Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Thiobencarb

MRID #: 434040-05

Matrix: Soil

Analysis: GC/NPD

Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Thiobencarb

MRID #: 434040-05

Matrix: Water

Analysis: GC/NPD

APPENDIX III

RESIDUE METHODS

CHEVRON CHEMICAL COMPANY
ORTHO AGRICULTURAL CHEMICALS DIVISION
RESIDUE CHEMISTRY LABORATORY
RICHMOND, CALIFORNIA

DETERMINATION OF THIOBENCARB, THIOBENCARB SULFOXIDE AND 4-CHLOROBENZYLMETHYLSULFONE IN SOIL
RESIDUE METHOD RM-16A-4S

DATE: AUGUST 1, 1988
FILE NO: 740.01/BOLERO

INTRODUCTION

This method describes the determination of thiobencarb, (S[(4-chlorophenyl)methyl]diethyl carbamothioate), thiobencarb sulfoxide, (1-[((4-chlorophenyl)methyl)sulfinyl)-N,N-diethylformamide) and 4-chlorobenzylmethylsulfone in soil. This procedure combines the extraction and analysis of the three compounds into one unified method.

Briefly, this method involves the extraction of soil with ethyl acetate. All three compounds are analyzed by gas chromatography. Thiobencarb and thiobencarb sulfoxide are detected with a nitrogen-phosphorus detector and 4-chlorobenzylmethylsulfone with a flame-photometric detector.

REAGENTS

Thiobencarb - Reference standard

Thiobencarb sulfoxide - Reference standard

4-chlorobenzylmethylsulfone - Reference standard

Ethyl acetate - Pesticide quality

Sodium sulfate - AR grade, granular, acetone washed and air dried.

EQUIPMENT

DO NOT USE PLASTIC. THE COMPOUNDS MAY REACT WITH THE PLASTIC.

1-Liter Separatory Funnel

500-mL Roundbottom Flask

Rotary Vacuum Evaporators

Ultrasonic Cleaner

Omni-Mixer

INSTRUMENTATION

1. Gas Chromatograph (HP-5710 or equivalent) equipped with a nitrogen-phosphorus detector, autosampler and integrator.

Column: DB-1, 15 m x 0.53 mm I.D. megabore, J & W Scientific, Inc. (or equivalent).

Flow Rates:		
	Carrier Gas (He)	- 20 mL/min.
	Hydrogen	- 3.2 mL/min.
	Air	- 75 mL/min.

Temperatures (May vary to optimize resolution):

Column-Oven	- 185°C
Injector Port	- 250°C
Detector Port	- 300°C

2. Gas Chromatograph (HP-5890 or equivalent) equipped with a flame-photometric detector, autosampler and integrator.

Column: HP-1 (methyl silicone gum) 5 m x 0.53 mm x 2.65 um film thickness (or equivalent).

Flow Rates:		
	Carrier Gas (He)	- 10 mL/min.
	Auxiliary	- 25 mL/min.
	Hydrogen	- 77 mL/min.
	Oxygen	- 94 mL/min.

Temperatures (May vary to optimize resolution):

Column-Oven	- Initial - 145°C	Initial Time - 3 mins.
	Final - 250°C	Final Time - 2 mins.
	Program Rate - 30°C per min.	
Injector Port	- 275°C	
Detector Port	- 275°C	

EXTRACTION

Weigh 50 g of soil into a pint Mason jar. (For recovery purposes, fortify a control sample with acetone solutions of thiobencarb, thiobencarb sulfoxide and 4-chlorobenzylmethylsulfone at this point in the procedure.) Add 150 mL ethyl acetate and 15 g sodium sulfate pre-washed with acetone and ethyl acetate. Mix for 5 minutes using the Omni-Mixer. Decant the extract through a sodium sulfate filter and collect the filtrate into a 250 mL roundbottom flask. Rinse the jar with 50 mL ethyl acetate and filter the rinse into the same flask. Then rinse the filter with 25 mL ethyl acetate. Evaporate the filtrate to dryness and dissolve the residue in 10 mL ethyl acetate. Use the ultrasonic cleaner to ensure that all residue is dissoved in the ethyl acetate.

MEASUREMENT

A. Thiobencarb and thiobencarb sulfoxide - Gas Chromatograph (NPD)

Transfer the solutions to be measured into vials for use on the automatic sampler (HP-7671). To analyze both compounds simultaneously, load the tray in the following order: standard thiobencarb, standard thiobencarb sulfoxide, standard thiobencarb, standard thiobencarb sulfoxide, check, fortified, standard thiobencarb, standard thiobencarb sulfoxide, sample, sample, standard thiobencarb, standard thiobencarb sulfoxide... Set the syringe to deliver 1 µl. The standard vials should contain 0.5 µg/mL of thiobencarb or thiobencarb sulfoxide for samples fortified at 0.1 ppm.

OR thiobencarb and thiobencarb sulfoxide samples can be analyzed independently.

B. 4-chlorobenzylmethylsulfone - Gas Chromatograph (FPD)

Transfer the solutions to be measured into vials for use on the automatic sampler (HP-7673A). Load the tray in the following order: standards, check, fortified, standards, samples, standards... Set the syringe to deliver 4 µl. The standard vials should contain solutions of the standard 4-chlorobenzylmethylsulfone at concentrations of 0.1, 0.2, 0.5, 0.8, 1.0, 2.0 ug/mL. The GC column should be conditioned prior to sample analysis.

LIMIT OF DETECTION

The limit of detection of this method is approximately 0.01 ppm for all three compounds.

D. E. de Guzman
D. de GUZMAN

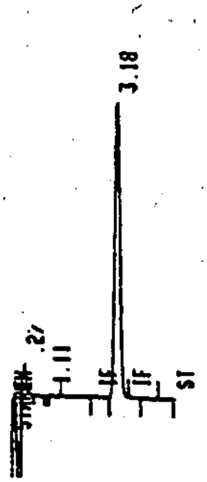
BHo
B. HO

Reviewed by: G O Breault

BH:gt

cc: G. O. Breault
R&D Files
Residue Files

FIGURE 1

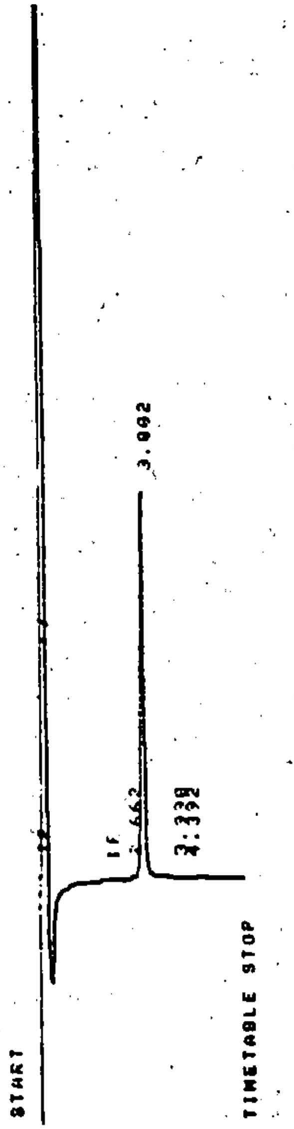


THIOBENCARB (1.0 ug/ml)
(GC conditions in text)

FIGURE 2

THIOBENCARB SULFOXIDE (1.0 ug/ml)
(GC conditions in text)

FIGURE 3



4-CHLOROBENZYLMETHYLSULFONE (1.0 ug/ml)
(GC conditions in text)

CHEVRON CHEMICAL COMPANY
ORTHO AGRICULTURAL CHEMICALS DIVISION
RESIDUE CHEMISTRY LABORATORY
RICHMOND, CALIFORNIA

DETERMINATION OF THIOBENCARB, THIOBENCARB SULFOXIDE AND 4-CHLOROBENZYLMETHYLSULFONE IN SOIL
RESIDUE METHOD RM-16A-5S

DATE: MARCH 6, 1989
FILE NO: 740.01/BOLERO

INTRODUCTION

This method describes the determination of thiobencarb, (S[(4-chlorophenyl)methyl]diethyl carbamothioate), thiobencarb sulfoxide, (1-[((4-chlorophenyl)methyl)sulfinyl)-N,N-diethylformamide) and 4-chlorobenzylmethylsulfone in soil. This procedure combines the extraction and analysis of the three compounds into one unified method. This revision of RM-16A-4S allows for the determination of thiobencarb sulfoxide by high performance liquid chromatography (photo-conductivity detector) and describes the residue calculations.

Briefly, this method involves the extraction of soil with ethyl acetate. Thiobencarb is analyzed by gas chromatography (nitrogen-phosphorus detector); 4-chlorobenzylmethylsulfone is analyzed by gas chromatography (flame photometric detector); and thiobencarb sulfoxide is analyzed by HPLC.

REAGENTS

Thiobencarb - Reference standard

Thiobencarb sulfoxide - Reference standard

4-chlorobenzylmethylsulfone - Reference standard

Ethyl acetate - Pesticide quality

Iso-Octane (2,2,4-Trimethylpentane) - HPLC grade

2-Propanol - HPLC grade

Methanol - HPLC grade

Sodium sulfate - AR grade, granular, acetone washed and air dried.

EQUIPMENT

DO NOT USE PLASTIC. THE COMPOUNDS MAY REACT WITH THE PLASTIC.

250-mL Roundbottom Flask
Rotary Vacuum Evaporators
Ultrasonic Cleaner
Omni-Mixer

INSTRUMENTATION

1. Gas Chromatograph (HP-5710 or equivalent) equipped with a nitrogen-phosphorus detector, autosampler and integrator.

   Column: DB-1, 15 m x 0.53 mm I.D. megabore, J & W Scientific, Inc. (or equivalent).

   Flow Rates:
   Carrier Gas (He) - 20 mL/min.
   Hydrogen - 3.2 mL/min.
   Air - 75 mL/min.

   Temperatures (May vary to optimize resolution):

   Column-Oven - 185°C
   Injector Port - 250°C
   Detector Port - 300°C

2. Gas Chromatograph (HP-5890 or equivalent) equipped with a flame-photometric detector, autosampler and integrator.

   Column: HP-1 (methyl silicone gum) 5 m x 0.53 mm x 2.65 um film thickness (or equivalent).

   Flow Rates:
   Carrier Gas (He) - 10 mL/min.
   Auxiliary - 25 mL/min.
   Hydrogen - 77 mL/min.
   Oxygen - 94 mL/min.

   Temperatures (May vary to optimize resolution):

   Column-Oven - Initial - 145°C Initial Time - 3 mins.
   Final - 250°C Final Time - 2 mins.
   Program Rate - 30°C per min.
   Injector Port - 275°C
   Detector Port - 275°C

3. High Performance Liquid Chromatograph (HP-1082B or equivalent) equipped with a photo-conductivity detector (Tracor 965 or equivalent), autosampler and integrator.

   Column: Ultrasphere Cyano (Altex), 5 µm, 4.6 mm x 25 mm (or equivalent).

   Mobile Phase: iso-octane:methanol:2-propanol (85:10:5); must equilibrate through detector before use.

   Flow Rate: 0.8 mL/min.

   Retention Time: Approximately 10 min.

EXTRACTION

Weigh 50 g of soil into a pint Mason jar. (For recovery purposes, fortify a control sample with acetone solutions of thiobencarb, thiobencarb sulfoxide and 4-chlorobenzylmethylsulfone at this point in the procedure.) Add 150 mL ethyl acetate and 15 g sodium sulfate pre-washed with acetone and ethyl acetate. Mix for 5 minutes using the Omni-Mixer. Decant the extract through a sodium sulfate filter and collect the filtrate into a 250 mL roundbottom flask. Rinse the jar with 50 mL ethyl acetate and filter the rinse into the same flask. Then rinse the filter with 25 mL ethyl acetate. Evaporate the filtrate to dryness and dissolve the residue in 5 mL ethyl acetate. Use the ultrasonic cleaner to ensure that all residue is dissoved in the ethyl acetate. For HPLC analysis, 1.0 mL of the ethyl acetate solution is evaporated to dryness and reconstituted in 1.0 mL of 85/15 iso-octane/2-propanol immediately before analysis.

MEASUREMENT

A. Thiobencarb - Gas Chromatograph (NPD)

Transfer the solutions to be measured into vials for use on the automatic sampler (HP-7671). Set the syringe to deliver 1 µl. The standard vials should contain 1.0 µg/mL of thiobencarb for samples fortified at 0.1 ppm; the coefficient of variation for the reproducibility of the reference standards should be ± 10%. Linearity should be verified using thiobencarb standards at concentrations of 0.1, 0.5, 1.0, 2.0 and 10 µg/mL; the response factor (response equivalent to 1 µg/mL) should have a coefficient of variation ± 10%.

B. 4-chlorobenzylmethylsulfone - Gas Chromatograph (FPD)

Transfer the solutions to be measured into vials for use on the automatic sampler (HP-7673A). Set the syringe to deliver 4 µl. The standard vials should contain solutions of the standard 4-chlorobenzylmethylsulfone at concentrations of 0.1, 0.2, 0.5, 0.8, 1.0, 2.0 µg/mL. The GC column should be conditioned prior to sample analysis.

C. Thiobencarb sulfoxide - High Performance Liquid Chromatography (PCD)

An injection volume of 20 µl should be used. The reference standard should be a 1 µg/mL solution of thiobencarb sulfoxide freshly reconstituted in 85/15 isooctane/2-propanol. The coefficient of variation for the reproducibility of the reference standard peak heights/areas should be ± 10%. Linearity should be verified using thiobencarb sulfoxide standards at concentrations of 0.1, 0.2, 0.5, 1.0 and 2.0 µg/mL; the response factors (response equivalent to 1 µg/mL) should have a coefficient of variation ± 10%.

CALCULATIONS

A. 4-chlorobenzylmethylsulfone

A non-linear curve of peak area/height versus standard concentration (µg/mL) is generated by computer using the equation:

$$y = Ax^B$$

y = peak area/height
x = standard concentration
A = constant (computer-generated; initial value is 10)
B = constant (computer-generated; initial value is 1)

After the generation of the curve, sample concentration (µg/mL) is determined by solving the above equation for x using the computer-generated values for A and B:

$$x = (y/A)^{1/B}$$

B. Thiobencarb and thiobencarb sulfoxide

$$\text{ppb} = \frac{\text{sample (peak area)}}{\text{standard (average peak area)}} \times 1\ \mu\text{g/mL} \times 5.0\ \text{mL} \times 1/50$$

LIMIT OF DETECTION

The limit of detection of this method is approximately 0.01 ppm for all three compounds.

Alexander C Munoz
A. MUNOZ

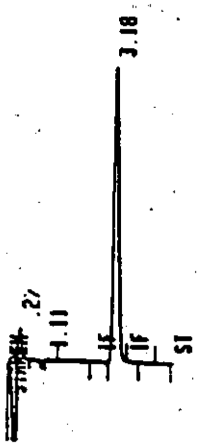
Ben Ho
B. HO

Reviewed by:

BH:gt

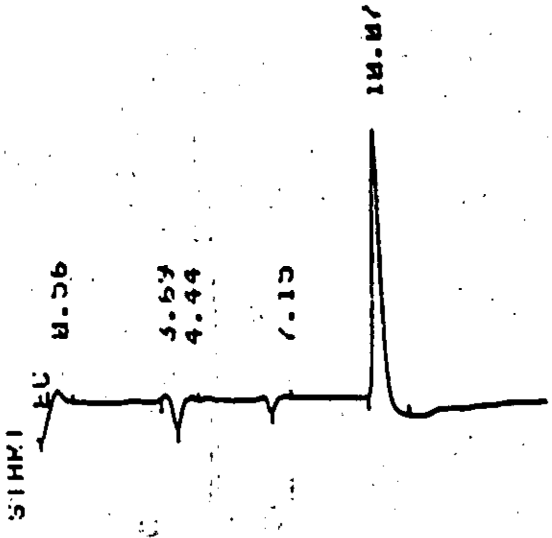
cc: G. O. Breault
Research Files
Residue Files

FIGURE 1



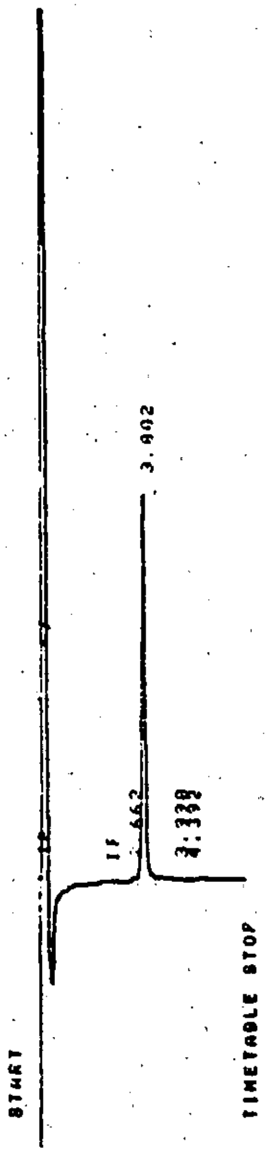
THIOBENCARB (1.0 ug/ml)
(GC conditions in text)

FIGURE 2



THIOBENCARB SULFOXIDE (1.0 ug/ml)
(HPLC conditions in text)

FIGURE 3



4-CHLOROBENZYLMETHYLSULFONE (1.0 ug/ml)
(GC conditions in text)

CHEVRON CHEMICAL COMPANY
ORTHO AGRICULTURAL CHEMICALS DIVISION
RESIDUE CHEMISTRY LABORATORY
RICHMOND, CALIFORNIA

DETERMINATION OF THIOBENCARB, THIOBENCARB SULFOXIDE AND 4-CHLOROBENZYLMETHYLSULFONE IN WATER
RESIDUE METHOD RM-16W-3

DATE: AUGUST 1, 1988
FILE NO: 740.01/BOLERO

INTRODUCTION

This method describes the determination of thiobencarb, (S[(4-chlorophenyl)methyl]diethyl carbamothioate, thiobencarb sulfoxide, (1-(((4-chlorophenyl)methyl)sulfinyl)-N,N-diethylformamide) and 4-chlorobenzylmethylsulfone in water. This procedure combines the extraction and analysis of the three compounds into one unified method.

Briefly, this method involves the extraction of water with hexane and dichloromethane. Thiobencarb is determined from hexane extract, thiobencarb sulfoxide is determined from the hexane and dichloromethane extracts and 4-chlorobenzylmethylsulfone is determined from the dichloromethane extract. All three compounds are analyzed by gas chromatography. Thiobencarb and thiobencarb sulfoxide are detected with a nitrogen-phosphorus detector and 4-chlorobenzylmethylsulfone is detected with a flame-photometric detector.

REAGENTS

Thiobencarb - Reference standard

Thiobencarb Sulfoxide - Reference standard

4-chlorobenzylmethylsulfone - Reference standard

Dichloromethane - Pesticide quality

Ethyl Acetate - Pesticide quality

Hexane - Pesticide quality

Sodium Sulfate - AR grade, granular, acetone washed and air dried.

Sodium Chloride - AR grade, crystals, acetone washed and air dried.

EQUIPMENT

DO NOT USE PLASTIC. THE COMPOUNDS MAY REACT WITH THE PLASTIC.

1-Liter Separatory Funnel
500-mL Roundbottom Flask
Rotary Vacuum Evaporators
Ultrasonic Cleaner

INSTRUMENTATION

1. Gas Chromatograph (HP-5710 or equivalent) equipped with a nitrogen-phosphorus detector, autosampler and integrator.

   Column: DB-1, 15 m x 0.53 mm I.D. megabore, J & W Scientific, Inc. (or equivalent).

   Flow Rates:
   Carrier gas (He) - 20 mL/min
   Hydrogen - 3.2 mL/min
   Air - 75 mL/min

   Temperatures (May vary to optimize resolution):

   Column Oven - 185°C
   Injector Port - 250°C
   Detector Port - 300°C

2. Gas Chromatograph (HP-5890 or equivalent) equipped with a flame-photometric detector, autosampler and integrator.

   Column: HP-1 (methyl silicone gum) 5 m x 0.53 mm x 2.65 um film thickness (or equivalent).

   Flow Rates:
   Carrier Gas (He) - 10 mL/min.
   Auxiliary - 25 mL/min.
   Hydrogen - 77 mL/min.
   Oxygen - 94 mL/min.

   Temperatures (May vary to optimize resolution):

   Column-Oven - Initial - 145°C Initial Time - 3 mins.
   Final - 250°C Final Time - 2 mins.
   Program Rate - 30°C per min.

   Injector Port - 275°C
   Detector Port - 275°C

EXTRACTION

Transfer 500 mL of water to a 1-liter separatory funnel. (For recovery purposes, fortify control sample with acetone solutions of thiobencarb, thiobencarb sulfoxide and 4-chlorobenzylmethylsulfone at this point in the procedure.) Add 200 mL hexane and about 15 g sodium chloride. Shake the mixture for about 2 minutes and let it settle. Drain the lower aqueous portion into a 1-liter container. Filter the hexane portion through anhydrous sodium sulfate into a 500-mL roundbottom flask. Rinse the filter with 25 mL hexane and combine the filtrate and rinse. Put the water back into the separatory funnel and add 100 mL dichloromethane. Shake the mixture for 2 minutes and let it settle. Filter the lower dichloromethane portion through the same filter previously used into a empty 500-mL roundbottom flask. Repeat dichloromethane extraction and combine the dichloromethane extracts. Evaporate both extracts of hexane and dichloromethane to dryness. Dissolve each extract with 2.5 mL ethyl acetate. Use the ultrasonic cleaner to ensure that all residue is dissolved in the ethyl acetate.

MEASUREMENT

A. Thiobencarb and Thiobencarb Sulfoxide - Gas Chromatography (NPD)

Transfer the solutions from the hexane extracts into the vials for use in the Automatic Sampler (HP-7671). Load the tray in the following order: standard thiobencarb, standard thiobencarb sulfoxide, standard thiobencarb, standard thiobencarb sulfoxide, check, fortified, standard thiobencarb, standard thiobencarb sulfoxide, sample, sample, standard thiobencarb, standard thiobencarb sulfoxide ... Then the dichloromethane extracts are loaded as follows: standard thiobencarb sulfoxide, standard thiobencarb sulfoxide, check, fortified, standard thiobencarb sulfoxide, sample, sample ... Set the syringe to deliver 1 µl. The standard vials should contain 1.0 µg/mL of thiobencarb or thiobencarb sulfoxide for samples fortified at 5.0 ppb.

<u>OR</u> analysis of thiobencarb and thiobencarb sulfoxide can be made independently.

NOTE: The thiobencarb sulfoxide residues in the hexane and dichloromethane portions should be added together.

B. 4-chlorobenzylmethylsulfone - Gas Chromatograph (FPD)

Transfer the solutions from the dichloromethane extracts into the vials for the automatic samples (HP-7673A). Load the tray in the following order: standards, check, fortified, standards, sample, sample, standards ... Set the syringe to deliver 4 µl. The standard vials should contain solutions of the standard 4-chlorobenzylmethylsulfone at concentrations of 0.1, 0.2, 0.5, 0.8, 1.0, 2.0 µg/mL. The GC column should be conditioned prior to sample analysis.

LIMIT OF DETECTION

The limit of detection of this method is approximately 0.5 ppb for all three compounds.

D. E. de Guzman
D. de GUZMAN

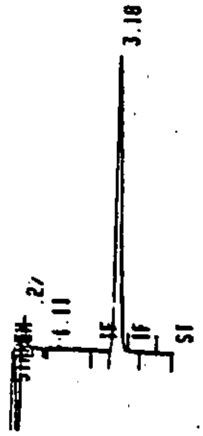
BHo
B. HO

Reviewed by: G. O. Breault

BH:gt

cc: G. O. Breault
R&D Files
Residue Files

FIGURE 1

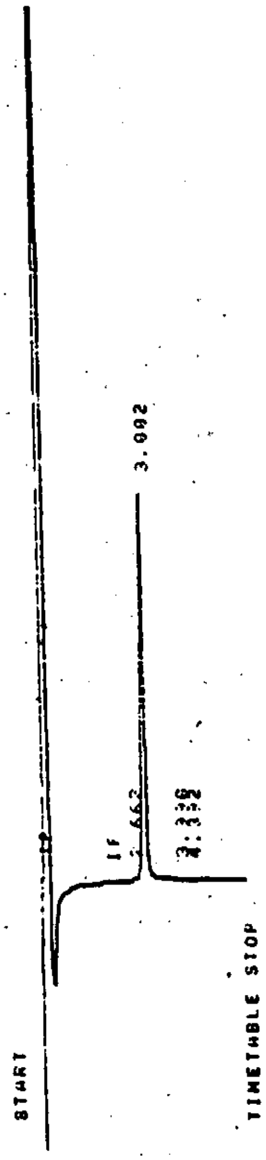


THIOBENCARB (1.0 ug/ml)
(GC conditions in text)

FIGURE 2

THIOBENCARB SULFOXIDE (1.0 ug/ml)
(GC conditions in text)

FIGURE 3



4-CHLOROBENZYLMETHYLSULFONE (1.0 ug/ml)
(GC conditions in text)

CHEVRON CHEMICAL COMPANY
ORTHO AGRICULTURAL CHEMICALS DIVISION
RESIDUE CHEMISTRY LABORATORY
RICHMOND, CALIFORNIA

DETERMINATION OF THIOBENCARB, THIOBENCARB SULFOXIDE AND 4-CHLOROBENZYLMETHYLSULFONE IN WATER
RESIDUE METHOD RM-16W-4

DATE: MARCH 6, 1989
FILE NO: 740.01/BOLERO

INTRODUCTION

This method describes the determination of thiobencarb, (S[(4-chlorophenyl)methyl]diethyl carbamothioate, thiobencarb sulfoxide, (1-(((4-chlorophenyl)methyl)sulfinyl)-N,N-diethylformamide) and 4-chlorobenzylmethylsulfone in water. This procedure combines the extraction and analysis of the three compounds into one unified method. This revision of RM-16W-3 allows for the determination of thiobencarb sulfoxide by high performance liquid chromatography (photo-conductivity detector) and describes the residue calculations.

Briefly, this method involves the extraction of water with hexane and dichloromethane. Thiobencarb is determined from the hexane extract, thiobencarb sulfoxide is determined from the hexane and dichloromethane extracts and 4-chlorobenzylmethylsulfone is determined from the dichloromethane extract. Thiobencarb is analyzed by gas chromatography (nitrogen-phosphorus detector); 4-chlorobenzylmethylsulfone is analyzed by gas chromatography (flame photometric detector); and thiobencarb sulfoxide is analyzed by HPLC.

REAGENTS

Thiobencarb - Reference standard

Thiobencarb Sulfoxide - Reference standard

4-chlorobenzylmethylsulfone - Reference standard

Dichloromethane - Pesticide quality

Ethyl Acetate - Pesticide quality

Hexane - Pesticide quality

Iso-Octane (2,2,4-Trimethylpentane) - HPLC grade

2-Propanol - HPLC grade

Methanol - HPLC grade

Sodium Sulfate - AR grade, granular, acetone washed and air dried.

Sodium Chloride - AR grade, crystals, acetone washed and air dried.

EQUIPMENT

DO NOT USE PLASTIC. THE COMPOUNDS MAY REACT WITH THE PLASTIC.

1-Liter Separatory Funnel
500-mL Roundbottom Flask
Rotary Vacuum Evaporators
Ultrasonic Cleaner

INSTRUMENTATION

1. Gas Chromatograph (HP-5710 or equivalent) equipped with a nitrogen-phosphorus detector, autosampler and integrator.

   Column: DB-1, 15 m x 0.53 mm I.D. megabore, J & W Scientific, Inc. (or equivalent).

   Flow Rates: Carrier gas (He) - 20 mL/min
   Hydrogen - 3.2 mL/min
   Air - 75 mL/min

   Temperatures (May vary to optimize resolution):

   Column Oven - 185°C
   Injector Port - 250°C
   Detector Port - 300°C

2. Gas Chromatograph (HP-5890 or equivalent) equipped with a flame-photometric detector, autosampler and integrator.

   Column: HP-1 (methyl silicone gum) 5 m x 0.53 mm x 2.65 um film thickness (or equivalent).

   Flow Rates: Carrier Gas (He) - 10 mL/min.
   Auxiliary - 25 mL/min.
   Hydrogen - 77 mL/min.
   Oxygen - 94 mL/min.

   Temperatures (May vary to optimize resolution):

   Column-Oven - Initial - 145°C Initial Time - 3 mins.
   Final - 250°C Final Time - 2 mins.
   Program Rate - 30°C per min.

   Injector Port - 275°C
   Detector Port - 275°C

3. High Performance Liquid Chromatograph (HP-1082B or equivalent) equipped with a photo-conductivity detector (Tracor 965 or equivalent), autosampler and integrator.

   Column: Ultrasphere Cyano (Altex), 5 µm, 4.6 mm x 25 mm (or equivalent).

   Mobile Phase: iso-octane:methanol:2-propanol (85:10:5); must equilibrate through detector before use.

   Flow Rate: 0.8 mL/min.

   Retention Time: Approximately 10 min.

EXTRACTION

Transfer 500 mL of water to a 1-liter separatory funnel. (For recovery purposes, fortify control sample with acetone solutions of thiobencarb, thiobencarb sulfoxide and 4-chlorobenzylmethylsulfone at this point in the procedure.) Add 200 mL hexane and about 15 g sodium chloride. Shake the mixture for about 2 minutes and let it settle. Drain the lower aqueous portion into a 1-liter container. Filter the hexane portion through anhydrous sodium sulfate into a 500-mL roundbottom flask. Rinse the filter with 25 mL hexane and combine the filtrate and rinse. Put the water back into the separatory funnel and add 100 mL dichloromethane. Shake the mixture for 2 minutes and let it settle. Filter the lower dichloromethane portion through the same filter previously used into a empty 500-mL roundbottom flask. Repeat dichloromethane extraction and combine the dichloromethane extracts. Evaporate both extracts of hexane and dichloromethane to dryness. Dissolve each extract with 2.5 mL ethyl acetate. Use the ultrasonic cleaner to ensure that all residue is dissolved in the ethyl acetate. For HPLC analysis, 1.0 mL of the ethyl acetate solution is evaporated to dryness and reconstituted in 1.0 mL of 85/15 iso-octane/2-propanol immediately before analysis.

MEASUREMENT

A. Thiobencarb - Gas Chromatography (NPD)

Transfer the solutions from the hexane extracts into the vials for use in the Automatic Sampler (HP-7671). Set the syringe to deliver 1 µl. The standard vials should contain 1.0 ug/mL of thiobencarb for samples fortified at 5.0 ppb; the coefficient of variation for the reproducibility of the reference standards should be ± 10%. Linearity should be verified using thiobencarb standards at concentrations of 0.1, 0.5, 1.0, 2.0 and 10 ug/mL; the response factor (response equivalent to 1 ug/mL) should have a coefficient of variation ± 10%.

B. 4-chlorobenzylmethylsulfone - Gas Chromatograph (FPD)

Transfer the solutions from the dichloromethane extracts into the vials for the automatic samples (HP-7673A). Set the syringe to deliver 4 µl. The standard vials should contain solutions of the standard 4-chlorobenzylmethylsulfone at concentrations of 0.1, 0.2, 0.5, 0.8, 1.0, 2.0 µg/mL.
The GC column should be conditioned prior to sample analysis.

C. Thiobencarb Sulfoxide - High Performance Liquid Chromatography (PCD)

The autosamples should be loaded first with the hexane extracts and then the dichloromethane extracts. An injection volume of 20 µl should be used. The reference standard should be a 1 µg/mL solution of thiobencarb sulfoxide freshly reconstituted in 85/15 iso-octane/2-propanol. The coefficient of variation for the reproducibility of the reference standard peak heights/areas should be ± 10%. Linearity should be verified using thiobencarb sulfoxide standards at concentrations of 0.1, 0.2, 0.5, 1.0 and 2.0 µg/mL; the response factors (response equivalent to 1 µg/mL) should have a coefficient of variation ± 10%.

CALCULATIONS

A. 4-chlorobenzylmethylsulfone

A non-linear curve of peak area/height versus standard concentration (µg/mL) is generated by computer using the equation:

$$y = Ax^B$$

y = peak area/height
x = standard concentration
A = constant (computer-generated; initial value is 10)
B = constant (computer-generated; initial value is 1)

After the generation of the curve, sample concentration (µg/mL) is determined by solving the above equation for x using the computer-generated values for A and B:

$$x = (y/A)^{1/B}$$

B. Thiobencarb and thiobencarb sulfoxide

$$\text{ppb} = \frac{\text{sample (peak area)}}{\text{standard (average peak area)}} \times 1\ \mu\text{g/mL} \times 2.5\ \text{mL} \times 1/500 \times 10^3$$

NOTE: The thiobencarb sulfoxide residues in the hexane and dichloromethane portions should be added together.

LIMIT OF DETECTION

The limit of detection of this method is approximately 0.5 ppb for all three compounds.

Alexander C. Munoz
A. MUNOZ

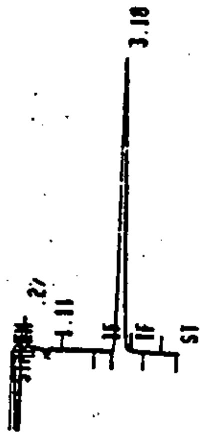
B Ho
B. HO

Reviewed by:

BH:gt

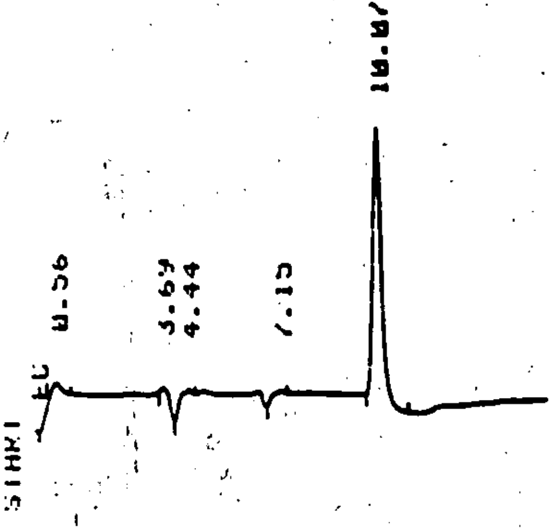
cc: G. O. Breault
Research Files
Residue Files

FIGURE 1



THIOBENCARB (1.0 ug/ml)
(GC conditions in text)

FIGURE 2



THIOBENCARB SULFOXIDE (1.0 ug/ml)
(HPLC conditions in text)

CHEVRON CHEMICAL COMPANY

RESIDUE LABORATORY

ANALYTICAL METHOD NO. RM-16W-4 VALIDATION REPORT

S.O.P. - 2.312 and 2.313	Reproducibility	Reproducibility (aged)	L.O.D.
Sample Matrix	WATER THIOBENCARB	SULFOXIDE	
Level:	10 ppb	1.0 ppb	
$\bar{X}$ =	10.3 ppb	0.96 ppb	
% of Nominal =	103 %	96 %	
C.V. =	5.0%	3.2	
n =	6	4	
Notebook Reference:	1044-43	10144-45	

Alexander C. [illegible] 7/7/89
Analyst(s) Date

7/10/89
Approved Date

Comments:

S.O.P. - 2.314 Efficacy of Extraction Procedure

Procedure used:

Notebook Reference:

Analyst(s) Date

Approved Date

Comments:

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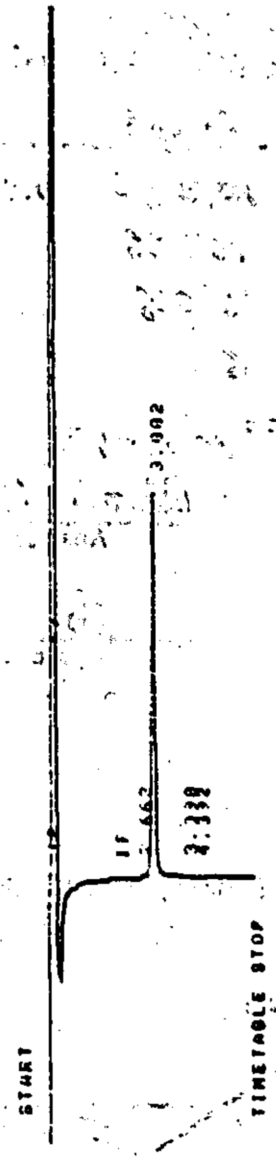
Reviewed by:

FIGURE 3



4-CHLOROBENZYLMETHYLSULFONE (1.0 ug/ml)
(GC conditions in text)