

Cover Sheet for
ENVIRONMENTAL CHEMISTRY METHOD

Pesticide Name: Thiobencarb

MRID #: 434040-05

Matrix: Soil

Analysis: GC/NPD

This method is provided to you by the Environmental Protection Agency's (EPA) Environmental Chemistry Laboratory (ECL). This method *is not* an EPA method but one which was submitted to EPA by the pesticide manufacturer to support product registration. EPA recognizes that the methods may be of some utility to state, tribal, and local authorities, but makes no claim of validity by posting these methods. Although the Agency reviews *all* Environmental Chemistry Methods submitted in support of pesticide registration, the ECL evaluates only about 30% of the currently available methods. Most methods perform satisfactorily but some, particularly the older methods, have deficiencies. Moreover, the print quality of the methods varies considerably because the methods originate from different sources. Therefore, the methods offered represent the best available copies.

If you have difficulties in downloading the method, or further questions concerning the methods, you may contact Elizabeth Flynt at 228-688-2410 or via e-mail at flynt.elizabeth@epa.gov.

100-1829-102

THE UNITED STATES GOVERNMENT

GENERAL LAND OFFICE

EXCISES - TAXES

REG. - STAMPS

CEMETERY - TOMBSTONES

The following rates of excise taxes are imposed by law upon
articles and articles used in the manufacture, sale, and distribution
and transportation of property, including tobacco, oil, salt, flour, sugar,
coffee, tea, and other articles imported from the foreign countries, and
upon the manufacture, sale, or distribution of such articles as may be
subject to excise taxes, and upon the manufacture, sale, and distribution
of such articles as may be subject to excise taxes.

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Cover Sheet for
ENVIRONMENTAL CHEMISTRY METHOD

Pesticide Name: Thiobencarb

MRID #: 434040-05

Matrix: Water

Analysis: GC/NPD

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REVIEW

THE SILENT SPHERE IN THE LITERATURE OF 1845

CHARLES H. COOPER

220 MASS.

1851

CHARLES

Charles H. Cooper's "The Silent Sphere in the Literature of 1845" is a detailed study of the year's output of American literature. The author begins by defining the "silent sphere" as the portion of the year's output that did not receive critical notice. He then goes on to analyze the remaining portion of the literature, examining the works of various authors and their contributions to the field. The study is comprehensive, covering a wide range of genres and topics. The author's writing style is clear and concise, making the information accessible to a general audience. The study is a valuable contribution to the field of literary history, providing a detailed look at the year's output of American literature.

The study is divided into several sections, each focusing on a different aspect of the literature. The first section, "Introduction," provides an overview of the year's output and sets the stage for the rest of the study. The second section, "The Silent Sphere," is the central focus of the study, providing a detailed analysis of the works that did not receive critical notice. The third section, "The Critical Sphere," provides a detailed analysis of the works that did receive critical notice. The fourth section, "Conclusion," summarizes the findings of the study and provides a final assessment of the year's output of American literature.

APPENDIX III

RESIDUE METHODS

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

DETERMINATION OF THIOBENCARB,
THIOBENCARB SULFOXIDE AND
4-CHLOROBENZYL METHYLSULFONE 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 dissolved 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 μ l. The standard vials should contain 0.5 μ g/mL of thiobencarb or thiobencarb sulfoxide for samples fortified at 0.1 ppm.

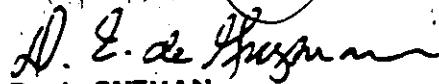
OR thiobencarb and thiobencarb sulfoxide samples can be analyzed independently.

B. 4-chlorobenzylmethylsulfone - Gas Chromatograph (FPD)

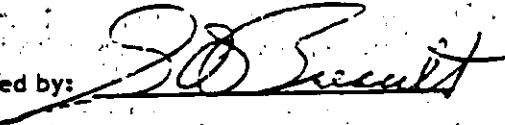
Transfer the solutions to be measured into vials for use on the automatic sampler (HP-7673A). Load the tray in the following order: standards, check, fortified, standards, samples, standards... Set the syringe to deliver 4 μ l. The standard vials should contain solutions of the standard 4-chlorobenzylmethylsulfone at concentrations of 0.1, 0.2, 0.5, 0.8, 1.0, 2.0 μ g/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
B. HO

Reviewed by:


G. O. Breault

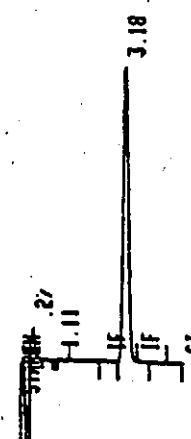
BH:gt

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

RM-16-A-45

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T-7230
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FIGURE 1



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

RM-16-A-4S

VALENT
T-7230
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FIGURE 2

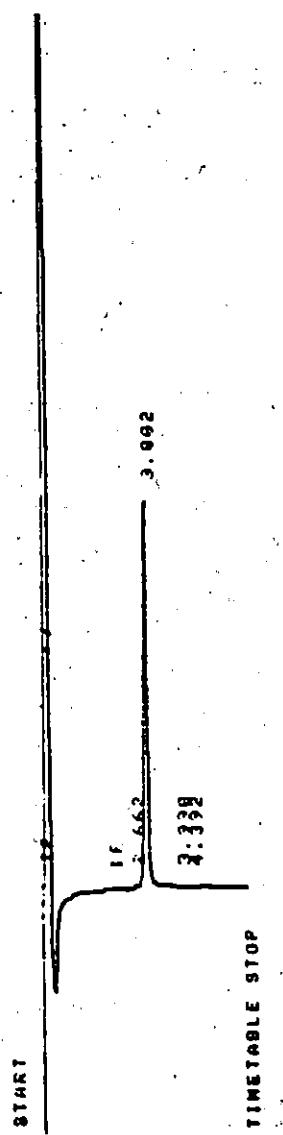


THIOBENCARB SULFOXIDE (1.0 ug/ml)
(GC conditions in text)

RM-1G-A-4S

SILENT
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FIGURE 3



4-CHLOROBENZYL METHYL SULFONE (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-CHLOROBENZYL METHYL SULFONE 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 μ m; 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 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 Chromatograph (NPD)

Transfer the solutions to be measured into vials for use on the automatic sampler (HP-7671). Set the syringe to deliver 1 μ L. The standard vials should contain 1.0 μ g/mL of thiobencarb for samples fortified at 0.1 ppm; the coefficient of variation for the reproducibility of the reference standards should be \pm 10%. Linearity should be verified using thiobencarb standards at concentrations of 0.1, 0.5, 1.0, 2.0 and 10 μ g/mL; the response factor (response equivalent to 1 μ g/mL) should have a coefficient of variation \pm 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 μ L. 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 μ g/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 $\mu\text{g/mL}$ 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 $\pm 10\%$. Linearity should be verified using thiobencarb sulfoxide standards at concentrations of 0.1, 0.2, 0.5, 1.0 and 2.0 $\mu\text{g/mL}$; the response factors (response equivalent to 1 $\mu\text{g/mL}$) should have a coefficient of variation $\pm 10\%$.

CALCULATIONS

A. 4-chlorobenzylmethylsulfone

A non-linear curve of peak area/height versus standard concentration ($\mu\text{g/mL}$) 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 ($\mu\text{g/mL}$) 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

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

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1-7288
Page 268

LIMIT OF DETECTION

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

Alexander C. Munoz
A. MUNOZ

B. HO

Reviewed by:

G.O. Breault

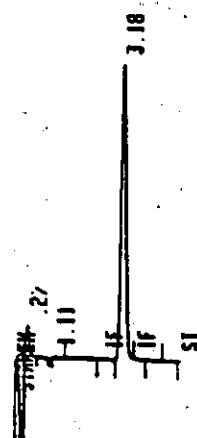
BH:gt

cc: G.O. Breault
Research Files
Residue Files

RM-16-A-5S

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FIGURE 1

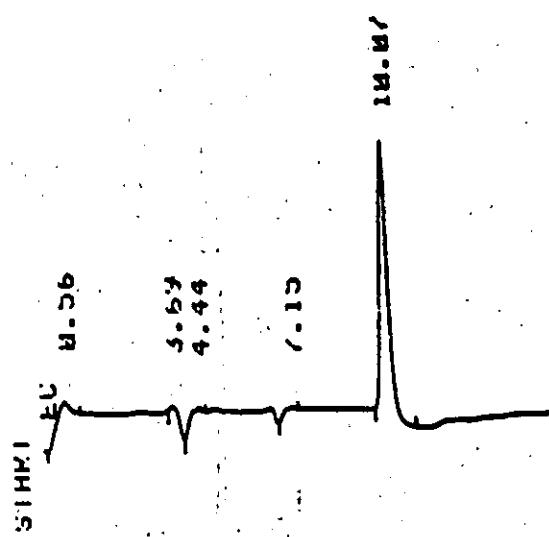


THIOBENCARB (1.0 ug/ml)
(GC conditions in text)

RM-16A-5S

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FIGURE 2

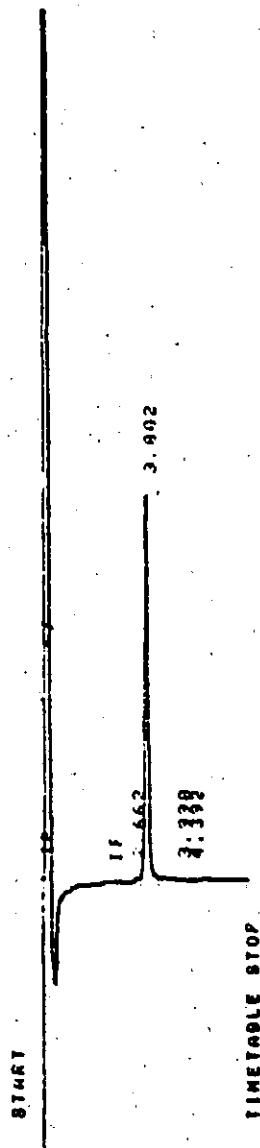


THIOBENCARB SULFOXIDE (1.0 ug/ml)
(HPLC conditions in text)

RM-16-A- 5S

VALENT
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FIGURE 3



4-CHLOROBENZYL METHYL SULFONE (1.0 ug/ml)
(GC conditions in text)

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ORTHO AGRICULTURAL CHEMICALS DIVISION
RESIDUE CHEMISTRY LABORATORY
RICHMOND, CALIFORNIA

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DETERMINATION OF THIOBENCARB,
THIOBENCARB SULFOXIDE AND
4-CHLOROBENZYL METHYLSULFONE
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, (I-((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 dichloroethane. 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 Evaporator

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.

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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 μ l. The standard vials should contain 1.0 μ g/mL of thiobencarb or thiobencarb sulfoxide for samples fortified at 5.0 ppb.

OR 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 μ l. 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 μ g/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

BB
B. HO

Reviewed by: *S. O. Breault*

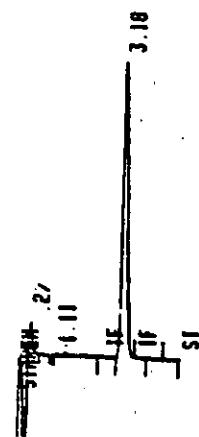
BH:gt

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

RM-16W-3

VALENT
I-7230
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FIGURE 1

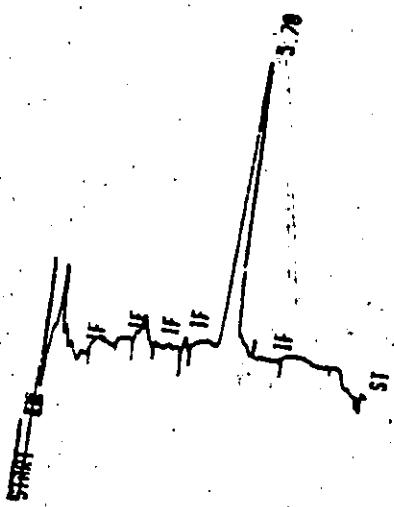


THIOBENCARB (1.0 ug/ml)
(GC conditions in text)

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RM-16W-3

FIGURE 2

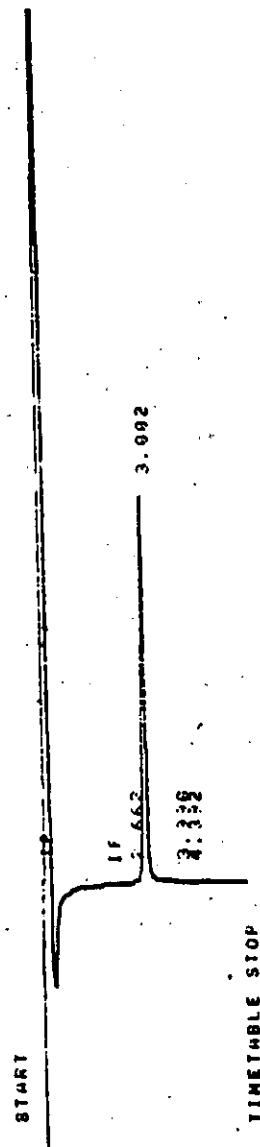


THIOBENCARB SULFOXIDE (1.0 $\mu\text{g/ml}$)
(GC conditions in text)

RM-16W-3

VALENT
1-7230
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FIGURE 3



4-CHLOROBENZYL METHYL SULFONE (1.0 ug/ml)
(GC conditions in text)

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

VALLET
T-720
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DETERMINATION OF THIOBENCARB,
THIOBENCARB SULFOXIDE AND
4-CHLOROBENZYL METHYLSULFONE
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

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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 $\mu\text{g}/\text{mL}$ of thiobencarb for samples fortified at 5.0 ppb; the coefficient of variation for the reproducibility of the reference standards should be $\pm 10\%$. Linearity should be verified using thiobencarb standards at concentrations of 0.1, 0.5, 1.0, 2.0 and 10 $\mu\text{g}/\text{mL}$; the response factor (response equivalent to 1 $\mu\text{g}/\text{mL}$) should have a coefficient of variation $\pm 10\%$.

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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 μ l. 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 μ g/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 μ l should be used. The reference standard should be a 1 μ g/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 \pm 10%. Linearity should be verified using thiobencarb sulfoxide standards at concentrations of 0.1, 0.2, 0.5, 1.0 and 2.0 μ g/mL; the response factors (response equivalent to 1 μ g/mL) should have a coefficient of variation \pm 10%.

CALCULATIONS

A. 4-chlorobenzylmethylsulfone

A non-linear curve of peak area/height versus standard concentration (μ g/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 (μ g/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.

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LIMIT OF DETECTION

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

Alexander C. Munoz
A. MUÑOZ

B. HO
B. HO

Reviewed by: J. D. Breslow

BH:gt

cc: G. O. Breault
Research Files
Résidue Files

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FIGURE I

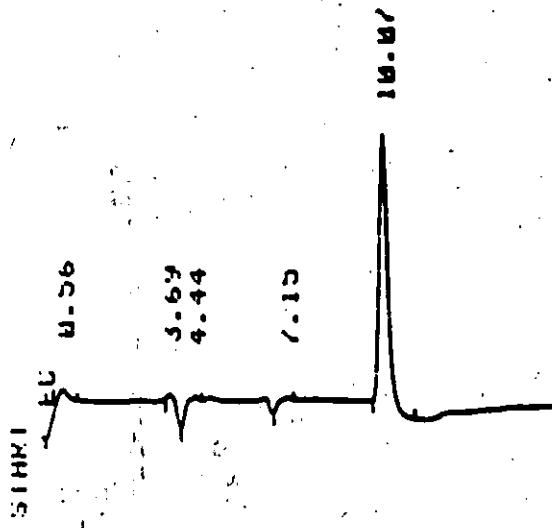


THIOBENCARB (1.0 ug/ml)
(GC conditions in text)

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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

Sample Matrix WATER THIOSENCARB SULFOXIDE

L.O.D.

Level: 10 ppb 1.0 ppb

X = 10.3 ppb 0.36 LLOQ ppb

% of Nominal = 103 % 96 %

C.V. = 5.0 % 3.2

n = 6 4

Notebook Reference: 10144-43 10144-45

Alexander C. Young 7/7/89
Analyst(s) Date

TSF
Approved

7/10/89
Date

Comments:

S.O.P. - 2.314

Efficacy of Extraction Procedure

Procedure used:

Notebook Reference:

Analyst(s)

Date

Approved

Date

Comments:

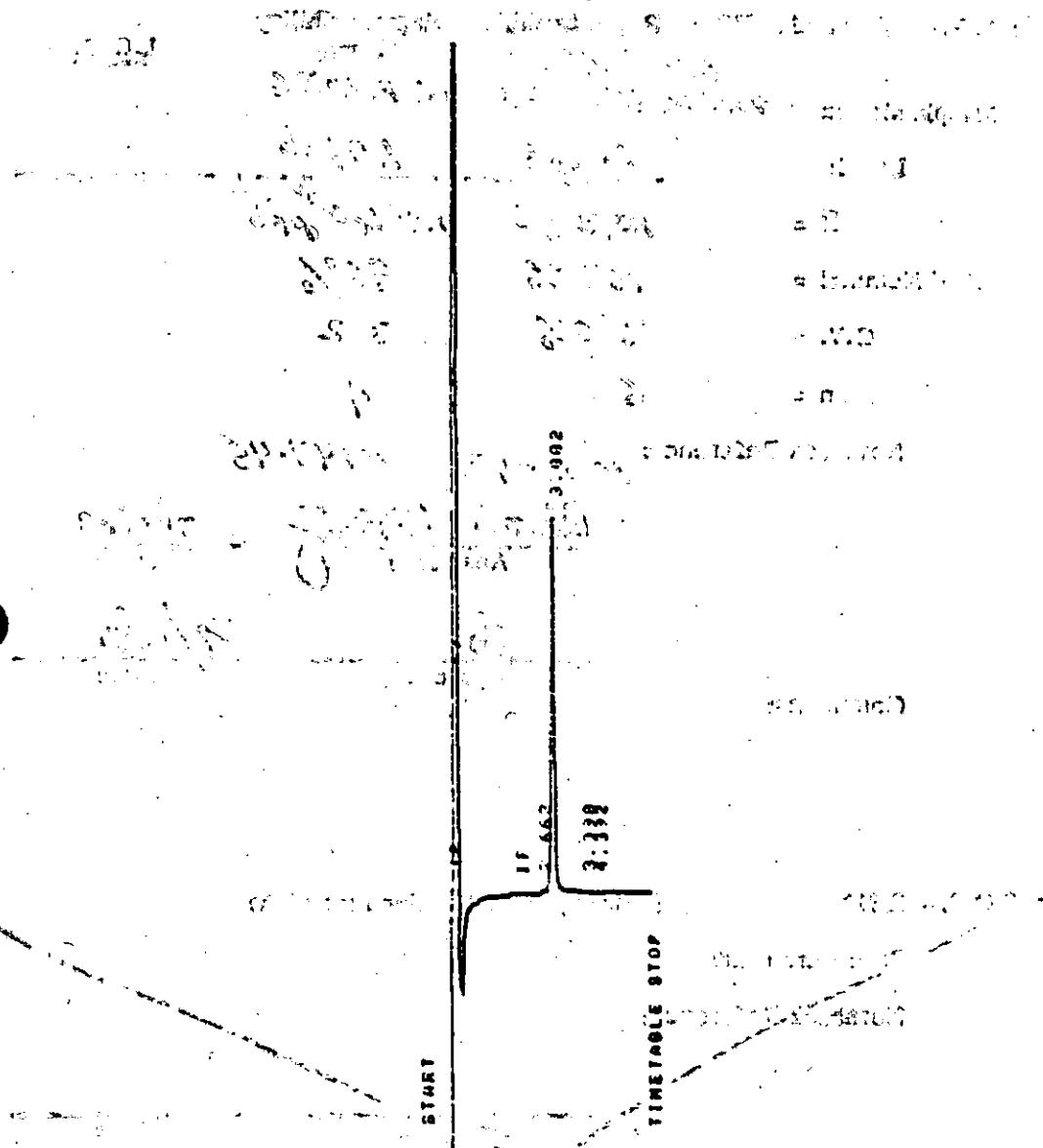
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FIGURE 3



4-CHLOROBENZYL METHYL SULFONE (1.0 ug/ml)
(GC conditions in text).