Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Oxydemeton-Methyl

MRID #: 414302-02

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.

$\phi 2$

WHEN REFERRING TO THIS REPORT USE THIS NUMBER

99118

Study Title

METASYSTOX-R and METASYSTOX-R Sulfone Method Development, Method Validation and Recoveries on Soil

Data Requirement

171-4 Residue Analytical Method
and
164-1 Dissipation-Field Soil

Authors

D.M. Naney, J.K. Kardatzke and W.D. Rhoads

Completion Date

May 15, 1989

Performing Laboratory

Colorado Analytical Research & Development Corporation
4720 Forge Road, Suite 108
Colorado Springs, Colorado 80907

Submitting Laboratory

Mobay Corporation
Agricultural Chemicals Division
Research and Development Department
17745 S. Metcalf Ave.
Stilwell, Kansas 66085

Laboratory Project ID

Mobay Project No. MS122101
Colorado Analytical Project No. Mobay 1102

METASYSTOX-R is a Registered TM of Bayer AG, Germany

File copy

BB-24

Oxydemeton methyl

EPA

MRID NUMBER

44320-02

99118

CONFIDENTIALITY STATEMENT

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

Company: Mobay Corporation, Agricultural Chemicals Division

Company Agent: D.R. Flint Date: 7/21/89

Manager, Biochemistry/Ecological Effects Group D.R. Flint
(Signature)

CERTIFICATE OF AUTHENTICITY

The subsequent pages of this document are presented as they were received from the performing laboratory. Mobay notebook 89R154 consists of raw data, protocol and correspondence and is not included as part of the report.

Company Agent: B.P. Smyser, Ph.D.
Senior Chemist, Biochemistry

Signature: B.P. Smyser

Date: July 28 1989

INQUIRIES

Inquiries should be directed to:

H.M. Chopade
Mobay Corporation
Research and Development Department
Mobay Research Park
17745 South Metcalf Avenue
Stilwell, Kansas 66085

Telephone: (913) 897-9321

Good Laboratory Practice Certification

Good laboratory practice requirements of 40 CFR Part 160 do not apply to the study described in this document.

Mobay Corporation
Agricultural Chemicals Division
Research and Development Department

Flagging Statements

No flagging statements are required for the study described in this document.

Mobay Corporation
Agricultural Chemicals Division
Research and Development Department

CERTIFICATION OF GOOD LABORATORY PRACTICE

Project No. Mobay 1102 (Mobay Project Number MS122101) "METASYSTOX-R and METASYSTOX-R Sulfone Method Development, Method Validation and Recoveries on Soil" has been performed in accordance with the good laboratory practice standards of Colorado Analytical Research and Development Corporation. Copies of all raw data, specimens and reports generated during the conduct of this study are retained in the Archives of Colorado Analytical Research & Development Corporation. The originals will be archived by Mobay Corporation.

STUDY DIRECTOR: William D. Rhoads, Ph.D.

STUDY SITE: Colorado Analytical Research & Development Corporation
4720 Forge Road, Suite 108
Colorado Springs, CO 80907
(719) 593-1165

SPONSOR: Mobay Corporation
Agricultural Chemicals Division
17745 South Metcalf Avenue
Stilwell, KS 66085

STUDY INITIATED: August 8, 1988

STUDY COMPLETED: May 15, 1989

FINAL REPORT DATE: July 20, 1989

Submitted By: William D. Rhoads Date 7/24/89
William D. Rhoads, Ph.D.

Doris M. Naney Date 7/24/89
Doris M. Naney, M.L.T., C.L.T.
Supervisor, Radiochemistry Laboratory

Janis K. Kardatzke Date 7-24-89
Janis K. Kardatzke, B.S.
Laboratory Technician II

Quality Assurance: Kenneth R. Weissenfluh Date 7/24/89
Kenneth R. Weissenfluh, B.S.
Director of Quality Assurance

99118

QUALITY ASSURANCE

FINAL REPORT STATEMENT

Study Title: METASYSTOX-R and METASYSTOX-R Sulfone Method Development, Method Validation and Recoveries on Soil

Test Articles: METASYSTOX-R and METASYSTOX-R Sulfone

This report has been reviewed by the Colorado Analytical Research & Development Corporation Quality Assurance Department in accordance with the United States Environmental Protection Agency FIFRA Good Laboratory Practice Standards as outlined in 40 CFR part 160, Federal Register Notice, November 29, 1983, Vol. 48, No. 230, effective May 2, 1984; Federal Register Notice, May 2, 1984, Vol. 49, No. 86.

Inspection of the Protocol for this study was conducted on August 12, 1988. A phase of the conduct of the study was inspected on March 8, 1989. Findings resulting from the inspection, from the data audit and from a review of the report were reported to management and the Study Director on August 12, 1988, March 8, 1989, June 20, 1989 and July 20, 1989. It was concluded that the final report accurately reflects the raw data for this study.

Kenneth R. Weissenfluh, B.S.
Director of Quality Assurance

99118

TABLE OF CONTENTS

ABSTRACT

This report presents the validation of the extraction of METASYSTOX-R and its oxidized metabolite METASYSTOX-R Sulfone from soil (Mobay Method No. 53204) coupled with Mobay preliminary method development studies for the separation of these compounds from soil extracts as performed by the staff members of Colorado Analytical Research & Development Corporation. The Mobay Corporation Biochemistry Study Specification is attached to this report (Appendix 1).

The validity of the analytical method was demonstrated from Fresno, California 0-6" sandy loam soil (Mobay Sample No. 1001) fortified from 0.01 to 2.0 ppm with both METASYSTOX-R and Meta-SYSTOX-R Sulfone. Recoveries ranged from a low of 74.7% to a high of 115.2% with an average recovery of 95.1% ± 12.3% (n = 16). Further validity of the method was demonstrated from Fresno, California sandy loam soil (Mobay Sample Numbers 1001 through 1007) and Chualar, California sandy loam soil samples (Mobay Sample Numbers 2001 through 2007) fortified with both METASYSTOX-R and METASYSTOX-R Sulfone at a residue level of 0.01 ppm for each 6 inch soil horizon representing zero to three foot depths as well as the three to four foot depths. Recoveries ranged from a low of 80.2% to a high of 136.4% with an average recovery of 95.1% ± 11.9% (n =28).

INTRODUCTION

The purpose of the study was to develop an analytical method for the determination of METASYSTOX-R and METASYSTOX-R Sulfone in soil at a screening level of 0.01 part per million using capillary gas chromatographic analysis. Mobay Method 53204 describes the determination of residues of METASYSTOX-R and its metabolite in plant, animal tissues and soil (Appendix 2). This report presents development of an analytical method based on Mobay Method 53204 and its validation on two California soils.

MATERIALS AND METHODS

APPARATUS

1.1 Bottle, Nalgene, 500 ml

1.2 Centrifuge

1.3 Filter paper, Whatman #1, 7 cm

1.4 Flask, filtering, 500 ml

1.5 Flask, round bottom, 100 ml, 250 ml, 500 ml

1.6 Funnel, Büchner, 7 cm

1.7 Funnel, long stem, 100 ml

1.8 Funnel, separatory, 250 ml

1.9 Orbit shaker, Lab Line or equivalent

1.10 Rotary evaporator, Büchi or equivalent

1.11 Sample vials, GC autosampler

REAGENTS

2.1 Acetone, distilled in glass

2.2 Chloroform, distilled in glass

2.3 Hexane, distilled in glass

2.4 Magnesium sulfate, reagent grade

2.5 Potassium permanganate, reagent grade

2.6 Sep Pak, silica gel, Waters, part No. 51900

2.7 Sodium chloride, reagent grade

2.8 Sodium sulfate, anhydrous, reagent grade

2.9 Water, deionized

SOILS

The method was validated for two sandy loam soils (Mobay Sample Numbers: 1001, 1002, 1003, 1004, 1005, 1006, 1007, 2001, 2002, 2003, 2004, 2005, 2006 and 2007) both supplied by Mobay Corporation. Characteristics of these soils are presented in Appendix 3.

STANDARDS

METASYSTOX-R (95.4% purity) and METASYSTOX-R Sulfone (96.3% purity) analytical standards were supplied by Mobay Corporation.

ANALYTICAL METHODOLOGY

3.1 Extraction

3.1.1 Weigh 25 grams of a well-homogenized, stone-free soil sample into a 500 ml Nalgene screw cap bottle. Add 250 ml of 10% (v/v) water/acetone. Cap the bottle securely.

3.1.2 Place the bottle on an orbital shaker and shake for 30 minutes at 2500 rpm.

3.1.3 Vacuum filter the sample through Whatman #1, 7 cm filter paper into a 500 ml filtering flask.

3.1.4 Wash the soil filter cake with 25 ml of 10% (v/v) water/acetone.

3.2 Partition

3.2.1 Transfer the combined extracts from steps 3.1.3 and 3.1.4 to a 500 ml round bottom flask.

3.2.2 Add 25 ml of water and remove the acetone by vacuum rotary evaporation (bath temperature 35°C).

3.2.3 Transfer the aqueous sample (approximately 50 ml) to a 250 ml separatory funnel and partition once with 150 ml of hexane using a 1 minute shake. Allow the layers to separate and discard the hexane.

3.2.4 Add 5 ml of saturated sodium chloride to the aqueous phase from step 3.2.3 and partition three times with 50 ml portions of chloroform using 30 second shakes. Drain each chloroform partition sample through a bed of anhydrous sodium sulfate into a 250 ml round bottom flask. After the last chloroform partition sample has been drained through the anhydrous sodium sulfate bed, rinse the bed with 25 ml of chloroform. Discard the water phase.

3.3 Silica Gel Sep Pak

3.3.1 Evaporate the chloroform just to dryness using a vacuum rotary evaporator (bath temperature 35°C). Blow off residual chloroform with a stream of nitrogen.

3.3.2 Dissolve the sample from step 3.3.1 in 5 ml of 50/50 acetone/hexane and load the sample onto a silica gel Sep Pak which has previously been washed with 20 ml of hexane. Use a 100 ml round bottom flask to collect the eluant.

3.3.3 Rinse the sample container from step 3.3.2 twice with 5 ml portions of 50/50 acetone/hexane and load these onto the Sep Pak. NOTE: THIS ELUANT CONTAINS THE METASYSTOX-R SULFONE.

3.3.4 Place a fresh 100 ml round bottom flask under the Sep Pak and elute with 15 ml of acetone. NOTE: THIS ELUANT CONTAINS THE METASYSTOX-R.

3.3.5 Remove the acetone/hexane from the eluant collected in step 3.3.3 by vacuum rotary evaporation (bath temperature 35°C).

3.3.6 Bring the sample from step 3.3.5 to volume with 2.0 ml of acetone and analyze by capillary gas chromatography.

3.4 Oxidation

3.4.1 Remove the acetone from the eluant collected in step 3.3.4 by vacuum rotary evaporation (bath temperature 35°C).

3.4.2 Dissolve the residue from step 3.4.1 in 2 ml of acetone. Add 5 ml of a 20% aqueous $MgSO_4$ solution followed by the addition of 25 ml of 0.1 M aqueous $KMnO_4$ solution. Let the sample sit for 30 minutes with occasional shaking.

3.4.3 Transfer the sample from step 3.4.2 into a 250 ml separatory funnel and partition three times with 25 ml portions of chloroform using 30 second shakes. Drain each chloroform partition sample through a bed of anhydrous sodium sulfate. After the last chloroform partition sample has been drained through the anhydrous sodium sulfate bed, rinse the bed with 10 ml of chloroform. NOTE: In general, emulsions will be present in the permanganate chloroform partition samples. Centrifuging may be necessary for all three partitions. Centrifuge the samples for 5 minutes at 3000 rpm.

3.4.4 Remove the chloroform from the sample obtained in step 3.4.3 by vacuum rotary evaporation (bath temperature 35°C).

3.4.5 Bring the sample from step 3.4.4 to volume with 2.0 ml of acetone and analyze by capillary gas chromatography.

The flow diagram for the method is shown in Figure 1.

CAPILLARY GAS CHROMATOGRAPHIC ANALYSIS

The samples from steps 3.3.6 and 3.4.5 are analyzed by capillary gas chromatography using a nitrogen phosphorous specific detector. The chromatographic conditions are given in Table I.

4.1 Preparation of Standard METASYSTOX-R Sulfone

4.1.1 Weigh 10.0 mg of METASYSTOX-R Sulfone (corrected for purity) into a 100 ml volumetric flask and bring to volume with acetone. This standard solution represents 100 micrograms of METASYSTOX-R Sulfone per ml. Prepare a 1.33 microgram per ml METASYSTOX-R Sulfone gas chromatographic standard by pipetting 1.0 ml of the stock 100 microgram per ml solution into 74 ml of

acetone. This gas chromatographic standard is equivalent to 1.25 micrograms per ml of METASYSTOX-R when a 0.939 multiplication factor for the difference in the molecular weights of METASYSTOX-R to METASYSTOX-R Sulfone (246.275/262.270), METASYSTOX-R MW/METASYSTOX-R Sulfone MW) is used.

4.2 Preparation of METASYSTOX-R and METASYSTOX-R Sulfone Soil Spiking Solutions

4.2.1 Weigh 10 mg of METASYSTOX-R (corrected for purity) into a 100 ml volumetric flask. Weigh 10.0 mg of METASYSTOX-R Sulfone (corrected for purity) into the same volumetric flask. Bring to volume with acetone. This standard solution represents 100 micrograms of METASYSTOX-R and METASYSTOX-R Sulfone per ml. Serially dilute this stock solution with acetone to obtain spiking solutions containing 10.0, 2.5, 1.0 and 0.5 micrograms of METASYSTOX-R and METASYSTOX-R Sulfone per ml.

4.3 Preparation of Spiked Soil Samples for Recovery Determinations

4.3.1 The spiking level chosen for the recovery sample will dictate which standard solution, prepared in Step 4.2, is used for the recovery sample. It is desirable to keep the spiking volume within 1.0 - 2.0 ml. The 25 gm soil aliquot is spiked immediately after weighing and prior to the addition of the extracting solvent. The recovery samples are taken through the complete method and are run concurrently with control and treated samples.

4.4 Standardization of Gas Chromatograph

4.4.1 Prior to any gas chromatographic analysis of standards and samples, the gas chromatographic column must be "primed". Priming is accomplished by injecting two 2 microliter aliquots of a soil gas chromatographic sample and two 2 microliter aliquots of a 10.0 microgram per ml METASYSTOX-R Sulfone standard. This priming reduces the enhancement problems associated with the analysis. See the discussion section for more detailed information regarding the enhancement observed for METASYSTOX-R Sulfone.

4.4.2 Inject a 2 microliter aliquot of the 1.33 microgram per ml METASYSTOX-R Sulfone standard and adjust the attenuation of the gas chromatograph to obtain a greater or equal to 50% full scale deflection.

4.3 Determination of Sample Residues

4.3.1 Following the injection pattern of standard, sample, sample, standard, inject 2.0 microliter aliquots of the samples from steps 3.3.6 and 3.4.5 into the into the gas chromatograph. Typical chromatograms of the standard and soil samples are presented in Figure 2.

With each analytical set, a minimum of one control soil and one control soil fortified with both METASYSTOX-R and METASYSTOX-R Sulfone is required for purposes of recovery validation. The recovery samples should represent a range covering the screening level of the method, 0.01 ppm, to the highest residue found in treated samples.

CALCULATIONS

Calculation of METASYSTOX-R and METASYSTOX-R Sulfone residues in soil samples is by the following:

The 1.33 microgram per ml METASYSTOX-R Sulfone standard represents 2.66 nanograms injected from a 2 microliter aliquot. This represents 2.50 nanograms of equivalent METASYSTOX-R when corrected for the 0.939 molecular weight factor.

Determine the average integrator peak area for the 2.50 nanogram equivalent METASYSTOX-R standard.

Determine the nanograms found for soil samples from the following equations:

$$\text{nanograms METASYSTOX-R found} = \frac{\text{peak area of soil sample}}{\text{average peak area of the standard}} \times 2.5$$

$$\text{nanograms METASYSTOX-R Sulfone found} = \frac{\text{peak area of soil sample}}{\text{average peak area of the standard}} \times 2.66$$

Soil residue data are reported on a dry weight basis. Oven dry a 10 to 20 gram soil aliquot at 110°C for 16 hours, and determine the moisture content using the following equation:

$$\text{percent soil moisture} = \frac{\text{net weight of wet soil} - \text{net weight of dry soil}}{\text{net weight of wet soil}} \times 100$$

The METASYSTOX-R and METASYSTOX-R Sulfone residue values for soil samples, expressed in parts per million on a dry weight basis, are obtained from the following equation:

$$ppm = \frac{\text{nanograms METASYSTOX-R or METASYSTOX-R Sulfone found}}{\text{(milligrams equivalent soil injected)(M)}}$$

$$\text{milligrams equivalent soil injected} = \frac{\text{25 gm soil sample}}{\text{final sample volume}} \times \text{2 microliters injected}$$

M is the dry weight factor for the moisture content of the soil and is expressed as a decimal (11.84% soil moisture yields 2.96 ml of water from a 25 gram soil sample).

$$M = \frac{25.00 - 2.96}{25.00} = 0.882$$

Parts per million METASYSTOX-R Sulfone are reported as ppm equivalent METASYSTOX-R residue. The following equation accomplishes this conversion.

$$\text{ppm equivalent METASYSTOX-R} = \text{ppm METASYSTOX-R Sulfone found (dry basis)} \times 0.939$$

Recovery of METASYSTOX-R and METASYSTOX-R Sulfone from control samples fortified with the analytes is calculated from the following:

$$\frac{\text{ppm found} - \text{ppm found in control soil}}{\text{ppm added}} \times 100$$

RESULTS AND DISCUSSION

LINEARITY OF THE DETECTOR RESPONSE TO METASYSTOX-R SULFONE

Table II presents the linear response data for METASYSTOX-R Sulfone in soil matrix. From data outlined in Table II, a coefficient of determination of 0.9984 was obtained for recoveries from soil matrix representing equivalent 0.005 to 5.0 ppm METASYSTOX-R Sulfone. Also presented in Table II are ppm METASYSTOX-R Sulfone found by back calculation using least squares linear regression. These ppm values demonstrate reasonable linearity from 0.005 to 5.0 ppm METASYSTOX-R Sulfone. Figure 3 presents the linearity of this study in graphic format.

Staff members of Colorado Analytical Research & Development Corporation, prior to this method development study, developed analytical methods on a variety of agricultural crops for both METASYSTOX-R and METASYSTOX-R Sulfone. Enhanced recoveries were often observed. The enhanced recovery problems observed from these studies were traced to competitive adsorption on the GC column between METASYSTOX-R Sulfone and component(s) in the biological matrix. At the lower spiking levels, the mass ratio of standard/matrix is much lower than at higher spiking levels, resulting in a proportionately lower amount of standard being adsorbed by the column. The variable detector response obtained under these conditions was clearly apparent when compared to an analytical standard in solvent only (no matrix) for quantitation.

The enhancement problems observed from soil were generally from high residue levels of METASYSTOX-R and METASYSTOX-R Sulfone, specifically for residues greater than 0.1 ppm equivalent METASYSTOX-R. Enhancement of recoveries of 106-132%, 108-136% and 117-154% were obtained from soil samples fortified with METASYSTOX-R and METASYSTOX-R Sulfone at the 0.5, 1.0 and 2.0 ppm levels, respectively, and from samples brought up in a 2 ml final GC volume. The gas chromatographic standard (2.66 manograms METASYSTOX-R Sulfone) used for the analysis represents equivalent 0.1 ppm METASYSTOX-R residue levels. The enhancement problems observed at the higher residue levels of METASYSTOX-R and METASYSTOX-R Sulfone were eliminated by dilution of these samples to achieve an approximate 2.50 nanogram level of injected METASYSTOX-R Sulfone. Using this methodology recoveries of 81-106%, 90-106% and 84-105% were obtained for soil samples fortified at 0.5, 1.0 and 2.0 ppm METASYSTOX-R and METASYSTOX-R Sulfone, respectively.

RECOVERIES

The validity of the analytical method was demonstrated from Fresno, California 0-6" sandy loam soil (Mobay Sample Number 1001) fortified from 0.01 to 2.0 ppm with both METASYSTOX-R and METASYSTOX-R Sulfone. Recoveries ranged from a low of 74.7% to a high of 115.2% with an average recovery of 95.1% ± 12.3% (n = 16). Further validity of the method was demonstrated from Fresno, California sandy loam soil (Mobay Sample Numbers 1001 through 1007) and Chualar, California sandy loam soil samples (Mobay Sample Numbers 2001 through 2007) fortified with both METASYSTOX-R and METASYSTOX-R Sulfone at a residue level of 0.01 ppm for each 6 inch soil horizon representing zero to three foot depths as well as the three to four foot depths. Recoveries ranged from a low of 80.2% to a high of 136.4% with an average recovery of 95.1% ± 11.9% (n = 28).

Table III presents the complete method validation data for the determination of METASYSTOX-R and METASYSTOX-R Sulfone residues in soil and represents the recovery of METASYSTOX-R and METASYSTOX-R Sulfone from a 0-6" Fresno sandy loam soil horizon representing a 0.01 to 2.0 ppm residue range.

Table IV presents the complete method validation data for the determination of METASYSTOX-R and METASYSTOX-R Sulfone residue in soil as a function of soil depth. All soils were fortified at a residue level of 0.01 ppm for both METASYSTOX-R and METASYSTOX-R Sulfone.

Data outlined in Tables III and IV demonstrate reliability of the soil method from a limit of detection of 0.01 ppm to the analytical level of 2.0 ppm.

Data outlined in Table IV also demonstrate that the soil, which represents actual METASYSTOX-R soil dissipation sites at Fresno, California and Chualar, California, are free of any background interferences of METASYSTOX-R and METASYSTOX-R Sulfone. Data outlined in Table IV demonstrate no affect of soil depth versus recovery of METASYSTOX-R or METASYSTOX-R Sulfone at the screening level of the method.

Since Analytical Method: Colorado Analytical-1102-MSR uses a METASYSTOX-R Sulfone gas chromatographic standard for analysis, a comparison of that standard to an oxidized METASYSTOX-R standard was done. Three METASYSTOX-R standards, equivalent to 2.66 nanograms of METASYSTOX-R Sulfone injected into the gas chromatograph, were taken through the permanganate oxidation step of the analytical method and compared side by side with the METASYSTOX-R Sulfone gas chromatographic standard. Some enhancement of the oxidized standard was found with an overall comparison of oxidized METASYSTOX-R to the METASYSTOX-R Sulfone of 122.7%. One side by side comparison of the oxidized METASYSTOX-R to the METASYSTOX-R Sulfone was 99.7%.

CONCLUSIONS

The validity of this analytical method was demonstrated in the laboratories of Colorado Analytical Research & Development Corporation. Fresno, California 0-6" soil was fortified from 0.01 to 2.0 ppm with both METASYSTOX-R and METASYSTOX-R Sulfone. Recoveries ranged from a low of 74.7% to a high of 115.2% with an average recovery of 95.1% ± 12.3% (n = 16). Further validity of the method was demonstrated from Fresno, California and Chualar, California soil samples fortified with both METASYSTOX-R and METASYSTOX-R Sulfone at a residue level of 0.01 ppm for each 6 inch soil horizon representing zero to four foot depths. Recoveries ranged from a low of 80.2% to a high of 136.4% with an average recovery of 95.1% ± 11.9% (n = 28).

CERTIFICATION

To the best of my knowledge, there were no significant deviations from the Good Laboratory Practice Regulations which affected the quality or integrity of the study nor were there any deviations from the study protocol. This final report accurately reflects the raw data obtained from this study.

Approved and Submitted By: William D. Rhoads 7/24/89

William D. Rhoads, Ph.D. — Date
President
Study Director

LIST OF TABLES

TABLE I

CAPILLARY GAS CHROMATOGRAPHIC CONDITIONS

Instrument:	Hewlett-Packard Model 5880 Capillary Gas Chromatograph with Model 7672A or Model 7673A Automatic Sampler.
Carrier Gas:	Helium, flow adjusted to give 15 psi (1-2 cc per minute).
Makeup Gas:	Helium, 30 cc per minute.
Column:	J&W DB-5, 1.0 u, 0.32-mm I.D., 15 meters.
Injection:	Splitless.
Detector:	Nitrogen phosphorous specific.
Temperatures:	
Injector:	250°C
Detector:	275°C

Oven Program and Run Table

PROGRAM: (ANNOTATION OFF)

```
10    VALVE 5 ON
20    OVEN TEMP 60
30    OVEN TEMP EQUIB TIME 1
40    OVEN TEMP INITIAL VALUE 60
50    OVEN TEMP INITIAL TIME 1
60    OVEN TEMP PRGM RATE 30
70    OVEN TEMP FINAL VALUE 187
80    OVEN TEMP FINAL TIME 7
90    OVEN TEMP POST VALUE 187
100   OVEN TEMP POST TIME 5
110   ATTN 2↑10
120   CHART SPEED 0.1
```

(Continued on the following page)

TABLE I (continued)

CAPILLARY GAS CHROMATOGRAPHIC CONDITIONS

```
130   %OFFSET 15
140   RUN TIME ANNOTATION OFF
150   RUN TBL ANNOTATION OFF
160   REPORT ANNOTATION OFF
170   REPORT ON
180   OVEN TEMP ANNOTATION OFF
190   DELETE RUN TBL
200   DELETE REPORT TBL
210   PEAK WIDTH 0.087
220   THRESHOLD -1
230   RUN TIME 0 VALVE 5 ON
240   RUN TIME 0.1 INTG OFF
250   RUN TIME 0.5 VALVE 5 OFF
260   RUN TIME 7.74 CHART SPEED 2
270   RUN TIME 7.75 ATTN 2↑2
280   RUN TIME 7.76 INTG ON
290   RUN TIME 7.77 RUN TIME ANNOTATION ON
300   RUN TIME 7.78 ZERO
310   RUN TIME 11.5 VALVE 5 ON
320   RUN TIME 11.51 RUN TIME ANNOTATION OFF
330   EDIT AUTO SEQ 1,1
340   SIGNAL B DEVICE# 1
350   AREA%
360   REPORT TIME 0 REJECT 0.1
```

Volume Injected: 2 ul

Retention Time: 8.84 minutes ± 0.02 minute

TABLE II

LINEAR RESPONSE DATA

Analysis Location:
Colorado Analytical Research & Development Corporation
Analysis Method:
Colorado Analytical-1102-MSR
Analysis Type: Capillary Gas Chromatography

Matrix: Soil, 0-6", Fresno, CA

(Lab) Sample No.	Date ANALYZED	STD Conc (ppm) *	STD Response Intg Area	ppm Pound **	Matrix Present (Y/N)
76	5/5/89	0.000	<0.10	0.000	Y
77	5/5/89	0.005	3.89	0.067	Y
78	5/5/89	0.010	7.75	0.069	Y
79	5/5/89	0.050	53.13	0.094	Y
80	5/5/89	0.100	109.35	0.124	Y
81	5/5/89	0.200	228.44	0.189	Y
82	5/5/89	0.250	323.67	0.240	Y
83	5/5/89	0.625	898.42	0.552	Y
84	5/5/89	1.250	1934.04	1.113	Y
85	5/5/89	2.500	4484.94	2.495	Y
86	5/5/89	5.000	9190.95	5.045	Y

* Measured as ppm relative to matrix
** Back calculated by Least Squares Linear Regression

Regression Output:

Constant	-120.1275
Std Err of Y Est	46.9597
R Squared	0.9984
No. of Observations	10
Degrees of Freedom	9
X Coefficient(s)	1845.4310
Std Err of Coef.	25.7267

Entered by: M. Varney Date: 7/20/89
Reviewed by: K R Weisenfluh Date: 7/24/89

TABLE III

METASYSTOX-R and METASYSTOX-R Sulfone in Soil,
0-6", 0.01 to 2.0 ppm

Analysis Location: Colorado Analytical Research & Development Corporation
Analysis Method: Colorado Analytical-1102-MSR
Analysis Type: Capillary Gas Chromatography

Matrix: Soil from Fresno, CA

(Lab) Sample No.	MOBAY Soil Number	Soil Depth, in.	Compound	Dates EXTN	Dates ANALYSIS	Sample Wt (g)	Final Vol (mL)	Dil Factor	Raw Data Integrator Area SAMPLE	Raw Data Integrator Area STANDARD	STD Mg Inj *	Gross Residue (ppm)	Conc Added (ppm)	% Recovery
STD			SULFONE		5/5/89					108.03	2.50			
87 CNTROL for SULF	1001	0-6	none	5/3/89	5/5/89	25.00	2.00		<0.1			<0.00009	0.00	---
87 CONTROL for MSR	1001	0-6	none	5/3/89	5/5/89	25.00	2.00		<0.1			<0.00008	0.00	---
STD			SULFONE		5/5/89					112.76	2.50			
88 CTRL+0.01 SULF	1001	0-6	MSR/SULF	5/3/89	5/5/89	25.00	2.00		9.87			0.009	0.01	93.2
88 CTRL+0.01 MSR	1001	0-6	MSR/SULF	5/3/89	5/5/89	25.00	2.00		10.49			0.009	0.01	93.1
STD			SULFONE		5/5/89					120.75	2.50			
89 CTRL+0.01 SULF	1001	0-6	MSR/SULF	5/3/89	5/5/89	25.00	2.00		11.29			0.011	0.01	106.6
89 CTRL+0.01 MSR	1001	0-6	MSR/SULF	5/3/89	5/5/89	25.00	2.00		8.41			0.007	0.01	74.7
STD			SULFONE		5/5/89					116.71	2.50			
90 CTRL+0.02 SULF	1001	0-6	MSR/SULF	5/3/89	5/5/89	25.00	2.00		23.61			0.022	0.02	111.5
90 CTRL+0.02 MSR	1001	0-6	MSR/SULF	5/3/89	5/5/89	25.00	2.00		18.23			0.016	0.02	80.9
STD			SULFONE		5/5/89					108.75	2.50			
91 CTRL+0.05 SULF	1001	0-6	MSR/SULF	5/3/89	5/5/89	25.00	2.00		60.99			0.058	0.05	115.2
91 CTRL+0.05 MSR	1001	0-6	MSR/SULF	5/3/89	5/5/89	25.00	2.00		48.11			0.043	0.05	85.4
STD			SULFONE		5/5/89					101.76	2.50			
92 CTRL+0.10 SULF	1001	0-6	MSR/SULF	5/3/89	5/5/89	25.00	2.00		104.85			0.099	0.10	99.0
92 CTRL+0.10 MSR	1001	0-6	MSR/SULF	5/3/89	5/5/89	25.00	2.00		102.67			0.091	0.10	91.1
STD			SULFONE		5/5/89					109.63	2.50			
STD			SULFONE		5/5/89					104.79	2.50			
STD			SULFONE		5/5/89					127.54	2.50			
STD			SULFONE		5/5/89					115.78	2.50			

MSR = METASYSTOX-R, found in 100% fraction
SULF = METASYSTOX-R Sulfone, found in 50% fraction
* Nanograms injected from 2 microliters, METASYSTOX-R equivalent

Data calculation equations provided at end of Table III.

Entered by: M. Vaughn
Reviewed by: K. Weidenfeld

Date: 7/20/89
Date: 7/24/89

+ sulfone
+ MSR
+ sulfone
+ MSR
+ MSR

TABLE III (continued)

METASYSTOX-R and METASYSTOX-R Sulfone in Soil,
0-6", 0.01 to 2.0 ppm

Analysis Location: Colorado Analytical Research & Development Corporation
Analysis Method: Colorado Analytical-1102-MSR
Analysis Type: Capillary Gas Chromatography

Matrix: Soil from Fresno, CA

(Lab) Sample No.	MOBAY Soil Number	Soil Depth, in.	Compound	Dates EXTN	Dates ANALYSIS	Sample Wt (g)	Final Vol (mL)	Dil Factor	Raw Data Integrator Area SAMPLE	Raw Data Integrator Area STANDARD	STD Ng Inj *	Gross Residue (ppm)	Conc Added (ppm)	% Recovery
STD			SULFONE		5/10/89					218.79	2.50			
93 CTRL+0.50 SULF	1001	0-6	MSR/SULF	5/3/89	5/10/89	25.00	2.00	5.00	228.23			0.532	0.50	106.4
93 CTRL+0.50 MSR	1001	0-6	MSR/SULF	5/3/89	5/10/89	25.00	2.00	5.00	183.76			0.402	0.50	80.5
STD			SULFONE		5/10/89					241.59	2.50			
94 CTRL+1.0 SULF	1001	0-6	MSR/SULF	5/3/89	5/10/89	25.00	2.00	10.00	227.08			1.058	1.00	105.8
94 CTRL+1.0 MSR	1001	0-6	MSR/SULF	5/3/89	5/10/89	25.00	2.00	10.00	204.20			0.895	1.00	89.5
STD			SULFONE		5/10/89					219.05	2.50			
95 CTRL+2.0 SULF	1001	0-6	MSR/SULF	5/3/89	5/10/89	25.00	2.00	20.00	224.68			2.095	2.00	104.7
95 CTRL+2.0 MSR	1001	0-6	MSR/SULF	5/3/89	5/10/89	25.00	2.00	20.00	191.35			1.677	2.00	83.8
STD			SULFONE		5/10/89					233.66	2.50			

MSR = METASYSTOX-R, found in 100% fraction
SULF = METASYSTOX-R Sulfone, found in 50% fraction
* Nanograms injected from 2 microliters, METASYSTOX-R equivalent

Data calculation equations provided at end of table.

Entered by: M. Verhey Date: 7/20/89
Reviewed by: K. Weinmiller Date: 7/24/89

TABLE III (continued)

CALCULATIONS

MSR = METASYSTOX-R, found in 100% fraction
SULF = METASYSTOX-R Sulfone, found in 50% fraction

$$\text{Ng Found} = \frac{\text{Integrator Area, sample}}{\text{Average Integrator Area, standard}} \times \text{correction factor}$$

correction factor = 2.5 for MSR, = 2.66 for SULF.
Reflects STD Ng injected for standard of interest.

$$\frac{\text{Ng Found}}{\text{Sample Weight (g)}} \times \text{Dil Factor} = \text{Gross Residue (ppm)}$$

Dil factor = 1 unless noted otherwise.

$$\% \text{ Recovery} = \frac{\text{Gross Residue (ppm)}}{\text{Conc added (ppm)}}$$

TABLE IV

METASYSTOX-R and METASYSTOX-R Sulfone in Soil,
0-42", 0.01 ppm

Analysis Location: Colorado Analytical Research & Development Corporation
Analysis Method: Colorado Analytical-1102-MSR
Analysis Type: Capillary Gas Chromatography

Matrix: Soil from Fresno, CA

(Lab) Sample No.	MOBAY Soil Number	Soil Depth, in.	Compound	Dates EXTN	Dates ANALYSIS	Sample Wt (g)	Final Vol (mL)	Dil Factor	Raw Data Integrator Area SAMPLE	Raw Data Integrator Area STANDARD	STD Ng Inj *	Gross Residue (ppm)	Conc Added (ppm)	% Recovery
STD			SULFONE		5/6/89					92.68	2.50			
96 CNTROL for SULF	1001	0-6	none	5/4/89	5/6/89	25.00	2.00		<0.1			<0.0001	0.00	---
96 CONTROL for MSR	1001	0-6	none	5/4/89	5/6/89	25.00	2.00		1.12			0.001	0.00	---
STD			SULFONE		5/6/89					110.04	2.50			
97 CTRL+0.01 SULF	1001	0-6	MSR/SULF	5/4/89	5/6/89	25.00	2.00		10.84			0.012	0.01	120.2 + Sulfa
97 CTRL+0.01 MSR	1001	0-6	MSR/SULF	5/4/89	5/6/89	25.00	2.00		9.78			0.010	0.01	101.9 + MSR
STD			SULFONE		5/6/89					105.19	2.50			
98 CNTROL for SULF	1002	6-12	none	5/4/89	5/6/89	25.00	2.00		<0.1			<0.0001	0.00	---
98 CONTROL for MSR	1002	6-12	none	5/4/89	5/6/89	25.00	2.00		<0.1			<0.0001	0.00	---
STD			SULFONE		5/6/89					96.49	2.50			
99 CTRL+0.01 SULF	1002	6-12	MSR/SULF	5/4/89	5/6/89	25.00	2.00		8.62			0.010	0.01	95.6 + SULFa
99 CTRL+0.01 MSR	1002	6-12	MSR/SULF	5/4/89	5/6/89	25.00	2.00		9.47			0.010	0.01	98.7 + MSR
STD			SULFONE		5/6/89					90.00	2.50			
100 CNTRL for SULF	1003	12-18	none	5/4/89	5/5/89	25.00	2.00		<0.1			<0.0001	0.00	---
100 CNTROL for MSR	1003	12-18	none	5/4/89	5/6/89	25.00	2.00		<0.1			<0.0001	0.00	---
STD			SULFONE		5/6/89					100.89	2.50			
101 CTRL+0.01 SULF	1003	12-18	MSR/SULF	5/4/89	5/6/89	25.00	2.00		8.49			0.009	0.01	94.1 - SULFa
101 CTRL+0.01 MSR	1003	12-18	MSR/SULF	5/4/89	5/6/89	25.00	2.00		9.07			0.009	0.01	94.5 - MSR
STD			SULFONE		5/6/89					84.86	2.50			

(continued on next page)

Data calculation equations provided at end of table.

MSR = METASYSTOX-R, found in 100% fraction
SULF = METASYSTOX-R Sulfone, found in 60% fraction
* Nanograms injected from 2 microliters, METASYSTOX-R equivalent

Entered by: M. Smith Date: 7/20/89
Reviewed by: K.W. Eisenfluh Date: 7/24/89

TABLE IV (continued)

METASYSTOX-R and METASYSTOX-R Sulfone in Soil,
0-42", 0.01 ppm

Analysis Location: Colorado Analytical Research & Development Corporation
Analysis Method: Colorado Analytical-1102-MSR
Analysis Type: Capillary Gas Chromatography

Matrix: Soil from Fresno, CA

(lab) Sample No.	MOBAY Soil Number	Soil Depth, in.	Compound	Dates EXTN	Dates ANALYSIS	Sample Wt (g)	Final Vol (mL)	Dil Factor	Raw Data Integrator Area SAMPLE	Raw Data Integrator Area STANDARD	STD Ng inj *	Gross Residue (ppm)	Conc Added (ppm)	% Recovery
continued from previous page														
102 CNTRL for SULF	1004	18-24	none	5/4/89	5/6/89	25.00	2.00		<0.1			<0.0001	0.00	---
102 CNTROL for MSR	1004	18-24	none	5/4/89	5/6/89	25.00	2.00		<0.1			<0.0001	0.00	---
STD			SULFONE		5/6/89					97.50	2.50			
103 CTRL+0.01 SULF	1004	18-24	MSR/SULF	5/4/89	5/6/89	25.00	2.00		8.59			0.010	0.01	95.2 — Sulfn
103 CTRL+0.01 MSR	1004	18-24	MSR/SULF	5/4/89	5/6/89	25.00	2.00		8.14			0.008	0.01	(84.8) — MSR
STD			SULFONE		5/6/89					92.60	2.50			
104 CNTRL for SULF	1005	24-30	none	5/4/89	5/6/89	25.00	2.00		<0.1			<0.0001	0.00	---
104 CNTROL for MSR	1005	24-30	none	5/4/89	5/6/89	25.00	2.00		<0.1			<0.0001	0.00	---
STD			SULFONE		5/6/89					96.01	2.50			
105 CTRL+0.01 SULF	1005	24-30	MSR/SULF	5/4/89	5/6/89	25.00	2.00		7.27			0.008	0.01	80.6 — Sulfn
105 CTRL+0.01 MSR	1005	24-30	MSR/SULF	5/4/89	5/6/89	25.00	2.00		9.60			0.010	0.01	(100.0) — MSR
STD			SULFONE		5/6/89					89.17	2.50			
106 CNTRL for SULF	1006	30-36	none	5/4/89	5/6/89	25.00	2.00		<0.1			<0.0001	0.00	---
106 CNTROL for MSR	1006	30-36	none	5/4/89	5/6/89	25.00	2.00		<0.1			<0.0001	0.00	---
STD			SULFONE		5/6/89					91.19	2.50			
107 CTRL+0.01 SULF	1006	30-36	MSR/SULF	5/4/89	5/6/89	25.00	2.00		7.92			0.009	0.01	87.8 — Sulfn
107 CTRL+0.01 MSR	1006	30-36	MSR/SULF	5/4/89	5/6/89	25.00	2.00		8.21			0.009	0.01	(85.6) — MSR
STD			SULFONE		5/6/89					91.66	2.50			

continued on next page

MSR = METASYSTOX-R, found in 100% fraction
SULF = METASYSTOX-R Sulfone, found in 50% fraction
* Nanograms injected from 2 microliters, METASYSTOX-R equivalent

Data calculation equations provided at end of table.

Entered by: M. Vaught Date: 7/20/89
Reviewed by: K. Weissenfluh Date: 7/24/89

99118

TABLE IV (continued)

METASYSTOX-R and METASYSTOX-R Sulfone in Soil,
0-42", 0.01 ppm

Matrix: Soil from Fresno, CA

Analysis Location: Colorado Analytical Research & Development Corporation
Analysis Method: Colorado Analytical 1102-MSR
Analysis Type: Capillary Gas Chromatography

(Lab) Sample No.	MOBAY Soil Number	Soil Depth, in.	Compound	Dates EXTN	Dates ANALYSIS	Sample Wt (g)	Final Vol (mL)	Dil Factor	Raw Data Integrator Area SAMPLE	Raw Data Integrator Area STANDARD	STD Ng Inj *	Gross Residue (ppm)	Conc Added (ppm)	% Recovery
continued from previous page														
108 CNTRL for SULF	1007	36-46	none	5/4/89	5/6/89	25.00	2.00		<0.1			<0.0001	0.00	---
108 CNTROL for MSR	1007	36-46	none	5/4/89	5/6/89	25.00	2.00		<0.1			<0.0001	0.00	---
STD			SULFONE		5/6/89					94.70	2.60			
109 CTRL+0.01 SULF	1007	36-46	MSR/SULF	5/4/89	5/6/89	25.00	2.00		7.96			0.009	0.01	88.3 - SUL
109 CTRL+0.01 MSR	1007	36-46	MSR/SULF	5/4/89	5/6/89	25.00	2.00		7.96			0.008	0.01	83.0 - MSR
STD			SULFONE		5/6/89					97.46	2.50			

Average Recovery 93.6% + 10.1%

MSR = METASYSTOX-R, found in 100% fraction
SULF = METASYSTOX-R Sulfone, found in 50% fraction
* Nanograms injected from 2 microliters, METASYSTOX-R equivalent

Data calculation equations provided at end of table.

Entered by: M. Valley
Reviewed by: K.K. Weinmfluk

Date: 7/24/89
Date: 7/24/89

TABLE IV (continued)

METASYSTOX-R and METASYSTOX-R Sulfone in Soil,
0-42", 0.01 ppm

Matrix: Soil from Chualar, CA

Analysis Location: Colorado Analytical Research & Development Corporation
Analysis Method: Colorado Analytical-1102-MSR
Analysis Type: Capillary Gas Chromatography

(Lab) Sample No.	MOBAY Soil Number	Soil Depth, in.	Compound	Dates EXTN	Dates ANALYSIS	Sample Wt (g)	Final Vol (mL)	Dil Factor	Raw Data Integrator Area SAMPLE	Raw Data Integrator Area STANDARD	STD Ng Inj s	Gross Residue (ppm)	Conc Added (ppm)	% Recovery
STD			SULFONE		5/9/89					160.19	2.50			
110 CNTRL for SULF	2001	0-6	none	5/8/89	5/9/89	25.00	2.00		1.01			0.001	0.00	---
110 CNTROL for MSR	2001	0-6	none	5/8/89	5/9/89	25.00	2.00		<0.1			<0.00005	0.00	---
STD			SULFONE		5/9/89					210.83	2.50			
111 CTRL+0.01 SULF	2001	0-6	MSR/SULF	5/8/89	5/9/89	25.00	2.00		28.02			0.014	0.01	136.4 ~~MSR~~
111 CTRL+0.01 MSR	2001	0-6	MSR/SULF	5/8/89	5/9/89	25.00	2.00		17.54			0.009	0.01	86.4 MSR
STD			SULFONE		5/9/89					212.30	2.50			
112 CNTRL for SULF	2002	6-12	none	5/8/89	5/9/89	25.00	2.00		<0.1			<0.00005	0.00	---
112 CNTROL for MSR	2002	6-12	none	5/8/89	5/9/89	25.00	2.00		<0.1			<0.00005	0.00	---
STD			SULFONE		5/9/89					219.99	2.50			
113 CTRL+0.01 SULF	2002	6-12	MSR/SULF	5/8/89	5/9/89	25.00	2.00		19.87			0.010	0.01	104.2
113 CTRL+0.01 MSR	2002	6-12	MSR/SULF	5/8/89	5/9/89	25.00	2.00		18.38			0.009	0.01	90.8 MSR
STD			SULFONE		5/9/89					217.52	2.50			
114 CNTRL for SULF	2003	12-18	none	5/8/89	5/9/89	25.00	2.00		0.53			0.0003	0.00	---
114 CNTROL for MSR	2003	12-18	none	5/8/89	5/9/89	25.00	2.00		<0.1			<0.00005	0.00	---
STD			SULFONE		5/9/89					188.60	2.50			
116 CTRL+0.01 SULF	2003	12-18	MSR/SULF	5/8/89	5/9/89	25.00	2.00		18.02			0.009	0.01	94.5
115 CTRL+0.01 MSR	2003	12-18	MSR/SULF	5/8/89	5/9/89	25.00	2.00		21.06			0.010	0.01	103.8 MSR
STD			SULFONE		5/9/89					211.09	2.50			

continued on next page.

MSH = METASYSTOX-R, found in 100% fraction
MSF = METASYSTOX-R Sulfone, found in 50% fraction
Areas injected from 2 microliters, METASYSTOX-R equivalent

Data calculation equations provided at end of table.

M. Vaughn
Reviewed by

Date: 7/27/89
Date: 7/24/89

TABLE IV (continued)

METASYSTOX-R and METASYSTOX-R Sulfone in Soil,
0-42", 0.01 ppm

Matrix: Soil from Chualar, CA

Analysis Location: Colorado Analytical Research & Development Corporation
Analysis Method: Colorado Analytical-1102-MSR
Analysis Type: Capillary Gas Chromatography

(Lab) Sample No.	MOBAY Soil Number	Soil Depth, in.	Compound	Dates EXTN	Dates ANALYSIS	Sample Wt (g)	Final Vol (mL)	Dil Factor	Raw Data Integrator Area SAMPLE	Raw Data Integrator Area STANDARD	STD Ng Inj e	Gross Residue (ppm)	Conc Added (ppm)	% Recovery
continued from previous page														
116 CNTRL for SULF	2004	18-24	none	5/8/89	5/9/89	25.00	2.00		<0.1			<0.00005	0.00	---
116 CNTROL for MSR	2004	18-24	none	5/8/89	5/9/89	25.00	2.00		0.71			0.0003	0.00	---
STD			SULFONE		5/9/89					198.05	2.50			
117 CTRL+0.01 SULF	2004	18-24	MSR/SULF	5/8/89	5/9/89	25.00	2.00		18.34			0.010	0.01	96.2
117 CTRL+0.01 MSR	2004	18-24	MSR/SULF	5/8/89	5/9/89	25.00	2.00		19.80			0.010	0.01	97.6 + MSR
STD			SULFONE		5/9/89					198.96	2.50			
118 CNTRL for SULF	2005	24-30	none	5/8/89	5/9/89	25.00	2.00		<0.1			<0.00005	0.00	---
118 CNTROL for MSR	2005	24-30	none	5/8/89	5/9/89	25.00	2.00		<0.1			<0.00005	0.00	---
STD			SULFONE		5/9/89					184.14	2.50			
119 CTRL+0.01 SULF	2005	24-30	MSR/SULF	5/8/89	5/9/89	25.00	2.00		17.42			0.009	0.01	91.3
119 CTRL+0.01 MSR	2005	24-30	MSR/SULF	5/8/89	5/9/89	25.00	2.00		18.52			0.009	0.01	91.3 + MSR
STD			SULFONE		5/9/89					201.82	2.50			
120 CNTRL for SULF	2006	30-36	none	5/8/89	5/9/89	25.00	2.00		<0.1			<0.00005	0.00	---
120 CNTROL for MSR	2006	30-36	none	5/8/89	5/9/89	25.00	2.00		<0.1			<0.00005	0.00	---
STD			SULFONE		5/9/89					209.03	2.50			
121 CTRL+0.01 SULF	2006	30-36	MSR/SULF	5/8/89	5/9/89	25.00	2.00		18.51			0.010	0.01	102.3
121 CTRL+0.01 MSR	2006	30-36	MSR/SULF	5/8/89	5/9/89	25.00	2.00		16.71			0.008	0.01	82.3 + MSR
STD			SULFONE		5/9/89					200.98	2.50			

continued on next page

MSR = METASYSTOX-R, found in 100% fraction
SULF = METASYSTOX-R Sulfone, found in 80% fraction
a Nanograms injected from 2 microliters, METASYSTOX-R equivalent

Data calculation equations provided at end of table.

Entered by: M. Vorhees
Reviewed by: A.R. Weissenfluh

Date: 7/20/89
Date: 11/4/89

99118

TABLE IV (continued)

METASYSTOX-R and METASYSTOX-R Sulfone in Soil,
0-42", 0.01 ppm

Analysis Location: Colorado Analytical Research & Development Corporation
Matrix: Soil from Chualar, CA
Analysis Method: Colorado Analytical-1102-MSR
Analysis Type: Capillary Gas Chromatography

(Lab) Sample No.	MOBAY Soil Number	Soil Depth, in.	Compound	Dates EXTN	Dates ANALYSIS	Sample Wt (g)	Final Vol (mL)	Dil Factor	Raw Data Integrator Area SAMPLE	Raw Data Integrator Area STANDARD	STD Ng Inj *	Gross Residue (ppm)	Conc Added (ppm)	% Recovery
continued from previous page														
122 CNTRL for SULF	2007	36-42	none	5/8/89	5/9/89	25.00	2.00		<0.1			<0.00005	0.00	---
122 CNTROL for MSR	2007	36-42	none	5/8/89	5/9/89	25.00	2.00		<0.1			<0.00005	0.00	---
STD			SULFONE		5/9/89					207.86	2.50			
123 CTRL+0.01 SULF	2007	36-42	MSR/SULF	5/8/89	5/9/89	25.00	2.00		18.32			0.010	0.01	96.0
123 CNTRL+0.01 MSR	2007	36-42	MSR/SULF	5/8/89	5/9/89	25.00	2.00		16.28			0.008	0.01	80.2 MSR
STD			SULFONE		5/9/89					225.02	2.50			
					Data calculation equations provided at end of table.						Average Recovery			96.7% + 13.6%

MSR = METASYSTOX-R, found in 100% fraction
SULF = METASYSTOX-R Sulfone, found in 50% fraction
* Nanograms injected from 2 microliters, METASYSTOX-R equivalent

Entered by: M. Sorley Date: 7/20/89
Reviewed by: KR Weissenfluh Date: 7/24/89

TABLE IV (continued)

CALCULATIONS

MSR = METASYSTOX-R, found in 100% fraction
SULF = METASYSTOX-R Sulfone, found in 50% fraction

$$\text{Ng Found} = \frac{\text{Integrator Area, sample}}{\text{Average Integrator Area, standard}} \times \text{correction factor}$$

correction factor = 2.5 for MSR, = 2.66 for SULF.
Reflects STD Ng injected for standard of interest.

$$\frac{\text{Ng Found}}{\text{Sample Weight (g)}} \times \text{Dil Factor} = \text{Gross Residue (ppm)}$$

Dil Factor = 1 unless noted otherwise.

$$\% \text{ Recovery} = \frac{\text{Gross Residue (ppm)}}{\text{Conc added (ppm)}}$$

LIST OF FIGURES

Figure 1

FLOW DIAGRAM FOR THE DETERMINATION OF METASYSTOX-R AND METASYSTOX-R SULFONE IN SOIL

25 gm soil sample

↓

Shake at 2500 rpm for 30 minutes with 250 ml 10% water/90% acetone

↓

Vacuum filter using Whatman #1 paper

↓

Wash filter cake with 25 ml 10% water/90% acetone

↓

Transfer total sample to a 500 ml round bottom flask

↓

Add 25 ml water

↓

Rotovap to water phase (~50 ml) at 35°C

↓

Transfer water phase to 250 ml separatory funnel

↓

Partition with 150 ml hexane

Discard hexane ←

↓

Add 5 ml saturated sodium chloride solution
Partition 3 times with 50 ml chloroform
Drain chloroform through anhydrous sodium sulfate
Rinse sodium sulfate with 25 ml chloroform

Discard water phase ←

↓

Rotovap just to dryness (blow off residual chloroform with nitrogen)

↓

Dissolve residue in 5 ml 50/50 acetone/hexane solution

↓

Prewash silica gel sep-pak with 20 ml hexane

Discard hexane rinse ←

↓

Place collection flask under sep-pak
Transfer sample to sep-pak

↓

Rinse sample container 2 times with 5 ml 50/50 acetone/hexane solution and run each rinse through sep-pak
The resultant sep-pak eluant, Eluant 1, contains METASYSTOX-R Sulfone

↓

Figure 1 (continued)

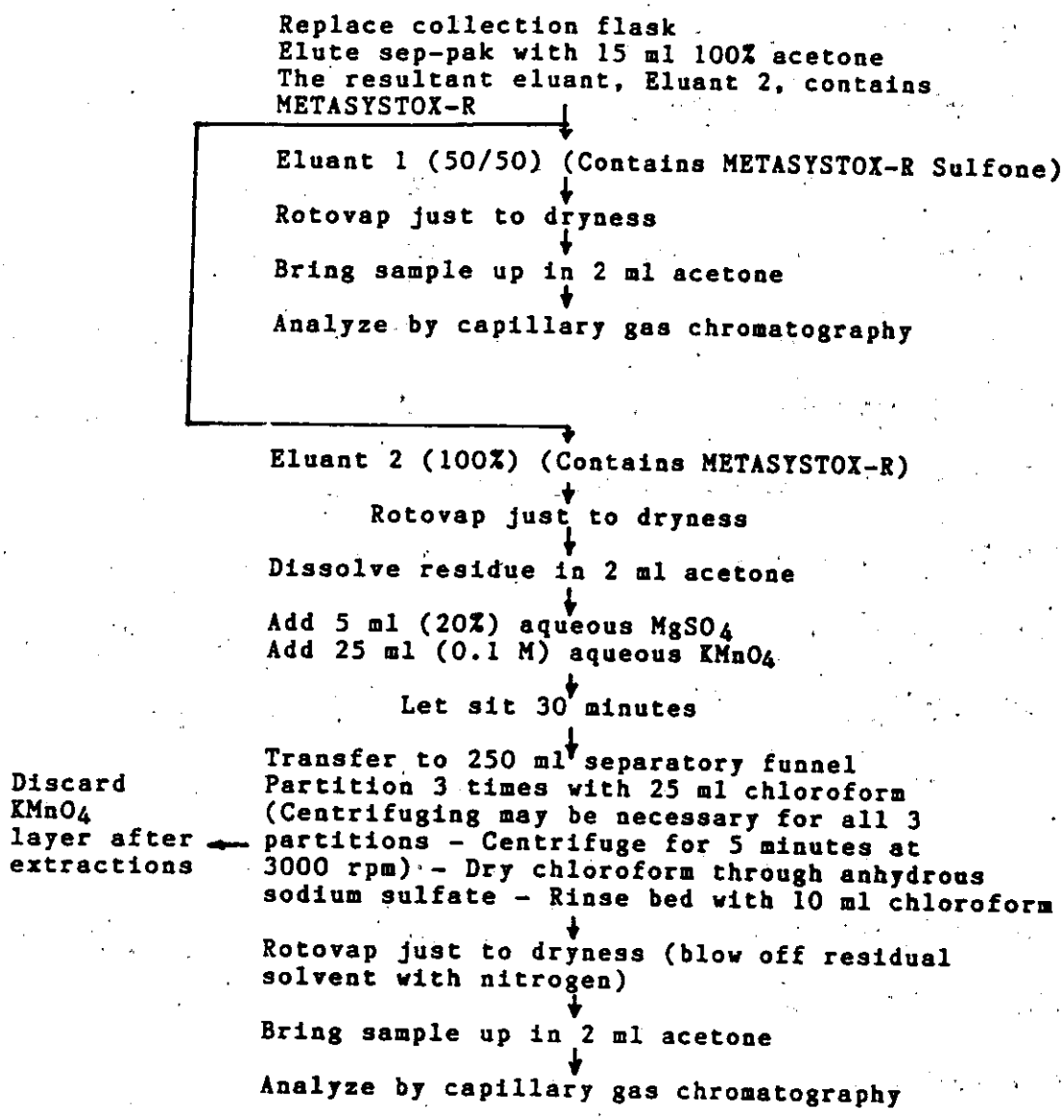
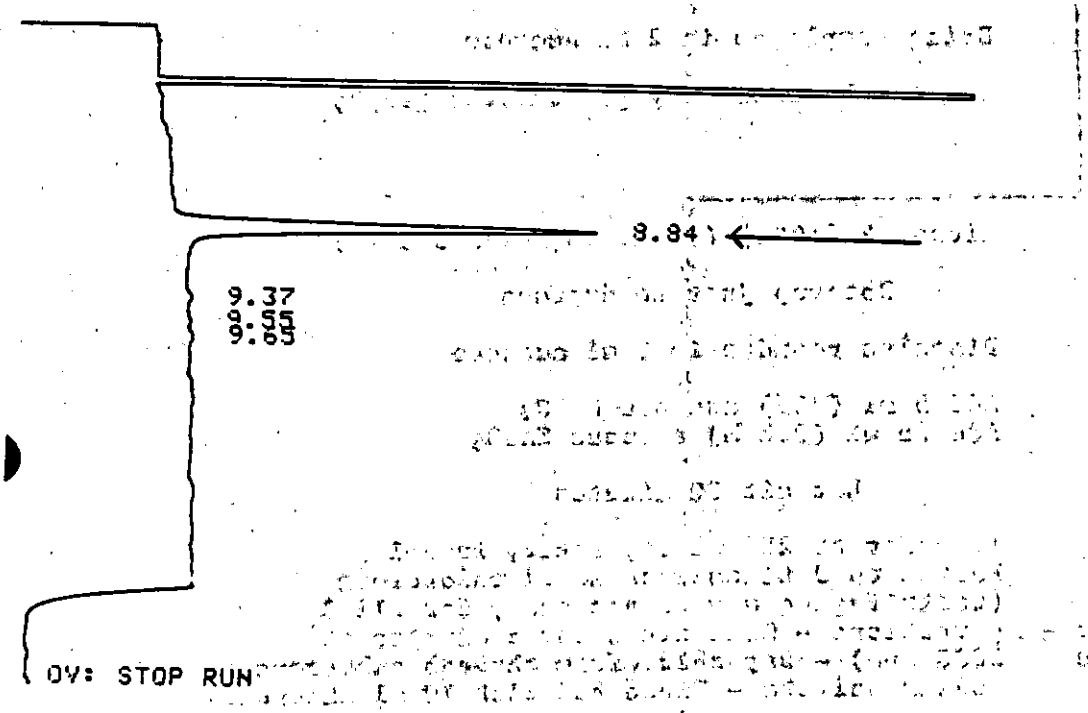


Figure 2

TYPICAL GAS CHROMATOGRAMS

2.50 ng Equivalent METASYSTOX-R as METASYSTOX-R Sulfone



OV: STOP RUN

5880A SAMPLER INJECTION @ 08:51 MAY 6, 1989

SAMPLE # : ID CODE :

45 2.5 ng STD

:A %

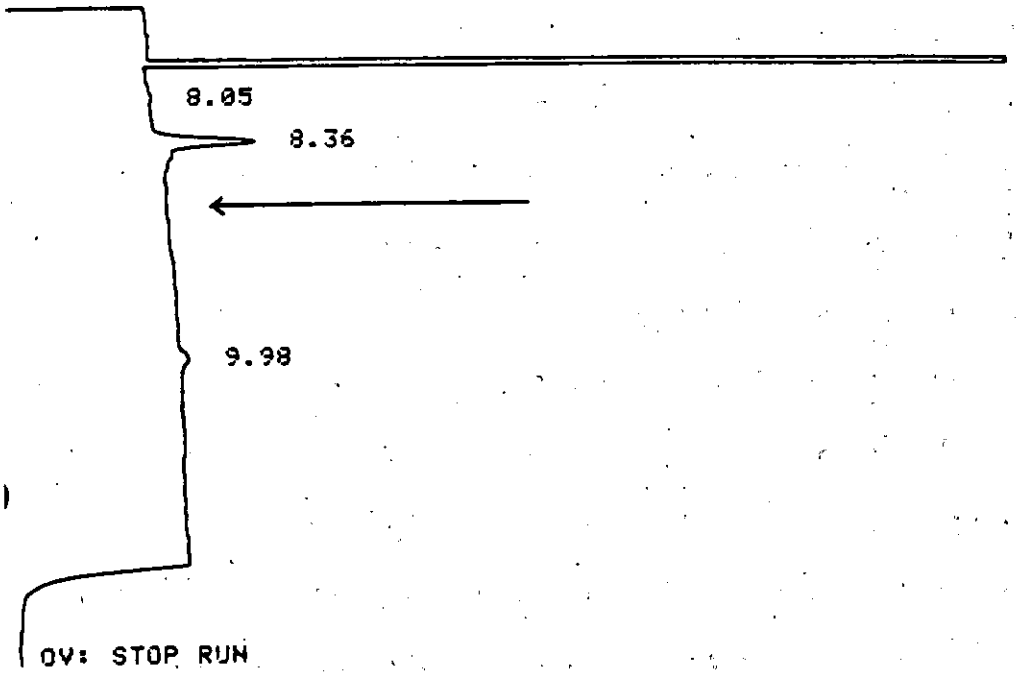
RT	AREA	TYPE	AREA %
3.84	110.04	BB	98.261
9.37	0.93	BB	0.832
9.55	0.26	BB	0.229
9.65	0.76	BB	0.679

TAL AREA = 111.99

.TIPLIER = 1

Figure 2 (continued)

Control Soil, METASYSTOX-R Sulfone Fraction



OV: STOP RUN

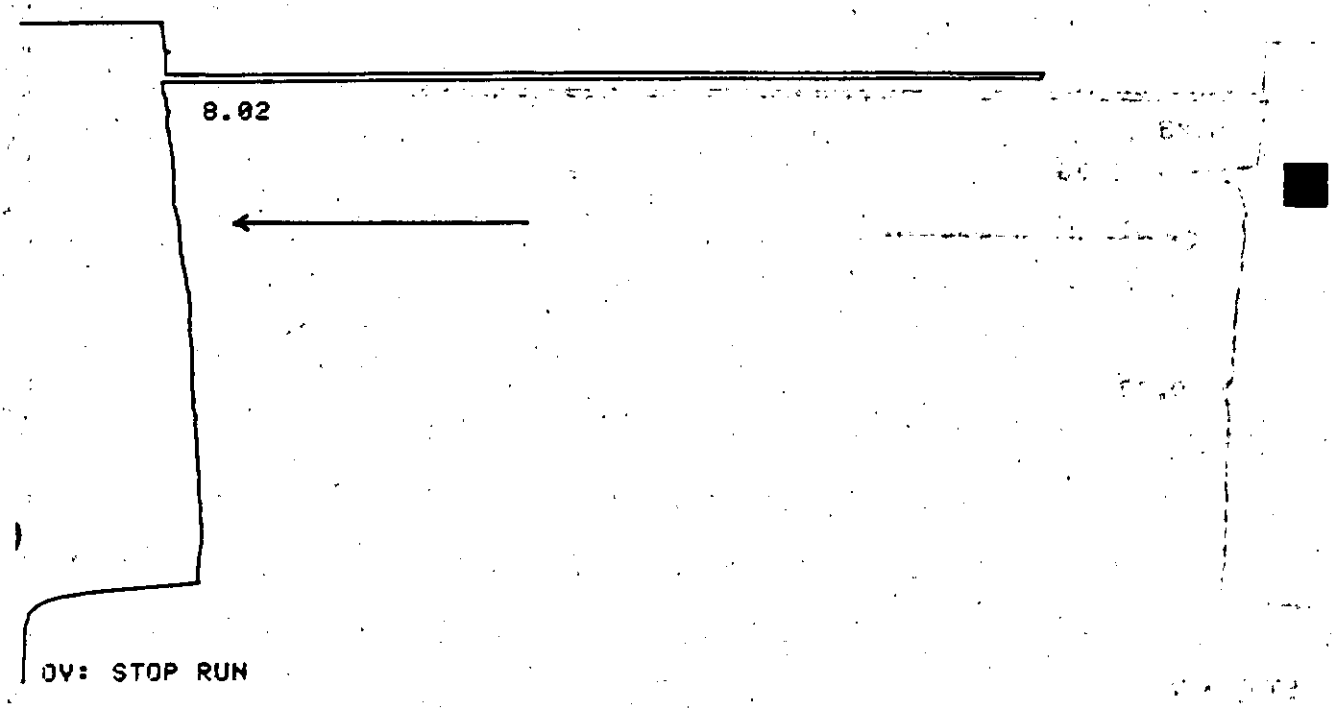
5880A SAMPLER INJECTION @ 10:22 MAY 6, 1989
AMPLE # : ID CODE :
49 98-50 % Fraction Mobay Soil #1001, 0-6"
A %

RT	AREA	TYPE	AREA %
.05	0.94	BB	3.326
.36	24.79	BV	87.579
.98	2.57	BB	9.095

AL AREA = 28.31
TIPLIER = 1

Figure 2 (continued)

Control Soil, METASYSTOX-R Fraction



OV: STOP RUN

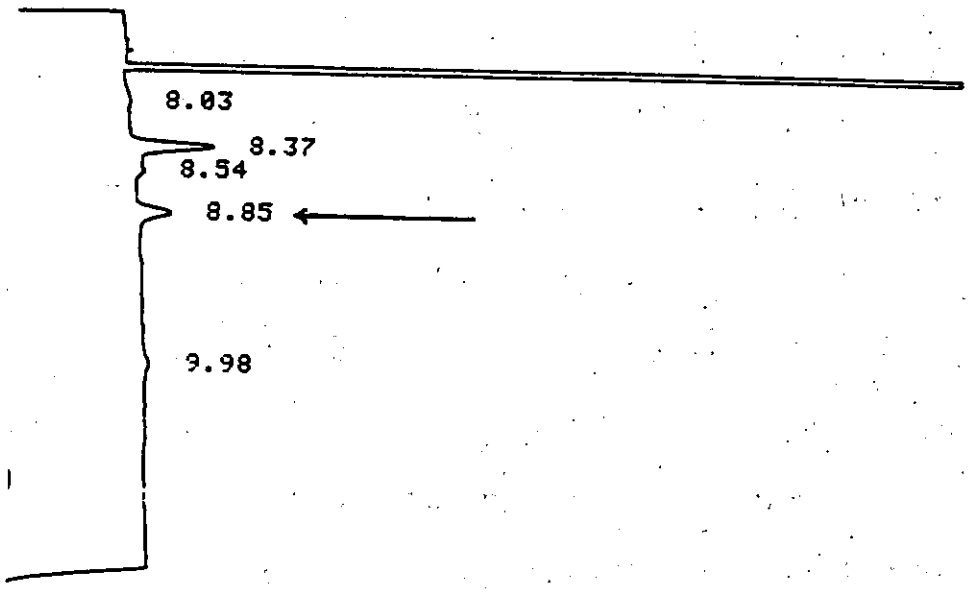
>] 5880A SAMPLER INJECTION @ 10:45 MAY 6, 1989
SAMPLE # : ID CODE :
50 98-100% Fraction Mobay Soil #1001, 0-6"
EA %

RT	AREA	TYPE	AREA %
3.02	0.28	BB	100.000

TAL AREA = 0.28
LTIPLIER = 1

Figure 2 (continued)

Control Soil + 0.01 ppm METASYSTOX-R Sulfone
95.6% Recovery



)V: STOP RUN

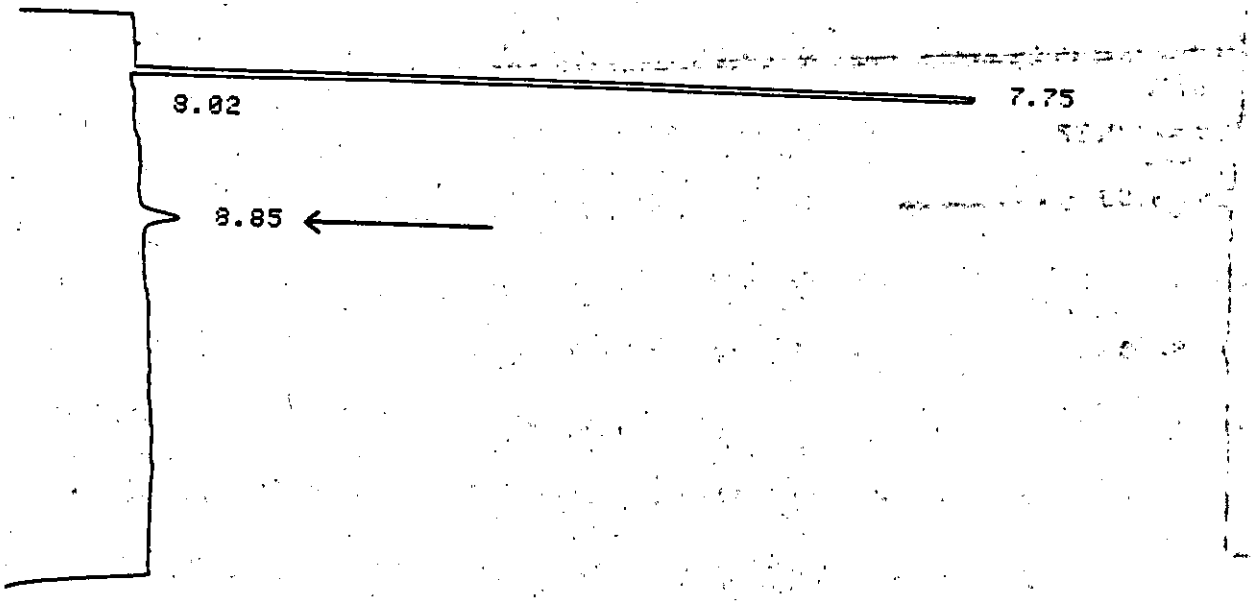
5880A SAMPLER INJECTION @ 11:30 MAY 6, 1989
1PLE # : ID CODE :
52 99-50% Fraction Mobay Soil #1001, 0-6"
%

T	AREA	TYPE	AREA %
33	1.40	BB	4.599
37	18.24	BV	59.818
54	0.76	BB	2.488
35	8.62	BB	28.287
98	1.47	BB	4.809

L AREA = 30.49
IPLIER = 1

Figure 2 (continued)

Control Soil + 0.01 ppm METASYSTOX-R
98.7% Recovery



DV: STOP RUN

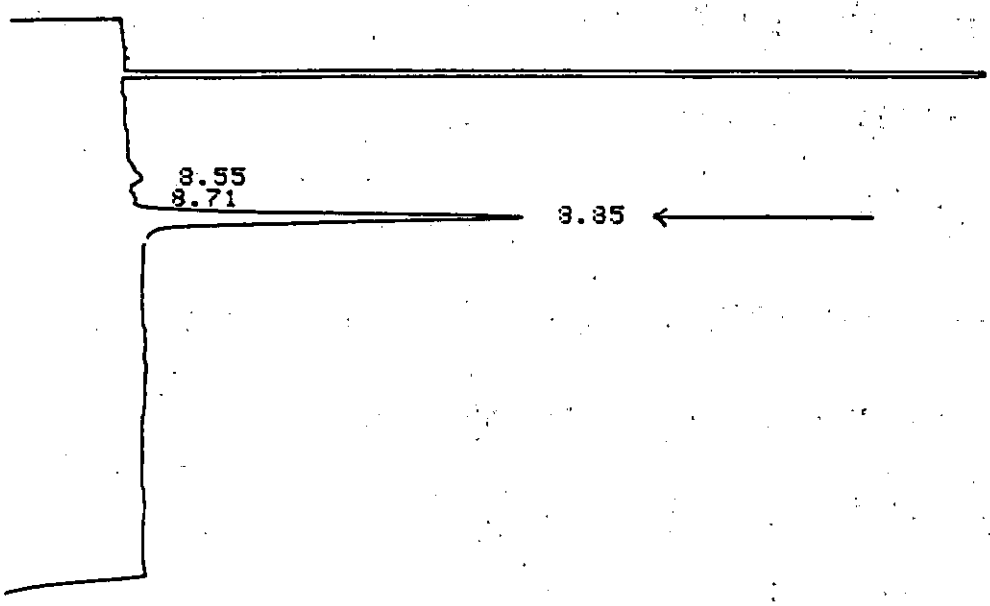
5880A SAMPLER INJECTION @ 11:53 MAY 6, 1989
IPLE # : ID CODE :
53 99-100% Fraction Mobay Soil #1001, 0-6"
%

	AREA	TYPE	AREA %
5	0.42	BB	4.122
2	0.19	BB	1.853
5	9.47	BB	94.025

AREA = 10.07
PLIER = 1

Figure 2 (continued)

Control Soil + 0.1 ppm METASYSTOX-R Sulfone
99.0% Recovery



OV: STOP RUN

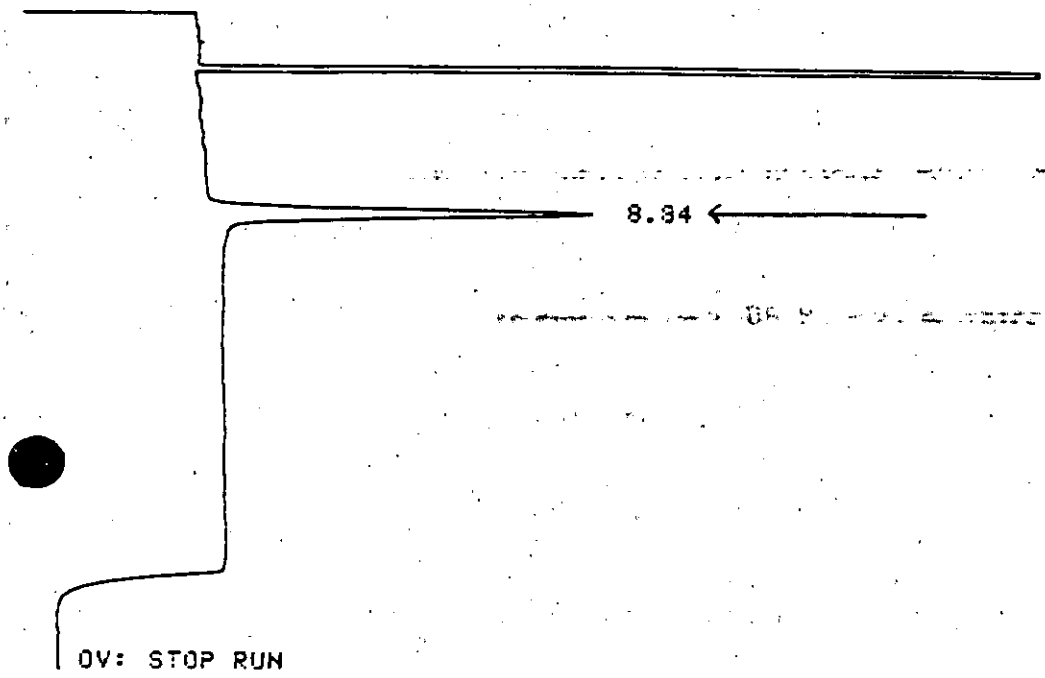
5880A SAMPLER INJECTION @ 21:33 MAY 5, 1989
MPLE # : ID CODE :
17 92-50% Fraction Mobay Soil#1001, 0-6"
%

T	AREA	TYPE	AREA %
55	4.34	BB	3.952
71	0.63	BV	0.571
85	104.85	VB	95.477

L AREA = 109.82
IPLIER = 1

Figure 2 (continued)

Control Soil + 0.1 ppm METASYSTOX-R
91.1% Recovery

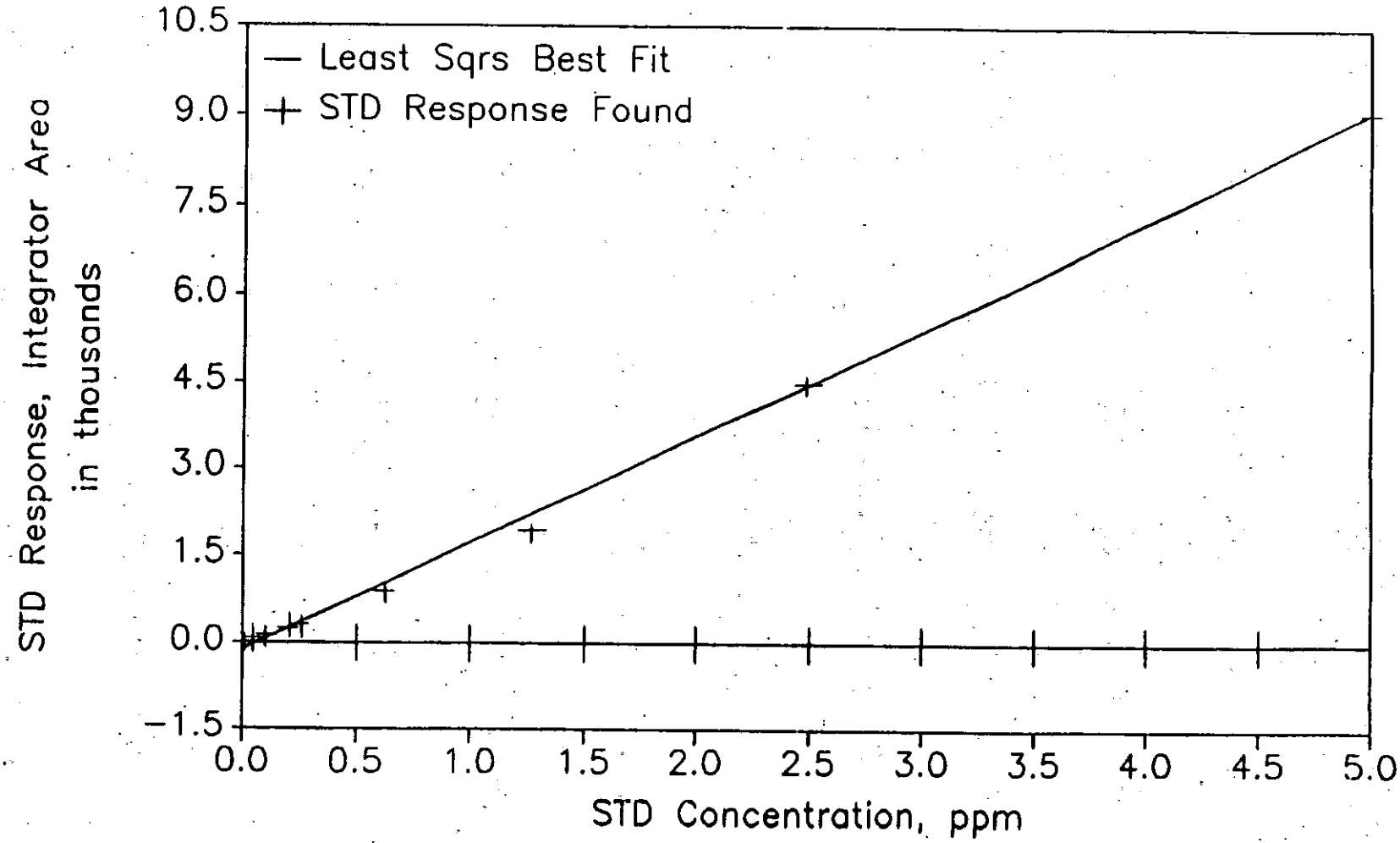


[hp] 5880A SAMPLER INJECTION @ 21:55 MAY 5, 1989
SAMPLE # : ID CODE :
18 92-100% Fraction Mobay Soil #1001, 0-6"
AREA %

RT	AREA	TYPE	AREA %
8.84	102.67	BB	100.000

TOTAL AREA = 102.67
MULTIPLIER = 1

FIGURE 3
LINEARITY OF METASYSTOX-R Sulfone in
FRESNO, CA SANDY LOAM SOIL



0.005 to 5.0 ppm standard curve.

LIST OF APPENDICES

APPENDIX 1

ATTACHMENT I

BIOCHEMISTRY STUDY SPECIFICATIONS

SUBJECT STUDY: METASYSTOX-R Analytical Method Development

1. Colorado Analytical Research and Development Corp., Colorado Springs, CO (Colorado Analytical) will provide Mobay with reports of progress of the subject study in the following manner:

   a) Weekly, verbal and/or written summary of highlights of results;

   b) Written monthly progress reports of all data generated during the testing periods unless advised to the contrary by Mobay;

   c) Final complete report of the subject study when the study is finished or otherwise terminated.

2. The information provided by Mobay to Colorado Analytical as well as the information developed by Colorado Analytical for Mobay in the course of conduct of the subject study is confidential and shall only be disclosed to those in the Colorado Analytical organization on a need to know basis. The personnel of Colorado Analytical who receive or develop the information will be advised by the study director as to its confidential nature and of their obligation to maintain secrecy of the information. Colorado Analytical shall make no use of the information except in the development of the methodology and/or the evaluation of the results as specifically required for and by Mobay. Colorado Analytical shall not disclose the information to a third party without the express written consent of Mobay. At the end of the testing and reporting periods, Colorado Analytical will return all written confidential information generated by Colorado Analytical for Mobay.

3. Colorado Analytical and its agents shall notify and assign to Mobay all rights and interests to any and all patentable inventions which may occur as a direct result of work by Colorado Analytical for Mobay in the course of conduct of the subject study.

4. The study shall be performed hereunder by Colorado Analytical in complete conformity with the protocol and/or testing requirements as specified by Mobay. Colorado Analytical shall call to the attention of Mobay upon discovery, any testing procedure or practice utilized which is not in full compliance or conformity as specified in the study protocol or testing requirements.

APPENDIX 1 (continued)

5. If during the conduct of the subject study, information becomes available to indicate that further work is unnecessary, then in such event, Mobay shall have the right to terminate such work by Colorado Analytical by providing notice to Colorado Analytical in writing, and Mobay shall have no obligations hereunder except to pay Colorado Analytical for the work that has been performed on a pro-rata basis to date.

The BIOCHEMISTRY STUDY SPECIFICATIONS described above are accepted by Colorado Analytical for development of a METASYSTOX-R analytical method.

BY: William D. Woods of Colorado Analytical

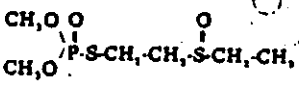
DATE: August 12, 1988

Determination of Residues of Metasystox-R and Metabolite in Plant and Animal Tissues and Soil

John S. Thornton,* Thomas J. Olson, and Klaus Wagner[1]

A gas chromatographic procedure is described for the analysis of residues of Metasystox-R and its sulfone metabolite in a wide variety of plant and animal tissues and soil. Varied extraction procedures are described for most efficient removal of residues from specific samples of differing physical characteristics. Following this, residues are partitioned into water and then extracted into chloroform, taking advantage of the dual solubility characteristics of the compounds to effect cleanup. The extract is oxidized to convert all active residues to the sulfone, which is then measured by gas chromatography with alkali-flame detection. Recovery for all sample types is generally 80–100% with limit of sensitivity at least 0.01 ppm.

Metasystox-R, *S*-[2-(ethylsulfinyl)ethyl] *O,O*-dimethyl phosphorothioate, sometimes called oxydemeton methyl or methylisosystox sulfoxide, is a systemic organophosphate insecticide exhibiting marked specificity in its action against aphids, mites, leafhoppers and similar plant sucking insects. It is also unique because of its total water solubility as well as being soluble in most organic solvents. The structural formula is:



Early metabolism studies have well documented the oxidative conversion of Systox and Metasystox-type compounds in biological systems (Muhlmann and Tietz, 1956; Tietz, 1960). The primary concern in developing a suitable residue analysis method for Metasystox-R was to account for the parent compound and its oxidative metabolite with adequate sensitivity and specificity.

The earliest residue analysis procedure for Metasystox compounds was a cholinesterase inhibition method developed by Hensel (1954) for Systox residues. This was unsatisfactory, however, due to the low inhibitory effect of the Metasystox compounds. Later, Laws and Webley (1959) developed a total phosphorus colorimetric procedure for Metasystox residues in plant material.

A number of workers have identified residue amounts of Metasystox-R in the presence of other organophosphorus compounds using thin-layer chromatography, including Eichenberger and Gay (1960), Ragab (1967), Smart and Hill (1967), Guth (1967), and Getz and Wheeler (1968).

Infrared spectroscopy (IR) has been used as a method of quantitation for Metasystox-R. Crosby and Laws (1964) used preparative gas chromatography to separate residues of Metasystox-R from crop extractives prior to measurement by IR.

Gas chromatography has recently become of interest for Metasystox-R residue analysis. Its advantage of sensitivity and specificity over the total phosphorus and other nonspecific methods was obvious. Burke and Holswade (1966) chromatographed Metasystox-R on a mixed phase column of 15% QF-1 and 10% DC 200 on Gas Chrom Q but found it necessary to inject 2000–3000 ng for suitable response with electron-capture detection. Bowman et al. (1969) reported their published method for disulfoton and metabolites in tobacco plants would also detect Metasystox-R and its sulfone, although the procedure was not tested with crop samples. McCully (1970) recognized the entire demeton group of compounds could be analyzed by the disulfoton residue procedure of Thornton and Anderson (1968), although no specific extraction and cleanup procedures or recoveries were described for thiono Systox or Metasystox-type compounds.

A flame photometric method by van der Merwe and Taylor (1971) for demeton-*S*-methyl utilized the precipitation cleanup of Thornton and Anderson (1968) and included some recovery data for Metasystox-R and its sulfone from sorghum foliage.

The procedure described in this paper takes advantage of the dual solubility characteristics of Metasystox-R and its sulfone in extraction and cleanup schemes for a wide variety of crops and tissues. Following initial extraction and partitioning into water and then into chloroform, most extracts are sufficiently clean to be readily oxidized with permanganate with the resulting sulfone measured by alkali-flame gas chromatography. Preliminary work showed both compounds could be separated using gas chromatography. However, a multicomponent analysis has the disadvantage of the increased possibility of interference from crop extractives or other pesticides.

ANALYTICAL METHOD

Apparatus. A Hewlett-Packard Model 5750 gas chromatograph equipped with a flame ionization detector modified for alkali-flame operation as previously described by Thornton and Anderson (1968) was used. Explosion-proof blender motors were used to minimize the fire hazard from volatile organic solvents.

Reagents. All solvents were pesticide quality (nanograde). Other reagents were Analytical Reagent grade or equivalent.

Sample Preparation. Grind wet crops, oily crops, and animal tissues in a Hobart food cutter in the presence of dry ice and place the samples in frozen storage overnight to allow the dry ice to sublime. Grind dry samples in a Wiley mill to pass a No. 3 screen.

Sample Extraction. *Extraction of High Moisture Content Crops.* Place 100 g of chopped and mixed sample into a Waring blender jar marked at the 300-mL level. Add 200 mL of acetone and blend for 3 min at high speed. Dilute to the 300-mL mark with water and blend for 1 additional min. Filter through 32-cm Whatman No. 2V fluted filter paper and collect 150 mL of the filtrate in a graduated cylinder. Transfer the filtrate to 1-L separatory

Chemagro Agricultural Division, Mobay Chemical Corporation, Kansas City, Missouri 64120.
[1]Present address: Bayer AG, Pflanzenschutz Anwendungstechnik, Biologiche Forschung, Leverkusen, West Germany.

Reprinted from AGRICULTURAL AND FOOD CHEMISTRY, Vol. 25, No. 3, Page 573, May/June 1977

funnel and add 150 mL of hexane. Shake the funnel for 30 s, allow the phases to separate, and drain the lower (acetone–water) phase into a 500-mL separatory funnel. Extract the acetone–water mixture successively with 200- and 50-mL portions of chloroform. Evaporate the combined chloroform extracts just to dryness on a rotary vacuum evaporator using a 40 °C water bath. Remove last traces of solvent with a gentle stream of air. Proceed to the "Oxidation" section.

→*Extraction of Oily Crops, i.e., Nut Meats, Cottonseed.* Weigh 50 g of chopped and mixed sample into a blender jar and add 300 mL of chloroform. Blend at high speed for 5 min. Filter with vacuum through Whatman No. 42 filter paper covered with a 0.25-in. layer of Hyflo Super-Cel in a Büchner funnel. Wash the filter cake with 100 mL of fresh chloroform. Transfer the extract to a 1-L round-bottomed flask and evaporate the solvent on a rotary vacuum evaporator in a water bath at 40 °C. Proceed to the "Hexane–Water Partition" section.

Extraction of Animal Tissues (Except Fat). Weigh 50 g of chopped and mixed tissue into a blender jar. Add 50 g of powdered, anhydrous sodium sulfate, 10 g of Hyflo Super-Cel, and 200 mL of acetonitrile and blend at high speed for 2 min. Filter with vacuum through Whatman No. 42 filter paper covered with a 0.25-in. layer of Hyflo Super-Cel in a Büchner funnel. Return the filter cake to the blender and reblend with 300 mL of hexane for 2 min. Filter as before, omitting any additional filter aid. Rinse the blender with 100 mL of fresh hexane and use this to wash the filter cake. Transfer the combined filtrate to a 1-L separatory funnel using a few milliliters of fresh acetonitrile to complete the transfer. Shake the separatory funnel for 30 s, allow the phases to separate, and drain the lower phase into a 500-mL round-bottomed flask. Evaporate the combined acetonitrile extract just to dryness on a rotary vacuum evaporator in a 40 °C water bath. Proceed to the "Hexane–Water Partition" section.

Extraction of Fat. Weigh 50 g of chopped and mixed fat tissue into a blender jar. Add 300 mL of hexane and blend for 2 min at high speed. Filter with vaccum through Whatman No. 42 filter paper covered with a 0.25-in. layer of Hyflo Super-Cel in a Büchner funnel. Return the filter cake to the blender and reblend with 200 mL of acetonitrile for 2 min. Filter as before but omit any additional filter aid. Rinse the blender with 100 mL of hexane and use this to wash the filter cake. Transfer the combined filtrate to a 1-L separatory funnel and continue the hexane acetonitrile partition steps as described for animal tissues (above).

Extraction of Milk. Mix milk samples thoroughly to disperse the cream. Place 100 g of milk in a blender jar and extract as described for animal tissues, omitting the addition of granular sodium sulfate.

Extraction of Eggs. Break one egg into a blender jar and record the weight. Add 15 g of Hyflo Super-Cel and 200 mL of acetone and blend for 2 min at high speed. Filter with vacuum through Whatman No. 42 filter paper covered with a 0.25-in. layer of Hyflo Super-Cel in a Büchner funnel. Rinse the blender jar with 300 mL of chloroform and use this to wash the filter cake. Transfer the filtrate to a 1-L separatory funnel using a few milliliters of fresh chloroform to complete the transfer. Shake the funnel for 30 s, allow the phases to separate, and drain the lower, organic phase through a 32-cm Whatman No. 2V fluted filter paper into a 1-L round-bottomed flask. Rinse the filter paper with 5–10 mL of fresh chloroform. Evaporate the organic extract just to dryness on a rotary vacuum evaporator in a water bath at 40 °C. Dissolve the residue from the previous steps in 300 mL of hexane and transfer to a 500-mL separatory funnel. Rinse the flask with 50 mL of acetonitrile and add to the separatory funnel. Shake the separatory funnel for 30 s, allow the phases to separate, and drain the lower phase into a 300-mL round-bottomed flask. Repeat the extraction twice more with fresh 50-mL portions of acetonitrile. Evaporate the combined acetonitrile extracts just to dryness on a rotary vacuum evaporator in a water bath at 40 °C. Proceed to the "Hexane–Water Partition" section.

Extraction of Soil. Weigh 50 g of air-dried and mixed soil into a Soxhlet extraction thimble. Weigh a companion sample into a beaker for moisture determination if residues are to be reported on a dry weight basis. Place the thimble into a Soxhlet extraction apparatus and extract for 4 h using 300 mL of a 1:1 chloroform–methanol (v/v) mixture at a rate of five–six exchanges per hour. Cool and evaporate the extract just to dryness on a rotary vacuum evaporator in a water bath at 40 °C. Proceed to the "Oxidation" section.

Hexane–Water Partition. Dissolve the residue from the previous steps in 400 mL of hexane and transfer to a 500-mL separatory funnel. Rinse the flask with 100 mL of water and add to the separatory funnel. Shake the funnel for 30 s. Allow the phases to separate and drain the lower, water phase into a clean 250-mL separatory funnel. Extract the water with 100- and 50-mL portions of chloroform and drain into a 250-mL round-bottomed flask. Evaporate the chloroform extract just to dryness on a rotary vacuum evaporator at 40 °C.

Oxidation. Place 5 μg of Metasystox-R standard in a 100-mL round-bottomed flask in 2 mL of acetone solution and carry through the oxidation procedure. Dissolve the sample residue from the previous steps in 2 mL of acetone. Add 5 mL of 20% (w/v) magnesium sulfate solution and 25 mL of a 0.1 M $KMnO_4$ solution, washing down the sides of the flasks during the addition. Mix and let stand with occasional swirling for 30 min, making sure there is an excess of permanganate the entire time. Transfer the oxidation mixture to a 125-mL centrifuge type separatory funnel. Rinse the oxidation flask with 25 mL of chloroform and add this to the separatory funnel containing the oxidation mixture. Shake the separatory funnel for 30 s to extract, allow the phases to separate (centrifuge if necessary), and drain the lower phase through 15 to 20 g of powdered, anhydrous sodium sulfate retained in a powder funnel with a loose plug of glass wool. Collect the filtrate in a 250-mL round-bottomed flask. Repeat the extraction twice more with fresh 25-mL portions of chloroform. After the final extraction, rinse the sodium sulfate with 5–10 mL of chloroform. Evaporate the combined extracts just to dryness on a rotary vacuum evaporator at 40 °C. Remove any last traces of solvent with a stream of dry air at room temperature.

Gas Chromatographic Analysis. Dissolve the standard and sample residues from the previous steps in 2 mL of acetone and inject an appropriate aliquot into the alkali-flame modified gas chromatograph maintained at the following conditions: column, 3.5 ft × $^1/_8$ in o.d. (approximately $^1/_{10}$ in. i.d.) borosilicate glass column, packed with 10% DC 200 and 1.5% QF-1 solution coated on 80–100 mesh Chromosorb W (HP); gas flows, helium carrier gas, 60 mL/min; hydrogen, adjust hydrogen flow after other gasses are set so that at least a one-half scale peak results from a 10-ng standard injected; temperatures, column, 210 °C; injection port, 225 °C; detector, 240 °C.

Identify the Metasystox-R sulfone peak by its retention time and measure the area or peak height produced on the

Table I. Recovery of Metasystox-R and Its Sulfone from Representative Samples

99116

Crop	Ppm added[a]	Recovery, %[b]	
		Metasystox-R	Sulfone
Apples	0.06–0.10	108.4 ± 10.3(8)	94.0 ± 6.6(6)
Grapes	0.05–0.10	103.0 ± 5.2(3)	84.7 ± 2.9(3)
Lettuce	0.05–0.50	92.7 ± 7.8(10)	98.7 ± 10.8(12)
Nut meat	0.05–0.10	99.5 ± 13.1(6)	101.6 ± 9.1(5)
Animal tissue	0.05–0.10	93.8 ± 7.8(17)	92.2 ± 8.4(13)
Animal fat	0.05–0.10	93.0 ± 4.2(5)	94.4 ± 3.7(5)
Bovine milk	0.005–0.01	93.3 ± 6.5(6)	96.5 ± 13.0(6)

[a] Control values were negligible compared with the fortified levels in all cases. [b] Average percent recoveries are followed by the standard deviation and the number of individual determinations. All recoveries were fortified before extraction.

recorder strip chart. At the gas chromatographic conditions employed, Metasystox-R sulfone has a retention time of 3.5 min.

Calculate parts per million of residue in a sample by comparing the response obtained for the unknown with the response obtained for a known amount of Metasystox-R standard started at the oxidation steps, including appropriate factors for sample size, aliquots, and dilutions. An appropriate dilution of Metasystox-R sulfone, if available, may be directly injected into the gas chromatograph for use as a standard. Oxidation of Metasystox-R itself is recommended because the pure sulfone is not readily available to all workers.

DISCUSSION

Sulfoxide compounds such as Metasystox-R are, in general, difficult to chromatograph because of adsorption and tailing. Many workers including Burke and Holswade (1966) have tried to overcome this problem with massive conditioning injections to build up sensitivity. The method described in this paper utilizes permanganate oxidation to convert Metasystox-R to the sulfone which exhibits much less tailing and is easier to chromatograph. In addition, all active residue is concentrated into one peak adding further simplicity and sensitivity.

Room temperature oxidation is quantitative using 0.1 M potassium permanganate (Tietz and Frehse, 1960) for 30 min. Oxidation also converts most tissue extractives and pigments to a water-soluble form, making them easy to remove. The unique water soluble character of the Metasystox compounds allows cleanup procedures to be relatively simple. Initial crop or tissue extracts may be partitioned back and forth between water and various polar and nonpolar organic solvents to yield extremely well-purified extracts prior to oxidation. Oxidized extracts are relatively free from severe crop or tissue interferences on the gas chromatograph.

Recovery experiments were run on a large number of different crops and various animal tissues by fortifying the samples with 0.005 to 5 ppm of Metasystox-R or its sulfone prior to blending. Representative recovery values for a general cross section of the crops and tissues are presented in Table I. Control values in each case were negligible compared with the level at which the recovery check was run. In addition to the samples shown in Table I, the method has been used successfully since 1967 for the following crops and tissues: alfalfa, barley, beans, broccoli, brussels sprouts, carrots, cattle tissues (brain, fat, heart, kidney, liver, muscle, and milk), cauliflower, cherries, clover, grass, mint, onions, peas, plums, poultry tissues (fat, giblets muscle, eggs), soils, sorghum, strawberries, sugar beets, tomatoes, and wheat. Representative control and recovery chromatograms are shown in Figure 1 for recovery of 0.1 ppm Metasystox-R from walnut meat. Chromatograms for other types of samples were similar.

Table II. Chemicals Tested for Possible Interference with the Metasystox-R Residue Analysis Procedure

Chemical name	Ppm level tested[a]
Azodrin	5.0
Bensulide	5.0
Bidrin	5.0
Chlorfenvinphos	5.0
Clodrin	5.0
Co-Ral	1.0
Dasanit	5.0
DDVP	5.0
Def	5.0[b]
Delnav	5.0
Diazinon	40.0[b]
Dibrom	5.0
Dicapthon	5.0
Dimethoate	5.0[b]
Di-Syston	12.0
Diuron	2.0
Dyfonate	5.0[b]
Dylox	240.0
EPN	5.0
Ethephon	36.0
Ethion	5.0
Ethrel	36.0
Fenthion	18.0
Famphur	0.1
Folex	5.0
Gardona	110.0
Guthion	5.0
Imidan	40.0
Kelthane	25.0
Malathion	135.0[b]
Methyl parathion	5.0[b]
Mocap	5.0
Monitor	1.0
Nemacur	0.1
OMPA	0.75[d]
Orthene	10.0
Parathion	5.0[b]
Phosalone	40.0[b]
Phosdrin	5.0
Phosphamidon	0.5
Ronnel	10.0
Ruelene	1.0[b]
Supracide	6.0
Systox	12.0[c]
TEPP	5.0
Terbacil	1.0
Tetradifon	100.0
Thimet	5.0[a]
Torak	1.5
Trifluralin	1.0
Trithion	5.0
Zinophos	5.0
Zytron	5.0

[a] Ppm relative to a 50-g sample size. [b] Interferes with standard GC method but can be separated using a 40 cm × 3 mm i.d. glass column packed with 6% QF-1 coated on 80–100 mesh Gas Chrom Q. [c] Can be separated from Metasystox-R at 180 °C. [d] Interference eliminated by using flame photometric detector (sulfur mode).

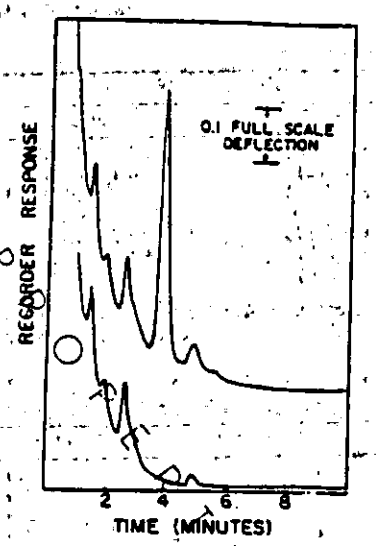


Figure 1. Gas chromatograms of walnut meat control (lower curve) and walnut meat fortified with 0.1 ppm of Metasystox-R (upper curve).

The slurry filtration (solution coating) technique described by Supina (1974) was used to prepare the gas chromatographic column packing. A 1:1 mixture of acetone and hexane was used to dissolve the DC-200, QF-1 mixture. This coating procedure was by far the best method for consistently preparing a packing which would allow Metasystox-R sulfone to be chromatographed without tailing or adsorption. The empty glass columns were also treated with a 5% solution of dimethyldichlorosilane in toluene and then flushed with toluene and methanol and dried before packing. After packing, new columns were purged with carrier gas at room temperature to remove oxygen, the exit end capped and the column conditioned with no flow for 8 h at 250 °C. Then, after normal flow conditioning at operating conditions overnight, the columns generally would allow 5 ng of Metasystox-R sulfone to yield one-half to full-scale recorder response with <1% noise.

A standard curve was run to determine linearity of response in the gas chromatograph for Metasystox-R sulfone. Response was linear over at least a 100-fold range up to 80 ng injected. Samples containing residues in excess of this amount in the injection volume should be diluted and re-injected to ensure that response falls within the linear portion of the response curve.

If 0.1 sq in. is considered the smallest area which can be accurately measured with a polar planimeter, the level of sensitivity is determined by the amount of Metasystox-R sulfone necessary to produce this area. In general, 0.1 ppm (10 ng) of standard produces a peak of 1 sq in. or better, indicating the sensitivity of the method to be approximately 0.01 ppm. If the criteria of 2 × the noise level is selected as the limiting factor, sensitivity would be somewhat better.

To determine the specificity of the method for Metasystox-R in the presence of other pest control chemicals, an interference study was run. Only phosphorus-containing chemicals were tested because of the phosphorus-specific nature of the alkali-flame detector. All organophosphorus chemicals currently registered for use on the above mentioned crops as reported in the U.S. Federal Register and listed in Table II were tested for interference with the analysis procedure. One-tenth part per million of Metasystox-R could readily be analyzed in the presence of any of these chemicals at their maximum registered level.

The method described above has been used extensively for the analysis of field residue and animal-feeding study samples. The various extraction procedures which were described include all of the modifications which have been found necessary to prepare any sample which has been analyzed for Metasystox-R in this laboratory and in various contract laboratories during the past nine years.

LITERATURE CITED

Bowman, M. C., Beroza, M., Gentry, C. R., *J. Assoc. Off. Anal. Chem.* **52**, 157 (1969).
Burke, J., Holswade, W., *J. Assoc. Off. Anal. Chem.* **48**, 374 (1966).
Crosby, N. T., Laws, E. Q., *Analyst (London)* **89**, 319 (1964).
Eichenberger, J., Gay, L., *Mitt. Geb. Lebensmitteluntersuch. Hyg.* **51**, 423 (1960); *Chem. Abstr.* **55**, 12752g (1961).
Getz, M. E., Wheeler, W. G., *J. Assoc. Off. Anal. Chem.* **51**, 1101 (1968).
Guth, J. A., *Pflanzenschutzberichte* **38**, 129 (1967); *Chem. Abstr.* **67**, 72784q (1967).
Hensel, J., Chemagro Division, Mobay Chemical Corp. Report No. 484, K.C. MO. (1954).
Laws, E. Q., Webley, D. J., *Analyst (London)* **84**, 28 (1959).
McCully, K. A., *J. Assoc. Off. Anal. Chem.* **53**, 362 (1970).
Mühlmann, R., Tietz, H., *Hoefchen-Briefe (Engl. Ed.)*, 116 (1956).
Ragab, T. M. H., *J. Assoc. Off. Analyt. Chem.* **50**, 1088 (1967).
Smart, N. A., Hill, A. R. C., *J. Chromatogr.* **30**, 628 (1967).
Supina, W. R., "The Packed Column in Gas Chromatography", Supelco, Inc., Bellefonte, Pa., 1974, p 96–107.
Thornton, J. S., Anderson, C. A., *J. Agric. Food Chem.* **16**, 895 (1968).
Tietz, H., *Phytiatr.-Phytopharm.* **9**, 167 (1960).
Tietz, H., Frehse, H., *Hoefchen-Briefe (Engl. Ed.)* **4**, 212 (1960).
van der Merwe, J. H., Taylor, W. B., *Pflanzenschutz-Nachr. (Am. Ed.)* **24**, 259 (1971).

Received for review October 12, 1976. Accepted January 28, 1977.

APPENDIX 3

99118

SOIL NO.: 0371

DATE RECEIVED: 1-30-89

DATE COMPLETED: 2-1-89

SOIL SENDER: KAREN CAIN

SOIL DESCRIPTION: SOIL FROM FRESNO, CALIFORNIA
characterization needed to determine if
site is appropriate for soil dissipation study

TEXTURAL ANALYSIS (%)	SAMPLE NO. 0371	STANDARD SOIL
SAND	53	56
SILT	37	28
CLAY	10	16
CLASS	SANDY LOAM	SANDY LOAM
pH (in 0.01 M CaCl)	7.1	5.0

ANALYZED BY: V.J. Lemke

Notebook Ref.: 86-R-57 p. 84

% Organic Matter based on total organic carbon x 1.9

CEC determined by using sodium acetate, pH 8.2.

Particle density determined by use of Mobay Ag Chem Report No. 67681.

RESULTS SENT TO: KAREN CAIN 2/1/89

V.J. Lemke 2/2/89

REPORT NUMBER

W095-30

A & L WESTERN AGRICULTURAL LABORATORIES

1311 WOODLAND AVE. • MODESTO, CALIFORNIA 95351 • (209) 529-4080

SEND TO:
PLANT SCIENCES
514 CALABASAS RD.
WATSONVILLE
CA. 95076

GROWER
BENGARD #38

SAMPLES SUBMITTED BY.

EXACT COPY
NAME
DATE 6/12/89

DATE OF REPORT 4-6-89

PAGE

SOIL ANALYSIS REPORT
(SEE EXPLANATION ON BACK)

SAMPLE NUMBER	LAB NUMBER	ORGANIC MATTER % RATE	ORGANIC MATTER lbs/A	PHOSPHOROUS P_1 (Week Bray) ppm-P RATE	PHOSPHOROUS P_2 $NaHCO_3$-P ppm-P RATE	POTASSIUM K ppm-K RATE	MAGNESIUM Mg ppm-Mg RATE	CALCIUM Ca ppm-Ca RATE	SODIUM Na ppm-Na RATE	pH SOIL pH	pH BUFFER INDEX	HYDROGEN meq/100g	Cation Exchange Capacity C.E.C. meq/100g	PERCENT BASE SATURATION (COMPUTED) % K	% Mg	% Ca	% H	% Na
38	58816									7.3								

99118

Page 51 of 52

SAMPLE NUMBER	NITRATE NO_3 ppm-N RATE	SULFUR S ppm-S RATE	ZINC Zn ppm-Zn RATE	MANGANESE Mn ppm-Mn RATE	IRON Fe ppm-Fe RATE	COPPER Cu ppm-Cu RATE	BORON B ppm-B RATE	EXCESS LIME RATE	SOLUBLE SALTS mmhos/cm RATE	CHLORIDE Cl ppm-Cl RATE	SOLUBLE SODIUM Na ppm-Na RATE	PARTICLE SIZE ANALYSIS % SAND	% SILT	% CLAY	SOIL TEXTURE
38												74	12	14	SANDY LOAM

AC 6/5/89

This report applies only to the sample(s) tested. Samples are retained a maximum of thirty days after testing. Soil Analysis Prepared By

A & L WESTERN AGRICULTURAL LABORATORIES
Richard East
RICHARD EAST, AGRONOMIST

[redacted]

99118

APPENDIX 4

Supplement, Herbicide Screen

In conjunction with the potential use of herbicides at the METASYSTOX-R test sites three herbicides, Fusilade (Fluazifop-butyl), Surflan (Oryzalin) and Goal (Oxyfluorfen), were taken through the METASYSTOX-R and METASYSTOX-R Sulfone analytical methodology at an equivalent residue level of 2.0 ppm. No interferences were found from the METASYSTOX-R and METASYSTOX-R Sulfone methodologies.

William D. Rhoads, Ph.D.
Study Director

END