STUDY TITLE

Validation of Methods for the Analysis of Worker Exposure and Reentry Matrices for Diazinon and Malathion

Study Number ARF003

DATA REQUIREMENT

Series 875
Occupational and Residential Exposure
Test Guidelines

AUTHOR

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Study Director

FINAL REPORT DATE

February 23, 1999

TESTING FACILITY

ABC Laboratories, Inc.
Analytical Chemistry and Field Studies
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SPONSOR/SUBMITTER

Agricultural Reentry Task Force

Statement of No Data Confidentiality Claims

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

Paula Paul

Paula Paul
Submitter
Administrative Committee Chair
Agricultural Reentry Task Force

Oct 27, 1999

Date

Statement of Compliance with Good Laboratory Practice Standards

Agricultural Reentry Task Force (ARTF) Study ARF003, "Validation of Methods for the Analysis of Worker Exposure and Reentry Matrices for Diazinon and Malathion" was conducted according to the Good Laboratory Practice Standards (GLPs), 40 CFR Part 160 as described in the Federal Register, 54:34052-34074, August 17, 1989. There were no GLP deviations noted during this study.

Del A. Koch — 23 Feb 99
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Paula Paul — Oct. 27, 1999
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Agricultural Reentry Task Force
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ARTF Quality Assurance Unit Statement

Study ARF003 was inspected/audited by the Agricultural Reentry Task Force Quality Assurance Unity (QAU) for compliance with the EPA's Good Laboratory Practice Standards (40 CFR Part 160). All findings were reported to the Study Director and ARTF Management. The Quality Assurance Statement from the analytical laboratory is presented on page 5.

Phase Inspected	Date(s) of Inspection	Date Findings Reported to the Study Director/Management
Final (Draft) Report	April 13, May 15, and May 18, 1998	June 8, 1998
Final Report	January 20 and 21, 1999	January 25, 1999

Daniel Carey
QUALITY ASSOCIATES, INC.
ARTF Quality Assurance Officer

01 Mar 99
Date

ABC Laboratories' Quality Assurance Unit Statement

ABC Laboratories' Quality Assurance Unit reviewed Study #43767, "Validation of Methods for the Analysis of Worker Exposure and Reentry Matrices for Diazinon and Malathion," for the Agricultural Reentry Task Force. The following inspection/audits were conducted on this study.

Phase Inspected	Date(s) of Inspection	Date Reported to Study Director	Date Reported to Management
Protocol	01/10/97	01/10/97	09/15/97
Fortifications	06/2797	06/27/97	06/30/97
Column Clean-up	08/20/97	08/20/97	08/25/97
Elution	10/27/97	10/27/97	03/23/98
Draft Report and Raw Data	03/05/98	03/06/98	03/16/98
Final Report	02/05/99	02/05/99	02/16/99

The undersigned conducted the report and raw data audits. The audits indicate the report is an accurate reflection of the study as it was conducted by ABC Laboratories, Inc.

Nancy G. Shikles
Senior Quality Assurance Specialist

2/23/99
Date

Study Identification and Approval

Sponsor:	Agricultural Reentry Task Force c/o Harold Himmelman Beverage & Diamond 1350 Eye Street, N.W., Suite 700 Washington, D.C., 20005
Sponsor Contact:	David R. Johnson (660) 762-4240
Testing Facility:	ABC Laboratories, Inc. Analytical Chemistry and Field Studies 7200 E. ABC Lane Columbia, Missouri 65202
Study Director:	Del A. Koch ABC Laboratories, Inc.
Study Initiation Date:	February 5, 1997
Study Completion Date	February 23, 1999
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Jodie Wehrman	Associate Scientist

Study Identification and Approval con't

Data that are specific to the contracting laboratories will be archived at their respective facilities. All other raw data, protocols, and final reports are stored in the Agricultural Reentry Task Force archives at Quality Associates, Inc., 9017 Red Branch Road, Suite 102, Columbia, MD 21045.

This report is issued by:

23Feb99

Del A. Koch
ABC Laboratories, Inc.
Study Director

This report is approved by:

3/3/99

Jim Clark
Technical Committee Chair
Agricultural Reentry Task Force

3/8/99

Luis Castro
Analytical Monitor
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1.0 INTRODUCTION AND BACKGROUND

In October 1995, the Environmental Protection Agency (EPA) issued a Data Call-In (DCI) notice to all pesticide registrants requiring data on dislodgeable foliar residues (DFR) and transfer coefficients (TC) on virtually all pesticides applied to agricultural crops. The data are used in assessing post-application exposure to agricultural workers upon entering treated fields and in calculating safe reentry intervals.

In anticipation of the DCI, the Agricultural Reentry Task Force (ARTF) was formed on December 28, 1994. The DCI requires data on dermal Transfer Coefficients. To accomplish this, the member companies of the ARTF are collectively conducting a series of studies. The data generated from these studies will become a comprehensive database of exposure that will be used to calculate Transfer Coefficients applicable to all pesticides, crops and activities. This report covers the validation of the analytical methods used in quantifying the residues of diazinon and malathion used in some of these studies. The study is designed to fulfill the requirements of the USEPA Series 875; Occupational and Residential Exposure Test Guidelines in accordance with EPA FIFRA Good Laboratory Practices Standards, 40 CFR 160. Details on the study design are presented in the protocol in Appendix A.

The objective of this particular study was to validate the analytical methods of analysis for the quantification of diazinon and malathion in dermal and inhalation worker exposure matrices.

2.0 STUDY OVERVIEW

Analytical methods were validated for the quantification of diazinon and malathion residues in/on matrices associated with the worker exposure and reentry studies being conducted by the Agricultural Reentry Task Force (ARTF). The accuracy and precision of the methods were evaluated. Draft methods were developed by Horizon Laboratories, Inc., of Columbia, Missouri, and were provided to ABC Laboratories, Inc., for evaluation, modification, and validation. The methods validated were assigned the following titles and reference numbers:

ARTF-AM-005	Determination of Diazinon and Malathion in Inner Dermal Dosimeters
ARTF-AM-006	Determination of Diazinon and Malathion in Hand Wash Solutions
ARTF-AM-007	Determination of Diazinon and Malathion in Leaf Wash Solutions
ARTF-AM-008	Determination of Diazinon and Malathion in Outer Dermal Dosimeters
ARTF-AM-009	Determination of Diazinon and Malathion in OVS Air Sampling Tubes

ARTF-AM-010 Determination of Diazinon and Malathion in Facial/Neck Wipes

Overall validation results for each matrix are summarized below:

Matrix	Diazinon			Malathion		
	Number of Analyses	Average % Recovery	Standard Deviation	Number of Analyses	Average % Recovery	Standard Deviation
Inner Dermal Dosimeters	12	99.9%	8.62%	12	98.5%	9.83%
Hand Wash Solutions	12	99.3%	9.97%	12	105%	9.23%
Leaf Wash Solutions	12	92.5%	10.3%	12	97.5%	10.5%
Outer Dermal Dosimeters (Shirts)	18	86.7%	9.63%	18	92.4%	10.1%
Outer Dermal Dosimeters (Shirts) Ruggedness Testing	12	103%	13.9%	12	106%	8.96%
Outer Dermal Dosimeters (Pants)	12	92.7%	6.93%	12	103%	8.36%
OVS Air Sampling Tubes	12	96.6%	7.23%	12	103%	4.66%
Facial/Neck Wipes	12	92.3%	6.53%	12	96.3%	14.6%

3.0 ANALYTICAL PROCEDURE

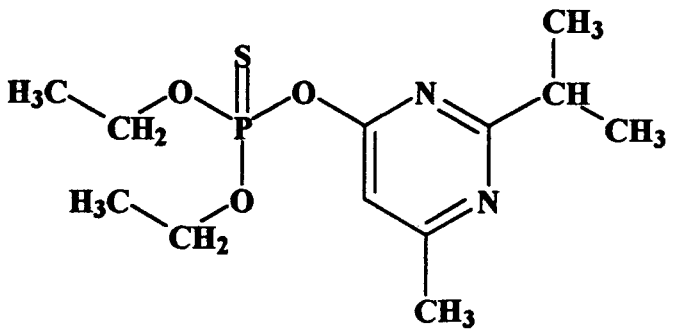
The validation of the analytical methods was performed by ABC Laboratories, Inc., of Columbia, Missouri. The methods were developed by Horizon Laboratories, Inc., also of Columbia, Missouri, and were transferred to ABC Laboratories for evaluation, revision, and validation. The protocol for the study was signed by the Study Director on February 5, 1997. The analytical test/reference substances were received from Bayer Corporation on March 21, 1997. For the validations, two sets of laboratory fortification samples were prepared on different days except for the outer dosimeter shirts in which three sets were prepared on different days. Each validation set consisted of a control, and duplicate fortifications prepared at three different levels ranging from the proposed limit of quantification (LOQ) for the method upward. Thus, each set consisted of seven samples fortified with both compounds. Summary

information is presented below with regard to the individual matrices. A summary of the important dates pertaining to these method validations are shown in Table 1.

3.1 Materials

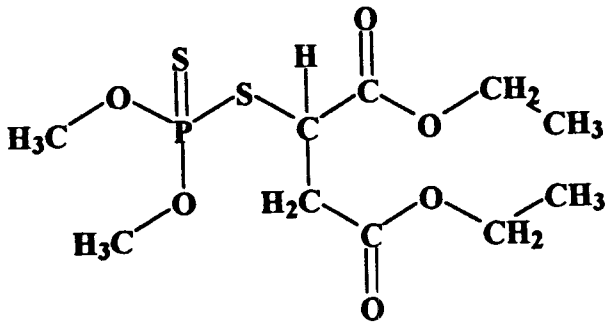
3.1.1 Test/Reference Substances

The analytical test/reference substances of diazinon and malathion were supplied and characterized by Bayer Corporation, where the documentation is maintained. These materials were used as test substances to fortify control worker exposure matrices and also as reference substances to quantify the recovery through each method. When not in use, the analytical test/reference substances were stored in a freezer at approximately -20 °C. The standards were received at ABC Laboratories on March 21, 1997. An expiration date of 12/97 was provided for both compounds on the Certificates of Analysis received with the analytical test/reference substances. This expiration date was later extended and new Certificates of Analysis issued. Compound structures and other information are as follows.



Chemical Name: O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate

Name:	Diazinon	Reference Number:	95R-31-45C
CAS Number:	333-41-5	Expiration Date:	September 14, 1998
Purity:	87.7%	Lot (ID) Number:	09467
Source:	Bayer Corporation		



Chemical Name:	O,O-dimethyl phosphorothioate of diethyl mercaptosuccinate		
Name:	Malathion	Reference Number:	95R-31-44E
CAS Number:	121-75-5	Expiration Date:	December 12, 1999
Purity:	95.0%	Lot (ID) Number:	CS030
Source:	Bayer Corporation		

3.1.2 Test System

The test system for this study is composed of the various test matrices associated with the worker exposure and reentry studies being conducted by the ARTF.

A supply of the various matrices were received from Stewart Agricultural Research Services, Inc., on an as needed basis. The test matrices consisted of 100% cotton shirts and pants for outer dermal dosimeters, 100% cotton union suits for inner dermal dosimeters, and 100% cotton gauze swabs for facial/neck wipes. The cotton matrices were received and used unwashed. In addition, OSHA Versatile Sampling (OVS) air tubes containing two beds of XAD-2 adsorbent resin were used. These control matrices were stored at room temperature in the Study Director's office until needed.

The 100% cotton shirts and pants for outer dermal dosimeters were obtained by Stewart from Universal Overall Company, 1060 W. Van Buren Street, Chicago, IL 60607. The 100% cotton union suits were obtained by Stewart from Unity Knitting Mills, Inc., P.O. Box 827, Highway 52 South, Wadesboro, NC 28170. The 100% cotton gauze swabs (Johnson & Johnson, 4 in x 4 in, 8-ply) for facial/neck wipes were obtained by Stewart from VWR Scientific Products, 800 E. Fabyan Parkway, Batavia, IL 60510. The OVS air tubes were obtained by Stewart from Gulf Coast, Inc., 9827 Whithorn Drive, Houston, TX 77095-5027.

Solutions of 0.01% Aerosol OT (AOT) were prepared from concentrated reagent grade 75% AOT purchased from Fisher Chemical. This reagent was used in the outer dermal dosimeter, hand wash, leaf wash, and final facial/neck wipe methods. This reagent was prepared on an as needed basis, and was stored at room temperature in the laboratory.

Leaf wash matrix was prepared using spinach leaves purchased at a local grocery. The appropriate surface area of the spinach leaves were extracted with 0.01% AOT solution for use in the method validation study.

3.1.3 Reagents

Solvent/Reagent	Manufacturer	Grade	Lot Numbers
Acetone	Burdick and Jackson	Pesticide	BO369, BO512, BO920, BP707, BQ210
Di(ethylene glycol) diethyl ether (DEGDEE)	Sigma Chemical Company	Reagent	02321HG
Hexane	Burdick and Jackson	Pesticide	BN237, BN936
Diethyl ether	Burdick and Jackson	Pesticide	BM863, BN234
Florisil® 100-200 mesh	Fisher Chemical Company	Analytical	964720
Deionized Water	Labconco	Reagent	N/A
75% Aerosol® OT (AOT)	Fisher Chemical Company	Reagent	963392
Methylene Chloride (DCM)	Burdick and Jackson	Pesticide	BN794
Methanol	Burdick and Jackson	Pesticide	BO820, BP026
Varian Mega Bond Elut® C-18 SPE Cartridges (1 g x 6 mL)	Varian Sample Preparation	N/A	071340

4.0 METHODS

4.1 Preparation of Spiking Solutions

Two sets of fortification solutions were used for the method validations described herein. The fortification solutions used for the validation of the inner dermal dosimeter, hand wash, leaf wash, and air tubes were diluted from primary stock solutions prepared on March 24, 1997. These

primary stock solutions were prepared at concentrations of 9.92 mg/mL diazinon and 10.2 mg/mL malathion in acetone.

The fortification solution used for the validation of the outer dermal dosimeter matrices were diluted from primary stock solutions prepared on July 24, 1997. These primary stock solutions were prepared at concentrations of 10.0 mg/mL diazinon and 10.0 mg/mL malathion in acetone.

Mixed fortification solutions were prepared from these primary stock solutions, or mixed dilutions thereof, at the appropriate concentrations for use in the various method validations, and assigned a unique identification name. All dilutions were prepared using class A volumetric glassware using acetone as the dilution solvent and are documented in the raw data. These dilutions were assigned expiration dates corresponding to six months after the date each dilution was made. The fortification solutions were stored in a freezer set at approximately -20 °C (typical range was -14 to -25°C) when not in use.

4.2 ARTF-AM-005 Determination of Diazinon and Malathion in Inner Dermal Dosimeters

The draft method for the analysis of diazinon and malathion in inner dermal dosimeters was received from Horizon Laboratories. The method was originally for the analysis of both the inner dosimeters and facial/neck wipe samples, but a separate method (ARTF-AM-010) was developed, validated, and written for the facial/neck wipe matrix. See Section 4.7 for the explanation of the need to develop a separate method.

The validation sets were fortified on April 7, and April 23, 1997. Control 100% cotton inner dermal dosimeters (union suits) were cut into the various segments according to ARTF SOP ARTF-8E/1 on an as needed basis. The segments were placed onto a sheet of aluminum foil and fortified, using volumetric pipets, at the appropriate levels. The samples were transferred to a 0.5 gallon, wide-mouth glass jar, and the foil was rinsed with a minimum of 50 mL acetone (which was included in a 1 L total extraction volume). The aluminum foil was discarded after a single use.

The samples were extracted with 1 liter of acetone by shaking for approximately 15 minutes. Loose particulate matter was allowed to settle, and a 50-mL sample aliquot was pipetted into a 125-mL evaporation flask. The extracted segment was discarded. The sample was vacuum-evaporated to dryness.

A 50-mL aliquot of deionized water was added to the sample flask, which was capped and shaken well. Exactly 20 mL of hexane was pipetted

onto the aqueous sample which was capped and shaken vigorously for approximately 15 seconds. The phases were allowed to separate, and at least 12 mL of the hexane phase (top layer) was transferred to a clean, dry, 50-mL centrifuge tube. An additional 5-mL aliquot of deionized water was added to the hexane extract in the centrifuge tube, which was capped and shaken vigorously for approximately 15 seconds. The centrifuge tubes were balanced with deionized water, then centrifuged for 2 minutes at approximately 1000x g.

A dry-packed activated Florisil® clean-up column was prepared by seating a small plug of glass wool into an 11 mm i.d. glass column. The column and glass wool were rinsed with diethyl ether and allowed to air-dry. One gram of fully-activated Florisil® was added to the column, and an 8-mL aliquot of the hexane phase (top layer) from the centrifuge tube was applied onto the column, taking care not to include any water droplets with the hexane. The hexane was allowed to percolate onto the column at approximately 2 drops per second, and the column was washed with 8 mL of neat hexane. The rinse was allowed to percolate through the column at the same slow flow rate, and the flow was stopped with approximately 1 cm of hexane rinse remaining over the top of the Florisil®. All eluates up to this point were discarded. The diazinon and malathion were eluted from the column with 120 mL of 15% diethyl ether in hexane. The eluant was collected in a 250-mL evaporation flask, and vacuum-evaporated to dryness. The dry residues were dissolved in a known volume of 1.5% DEGDEE in acetone (generally 2.0 mL for LOQ residues). The samples were quickly transferred to culture tubes to minimize evaporation of the solvent. Dilutions were prepared, with the same solvent, as necessary to maintain analyte concentrations within the standard curve range. Samples were analyzed by gas chromatography with flame photometric detection in the phosphorus mode [GC/FPD(P)] as described in Section 4.8.

4.3 ARTF-AM-006 Determination of Diazinon and Malathion in Hand Wash Solutions

The draft method for the analysis of diazinon and malathion in hand wash solutions was received from Horizon Laboratories. The validation sets were fortified on June 16, and June 23, 1997. Five hundred milliliter aliquots of 0.01% AOT were placed into a glass beakers, fortified at the appropriate levels, using volumetric pipets, and mixed thoroughly. One gram C-18 SPE cartridges were conditioned by placing cartridges on a vacuum manifold, and washing the cartridges successively with 2 x 5 mL of hexane, 2 x 5 mL of methanol, and 2 x 5 mL of water. The vacuum was limited throughout the loading, washing, and eluting procedure to achieve flows of only approximately 1 to 2 drops per second. Ten milliliters of the sample (2 x 5 mL aliquots) were pipetted onto the C-18 column. Samples were percolated into the column and the column

was washed with 5 mL of water. All eluates up to this point were discarded.

With full vacuum (> 20" Hg) on the manifold, the columns were air-dried for at least 45 minutes. The columns were washed with 5 mL of hexane, and the diazinon and malathion were eluted from the column with 8 mL of DCM. The eluate was collected in a 15-mL culture tube, transferred to a 125-mL evaporation flask, and the tube was rinsed twice with approximately 2 mL DCM which were added to the flask. The samples were vacuum-evaporated to dryness, and the dry residues were dissolved in a known volume of 1.5% DEGDEE:acetone (generally 2.5 mL for LOQ residues). The samples were quickly transferred to culture tubes to minimize evaporation of the solvent. Dilutions were prepared with the same solvent as necessary to maintain analyte concentrations within the standard curve range. Samples were analyzed by GC/FPD(P) as described in Section 4.8.

4.4 ARTF-AM-007 Determination of Diazinon and Malathion in Leaf Wash Solutions

The draft method for the analysis of diazinon and malathion in leaf wash solutions (0.01% AOT) was received from Horizon Laboratories. The validation sets were fortified on June 27, and June 30, 1997. Approximately 3.8 L of control dislodging solution was prepared using spinach leaves. Two-hundred-milliliter aliquots of this solution were placed into beakers, fortified at the appropriate levels, using volume pipets, and thoroughly mixed. One-gram C-18 SPE cartridges were conditioned by placing cartridges on a vacuum manifold. The cartridges were washed successively with 2 x 5 mL of methanol and 2 x 5 mL of water. The vacuum was limited throughout the loading, washing, and eluting procedure to achieve flows of only approximately 1 to 2 drops per second. Five milliliters of the sample were pipetted onto the C-18 column. Samples were percolated into the column and the column was washed with 10 mL of water. All eluates up to this point were discarded.

With full vacuum (>20" Hg) on the manifold, the columns were air-dried for at least 45 minutes. The diazinon and malathion were eluted from the column with 16 mL of DCM. The eluate was collected in a 15-mL culture tube, transferred to a 125-mL evaporation flask, and the tube was rinsed twice with approximately 2 mL DCM which were added to the flask. The samples were vacuum-evaporated to dryness, and the dry residues were dissolved in a known volume of 1.5% DEGDEE:acetone (generally 6.0 mL for LOQ residues). The samples were quickly transferred to culture tubes to minimize evaporation of the solvent. Dilutions were prepared with the same solvent as necessary to maintain analyte concentrations within the standard curve range. Samples were analyzed by GC/FPD (P) as described in Section 4.8.

4.5 ARTF-AM-008 Determination of Diazinon and Malathion in Outer Dermal Dosimeters

The draft method for the analysis of diazinon and malathion on outer dermal dosimeters was received from Horizon Laboratories. Method development and revision were necessary prior to application of the method to the validations (See Section 4.9). The validation sets for the outer dermal pants were fortified on August 20, and August 21, 1997. Three validation sets were performed for the outer dermal shirts, which were fortified on August 29, September 2, and September 4, 1997. Control 100% cotton outer dermal dosimeters (shirts and pants) were cut into the various segments according to ARTF SOP ARTF-8D/0 on an as-needed basis. The segments were placed onto a sheet of aluminum foil and fortified, using volumetric pipets, at the appropriate levels. The samples were transferred to a 1 gallon, wide-mouth glass jar, and the foil was rinsed with a minimum of 50 mL acetone (which was included in a 2.5 L total extraction volume). The aluminum foil was discarded after a single use.

The samples were extracted with 2.5 liters of acetone, shaking for approximately 15 minutes. Loose particulate matter was allowed to settle, and a 50-mL sample aliquot was pipetted into a 125-mL evaporation flask. The extracted segment was discarded. The sample was vacuum-evaporated to dryness.

Twenty milliliters of deionized water were added to the sample flask, which was sonicated for approximately 5 minutes, tipping and rotating the flask to remove residue on the sides of the flask. A 7.5-mL aliquot of diethyl ether was pipetted onto the aqueous sample and mixed well for approximately 15 seconds. A 7.5-mL aliquot of hexane was pipetted onto the diethyl ether:aqueous sample and mixed well for approximately 15 seconds. The sample was transferred to a clean, dry, 50-mL centrifuge tube, capped, and vortexed for approximately 15 seconds, thoroughly mixing the two phases. The tubes were balanced with deionized water, and centrifuged for 5 minutes at approximately 1000x g. The top (organic) layer was removed and placed in a 125-mL evaporation flask. The original 125-mL evaporation flask was rinsed with 15 mL of 50:50 diethyl ether:hexane, which was transferred to the centrifuge tube, and vortexed for approximately 15 seconds, thereby thoroughly mixing the two phases. The tubes were balanced with deionized water, and centrifuged for 5 minutes at approximately 1000x g. The top (organic) layer was removed and combined with the first organic extract in a 125-mL evaporation flask. This partition was repeated once more, and the samples vacuum-evaporated to dryness. The residues were reconstituted in 15 mL of 0.01% AOT in the 125-mL evaporation flask and

sonicated for approximately 5 minutes, tipping and rotating the flask to remove residue on the sides of the flask.

One gram C-18 SPE cartridges were conditioned by placing cartridges on a vacuum manifold. The cartridge was washed successively with 2 x 5 mL of methanol, and 2 x 5 mL of water. The vacuum was limited throughout the loading, washing, and eluting procedure to achieve flows of only approximately 1 to 2 drops per second. Five milliliters of the sample were pipetted onto the C-18 column. Samples were percolated into the column and the column was washed with 2 x 5 mL of water. All eluates up to this point were discarded.

With full vacuum (> 20" Hg) on the manifold, the columns were air-dried for at least 45 minutes. The diazinon and malathion were eluted from the column with 12 mL (pants) or 16 mL (shirts) of DCM. The eluate was collected in a culture tube of suitable volume, transferred to a 125-mL evaporation flask, and the tube rinsed twice with approximately 2 mL DCM, which were added to the flask. The samples were vacuum-evaporated to dryness, and the dry residues were dissolved in a known volume of 1.5% DEGDEE:acetone (generally 2.0 mL for LOQ residues). The samples were quickly transferred to culture tubes to minimize evaporation of the solvent. Dilutions were prepared, with the same solvent, as necessary to maintain analyte concentrations within the standard curve range. Samples were analyzed by GC/FPD(P) as described in Section 4.8.

4.6 ARTF-AM-009 Determination of Diazinon and Malathion in OVS Air Sampling Tubes

The draft method for the analysis of diazinon and malathion in OVS (XAD-2) air sampling tubes was received from Horizon Laboratories. The validation sets were fortified on July 9, and July 16, 1997. A high bias at the LOQ was observed in the first set, so a minor method modification was made prior to fortifying the second set, and a third set consisting only of a control and duplicate LOQ fortifications was prepared on July 18, 1997. Fortifications were made into the sorbent material by injecting 10 µL of the appropriate fortification solution just under the glass fiber disk into the center of the resin bed with a syringe. The tubes were allowed to stand at ambient temperature for 30 minutes to allow the acetone to evaporate. The entire contents of the tube were transferred to a 30-mL culture tube, including the Teflon® retainer ring. The tubes were rinsed with approximately 3 mL of acetone, which was added to the culture tube. Ten milliliters of acetone were added to each sample. The culture tube was capped tightly with a PTFE-lined lid, and the contents were mixed for approximately 30 seconds on a vortex mixer. The acetone was transferred into a 125-mL evaporation flask, and the extraction repeated two more times. The samples were vacuum-

evaporated to dryness. Prior to addition of the solvent for reconstitution of the residues, the flasks were placed into an ice-water bath to chill, and then a known volume of 1.5% DEGDEE in acetone (generally 1.00 mL for LOQ residues) was added. The samples were quickly transferred to culture tubes to minimize evaporation of the solvent. Dilutions were prepared, with the same solvent, as necessary to maintain analyte concentrations within the standard curve range. Samples were analyzed by GC/FPD(P) as described in Section 4.8.

4.7 ARTF-AM-010 Determination of Diazinon and Malathion in Facial/Neck Wipes

A draft method for the analysis of diazinon and malathion in facial/neck wipes was received from Horizon Laboratories. The method was originally for the analysis of both the inner dosimeters and facial/neck wipe samples, but a separate method (ARTF-AM-010) was developed, validated, and written for the facial/neck wipe matrix after the original method failed during subsequent analysis of field validation samples from ARTF Study ARF006. The separate method was modeled after the hand wash method (ARTF-AM-006). The validation sets were fortified on October 27, and October 28, 1997. Untreated control gauze samples were placed into a quart size, wide-mouth glass jar. Eight milliliters of 0.01% AOT solution were pipetted onto the gauze, and the samples were fortified, using volumetric pipets, with appropriate amounts of diazinon and malathion in acetone. For the companion unfortified QC sample, 8 mL of 0.01% AOT solution was added to the gauze, but no fortification made. Five hundred milliliters of 0.01% AOT were added to the jar, and the samples were shaken for 15 minutes. One gram C-18 SPE cartridges were prepared by placing cartridges on a vacuum manifold. The cartridges were washed successively with 2 x 5 mL 50:50 DCM:methanol, 2 x 5 mL methanol, and 2 x 5 mL water. The vacuum was limited throughout the loading, washing, and eluting procedure to achieve flows of only approximately 1 to 2 drops per second. Ten milliliters of the sample (2 x 5 mL aliquots) were pipetted onto the C-18 column. Samples were percolated through the column and the column was washed with 5 mL of water. All eluates up to this point were discarded.

With full vacuum (> 20" Hg) on the manifold, the columns were air-dried for at least 45 minutes. The diazinon and malathion eluted from the column with 8 mL of 50:50 DCM:methanol. The eluate was collected in a 15-mL culture tube, transferred to a 125-mL evaporation flask, and the tube rinsed twice with approximately 2 mL 50:50 DCM:methanol which was added to the flask. The samples were vacuum-evaporated to dryness and the dry residues were dissolved in a known volume of 1.5% DEGDEE:acetone (generally 2.0 mL for LOQ residues). The samples were quickly transferred to culture tubes to minimize evaporation of the

solvent. Dilutions were prepared, with the same solvent, as necessary to maintain analyte concentrations within the standard curve range. Samples were analyzed by GC/FPD(P) as described in Section 4.8.

4.8 Calibration Standards and Gas Chromatographic Analysis

Two sets of mixed calibration standards were used for the method validations described herein. The mixed calibration standards used for the validation of the inner dermal dosimeter, hand wash, leaf wash, and air tubes were diluted from primary stock solutions prepared on March 24, 1997. These primary stock solutions were prepared at concentrations of 9.92 mg/mL diazinon and 10.2 mg/mL malathion in acetone.

The mixed calibration standards used for the validation of the outer dermal dosimeter matrices were diluted from primary stock solutions prepared on July 24, 1997. These primary stock solutions were prepared at concentrations of 10.0 mg/mL diazinon and 10.0 mg/mL malathion in acetone.

Mixed fortification solutions were prepared from mixed dilutions and assigned a unique identification. All dilutions were prepared using class A volumetric glassware using 1.5% DEGDEE in acetone as the dilution solvent. They are documented in the raw data. These dilutions were assigned expiration dates corresponding to six months after the date each dilution was made. Six calibration standards were prepared in a range from approximately 4 to 100 ng/mL. The fortification solutions were stored in a freezer set at approximately -20 °C when not in use.

The samples were analyzed using gas chromatography with flame photometric detection in the phosphorus mode. The following conditions were typical of those employed in the analysis of the actual method validation samples. The actual conditions of the individual analysis sets are included in the raw data.

Instrument:	HP 5890 Series II
Autoinjector:	HP 7673B
Column:	HP-5MS, 30 M X 0.25 mm, 0.25 µm film thickness
Electrometer:	Range 4
Temperatures:	Injector (°C): 230
	Detector (°C): 230
Column:	
Initial Temp.(C):	95
Initial Time:	1.0 min.
Program Rate 1:	30 °C/min to 230 °C, hold 4 min

Program Rate 2:	40 °C/min to 290 °C, hold 4 min
Carrier Gas Flow Rate:	He 2.2 mL/min
Septum Purge:	He 2.0 mL/min
Make Up Gas:	N_2 28 mL/min
Air Flow Rate:	95 mL/min.
Hydrogen Flow Rate:	78 mL/min.
Purge Valve:	Off at 0 min, on at 0.75 min
Injection Volume:	2 µL

4.9 Changes to the Analytical Procedure

Numerous textual revisions, such as increasing the specificity of the reagent and glassware description, were made to the draft methods provided by Horizon Laboratories, Inc., which are not documented here. The modifications made to the technical aspect of the analytical method in order to obtain acceptable validation results are presented in this section with discussion.

Draft method ARTF-AM-005 originally contained both the inner dermal dosimeter and facial/neck wipe method. The facial/neck wipe method was validated as described; however, it subsequently failed to perform adequately with field validation samples. As a result, a new method was applied based on the hand wash method which used C-18 SPE cleanup instead of Florisil®.

The draft method ARTF-AM-005 was validated for use with inner dermal dosimeters as written except that triple the volume of 15% diethyl ether in hexane was used to quantifiably elute the two compounds from the Florisil®. The method included a description of a procedure for profiling the column cleanup step. It was determined that 120 mL of elution solvent was required instead of the 40 mL listed in the method. No investigation was made into the effects of increasing the solvent strength (e.g., 25% diethyl ether in hexane) on recovery or interferences. A modification such as a change in the elution volume is typical of the variability found between manufacturers and lots of cleanup media such as Florisil®, so a laboratory must routinely profile such a procedure to ensure adequate performance. The method specified that such a profile should be done with each lot of Florisil® used.

The draft method ARTF-AM-006 was validated for use with hand wash solutions, and was adapted for use with facial/neck wipes as a separate method (ARTF-AM-010). The draft method for the hand wash solutions was used as written with the exception that collection of the diazinon and malathion was performed into culture tubes, with the eluant then transferred to the evaporation flasks. This was necessary because of the

limited size of the vacuum manifolds used in this laboratory. The method validation was performed using 8 mL of methylene chloride as the elution solvent (as written). The method allowed for the adjustment of this elution volume, and the proposed final method allows for adjustment of both the volume and the composition to obtain quantitative recoveries with the matrix. Examples of this may be the use of 50:50 methanol:methylene chloride to improve solvent strength, or a mixture of hexane:methylene chloride to reduce coelution of interfering compounds.

The draft method ARTF-AM-007 was validated for use with leaf wash solutions. The draft method for the leaf wash solutions was used as written with the exception that collection of the diazinon and malathion was done into culture tubes, with the eluant then transferred to the evaporation flasks. This was necessary because of the limited size of the vacuum manifolds used in this laboratory. The method validation was performed using 8 mL of methylene chloride as the elution solvent (as written). The method allowed for the adjustment of this elution volume, and the proposed final method allowed for adjustment of both the volume and the composition to obtain quantifiable recoveries with the matrix. Examples of this may be the use of 50:50 methanol:methylene chloride to improve solvent strength, or a mixture of hexane:methylene chloride to reduce coelution of interfering compounds.

The draft method ARTF-AM-008 was validated for use with outer dermal dosimeter shirts and pants. The draft method required several method trials. A revision was made to the description of the technique and extract volumes prior to yielding acceptable results. The volume of water required to keep coextractants in solution during the subsequent aqueous:organic partition was increased from 15 mL to 20 mL. A corresponding increase in the volume of hexane and diethyl ether was made from 5 mL to 7.5 mL for the initial partition, and from 10 mL of 50:50 hexane:diethyl ether to 15 mL in the second and third partitions. The increase in the volume of aqueous phase yielded a reduction in the formation of precipitates, and reduced a gelatinous emusive interface that formed during the partitions that did not disperse upon centrifugation.

In addition, collection of the diazinon and malathion was done in culture tubes, with the eluant then transferred to the evaporation flasks. This was necessary because of the limited size of the vacuum manifolds used by this laboratory. The method validation was performed using 12 mL of methylene chloride as the elution solvent for the pants, and 16 mL for the shirts, instead of the 8 mL as originally written. The method allowed for the adjustment of this elution volume, and the proposed final method allowed for adjustment of both the volume and the composition to obtain quantifiable recoveries from the matrix. Examples of this may be the use of 50:50 methanol:methylene chloride to improve solvent strength, or a

mixture of hexane:methylene chloride to reduce coelution of interfering compounds.

The draft method ARTF-AM-009 was validated for use with OVS air sampling tubes containing XAD-2 adsorbent resin. The draft method for the air tubes was used as written with slight modifications. The validation was performed on the entire contents (front and back sections together) of the air tubes. A 50-mL culture tube was used for the extraction vessel. The interiors of the glass tubes were rinsed with approximately 3 mL of acetone after transfer of the tube contents, and the vortexing period was decreased from 30 seconds to approximately 15 seconds to improve sample throughput. In addition, the final volume for LOQ residues was changed from 1.25 mL to 1.00 mL. A high bias was encountered for the LOQ samples, possibly due to the small volume (1.00 mL) of 1.5% DEGDEE in acetone used to reconstitute the residues in a 125-mL evaporation flask. The method was also modified to include the immersion of the evaporation flask in an ice water bath to reduce the volatilization of acetone from the flask walls. The proposed final method included a description of handling the OVS tubes in which the front and back sections are analyzed separately as well as together, and the differences in handling field samples versus controls and fortification samples (both laboratory and field).

The draft method ARTF-AM-010 was validated for use with facial/neck wipes. It was adapted from the hand wash method (ARTF-AM-006). A procedure similar to the original facial/neck wipe method was incorporated into the inner dermal dosimeter method (ARTF-AM-005). The original draft method was validated, but subsequently failed with field validation samples. Therefore, a new method was adapted from the hand wash method using C-18 SPE cartridges instead of Florisil® in the cleanup step.

The draft method for the hand wash solutions was adapted and used as written for the facial/neck wipe samples with the following exceptions. No hexane wash was included in the C-18 SPE cleanup step in order to speed sample throughput. The method allowed for the use of hexane and other modifications to the C-18 cleanup as dictated by need. Collection of the diazinon and malathion was performed into culture tubes, with the eluant then transferred to the evaporation flasks. This was necessary because of the limited size of the vacuum manifolds used in this laboratory. The method validation was performed using 8 mL of 50:50 methanol:methylene chloride as the elution solvent. The method originally called for the use of 8 mL of neat methylene chloride, but column profile results indicated that as much as a 10-15% improvement in recovery was obtained using the more polar elution solvent without compromising the cleanup. The proposed final method allowed for the adjustment of the elution volume and the composition to obtain

quantifiable recoveries from the matrix. Examples of this may be the use of 50:50 methanol:methylene chloride to improve solvent strength as was necessary for the validation, or a mixture of hexane:methylene chloride to reduce coelution of interfering compounds.

5.0 STATISTICAL METHODS AND CALCULATIONS

The recoveries reported for both diazinon and malathion for a given method validation set were corrected for the amount of respective compound detected and quantified in the control analyzed with the set. Confirmational analysis of apparent outliers was performed based on recommendations from the Analytical Monitor for the ARTF. Confirmational analysis, including ruggedness testing, was also performed at the request of the Analytical Monitor for some sets.

Statistical methods employed included linear regression with 1/y weighting based on an external standard curve. Data were acquired with a VG Multichrom data system. In general, six external standard levels were used ranging from approximately 4 to 100 ng/mL, from which a 1/y weighted regression curve was generated using height, in µV (for inner dosimeters only, area in µVsec was used), vs. concentration. Use of the 1/y weighting reduced the effect of the higher standards upon the curve line that was calculated, and typically resulted in smaller curve intercepts. This curve technique was used for all matrices. The minimum acceptable correlation coefficient (r) deemed acceptable was 0.995.

The results from the extrapolation and data manipulation performed by the system yielded results in units of µg/sample for diazinon and malathion residues.

Examples of the specific equations are given below. If dilutions were necessary to cause the responses of the diazinon or malathion to fall within the range of the standard curve, these factors were also introduced into the equation.

In addition, method validation results for the minimum two sets were subjected to statistical evaluation. In general, the mean and standard deviation for the twelve or eighteen samples included in the validation results were calculated to three significant figures, and the 95% confidence interval calculated based on the mean plus or minus two times the standard deviation.

5.1 Example Calculations

The following example is taken from the inner dermal dosimeter method validation set with sample 43767-009, an LOQ fortification sample. The 1/y weighted regression equations for the lines obtained from the area response of six external standards of diazinon and malathion concentrations of approximately 4, 10, 20, 40, 60, and 100 ng/mL, were:

$$y\,(\text{peak area in } \mu V\ sec) = (609.521\ \mu V\ sec/\ (ng\ /\ mL))\,(X\ ng\ /\ mL) + 462.428\ \mu V\ sec \text{ for diazinon}$$

and

$$y\,(\textit{peak area in } \mu V\ sec) = (497.859\ \mu V\ sec/\ (ng\ /\ mL))\,(X\ ng\ /\ mL) + 471.318\ \mu V\ sec\ \textit{for malathion}$$

For inner dosimeter LOQ fortification sample 43767-009, the diazinon peak area was 5008 µVs, and the malathion peak area was 3800 µVs. Thus,

$$X\ ng\ /\ mL\ diazinon = \frac{(5008\ \mu V\ sec - 462.428\ \mu V\ sec)}{(609.521\ ng\ /\ mL\ /\ \mu V\ sec)} = 7.4576\ ng\ /\ mL$$

and

$$X\ ng\ /\ mL\ malathion = \frac{(3800\ \mu V\ sec - 471.318\ \mu V)}{(497.859\ ng\ /\ mL\ /\ \mu V)} = 6.6860\ ng\ /\ mL$$

Conversion of the result in units of ng/mL to the reporting units of µg/segment was performed automatically by the data system with the following general equation:

$$\mu g\ found = \frac{(ng\ /\ mL\ found)\,(Final\ volume\ in\ mL)\,(Factor\ 1)}{(Factor\ 2)}$$

where final volume (mL) is the initial final volume of the reconstituted residues prior to any dilutions, factor 1 is the general conversion factor based on the algebraic numerators in the conversion equation, and factor 2 is the general conversion factor based on the algebraic denominators in the conversion equation. The numerator and denominator factors are based upon aliquot factors and unit conversion factors. The entire conversion equation is as follows:

$$\mu g\ found = \frac{(ng\ /\ mL\ found)\,(2.50\ mL\ final\ volume)\,(20.0\ mL)\,(1000\ mL)}{(1000\ ng\ /\ \mu g)\,(50.0\ mL)\,(8.00\ mL)}$$

This equation was summarized as the final volume, factor 1, and factor 2, which were entered into the VG Multichrom sequence file prior to acquisition of the data. Thus the data, when worked up after completion of the acquisition, were reported automatically in the proper units of ug/segment, as shown in the example below:

$$\mu g\ Diazinon\ found = \frac{(7.4576\ ng\ /\ mL)\,(2.50\ mL\ final\ volume)\,(20{,}000)}{(400{,}000)} = 0.932\ mg$$

Recovery was then calculated as shown below:

$$\%\ Recovery = \frac{(\mu g\ Diazinon\ found - \mu g\ found\ in\ set\ control)}{\mu g\ Diazinon\ applied} \times 100 = \frac{(0.932\ \mu g - 0\ \mu g)}{0.992\ \mu g}$$

$$= 94.0\%\ recovery$$

This general format was used for all matrices although the final volumes and algebraic equations were different for the various matrices, and thus these conversion factors varied from method to method. The general algebraic equations for the LOQ samples of the various methods are shown below. The equation would require modification for dilutions prepared from the final extract:

Method ARTF-AM-005, Inner Dermal Dosimeters

$$\mu g\ found = \frac{(ng / mL\ found)(Final\ Volume\ in\ mL)(20.0\ mL)(1000\ mL)}{(1000\ ng / \mu g)(50.0\ mL)(8.00\ mL)}$$

LOQ Final Volume:	2.50 mL
Factor 1:	20,000
Factor 2:	400,000

Method ARTF-AM-006, Hand Wash Solutions

$$\mu g\ found = \frac{(ng / mL\ found)(Final\ Volume\ in\ mL)(500\ mL)}{(1000\ ng / \mu g)(10.0\ mL)}$$

LOQ Final Volume:	2.50 mL
Factor 1:	500
Factor 2:	10,000

Method ARTF-AM-007, Leaf Wash Solutions

$$\mu g\ found = \frac{(ng / mL\ found)(Final\ Volume\ in\ mL)(200\ mL)}{(1000\ ng / \mu g)(5.00\ mL)}$$

LOQ Final Volume:	6.00 mL
Factor 1:	200
Factor 2:	5000

Method ARTF-AM-008, Outer Dermal Dosimeters

$$\mu g\ found = \frac{(ng / mL\ found)(Final\ Volume\ in\ mL)(2500\ mL)(15\ mL)}{(1000\ ng / \mu g)(25\ mL)(5\ mL)}$$

LOQ Final Volume:	2.00 mL
Factor 1:	37,500
Factor 2:	125,000

Method ARTF-AM-009, OVS Air Sampling Tubes

$$\mu g\ found = \frac{(ng / mL\ found)(Final\ Volume\ in\ mL)}{(1000\ ng / \mu g)}$$

LOQ Final Volume:	1.00 mL
Factor 1:	1
Factor 2:	1000

Method ARTF-AM-010, Facial/Neck Wipes

$$\mu g\ found = \frac{(ng / mL\ found)(Final\ Volume\ in\ mL)(500\ mL)}{(1000\ ng / \mu g)(10\ mL)}$$

LOQ Final Volume:	2.00 mL
Factor 1:	500
Factor 2:	10,000

6.0 RESULTS

6.1 ARTF-AM-005 Determination of Diazinon and Malathion in Inner Dermal Dosimeters

Method validation results for inner dermal dosimeters are presented in Table 2. Fortification levels used for the validation work were nominal 1, 10, and 1000 µg/segment. The average and standard deviation for the recovery of diazinon and malathion from the twelve fortification samples reported was 99.9% ± 8.62% and 98.5% ± 9.83%, respectively. The 95% confidence intervals based on these results were 82.7% to 117% for diazinon, and 78.8% to 118% for malathion. The results implied a slight high bias in the recoveries at the LOQ of 1 µg. All of the reported recoveries fell within the 70% to 120% range.

6.2 ARTF-AM-006 Determination of Diazinon and Malathion in Hand Wash Solutions

Method validation results for hand wash solutions are presented in Table 3. Fortification levels used for the validation work were nominal 1, 10, and 1000 µg/500 mL solution. The average and standard deviation for the recovery of diazinon and malathion from the twelve fortification samples reported was 99.3% ± 9.97% and 105% ± 9.23%, respectively. The 95% confidence intervals based on these results were 79.4% to 119% for diazinon, and 86.5% to 123% for malathion. The results implied a slight high bias in the recovery of malathion, although both diazinon and malathion showed a slight high bias in the first validation set. All of the reported recoveries fell within the 70% to 120% range.

6.3 ARTF-AM-007 Determination of Diazinon and Malathion in Leaf Wash Solutions

Method validation results for leaf wash solutions are presented in Table 4. Fortification levels used for the validation work were nominal 2, 20, and 2000 µg/200 mL solution. The average and standard deviation for the recovery of diazinon and malathion from the twelve fortification samples reported was 92.5% ± 10.3% and 97.5% ± 10.5%, respectively. The 95% confidence intervals based on these results were 71.9% to 113% for diazinon, and 76.5% to 119% for malathion. All of the reported recoveries fell within the 70% to 120% range except for one low fortification (LOQ) sample which yielded diazinon and malathion recoveries of 69.2% and 68.1%, respectively.

6.4 ARTF-AM-008 Determination of Diazinon and Malathion in Outer Dermal Dosimeters

Method validation results for outer dermal dosimeters are presented in Tables 5 and 6. Fortification levels used for the validation work were nominal 5, 50, and 10,000 µg/segment. Difficulties were encountered with the original draft method that resulted in modifications and additional validation and ruggedness testing at the request of the ARTF. For the outer dosimeter shirt segments, a third validation set (consisting of six fortification samples) was analyzed. In addition, two additional aliquots from the extracts of this third validation set were analyzed on two separate days in order to evaluate method ruggedness.

The average and standard deviation for the recovery of diazinon and malathion from the eighteen fortification samples reported in Table 5 for outer dosimeter shirt segments was 86.7% ± 9.63% and 92.4% ± 10.1%, respectively. The 95% confidence intervals based on these results were 67.4% to 106% for diazinon, and 72.2% to 113% for malathion. All of the reported recoveries fell within the 70% to 120% range except for one low

fortification (LOQ) sample which yielded a diazinon recovery of 65.1%. The malathion recovery for that same fortification sample was acceptable at 85.3%.

The results of the two additional analysis sets that were prepared on different days from the extracts of the final validation set are also presented in Table 5. In general, the recoveries were within the 70% to 120% range with the exception of a single diazinon recovery at the LOQ, demonstrating that the method was rugged in terms of consistently yielding acceptable recoveries.

The average and standard deviation for the recovery of diazinon and malathion from the twelve fortification samples reported in Table 6 for outer dosimeter pant segments was 92.7% ± 6.93% and 103% ± 8.36%, respectively. The 95% confidence intervals based on these results were 78.8% to 107% for diazinon, and 86.3% to 120% for malathion. All of the reported recoveries fell within the 70% to 120% range.

6.5 ARTF-AM-009 Determination of Diazinon and Malathion in OVS Air Sampling Tubes

Method validation results for OVS air tubes are presented in Table 7. Fortification levels used for the validation work were nominal 0.01, 1, and 100 µg/air tube. High bias was observed in the method at the LOQ in the first validation set, so the method was modified for the second validation set. A third set consisting of only a control and duplicate fortifications at the LOQ were prepared and used in the calculation of the mean and standard deviation. The average and standard deviation for the recovery of diazinon and malathion from the twelve fortification samples reported was 96.6% ± 7.23% and 103% ± 4.66%, respectively. The 95% confidence intervals based on these results were 82.1% to 111% for diazinon, and 93.7% to 112% for malathion. After modification of the method to account for the high bias at the LOQ, all of the reported recoveries fell within the 70% to 120% range.

6.6 ARTF-AM-010 Determination of Diazinon and Malathion in Facial/Neck Wipes

Method validation results for facial/neck wipes are presented in Table 8. Fortification levels used for the validation work were nominal 1, 10, and 1000 µg/gauze wipe. The original draft method provided by the method developers was similar to the inner dermal dosimeter method and was successfully validated. This method, however, failed in subsequent application to field fortification samples (which were generated as part of ARTF Study ARF006), so a new method was developed and validated based on the hand wash method reported herein. The results report in Table 8 are from the validation with the new facial/neck wipe method.

This new method employed a C-18 SPE cartridge cleanup procedure in place of the liquid-liquid partitioning and Florisil cleanup procedures specified in the original method.

The average and standard deviation for the recovery of diazinon and malathion from the twelve fortification samples reported was 92.3% ± 6.53% and 96.3% ± 14.6%, respectively. The 95% confidence intervals based on these results were 79.2% to 105% for diazinon, and 67.1% to 126% for malathion. All of the reported recoveries fell within the 70% to 120% range except for a single malathion recovery at the LOQ at 121%. The corresponding diazinon recovery for that sample was acceptable at 105%. The data imply that there may be bias for the recovery of malathion as a function of concentration. Recoveries, biased slightly high at the LOQ of 1 µg/wipe, were in the 90-100% range at 10 µg/wipe, and were lower, although acceptable, at 1000 µg/wipe.

Table 1. Chronological Listing of Events

		Date					
Validation Matrix	Draft Method Identification	First Validation Set Fortified	First Validation Set Analyzed	Second Validation Set Fortified	Second Validation Set Analyzed	Third Validation Set Fortified	Third Validation Set Analyzed
Inner Dermal Dosimeters	ARTF-AM-005	7-Apr-97	10-Apr-97	23-Apr-97	24-Apr-97	N/A	N/A
Hand Wash Solution	ARTF-AM-006	16-Jun-97	20-Jun-97	23-Jun-97	23-Jun-97	N/A	N/A
Leaf Wash Solution	ARTF-AM-007	27-Jun-97	27-Jun-97	30-Jun-97	1-Jul-97	N/A	N/A
Outer Dermal Dosimeters (Pants)	ARTF-AM-008	20-Aug-97	24-Aug-97	21-Aug-97	22-Aug-97	N/A	N/A
Outer Dermal Dosimeters (Shirts)	ARTF-AM-008	29-Aug-97	29-Aug-97	2-Sep-97	2-Sep-97	4-Sep-97	4-Sep-97
OVS Air Tubes	ARTF-AM-009	9-Jul-97	10-Jul-97	16-Jul-97	18-Jul-97	18-Jul-97[1]	18-Jul-97[1]
Facial/Neck Wipes	ARTF-AM-010	27-Oct-97	27-Oct-97	28-Oct-97	28-Oct-97	N/A	N/A

[1] The third validation set for the OVS air tubes consisted of a control and two controls each fortified at the LOQ.

Table 2 Validation Data for Inner Dermal Dosimeter Method ARTF-AM-005

	Diazinon			Malathion		
Sample ID	Fortification Level (ug/dosimeter)	Recovery (ug/dosimeter)	% Recovery	Fortification Level (ug/dosimeter)	Recovery (ug/dosimeter)	% Recovery
43767-001R	NA	Not Detected		NA	Not Detected	
43767-002R	0.992	1.10	111%	1.02	1.05	103%
43767-003R	0.992	1.12	113%	1.02	1.07	105%
43767-004R	9.92	9.51	95.9%	10.2	9.00	88.2%
43767-005R	9.92	9.94	100%	10.2	10.0	98.0%
43767-006R	992	924	93.1%	1020	947	92.8%
43767-007R	992	867	87.4%	1020	888	87.1%
43767-008	NA	Not Detected		NA	Not Detected	
43767-009	0.992	0.932	94.0%	1.02	0.836	82.0%
43767-010	0.992	1.11	112%	1.02	1.19	117%
43767-011	9.92	9.70	97.8%	10.2	10.4	102%
43767-012	9.92	10.4	105%	10.2	11.0	108%
43767-013	992	982	99.0%	1020	1040	102%
43767-014	992	896	90.3%	1020	990	97.1%
		Average % Recovery (n=12)	99.9%		Average % Recovery (n=12)	98.5%
		Standard Deviation (n=12)	8.62%		Standard Deviation (n=12)	9.83%
		Avg. + 2 Std. Dev.	117%		Avg. + 2 Std. Dev.	118%
		Avg. - 2 Std. Dev.	82.7%		Avg. - 2 Std. Dev.	78.8%

Table 3 Validation Data for Hand Wash Method ARTF-AM-006

	Diazinon			Malathion		
Sample ID	Fortification Level (ug/sample)	Recovery (ug/sample)	% Recovery	Fortification Level (ug/sample)	Recovery (ug/sample)	% Recovery
43767-029	NA	Not Detected		NA	Not Detected	
43767-030	0.992	1.02	103%	1.02	1.15	113%
43767-031	0.992	0.879	88.6%	1.02	0.928	91.0%
43767-032-1	9.92	10.9	110%	10.2	11.2	110%
43767-033-2	9.92	11.1	112%	10.2	11.6	114%
43767-034	992	1060	107%	1020	1150	113%
43767-035	992	1020	103%	1020	1170	115%
43767-036	NA	Not Detected		NA	Not Detected	
43767-037	0.992	0.897	90.4%	1.02	0.941	92.3%
43767-038	0.992	0.784	79.0%	1.02	0.952	93.3%
43767-039	9.92	9.17	92.4%	10.2	9.98	97.8%
43767-040	9.92	9.53	96.1%	10.2	10.4	102%
43767-041	992	1030	104%	1020	1070	105%
43767-042	992	1050	106%	1020	1140	112%
		Average % Recovery (n=12)	99.3%		Average % Recovery (n=12)	105%
		Standard Deviation (n=12)	9.97%		Standard Deviation (n=12)	9.23%
		Avg. + 2 Std. Dev.	119%		Avg. + 2 Std. Dev.	123%
		Avg. - 2 Std. Dev.	79.4%		Avg. - 2 Std. Dev.	86.5%

Table 4 Validation Data for Leaf Wash Method ARTF-AM-007

	Diazinon			Malathion		
Sample ID	Fortification Level (ug/sample)	Recovery (ug/sample)	% Recovery	Fortification Level (ug/sample)	Recovery (ug/sample)	% Recovery
43767-043	NA	Not Detected		NA	Not Detected	
43767-044	1.98	1.37	69.2%	2.04	1.39	68.1%
43767-045	1.98	1.62	81.8%	2.04	2.14	105%
43767-046	19.8	17.6	88.9%	20.4	19.5	95.6%
43767-047	19.8	18.3	92.4%	20.4	19.8	97.1%
43767-048	1980	1870	94.4%	2040	2010	98.5%
43767-049	1980	1800	90.9%	2040	1930	94.6%
43767-050	NA	Not Detected		NA	Not Detected	
43767-051	1.98	2.12	107%	2.04	2.19	107%
43767-052	1.98	1.70	85.9%	2.04	1.89	92.6%
43767-053	19.8	19.1	96.5%	20.4	20.4	100%
43767-054	19.8	19.3	97.5%	20.4	21.0	103%
43767-055	1980	2010	102%	2040	2060	101%
43767-056	1980	2030	103%	2040	2200	108%
		Average % Recovery (n=12)	92.5%		Average % Recovery (n=12)	97.5%
		Standard Deviation (n=12)	10.3%		Standard Deviation (n=12)	10.5%
		Avg. + 2 Std. Dev.	113%		Avg. + 2 Std. Dev.	119%
		Avg. - 2 Std. Dev.	71.9%		Avg. - 2 Std. Dev.	76.5%

Table 5 Validation Data for Outer Dermal Dosimeter Shirt Method ARTF-AM-008

	Diazinon			Malathion		
Sample ID	Fortification Level (ug/segment)	Recovery (ug/segment)	% Recovery (1)	Fortification Level (ug/segment)	Recovery (ug/segment)	% Recovery (1)
43767-126	NA	0.494		NA	0.0464	
43767-127	5.00	4.71	84.3%	5.00	4.61	91.3%
43767-128	5.00	3.75	65.1%	5.00	4.31	85.3%
43767-129	50.0	44.6	88.2%	50.0	47.4	94.7%
43767-130	50.0	40.5	80.0%	50.0	39.8	79.5%
43767-131	10000	7090	70.9%	10000	7840	78.4%
43767-132	10000	7780	77.8%	10000	7500	75.0%
43767-133	NA	0.648		NA	Not Detected	
43767-134	5.00	5.56	98.2%	5.00	5.67	113%
43767-135	5.00	5.30	93.0%	5.00	5.21	104%
43767-136	50.0	50.3	99.3%	50.0	51.1	102%
43767-137	50.0	45.1	88.9%	50.0	45.3	90.6%
43767-138	10000	9410	94.1%	10000	9380	93.8%
43767-139	10000	8390	83.9%	10000	8830	88.3%
43767-140	NA	Not Detected		NA	Not Detected	
43767-141	5.00	5.08	102%	5.00	5.15	103%
43767-142	5.00	4.21	84.2%	5.00	5.03	101%
43767-143	50.0	42.3	84.6%	50.0	42.8	85.6%
43767-144	50.0	47.6	95.2%	50.0	48.6	97.2%
43767-145	10000	8790	87.9%	10000	9560	95.6%
43767-146	10000	8320	83.2%	10000	8470	84.7%
		Average % Recovery (n=18)	86.7%		Average % Recovery (n=18)	92.4%
		Standard Deviation (n=18)	9.63%		Standard Deviation (n=18)	10.1%
		Avg. + 2 Std. Dev.	106%		Avg. + 2 Std. Dev.	113%
		Avg. - 2 Std. Dev.	67.4%		Avg. - 2 Std. Dev.	72.2%

(1) Corrected for ug found in respective control sample.

Table 5 Validation Data for Outer Dermal Dosimeter Shirt Method ARTF-AM-008 (continued)

	Diazinon			Malathion		
Sample ID	Fortification Level (ug/segment)	Recovery (ug/segment)	% Recovery (1)	Fortification Level (ug/segment)	Recovery (ug/segment)	% Recovery (1)
Ruggedness Testing						
43767-140A	NA	Not Detected		NA	Not Detected	
43767-141A	5.00	4.86	97.2%	5.00	4.74	94.8%
43767-142A	5.00	6.32	126%	5.00	5.96	119%
43767-143A	50.0	56.0	112%	50.0	54.3	109%
43767-144A	50.0	56.3	113%	50.0	59.2	118%
43767-145A	10000	7190	71.9%	10000	9870	98.7%
43767-146A	10000	9300	93.0%	10000	9540	95.4%
43767-140B	NA	Not Detected		NA	Not Detected	
43767-141B	5.00	5.33	107%	5.00	5.58	112%
43767-142B	5.00	5.75	115%	5.00	5.22	104%
43767-143B	50.0	55.1	110%	50.0	57.9	116%
43767-144B	50.0	52.0	104%	50.0	54.4	109%
43767-145B	10000	9830	98.3%	10000	9910	99.1%
43767-146B	10000	9390	93.9%	10000	9740	97.4%
	Average % Recovery (n=12)		103%	Average % Recovery (n=12)		106%
	Standard Deviation (n=12)		13.9%	Standard Deviation (n=12)		8.96%
	Avg. + 2 Std. Dev.		131%	Avg. + 2 Std. Dev.		124%
	Avg. - 2 Std. Dev.		75.2%	Avg. - 2 Std. Dev.		88.1%

(1) Corrected for μg found in respective control sample.

Table 6 Validation Data for Outer Dermal Dosimeter Pant Method ARTF-AM-008

	Diazinon			Malathion		
Sample ID	Fortification Level (ug/segment)	Recovery (ug/segment)	% Recovery (1)	Fortification Level (ug/segment)	Recovery (ug/segment)	% Recovery
43767-098	NA	0.765		NA	Not Detected	
43767-099	5.00	6.07	106%	5.00	5.73	115%
43767-100	5.00	5.64	97.5%	5.00	5.47	109%
43767-101	50.0	47.1	92.7%	50.0	51.6	103%
43767-102	50.0	44.3	87.1%	50.0	47.7	95.4%
43767-103	10000	8290	82.9%	10000	9380	93.8%
43767-104	10000	8620	86.2%	10000	9180	91.8%
43767-105	NA	0.609		NA	Not Detected	
43767-106	5.00	5.44	96.6%	5.00	5.30	106%
43767-107	5.00	5.46	97.0%	5.00	5.84	117%
43767-108	50.0	44.7	88.2%	50.0	52.5	105%
43767-109	50.0	50.5	99.8%	50.0	54.3	109%
43767-110	10000	8530	85.3%	10000	9470	94.7%
43767-111	10000	9250	92.5%	10000	10000	100%
		Average % Recovery (n=12)	92.7%		Average % Recovery (n=12)	103%
		Standard Deviation (n=12)	6.93%		Standard Deviation (n=12)	8.36%
		Avg. + 2 Std. Dev.	107%		Avg. + 2 Std. Dev.	120%
		Avg. - 2 Std. Dev.	78.8%		Avg. - 2 Std. Dev.	86.3%

(1) Corrected for ug found in respective control sample.

Table 7 Validation Data for OVS Air Tube Method ARTF-AM-009

	Diazinon			Malathion		
Sample ID	Fortification Level (ug/air tube)	Recovery (ug/air tube)	% Recovery (2)	Fortification Level (ug/air tube)	Recovery (ug/air tube)	% Recovery (2)
43767-057	NA	0.00096		NA	Not Detected	
43767-058 (1)	0.00992	0.0125	116%	0.0102	0.0118	116%
43767-059 (1)	0.00992	0.0138	129%	0.0102	0.0135	132%
43767-060	0.992	1.01	102%	1.02	1.09	107%
43767-061	0.992	0.994	100%	1.02	1.05	103%
43767-062	99.2	77.8	78.4%	102	104	102%
43767-063	99.2	101	102%	102	105	103%
43767-074	NA	Not Detected		NA	Not Detected	
43767-075	0.00992	0.0101	102%	0.0102	0.0108	106%
43767-076	0.00992	0.0103	104%	0.0102	0.0104	102%
43767-077	0.992	0.898	90.5%	1.02	1.10	108%
43767-078	0.992	1.01	102%	1.02	1.13	111%
43767-079	99.2	92.3	93.0%	102	103	101%
43767-080	99.2	92.9	93.6%	102	102	100%
43767-088	NA	Not Detected		NA	Not Detected	
43767-089	0.00992	0.00953	96.1%	0.0102	0.0101	99.0%
43767-090	0.00992	0.00944	95.2%	0.0102	0.00952	93.3%
		Average % Recovery (n=12)	96.6%		Average % Recovery (n=12)	103%
		Standard Deviation (n=12)	7.23%		Standard Deviation (n=12)	4.66%
		Avg. + 2 Std. Dev.	111%		Avg. + 2 Std. Dev.	112%
		Avg. - 2 Std. Dev.	82.1%		Avg. - 2 Std. Dev.	93.7%

(1) Not included in statistical results. The method was modified subsequent to these analyses to reduce the potential for the evaporation of a significant percentage of solvent for those samples reconstituted in 1 mL.

(2) Corrected for the ug found in the respective control sample.

Table 8 Validation Data for Facial/Neck Wipe Method ARTF-AM-010

	Diazinon			Malathion		
Sample ID	Fortification Level (ug/gauze wipe)	Recovery (ug/gauze wipe)	% Recovery	Fortification Level (ug/gauze wipe)	Recovery (ug/gauze wipe)	% Recovery
43767-147	NA	Not Detected		NA	Not Detected	
43767-148	1.00	0.935	93.5%	1.00	1.05	105%
43767-149	1.00	0.961	96.1%	1.00	1.07	107%
43767-150	10.0	8.80	88.0%	10.0	9.95	99.5%
43767-151	10.0	9.20	92.0%	10.0	9.94	99.4%
43767-152	1000	848	84.8%	1000	769	76.9%
43767-153	1000	841	84.1%	1000	754	75.4%
43767-154	NA	Not Detected		NA	Not Detected	
43767-155	1.00	1.05	105%	1.00	1.21	121%
43767-156	1.00	1.03	103%	1.00	1.14	114%
43767-157	10.0	8.98	89.8%	10.0	9.25	92.5%
43767-158	10.0	9.31	93.1%	10.0	9.77	97.7%
43767-159	1000	873	87.3%	1000	789	78.9%
43767-160	1000	904	90.4%	1000	880	88.0%
		Average % Recovery (n=12)	92.3%		Average % Recovery (n=12)	96.3%
		Standard Deviation (n=12)	6.53%		Standard Deviation (n=12)	14.6%
		Avg. + 2 Std. Dev.	105%		Avg. + 2 Std. Dev.	126%
		Avg. - 2 Std. Dev.	79.2%		Avg. - 2 Std. Dev.	67.1%

APPENDIX A

Study Protocol, Amendments and Deviations

ARTF Protocol Number

ARF003

Sponsor/Testing Facility

Agricultural Reentry Task Force
c/o David R. Johnson
Stewart Ag. Research Services, Inc.
P.O. Box 509
Macon, MO 63552

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Study Title

VALIDATION OF METHOD FOR THE ANALYSIS OF WORKER EXPOSURE AND REENTRY MATRICES FOR DIAZINON AND MALATHION

Testing Laboratory

ABC Laboratories
7200 E. ABC Lane
P.O. Box 1097
Columbia, MO 65205
TE 573/443-9003

Testing Laboratory Study Number

43767

Total No. of Pages : 7

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1.0 STUDY PURPOSE

The purpose of this study is to validate analytical methods for the determination of diazinon and malathion in worker exposure and reentry matrices, for their accuracy and precision.

2.0 GLP COMPLIANCE STATEMENT

This study will be conducted in compliance with ABC Laboratories' Safety Procedures, Standard Operating Procedures (SOPs) and EPA Good Laboratory Practices Guidelines (40 CFR §160).

3.0 TEST SYSTEM JUSTIFICATION AND IDENTIFICATION

The test system will consist of whole body dosimeters (inner union suits, shirts and pants), handwash solution (Aerosol OT®), OVS tubes with polyurethane foam, and facial/neck wipes that will be used in worker reentry monitoring during application of diazinon and malathion to crops.

4.0 STUDY PERIOD

Proposed Experimental Start Date: February 1, 1997

Proposed Experimental Termination Date: April 1, 1997

5.0 STUDY SITE

ABC Laboratories
7200 E. ABC Lane
P.O. Box 1097
Columbia, MO 65205
Phone 573/443-9003
Fax 573/443-9034

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6.0 TEST/REFERENCE SUBSTANCE

Common Name: diazinon
Chemical Name: 0,0-diethyl 0-(2-isopropyl-6 methyl-4-pyrimidinyl) phosphorothioate
Lot Number: 09467
Purity: 87.7%
CAS No.: 333-41-5

Common Name: malathion
Chemical Name: 0,0-dimethyl phosphorodithioate of diethyl mercaptosuccinate
Lot Number: CS030
Purity: 95.0%
CAS No.: 121-75-5

ARTF has retained a reserve sample of this chemical, and has documentation specifying the location of the synthesis and characterization information for this compound. The solubility and stability of the reference substance will be the responsibility of the sponsor.

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7.0 ANALYTICAL METHODS TO BE VALIDATED

1. Determination of Diazinon and Malathion in Dermal Dosimeters
2. Determination of Diazinon and Malathion in OVS Air Sampling Tubes with Polyurethane Foam
3. Determination of Diazinon and Malathion in Handwash Solutions
4. Determination of Diazinon and Malathion in Cotton Facial/Neck Wipes

Equivalent instrumentation and reagents may be substituted for those specified in the methods. All substitutions must be clearly documented in the raw data with reasons.

8.0 STUDY PROCEDURES

1. All analytical methods and matrices will be provided by the ARTF. Procedures and techniques described in the methods will be followed as rigidly as possible. No changes are permitted without the prior approval of the ARTF.

2. Each method validation procedures will be done in the following manner:

   For each method validation, two sets of samples will be run. Each set will consist of a control and three levels of spikes (5x, 25x, and 125x the LOQ of 0.01 µg for sorbent tubes, and 1.0 µg for all other matrices) in duplicate (total of 7 samples). Each set of samples will be run on a different day.

3. Recoveries of diazinon and malathion from spiked samples will be measured against a standard curve (five point minimum) that brackets the levels of the matrix spikes. A solvent blank for the standard solutions shall be injected prior to the standard solutions for each run.

4. The validation study will be acceptable to the ARTF providing that the mean recovery minus 2 standard deviations is greater or equal to 70% recovery and the mean plus 2 standard deviations is less than or equal to 120% recovery for each spike level for each matrix. The Contractor may at its discretion replicate any sample set upon approval from ARTF.

   Estimated number of analyses: 84

   Note: Procedures 8.3 and 8.4 will insure analytical integrity of the data and address any bias.

9.0 SAMPLE DESCRIPTION

Control samples for the study consisting of the various worker exposure matrices will be supplied by the ARTF.

The ARTF sample identifications will consist of the study number and the number of the sample. The laboratory may assign their own numbers as long as the ARTF number is cross referenced and included in the documentation of the sample.

10.0 STATISTICAL EVALUATION

Chromatographic quantitation will be achieved using a standard curve obtained from peak heights or areas of injections of several concentrations of standards. The standard curve will be a least squares fit unless otherwise approved by the ARTF Analytical Subcommittee. Mean and standard deviation calculations will be done on the data generated. **All data will be supplied in a columnar format showing actual results versus the mean for each fortification level and the relative standard deviation of the mean.**

11.0 RECORDS TO BE MAINTAINED

Along with the study final report, all study-specific original data generated in the course of this study, including but not limited to the following, shall be maintained and turned over to the Agricultural Reentry Task Force at the completion of the study.

1. The study protocol as an appendix to the final report.
2. Laboratory notebooks or bench sheets used to record details of the analyses.
3. Chromatograms and/or machine-generated analysis reports and data
4. Spreadsheets and other calculated data
5. Chain-of-custody records.

In addition to the above study-specific raw data, the following records must also be kept, and original or true copies submitted with the raw data.

a) Storage conditions for reference substances and samples

b) Reference substance use log

c) Communications logs or records

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When the study is completed, all raw data will be archived at an ARTF designated GLP-Archive.

12.0 REPORT

At the completion of the study, the Study Director will submit a report including validation data to the ARTF. The report is required to be in the PR Notice 86-5 format. The report must contain but is not limited to containing:

1. A GLP compliance statement (40 CFR §160) signed by the Study Director.
2. An ABC Laboratories QAU statement giving dates of inspections and dates that findings were reported to the Study Director and Management.
3. A detailed description of each method validation.
4. Example calculations.
5. A summary of each method validation procedure and a summary of the recovery data in the format described in the STATISTICAL METHODS SECTION.
6. Representative chromatograms of control samples, fortified control samples and calibration standards.
7. A typical standard curve.
8. All elements of the EPA DRG on Analytical Methods.

Specific details can be worked out by the Study Director and the ARTF when the report is in draft form.

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13.0 AMENDMENTS AND DEVIATIONS

Amendments

Amendments to this protocol must be approved by the Study Director and be acknowledged by the Sponsor. The attached Protocol Amendment Form will be used for all amendments, and will be retained with the protocol by the ARTF QAU.

Deviations

Any deviations to the protocol, lab SOPs or GLPs, or situations that may affect the integrity of the study must be communicated to the Study Director in a timely manner. Protocol deviations are to be documented using the attached Protocol Deviation Form. The dated signatures from the Study Director and Sponsor representative of the ARTF must be obtained. The original change form will be retained with the protocol by ARTF QAU.

SOP deviations are to be documented and authorized by the Study Director, and documented in the raw data.

GLP deviations are to be documented on the "Statement of GLP Compliance" in the report. A description of any and all changes to the protocol must appear in the final report. The Study Director must be notified of any GLP deviations as they occur.

14.0 QUALITY ASSURANCE

The performing laboratory's Quality Assurance Unit will inspect the study at appropriate intervals and will review the analytical phase report for consistency with the protocol, internal SOPs, and raw data. **All findings obtained during QAU inspections and the corrective actions taken must be documented and reported promptly to the Study Director and to the performing laboratory's management.**

15.0 PROTOCOL APPROVAL

Loren C. Schrier — 5 Feb 97
Study Director — Date

David R Johnson — 1/28/97
Sponsor — Date

Del A. Koch — 5 Feb 97
Testing Laboratory Management — Date

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BY Della Koch

16.0 DISTRIBUTION LIST

Sponsor Representative / D. Johnson, Stewart Ag. Research Services, Inc.

Study Director / Loren C. Schrier, ABC Laboratories

Testing Laboratory Management / Del A. Koch, ABC Laboratories

Quality Assurance / ABC Laboratories

Quality Assurance / Agricultural Reentry Task Force (ARTF)

Agricultural Re-entry Task Force
Protocol Amendment

Protocol Number: ARF003 Protocol Amendment No. 1
ABC Laboratories Study Number 43767

Effective Date: 04/01/97

I. Add forms required by Section 13.0:

With this amendment, the required Protocol Amendment Form and Protocol Deviation Form are attached to the protocol as described in Section 13.0.

Reason for this Addition:

These forms were not attached at the time the protocol was signed.

II. Change the fortification levels described in Section 8.2 to state:

(1x, 10x, and 1000x the LOQ...) instead of (5x, 25x, and 125x the LOQ...)

Reason for this Change:

This fortification range will provide validation of the methods from the LOQ to the highest fortification evaluated during the method tryout.

III. Change table of contents on page 2 of the protocol to state:

16.0 Distribution List 7

instead of

16.0 Distribution List 8

Reason for this Change:

The incorrect page number was given in the protocol.

Agricultural Re-entry Task Force
Protocol Amendment

Protocol Number: ARF003 Protocol Amendment No. 1
ABC Laboratories Study Number 43767

Effective Date: 04/01/97

IV. Change Section 7.1 and 7.4 to read as follows:

1. Method for the Analysis of Diazinon and Malathion in Inner Cotton Whole Body Dosimeters and Gauze Facial Wipes, Draft Method ARTF-AM-005.

Reason for this Change:

This is the actual title and reference number of the draft method for the validation with dermal dosimeters and cotton facial/neck wipes. Further revisions to section 7.0 will be made to identify the actual draft methods to be validated as they become available.

V. Add Section 7.5 to read as follows:

5. Determination of Diazinon and Malathion in Leaf Wash Solutions

Reason for this Change:

This matrix was inadvertently left out of the protocol. Further revisions to section 7.0 will be made to identify the actual draft methods to be validated as they become available.

VI. Change the reference to polyurethane foam in Section 3.0 to read as follows:

..., OVS tubes with XAD-2, ... instead of ..., OVS tubes with polyurethane foam, ...

Reason for this Change:

The sorbent material for the validation will be XAD-2 instead of polyurethane foam.

Agricultural Re-entry Task Force
Protocol Amendment

Protocol Number: ARF003
ABC Laboratories Study Number 43767

Protocol Amendment No. 1

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Effective Date: 04/01/97

VII. Change Section 7.2 to read as follows:

2. Determination of Diazinon and Malathion in OVS Air Sampling Tubes with XAD-2

Reason for this Change:

The sorbent material for the validation will be XAD-2 instead of polyurethane foam.

Approved by:

Loren C. Schrier — 1 Apr 97
Loren C. Schrier — **Date**
Study Director

David R Johnson — 2 April 1997
David R. Johnson, Ph.D. — **Date**
ARTF Sponsor Representative

Agricultural Re-entry Task Force
Protocol Amendment

Protocol Number: ARF003 Protocol Amendment No._____
ABC Laboratories Study Number 43767

Effective Date: mm/dd/yy

I. Change/Add Section _____ to state:

Description of changes

Reason for this Change/Addition:

Description of reason for changes

II. Change/Add Section _____ to state:

Description of changes

Reason for this Change/Addition:

Description of reason for changes

{Add as many individual sections as necessary.}

Approved by:

_____ _____
Loren C. Schrier Date
Study Director

_____ _____
David R. Johnson, Ph.D. Date
ARTF Sponsor Representative

Agricultural Re-entry Task Force **Deviation Form**

ARTF Protocol Number: ARF003 ABC Laboratories Study Number: 43767

Nature of Deviation:

GLP Deviation:

Date of Deviation:

Date Recorded/Initials:

Describe the Deviation:

Explain Why this Deviation Occured:

Describe Actions Taken:

Impact on Study (to be completed by the study director only):

Loren C. Schrier
Study Director

Date

David R. Johnson, Ph.D.
ARTF Sponsor Representative

Date

Agricultural Re-entry Task Force
Protocol Amendment

Protocol Number: ARF003 Protocol Amendment No. 2
ABC Laboratories Study Number 43767

Effective Date: 07/07/97

I. Change Section 7.3 and 7.5 (added in Protocol Amendment 1, Part V) to read as follows:

3. Method for the Analysis of Diazinon and Malathion in 0.01% Aerosol® OT Handwash Solutions, Draft Method ARTF-AM-006.

5. Method for the Analysis of Diazinon and Malathion in 0.01% Aerosol® OT Dislodging Solutions, Draft Method ARTF-AM-007.

Reason for this Change:

These are the actual titles and reference numbers of the draft methods used for the validation with handwash and dislodging solutions. Further revisions to section 7.0 will be made to identify additional actual draft methods to be validated as they become available.

Agricultural Re-entry Task Force
Protocol Amendment

Protocol Number: ARF003
ABC Laboratories Study Number 43767

Protocol Amendment No. 2

Effective Date: 07/07/97

II. Change Section 8.2 to read as follows:

Each method validation procedure will be done in the following manner:

For each method validation, two sets of samples will be run. Each set will consist of a control and three levels of spikes in duplicate for a total of 7 samples per set. These spikes will be at 1x, 10x, and 1000x the LOQ of 1.0 μg for the inner whole body dosimeters, handwash solutions, and gauze facial wipes. For the leaf wash solutions these spikes will be at 1x, 10x, and 1000x the LOQ of 2.0 μg. For the outer dosimeters, these spikes will be at 1x, 10x, and 2000x the LOQ of 5.0 μg. For the OVS air sampling tubes, these spikes will be at 1x, 100x, and 10,000x the LOQ of 0.01 μg. Each set of samples will be run on a different day.

Reason for this Change:

These are the actual LOQ values and fortification levels that are being validated.

Approved by:

Loren C. Schrier
Study Director

7 July 97
Date

David R. Johnson, Ph.D.
ARTF Sponsor Representative

7/9/97
Date

Agricultural Re-entry Task Force
Protocol Amendment

Protocol Number: ARF003
ABC Laboratories Study Number 43767

Protocol Amendment No. 3

Effective Date: 10/22/97

I. Change Section 7 to include the following paragraph:

Due to problems encountered with the Gauze Facial Wipes method, ARTF-AM-005, the Hand Wash method, ARTF-AM-006, will be adapted and a validation attempted for the face wipes matrix. Modifications to the hand wash method will be documented in the raw data, and a draft Neck/Face Wipe method issued upon successful validation. The format for the validation will be the same as previous work in that two sets will be prepared on separate days, and each set will consist of a control plus duplicate fortification samples at three different levels.

Reason for this Change:

Although the original method ARTF-AM-005 was successfully validated, application of the method to a field validation study failed to yield acceptable recoveries for both laboratory and field fortification samples. Preliminary data suggested that the hand wash method, ARTF-AM-006, could be successfully validated with some modifications and applied to future studies.

Approved by:

Loren C. Schrier
Study Director

22 Oct 97
Date

David R. Johnson, Ph.D.
ARTF Sponsor Representative

11/3/97
Date

Agricultural Re-entry Task Force
Protocol Amendment

Protocol Number: ARF003
ABC Laboratories Study Number 43767

Protocol Amendment No. 4

Effective Date: 06/24/98

I. The Study Director for ARTF Study ARF003 is changed from Loren Schrier to Del A. Koch. Del previously provided management oversight on the study, and that responsibility will be assumed by Lyle D. Johnson.

Reason for this Change:

Change in personnel at ABC Laboratories Missouri.

Approved by:

Del A. Koch
Study Director

24 Jun 98
Date

David R. Johnson, Ph.D.
ARTF Sponsor Representative

6/28/98
Date

Agricultural Re-entry Task Force
Protocol Deviation

Protocol Number: ARF003
ABC Laboratories Study Number 43767
Effective Date: 02/01/99

Protocol Deviation No. 1

Nature of Deviation:

Section 8.0, No. 4 of the protocol states: "The validation will be acceptable to the ARTF providing that the mean recovery minus 2 standard deviations is greater or equal than 70% recovery and the mean plus two standard deviations is less than or equal to 120% recovery for each spike level for each matrix." This criterion was not achieved in many instances, particularly at the limit of quantification. This criterion was subsequently deemed to be too restrictive and, in general, not readily achievable for these methods. The methods were therefore considered to be validated even though this criterion was not met in all cases.

Effect on the Study:

Since this protocol requirement is more restrictive than necessary for method acceptability, it is concluded by the study director that there is no adverse effect on the study in failing to meet the requirement in all instances.

Corrective Actions:

The only corrective action necessary is this written documentation of the deviation from the protocol.

Approved by:

Del A. Koch — 1 Feb 99
Del A. Koch
Study Director
Date

David R Johnson — 5 Feb 99
David R. Johnson
ARTF Sponsor Representative
Date

Attachment 1. Copies of the Proposed Final Analytical Methods

Determination of Diazinon and Malathion in Inner Dermal Dosimeters

Method ARTF-AM-005

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Loren C. Schrier Date

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Determination of Diazinon and Malathion in Inner Dermal Dosimeters

Method ARTF-AM-005

I. INTRODUCTION AND SUMMARY

A. Scope

Diazinon and malathion are organophosphate insecticides used for control of certain noxious insects on agriculturally important crops. To generate data which estimate human exposure to the insecticides during agricultural applications, a method of analysis is required for determination of diazinon and malathion residues in/on cotton-based worker exposure fabrics such as inner cotton whole body dosimeters (IWBD).

B. Principle

Diazinon and malathion residues in/on IWBD are extracted with acetone. Following evaporation of the solvent, the residues are suspended in water, then partitioned into hexane; the hexane is back-extracted against water. Further purification of the hexane extract is effected by activated Florisil® chromatography. Quantification of both analytes in the final extract is performed by GC with flame photometric detection in the phosphorous mode [FPD(P)]. The claimed limit of quantification (LOQ) for diazinon and malathion is 1.0 μg/sample[1].

Figure 1 presents the chemical structures of diazinon and malathion.

II. MATERIALS AND METHODS

A. Equipment

Equipment	Suggested Manufacturers:[2]
Aluminum Foil	Local Grocery

[1]This method analyzes diazinon and malathion residues in/on segments cut from IWBD matrices (e.g., upper arms, lower legs, front torso, etc.). One segment = one sample. The lowest limit of fortification during methods development research was 1.0 μg each of diazinon and malathion/sample.

[2]Equivalent sources of the listed equipment and reagents may be used.

Analytical Balance	Ohaus GA110
Centrifuge, IEC Clinical	VWR Scientific
Centrifuge Tubes, 50 mL Round-bottomed with PTFE-Lined Screw Caps	Fisher Scientific, Catalog #05-558-5B
Gas Chromatograph with a Flame Photometric Detector Phosphorous Mode Narrow-bore Capability Split-Splitless Injector	Hewlett-Packard Model 5890 Series II
Gas Chromatograph Column	J & W Scientific, DB-5, 30 m x 0.25 mm i.d., 0.25 μm film thickness
General Laboratory Glassware	Various
Glass Columns: 11 mm i.d. x 25 cm, equipped with a PTFE stopcock and a 200 mL reservoir	Fisher Scientific, #K420280-0213
Glass Jars, 0.5 Gallon, with PTFE or foil-lined Lids, Wide-Mouth	Fisher Scientific
Glass Storage Jars, 250-500 mL, with PTFE-Lined Lids	Fisher Scientific
Glass Wool	Fisher Scientific
Rotary Evaporator	Fisher Scientific
Shaker, Eberbach	VWR Scientific
Top-loading Balance	Ohaus E400

B. Reagents and Standards

Acetone:	Fisher Optima Grade
Di(ethyleneglycol)diethylether: (i.e., DEGDEE), HPLC grade)	Sigma/Aldrich Catalog #30,827-7
1.5% DEGDEE (w:v)	Dilute 7.5 g of DEGDEE to 500 mL with acetone. Mix and store at ambient temperature.
Hexane:	Fisher Optima Grade
Diethylether (EtOEt):	Fisher Scientific, Anhydrous
15% EtOEt in Hexane (v:v)	Mix 150 mL of EtOEt with 850 mL hexane.

Florisil®: 100-200 mesh, Fisher Scientific Catalog #F101-500

Activate Florisil® overnight at 150°C. Cool and store in a desiccator; the anhydrous reagent is stable for up to 12 months.

Water:	Distilled and/or deionized.
Untreated Control Inner Whole Body Dosimeters (IWBD), Cotton:	Stewart Agricultural Research Services, Inc., P.O. Box 509, Macon, MO 63552.

Diazinon, O,O-diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]-phosphorothioate, available from ARTF.

Malathion, [(Dimethoxyphosphinothioyl)thio]-butanedioic acid diethyl ester, available from ARTF.

C. Inner Whole Body Cotton Dosimeters: Analytical Procedure

C.1 Sample Preparation

Freeze the field sample pending analysis. For analysis, cut an appropriate piece (e.g., upper arm, lower leg, front torso, etc.) from the IWBD as

specified by protocol or appropriate SOP. Re-freeze the remainder of the sample.

C.2 Extraction

a. Place the field sample into a 0.5 gallon, wide-mouth glass jar. If sample is received in foil, rinse the foil with a minimum of 50 mL acetone and include this rinse as part of the 1 L total extraction volume.

b. QC fortifications are made at this point as follows: Lay an untreated control (UTC) IWBD sample onto a sheet of aluminum foil. Fortify the cloth with an appropriate amount of diazinon and malathion in acetone (Note 1, p. 13.). Fold or roll the sample, place the sample into a 0.5 gallon, wide-mouth glass jar, then proceed as in C.2.c below. Rinse the foil with a minimum of 50 mL acetone and include this rinse as part of the 1 L total extraction volume. Discard the aluminum foil after a single use.

c. Add 1 liter of acetone to the sample (including the foil rinse volume). Cap the sample tightly with a PTFE or aluminum foil-lined lid. Shake for 0.25 hr (ca. 2 excursions/sec, Note 2, p. 13).

d. Remove the sample jar from the shaker and allow loose particulate matter to settle (1-2 minutes). Pipet a 50-mL sample aliquot into a 125-mL evaporation flask; as a backup in the event of method failure, retain ca. 200 mL of the remaining extract in a labeled, PTFE-capped glass bottle, and store in a freezer. Discard the IWBD sample.

e. Vacuum-evaporate the 50-mL sample to dryness (ca. 25" Hg, ≤35°C). **Ensure that all acetone has been removed from the sample** (Note 3, p. 13).

C.3 Partitioning

a. Add 50 mL of deionized water to the sample flask, cap, and shake well (Note 4, p. 14). Pipet exactly 20 mL of hexane onto the aqueous sample; cap and shake vigorously for 0.25 minutes. Allow the phases to separate (Note 5, p. 14).

b. With a Pasteur pipette, transfer the hexane phase (top layer) to a clean, dry, 50-mL centrifuge tube; a quantitative transfer is not necessary, but recover at least 12 mL. The sample may be stored overnight in the freezer at this point. Add 5 mL of deionized water to the sample, cap, and shake vigorously for ca. 0.25 minutes. Allow the phases to separate (Note 6, p. 14). Balance the tubes with deionized water, then centrifuge the sample for 2 minutes at approximately 1000 g (e.g., 15 cm rotation radius at 2400 rpm, Note 7, p. 14).

C.4 Florisil® Chromatography

a. Prepare an activated Florisil® clean-up column as follows: Seat a small plug of glass wool into an 11 mm i.d. glass column. Rinse the column and glass wool with EtOEt and allow to air-dry. Add 1 (±0.05) gram of fully-activated Florisil® to the column. **Do not pre-equilibrate the column with solvent**. The column is now ready for use.

b. Do not allow the Florisil® to go dry at any point in the procedure. With a pipet, transfer 8 mL of the hexane phase from step C.3.b (top layer) onto the column, taking care not to include any water droplets with the hexane (See Note 8, p. 14).

c. Percolate the sample onto the column (ca. 2 drops/second), then wash the column sides with 8 mL of hexane. Percolate the rinse through the column, stopping the flow with approximately 1 cm of hexane rinse over the top of the Florisil®. Discard all eluants to this point.

d. Elute diazinon and malathion from the column with 120 mL of 15% EtOEt in hexane (**Important**: **See Note 9, p. 15**). Collect the eluant in a 250-mL evaporation flask.

e. Vacuum-evaporate the eluant to dryness. Dissolve the dry residue in a known volume of 1.5% DEGDEE in acetone (generally 2.0 mL for LOQ residues, see Note 10, p. 16). Dilute with the same solvent as necessary to maintain analyte concentrations within the standard curve range. Submit the sample for GC/FPD(P) analysis as described in Step D.

D. Gas Chromatographic Analysis

A gas chromatograph equipped with a Flame Photometric Detector (phosphorous mode) is required. Split-splitless injection and narrow-bore capabilities are recommended. The conditions described herein may be modified provided adequate performance of the analysis is demonstrated.

GC Column: J & W DB-5, 30 m length, 0.25 mm i.d., 0.25 μm film. Other columns may be substituted if they give satisfactory resolution between the analytes and any interferences.

Injector: 230°C

Detector: 220°C

Column:

Initial: 95°C, hold 1.0 min.
Ramp Rate 1: 30°C/min to 230°C, hold 4 minutes.
Ramp Rate 2: 40°C/min to 290°C, hold 5 minutes.

Carrier Gas: He, 1.7 mL/min at 95°C, head pressure = 20 psi. Constant flow off.

Septum Purge: He @ 3.0 mL/min.

Injector Liner: HP Liner, Deactivated, 4 mm i.d., with Deactivated Glass Wool Plug, Part #5062-3587, or
HP Liner, Deactivated, Double-tapered splitless, Part #5181-3315.

Split Vent: He @ 7.6 mL/min, on @ 0.75 min.

Detector Make-Up: N_2 @ 23 mL/min.

Detector Air: 95 mL/min.

Detector Hydrogen: 68 mL/min.

Injection: 2 μl, Split/Splitless

E. Calibration Procedures

E.1 Preparation of Standard Solutions

Individual stock solutions of diazinon and malathion are prepared in acetone and stored in a freezer; primary stock concentrations are approximately 10.0 mg/mL. Stability of these stock solutions during prolonged storage has not been evaluated as part of this developmental and validation work.

Dilutions of diazinon and malathion are made at appropriate concentrations for fortification standards. These dilutions are made in acetone, stored in a freezer, and prepared as mixed or individual standards; that is, each solution may contain either or both diazinon and malathion. The concentration range for these fortification solutions will vary from study to study, but generally will range from 10 μg/mL to 5 mg/mL.

Dilutions of diazinon and malathion for GC standards are made in 1.5% DEGDEE in acetone (Note 10, p. 16) and are stored in a freezer. The standard concentrations suggested are 4, 10, 20, 40, 60, and 100 ng/mL for each analyte[3].

E.2 Detector Calibration

The sensitivity of the FPD(P) detector is monitored by injecting diazinon and malathion before, between, and after the samples. The suggested mass range is 8 pg to 200 pg injected.

Under the conditions of this assay, diazinon and malathion elute from the GC column at ca. 6.4 and 7.4 minutes, respectively. The GC/FPD(P) limit of detection for diazinon and malathion (injected as a pure standard in 1.5% DEGDEE:acetone) is ca. 2 pg injected for both analytes.

---

[3]The analyst should choose standard concentrations appropriate for the standard curve model (See footnote 4). For linear or quadratic standard curve models, the standard concentrations should be constructed in a linear manner; for logarithmic models, the concentrations should be arrayed geometrically.

F. Methods of Calculation

F.1 Injection Sequence

Analysis sequences are started and ended with one or two standards; standard injections are made throughout the run, generally with no more than three or four sample injections between each standard. A standard curve of analyte concentration (ng/mL) versus peak height or area is constructed using a method of curve generation appropriate for the GC/FPD(P) instrumentation. The construction may be linear, quadratic, or logarithmic[4]. It is recommended that the column be equilibrated with several injections of matrix-laden extract if a matrix effect is observed between samples and standards.

F.2 Calculations

Calculate μg/sample values for diazinon and malathion residues in IWBD matrix using the following equation:

$$ug/Sample = \frac{(ng/mL\ Final\ Extract)\ X\ (mL\ Final\ Extract)\ X\ \frac{20\ mL\ Pre\text{-}Florisil\ Total\ Volume}{8\ mL\ Florisil\ Aliquot\ Volume}}{X\ \frac{1000\ mL\ Acetone\ Extract\ Volume}{50\ mL\ Acetone\ Aliquot\ Volume}\ X\ \frac{1\ ug}{1000\ ng}}$$

For reference, the molecular weights of diazinon and malathion are 304.34 g/mole and 330.35 g/mole, respectively.

For fortified-control samples, use the following equation to calculate percent recovery:

$$\%\ Recovery = \left(\frac{(ug/Sample\ Found) - (ug/Sample\ Control)}{ug/Sample\ Fortified} \right) X\ 100$$

[4]The choice of the standard curve model is instrument/detector/laboratory specific, and should be based upon the precision of back-calculated standard responses against the various least squares curve models.

G. Interferences

G.1 Sample Matrices

Chromatographic interferences from pristine IWBD matrix are absent with this assay. GC parameters may require optimization to maximize resolution between the analytes and any interferences which may be present in actual samples.

G.2 Other Pesticides

A specificity study has not been conducted for this method.

G.3 Solvents and Reagents

Solvents and reagents have contributed no interfering chromatographic peaks in this assay. The developer of the method noted that several (apparent) high-quality lots of EtOEt contained interferences which were detected by GC/ECD, but no such interferences were detected by GC/FPD(P) in this developmental research. If required, satisfactory purification of EtOEt is achieved by distilling (ca. 35° C) a stirred mixture of EtOEt (ca. 200 mL) and concentrated sulfuric acid (ca. 10 mL)[5].

G.4 Glassware

There are no known interferences from labware at the stated LOQs. Extraction glassware is thoroughly washed with hot, soapy water, rinsed with acetone, air-dried, then placed in an oven at 150°C for at least 1 hour prior to use. Glass vessels are recommended for all steps without substitutions with plastic.

III. METHODS VERIFICATION

A. Experimental Design

The method for IWBD matrix was validated by analysis of one unfortified control sample, two controls fortified at 1.0 μg/sample, two controls fortified at

[5]**Caution: Do not store purified EtOEt for more than 1 week. Distillation removes antioxidants which prevent formation of explosive peroxides.**

10.0 µg/sample, and two controls fortified at 1000 µg/sample, replicated over two days.

B. Analytical Reference Materials

Specific reference materials used during the conduct of the method validation study are described in Table 1.

C. Control Matrix

Untreated control (UTC) IWBD samples were provided by Stewart Agricultural Research Services, Inc., P.O. Box 509, Macon, MO 63552. IWBD samples had been cut into various sections upon receipt, and had not been pre-washed in detergent.

D. Verification Results

D.1 Inner Whole Body Dosimeters

Results from the IWBD method validation study are presented in Table 2. Example chromatograms are presented in Figures 2 through 5.

D.2 Summary and Conclusions

The techniques outlined in this document are suitable for analysis of diazinon and malathion in IWBD matrix at fortification levels ranging from 1.0 µg/sample to 1 mg/sample. **Critical features of the IWBD method include: (a) ensuring that acetone is completely evaporated from the residues prior to hexane/water partitioning, and (b) ensuring that the Florisil® sorbent is adequately calibrated prior to use. Interferences in IWBD matrix can dramatically impact Florisil® retention of both analytes; if the calibration is not controlled, analyte recoveries will be biased low.**

IV. NOTES

Note 1: With a pipet, drizzle the fortification solution over the sample as uniformly as possible.

Note 2: The shaker speed will vary between laboratories and equipment. The analyst should visually ensure that shaking appears sufficiently vigorous to extract residues from all parts of the sample.

Note 3: IWBD cloth contains a "sizing" or "bluing" agent(s) which can interfere with this analysis. The interference(s) is likely a surfactant polymer and is at least partially soluble in a variety of solvents ranging from water to hexane. During vacuum evaporation, the acetone extract develops an oily, white haze, particles of which float on the liquid surface. Solvent "bumping" is **not** observed during vacuum-evaporation. When dry, a thick, colorless, translucent film is deposited on the sides of the evaporation flask; no free-flowing liquid is evident.

Removing the acetone solvent is a critical step in this procedure; acetone will interfere with proper partitioning of residues into hexane during subsequent steps.

Developmental research for this method demonstrated no losses of either analyte during vacuum-evaporation of solvent, or during prolonged (up to 10 minutes) "dry" evaporation at ≤35°C and 25" Hg vacuum.

Note 4: The sizing/bluing interferences are partially soluble in water, but most of the film (See Note 3 above) remains attached to the sides of the flask; the water appears hazy and may possess a surface foam.

Note 5: Addition of hexane, then shaking, destroys any foam on the surface of the aqueous extract (See Note 4 above), and solubilizes/detaches any remaining film from the sides of the flask. Phase separation is rapid and complete. Several oil-like droplets may appear around the neck of the flask; these are either insoluble, matrix-related materials, or simply a water/hexane emulsion. In any event, these droplets are of no consequence to performance of the assay.

After phase separation, the hexane layer is clear and colorless; the cloudy aqueous phase may contain white flakes.

Note 6: After phase separation, the hexane and aqueous layers are cloudy.

Note 7: After centrifugation, the hexane layer is clear and colorless. The aqueous phase is colorless, but cloudy, and may contain particulates.

Note 8: Water droplets in the hexane extract will change the elution profile of Florisil®. Desiccation reagents such as anhydrous sodium sulfate are not recommended as these may irreversibly bind organophosphate residues, yielding biased-low recoveries.

The partitioning step with hexane, followed by back-extraction of the hexane with water, reduces the concentration of sizing/bluing interferences in the final pre-Florisil® hexane sample; **if not reduced or eliminated, these interferences**

dramatically reduce the retention of diazinon and malathion by Florisil® in the subsequent column clean-up step. Diazinon and, to a lesser extent, malathion, will wash through the column during sample loading if these interferences are not reduced to an acceptable level. The analyst should note that low recoveries of diazinon from quality control samples may be an indication that the hexane/water partitioning step C.3.b was insufficient, and the pre-Florisil® hexane sample should be further back-extracted with water, then centrifuged, to remove additional sizing/bluing interferences.

Note 9: Each lot of Florisil® should be pre-calibrated with matrix prior to use. **This is a critical step in the assay, since sizing/bluing interferences in IWBD cloth can change the retention characteristics of the Florisil®.** An example procedure is as follows.

Process an untreated control (UTC) IWBD sample through the method as described in steps C.1 through C.4.a. Separately, pipet an acetone solution (e.g., 1 mL) containing 0.50 μg each of diazinon and malathion into a 50-mL evaporation flask; vacuum-evaporate the solvent to just-dryness. Add 10 mL of the UTC pre-Florisil® hexane extract from C.3.b to the dry residue, then mix thoroughly. Pipet 8 mL of this solution onto the Florisil® column prepared in C.4.a, then process the sample as described in steps C.4.b through C.4.e with a 4.0 mL final extract volume (retain the load and hexane wash from C.4.c separately to this point). Analyze the final sample by GC/FPD(P) (See Step D) against a 100 ng/mL diazinon/malathion standard prepared in 1.5% DEGDEE:acetone (Step E.1). At 100% recovery, the GC/FPD(P) detector responses for both compounds from the sample and standard injections should be equivalent.

If the recovery for either compound is biased low, vacuum-evaporate the wash from C.4.c, dissolve the residue in 2 mL of 1.5% DEGDEE:acetone, then inject into the GC/FPD(P). Similarly, elute the column with additional 15% EtOEt in hexane, vacuum-evaporate to just-dryness, dissolve the residue, then inject into the GC/FPD(P). If necessary, increase the ratio of EtOEt to hexane to yield quantitative recovery from the column.

As observed in Note 8 above, the presence of diazinon in the load/wash fraction from Step C.4.c is an indication that the hexane/water partitioning step C.3.b has failed to remove sufficient sizing/bluing matrix interferences from the sample; in such an event, additional back-extraction of the pre-Florisil® hexane extract with water is indicated. Reducing the volume of the post-load column wash with hexane (C.4.c) is not an option, since diazinon is lost during the column load step, not the hexane wash step.

Low-biased malathion recoveries are an indication that further elution of the Florisil® with 15% EtOEt:hexane is necessary. Simply increase the elution volume from the recommended 40 mL for the IWBD samples to 50-60 mL, as indicated. If necessary, the ratio of EtOEt to hexane may be increased to yield quantiative recoveries.

Commercial Florisil® columns may also be used for the clean-up. As with the Florisil® columns prepared in the laboratory, each lot of commercial columns must be independently evaluated as described in this note.

Note 10: Diazinon and malathion standards prepared in neat acetone give unacceptable chromatography; standard curves exhibit poor linearity (especially for malathion), reproducibility, and sensitivity. "Priming" the GC with UTC extracts in and of itself does not correct the problem. Use of 1.5% DEGDEE in acetone solvent for GC standards and final sample extracts eliminates these problems and improves the signal/noise ratio for analyte detection at all concentrations. The mechanism of action for this effect is not known.

Even with the use of 1.5% DEGDEE in acetone, it was found that priming, or equilibrating, the GC with matrix extract was necessary prior to the analysis of a set of samples for IWBD. In general, a minimum of two injections of matrix-laden extract is recommended immediately prior to initiation of a sample set. In addition, routine maintenance was found to be necessary due to buildup in the injector liner and at the front of the analytical column. Replacement of the injector liner and removal of approximately 15" from the front of the analytical column was necessary after approximately every 100 sample injections. It was found that this maintenance was necessary to prevent a matrix effect (enhancement) on the malathion in matrix-laden samples.

If a high bias is observed with samples reconstituted in low volumes of 1.5% DEGDEE in acetone, it may be necessary to chill the evaporation flask prior to addition of the acetone-based solvent. This can be accomplished using an ice water bath.

V. SAFETY

The organic solvents utilized in this method represent both a general exposure and fire hazard. Provision must be made for working with these solvents for personnel safety.

VI. TABLES

Table 1. Standard Reference Materials.

STANDARD NAME	ABC STANDARD NUMBER	LOT NUMBER	PURITY:EXP. DATE	PHYSICAL CHARAC-TERISTICS
Diazinon, O,O-diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate, CAS #333-41-5.	PS-9824	95R-31-45C 09467	87.7%:9/14/98	Clear Yellow Liquid
Malathion, [(Dimethoxyphosphino-thioyl)thio]-butanedioic acid diethyl ester, CAS #121-75-5.	PS-9825	95R-31-44E CS030	95.0%:12/12/99	Clear Liquid

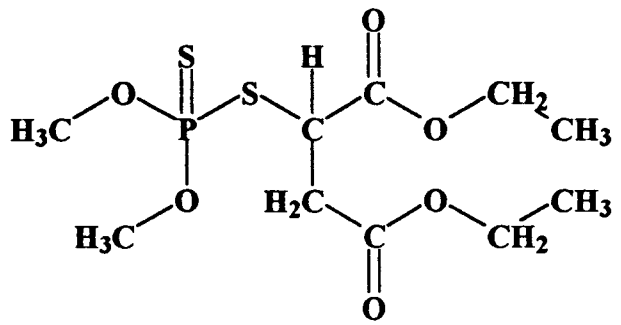
Table 2. Recovery of Diazinon and Malathion from Inner Whole Body Dosimeters

ABC Sample ID	Sample Description	µg Diazinon/ segment found	% Recovery Diazinon	µg Malathion/ segment found	% Recovery Diazinon
43767-001R	Control Upper Arms	0	N/A	0	N/A
43767-002R	Control Upper Arms + 0.992 µg Diazinon/1.02 µg Malathion	1.10	111	1.05	103
43767-003R	Control Front Torso + 0.992 µg Diazinon/1.02 µg Malathion	1.12	113	1.07	105
43767-004R	Control Lower Arms + 9.92 µg Diazinon/10.2 µg Malathion	9.51	95.9	9.00	88.2
43767-005R	Control Rear Torso + 9.92 µg Diazinon/10.2 µg Malathion	9.94	100	10.0	98.0
43767-006R	Control Lower Legs + 992 µg Diazinon/1020 µg Malathion	924	93.1	947	92.8
43767-007R	Control Upper Legs + 992 µg Diazinon/1020 µg Malathion	867	87.4	888	87.1
43767-008	Control Lower Arms	0	N/A	0	N/A
43767-009	Control Upper Arms + 0.992 µg Diazinon/1.02 µg Malathion	0.932	94.0	0.836	82.0
43767-010	Control Front Torso + 0.992 µg Diazinon/1.02 µg Malathion	1.11	112	1.19	117
43767-011	Control Rear Torso + 9.92 µg Diazinon/10.2 µg Malathion	9.70	97.8	10.4	102
43767-012	Control Lower Arms + 9.92 µg Diazinon/10.2 µg Malathion	10.4	105	11.0	108
43767-013	Control Lower Legs + 992 µg Diazinon/1020 µg Malathion	982	99.0	1040	102
43767-014	Control Upper Legs + 992 µg Diazinon/1020 µg Malathion	896	90.3	990	97.1
	Average Overall % Recovery (n=12)		99.9		98.5
	Overall Standard Deviation (n=12)		8.62		9.83
	% Relative Standard Deviation		8.63		9.98

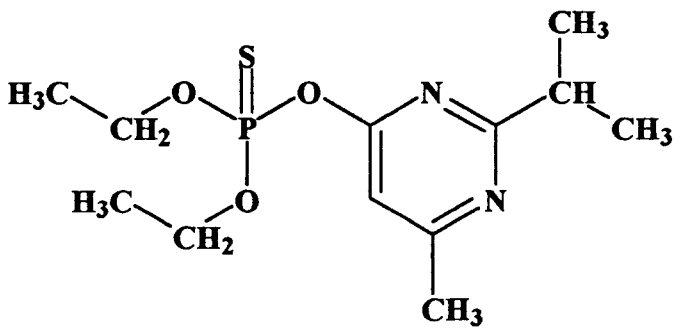
Recoveries corrected for the µg found in the respective controls of the sets.

VII. FIGURES

Figure 1. Chemical Structures of Diazinon and Malathion.



MALATHION
[(Dimethoxyphosphinothioyl)thio]-butanedioic acid diethyl ester



DIAZINON
O,O-Diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]-phosphorothioate

Figure 2. Representative Chromatogram of a Nominal 100 ng/mL Mixed External Standard

MCDO [43767] 29 767IWB03, 2, 1
GCMIX-1 NOMINAL 100 NG/ML
Acquired on 10-Apr-1997 at 17:23

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.43	59993	97.667
MALATHION	7.44	50100	99.684

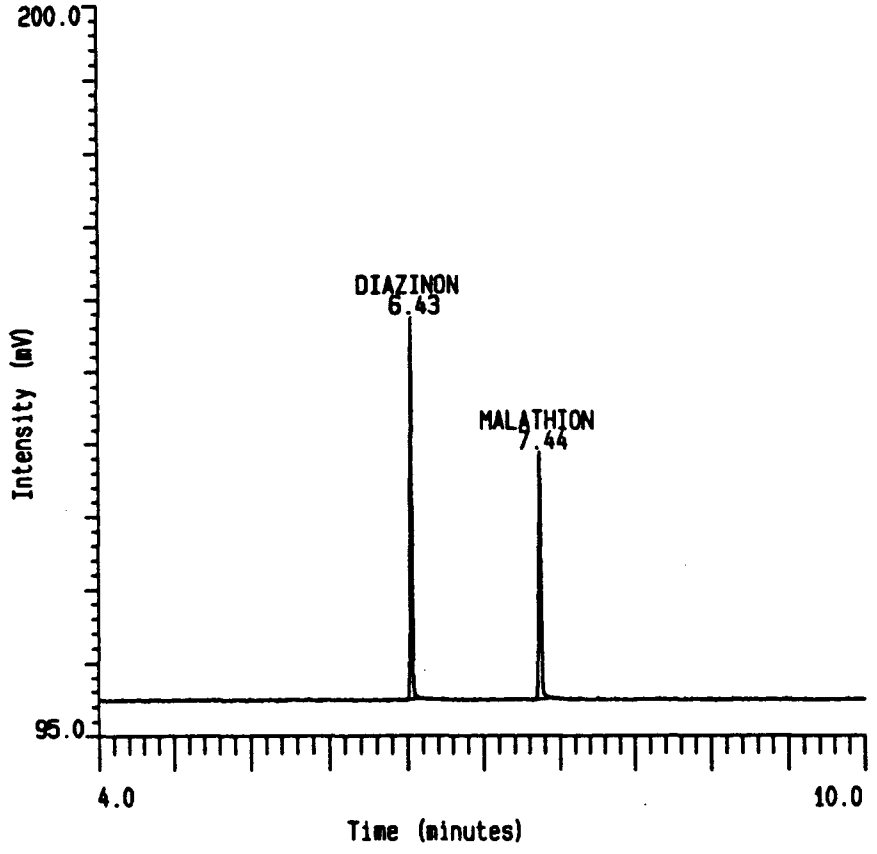


Figure 3. Representative Chromatogram of a Nominal 4.00 ng/mL Mixed External Standard

MCDO [43767] 29 767IWBD3, 14, 1
GCMIX-6 NOMINAL 4 NG/ML
Acquired on 10-Apr-1997 at 21:26

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.43	2567	3.453
MALATHION	7.45	2223	3.519

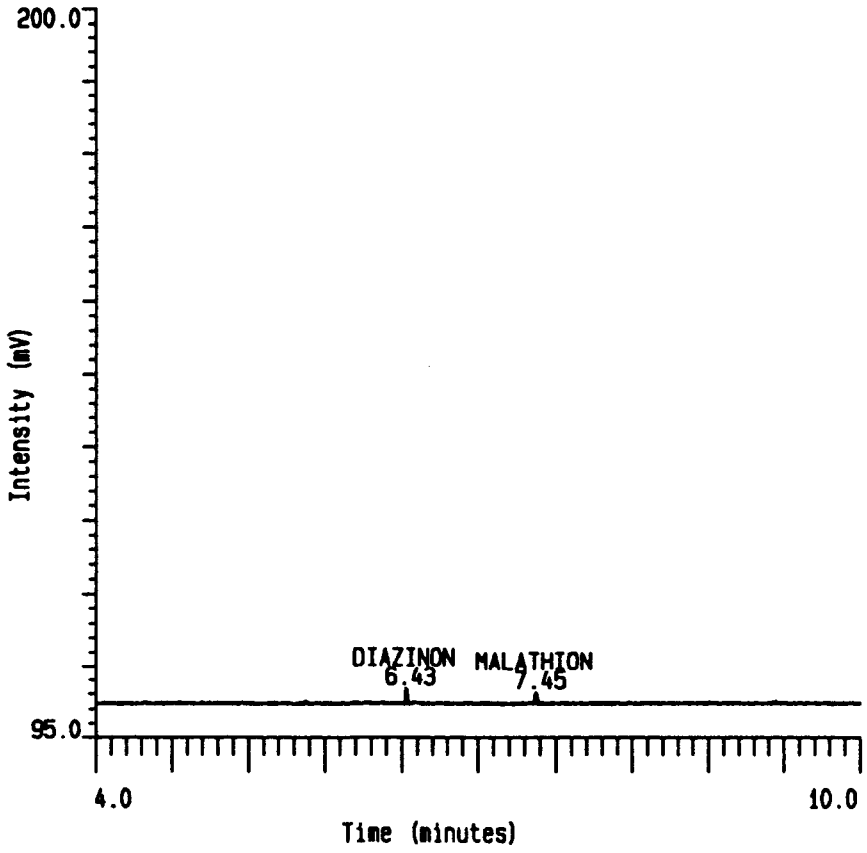


Figure 4. Representative Chromatogram of a Control Inner Whole Body Dosimeter Sample

MCDO [43767] 29 767IWBD3.4.1
43767-008
Acquired on 10-Apr-1997 at 18:03

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	0.00	0	0
MALATHION	0.00	0	0

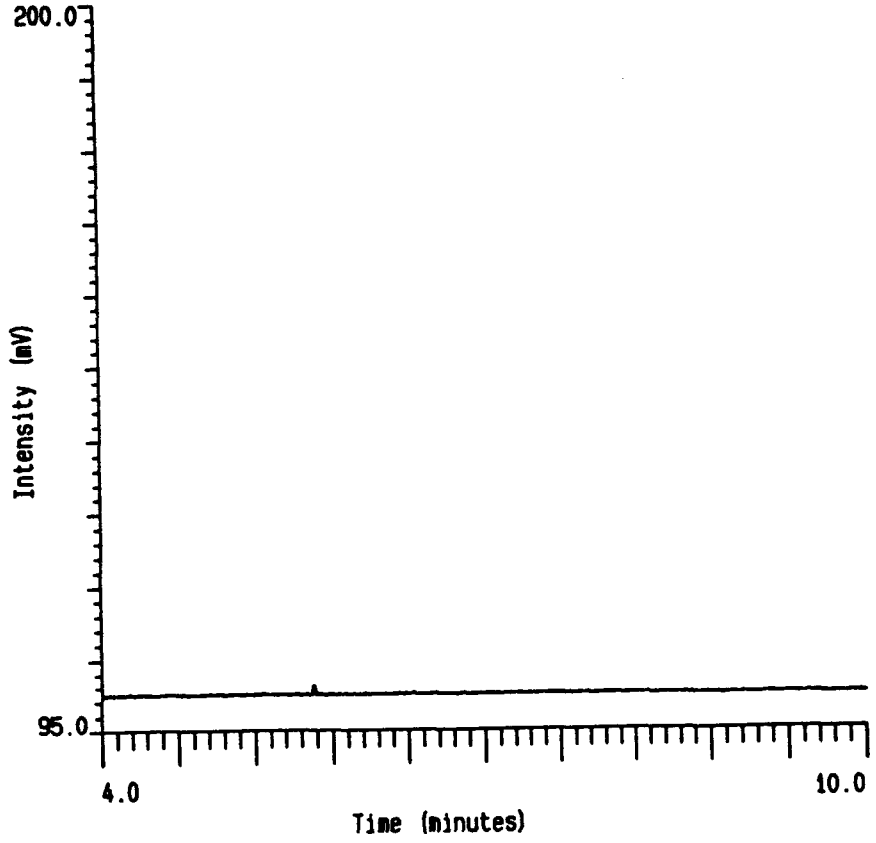
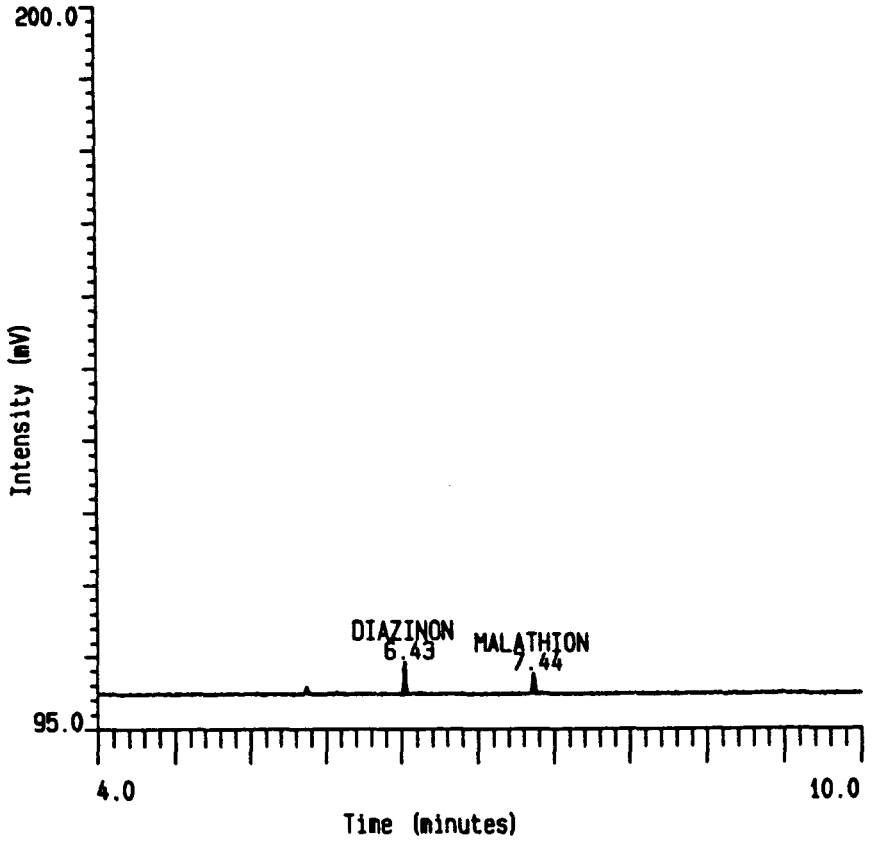


Figure 5. Representative Chromatogram of a Nominal 1 μg Inner Whole Body Dosimeter Fortification (LOQ) Sample

MCDO [43767] 29 767IWBD3, 5, 1
43767-009
Acquired on 10-Apr-1997 at 18:24

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.43	5008	0.932
MALATHION	7.44	3800	0.836



Determination of Diazinon and Malathion in Hand Wash Solutions

Method ARTF-AM-006

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Determination of Diazinon and Malathion in Hand Wash Solutions

Method ARTF-AM-006

I. INTRODUCTION AND SUMMARY

A. Scope

Diazinon and malathion are organophosphate insecticides used for control of certain noxious insects on agriculturally important crops. To generate data which estimate human exposure to the insecticides during agricultural applications, a method of analysis is required for determination of diazinon and malathion residues in 0.01% Aerosol® OT (AOT) hand wash solutions.

B. Principle

Diazinon and malathion residues in AOT hand wash solution are retained on a conditioned C-18 reverse phase (C-18RP) column. The column is washed with water, air-dried, then washed with hexane; the hexane is discarded. Analytes are eluted from the column with methylene chloride which is evaporated to dryness. The residues are dissolved in acetone-based solvent, then quantified by gas chromatography (GC) with flame photometric detection in the phosphorous mode [FPD(P)]. The claimed limit of quantification (LOQ) for diazinon and malathion is 1.0 μg/ sample[1].

Figure 1 presents the chemical structures of diazinon and malathion.

II. MATERIALS AND METHODS

A. Equipment

Equipment	Suggested Manufacturers:[2]
Analytical Balance	Ohaus GA110

[1]This method analyzes diazinon and malathion residues in AOT solution samples. One sample equals 500 mL. The lowest limit of fortification during methods development research was 1.0 μg each of diazinon and malathion/500 mL sample.

[2]Equivalent sources of the listed equipment and reagents may be used.

C-18, Reverse Phase, SPE 1 gram, 6-mL	Varian Sample Preparation Products, Catalog #1225-6001
Gas Chromatograph with a Flame Photometric Detector Phosphorous Mode Narrow-bore Capability Split-Splitless Injector	Hewlett-Packard Model 5890 Series II
Gas Chromatograph Column	J & W, DB-5, 30 m x 0.25 mm i.d., 0.25 μm film thickness
General Laboratory Glassware	Various
Rotary Evaporator	Fisher Scientific
Vacuum SPE Manifold	J & W Scientific

B. Reagents and Standards

Acetone:	Fisher Optima Grade
AOT 75 Solution, 75% w:w Aqueous	Fisher Scientific Catalog #A345-500
0.01% Aqueous AOT 75	Dissolve 0.4 mL of 75% AOT Solution in 3800 mL (nominal 1 gallon) of water. Mix well. This solution is good for 48 hours at room temperature.
Di(ethylene glycol)diethylether: (i.e., DEGDEE), HPLC grade	Sigma/Aldrich Catalog #30,827-7
1.5% DEGDEE (w:v)	Dilute 7.5 g of DEGDEE to 500 mL with acetone. Mix and store at ambient temperatures.
Hexane:	Fisher Optima Grade
Methanol:	Fisher Optima Grade

Methylene Chloride (DCM):	Fisher Optima Grade
Water:	Distilled and/or deionized.

Diazinon, O,O-diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]-phosphorothioate, available from ARTF.

Malathion, [(Dimethoxyphosphinothioyl)thio]-butanedioic acid diethyl ester, available from ARTF.

C. 0.01% AOT Hand Wash Solutions: Analytical Procedure

C.1 Sample Preparation

Freeze the field sample pending analysis. **IMPORTANT!: Thaw the entire sample prior to subsampling for analysis (See Note 1, page 12)**. Re-freeze the remainder of the sample.

C.2 C-18RP Clean-Up

a. Condition a 1 gram C-18RP SPE cartridge as follows: Place a cartridge on a clean vacuum manifold (See Note 2, page 12); the vacuum should be sufficient to achieve eluate flows of only ca. 1 → 2 drops/second. Wash the cartridge successively with 2 x 5 mL of hexane, 2 x 5 mL of methanol, and 2 x 5 mL of water. **Do not allow the column to go dry at any point in this procedure unless specified otherwise.**

b. QC fortifications are made at this point as follows: Place 500 mL of 0.01% AOT solution in a suitable glass beaker. Fortify the solution with an appropriate amount of diazinon and malathion in acetone (See Section E.1). Mix by stirring, then proceed as in C.2.c below.

c. Pipet 10 mL of sample onto the C-18RP column. With very little vacuum, percolate the sample into the column at a maximum flow rate of ca. 1 → 2 drops/second. Wash the sample into the column with 5 mL of water, again observing the 1 - 2 drops/second flow rate through the column (Note 3, p. 12). Discard all eluates to this point.

d. With full vacuum (≥ 20" Hg) on the manifold, air-dry the column for at least 45 minutes. **This is a critical step in the procedure; all water must be removed from the column!**

e. Wash the column with 5 mL of hexane (maximum rate of ca. 1 → 2 drops/second, see Note 4, p. 12). Discard the wash.

f. Elute diazinon and malathion from the column with 16 mL of DCM (maximum rate of ca. 1 → 2 drops/second, see Note 5, p. 12). Collect the eluate directly in a 125-mL evaporation flask, or in a culture tube of suitable size. Transfer the eluate from the culture tube to a 125-mL evaporation flask, and rinse the tube twice with ca. 2 mL DCM and add to the flask.

g. Vacuum-evaporate the sample to dryness (ca. 25" Hg, ≤35°C water bath). **Ensure that all DCM has been removed from the sample. Cautionary Note!: Discard and reanalyze any sample which contains droplets of water after complete evaporation of the DCM. Evaporation of the water to dryness will give profound losses of diazinon, but not malathion. (See Note 6, p. 14).**

h. Dissolve the dry residue in a known volume of 1.5% DEGDEE:acetone (generally 2.0 mL for LOQ residues, see Note 7, p. 14). Dilute with the same solvent as necessary to maintain analyte concentrations within the standard curve range. Submit the sample for GC/FPD(P) analysis as described in Step D.

D. Gas Chromatographic Analysis

A gas chromatograph equipped with a Flame Photometric Detector (phosphorous mode) is required. Split-splitless injection and narrow-bore capabilities are recommended. The conditions described herein may be modified provided adequate performance of the analysis is demonstrated.

GC Column: J & W DB-5, 30 m length, 0.25 mm i.d., 0.25 μm film. Other columns may be substituted if they give satisfactory resolution between the analytes and any interferences.

Injector: 230°C

Detector: 220°C

Column:

Initial:	95°C, hold 1.0 min.
Ramp Rate 1:	30°C/min to 230°C, hold 4 minutes.
Ramp Rate 2:	40°C/min to 290°C, hold 5 minutes.

Carrier Gas:	He, 1.7 mL/min at 95°C, head pressure = 20 psi. Constant flow off.
Septum Purge:	He @ 3.0 mL/min.
Injector Liner:	HP Liner, Deactivated, 4 mm i.d., with Deactivated Glass Wool Plug, Part #5062-3587, or HP Liner, Deactivated, Double-tapered splitless, Part #5181-3315.
Split Vent:	He @ 7.6 mL/min, on @ 0.75 min.
Detector Make-Up:	N_2 @ 23 mL/min.
Detector Air:	95 mL/min.
Detector Hydrogen:	68 mL/min.
Injection:	2 μl, Split/Splitless.

E. Calibration Procedures

E.1 Preparation of Standard Solutions

Individual stock solutions of diazinon and malathion are prepared in acetone and stored in a freezer; primary stock concentrations are approximately 10.0 mg/mL. Stability of these stock solutions during prolonged storage has not been evaluated as part of this developmental and validation work.

Dilutions of diazinon and malathion are made at appropriate concentrations for fortification standards. These dilutions are made in acetone, stored in a freezer, and prepared as mixed or individual standards; that is, each solution may contain either or both diazinon and malathion. The concentration range for these fortification solutions will vary from study to study, but generally will range from 10 μg/mL to 5 mg/mL.

Dilutions of diazinon and malathion for GC standards are made in 1.5% DEGDEE in acetone (Note 7, p. 14) and are stored in a freezer. The standard concentrations suggested are 4, 10, 20, 40, 60, and 100 ng/mL for each analyte[3].

E.2 Detector Calibration

The sensitivity of the FPD(P) detector is monitored by injecting diazinon and malathion before, between, and after the samples. The suggested mass range is 8 pg to 200 pg injected.

Under the conditions of this assay, diazinon and malathion elute from the GC column at ca. 6.0 and 6.8 minutes, respectively. The GC/FPD(P) limit of detection for diazinon and malathion (injected as a pure standard in 1.5% DEGDEE:acetone) is ca. 2 pg injected for both analytes.

F. Methods of Calculation

F.1 Injection Sequence

Analysis sequences are started and ended with one or two standards; standard injections are made throughout the run, generally with no more than three or four sample injections between each standard. A standard curve of analyte concentration (ng/mL) versus peak height or area is constructed using a method of curve generation appropriate for the GC/FPD(P) instrumentation. The construction may be linear, quadratic, or logarithmic[4]. It is recommended that the column be equilibrated with several injections of matrix-laden extract if a matrix effect is observed between samples and standards.

---

[3]The analyst should choose standard concentrations appropriate for the standard curve model (See footnote 4). For linear or quadratic standard curve models, the standard concentrations should be constructed in a linear manner; for logarithmic models, the concentrations should be arrayed geometrically.

[4]The choice of the standard curve model is instrument/detector/laboratory specific, and should be based upon the precision of back-calculated standard responses against the various least squares curve models.

F.2 Calculations

Calculate µg/sample values for diazinon and malathion residues in AOT hand wash solutions using the following equation:

$$ug/Sample = \frac{(ng/mL\ Final\ Extract)\ X\ (mL\ Final\ Extract)}{} X \frac{500\ mL\ Sample\ Volume}{10\ mL\ C\text{-}18RP\ Aliquot\ Volume} X \frac{1\ ug}{1000\ ng}$$

For reference, the molecular weights of diazinon and malathion are 304.34 g/mole and 330.35 g/mole, respectively.

For fortified-control samples, use the following equation to calculate percent recovery:

$$\%\ Recovery = \left(\frac{(ug/Sample\ Found) - (ug/Sample\ Control)}{ug/Sample\ Fortified} \right) X\ 100$$

G. Interferences

G.1 Sample Matrices

Chromatographic interferences from pristine AOT matrix are absent with this assay. GC parameters may require optimization to maximize resolution between the analytes and any other interferences that may be present in actual samples.

G.2 Other Pesticides

A specificity study has not been conducted for this method.

G.3 Solvents and Reagents

Solvents and reagents have contributed no interfering chromatographic peaks in this assay.

G.4 Glassware

There are no known interferences from labware at the stated LOQs. Extraction glassware is thoroughly washed with hot, soapy water, rinsed with acetone, air-dried, then placed in an oven at 150°C for at least 1 hour prior to use. Glass vessels are recommended for all steps without substitutions with plastic.

III. METHODS VERIFICATION

A. Experimental Design

The method for the hand wash matrix was tested by analysis of one unfortified control sample, three controls fortified at 1.0 µg/sample, three controls fortified at 10.0 µg/sample, and three controls fortified at 1.0 mg/sample, duplicated over two days. This design was used by the both the development and validation laboratories.

B. Analytical Reference Materials

Specific reference materials used during the conduct of the method validation study are described in Table 1.

C. Control Matrix

Concentrated AOT was purchased from Fisher Scientific. Solutions at 0.01% were prepared as needed, and were assigned a 2-day expiration date.

D. Verification Results

Results from the AOT method verification study are presented in Table 2, and example chromatograms are presented in Figures 2 through 5.

The techniques outlined in this document are suitable for analysis of diazinon and malathion in hand wash matrix at fortification levels ranging from 1.0 µg/sample to 1 mg/sample. This range was later expanded to 5 mg/sample during a field validation study by the validation laboratory. **Critical features of the method include: (a) proper drying of the C-18RP columns prior to elution, and (b) ensuring that the C-18RP sorbent is adequately calibrated prior to use, and (c) scrupulously cleansed labware. Interferences from AOT reagent can dramatically impact retention of both analytes onto C-18RP adsorbent; if the calibration is not controlled, analyte recoveries will be biased low.**

IV. NOTES

Note 1: **The entire sample must be thawed and mixed prior to subsampling for analysis**. During methods development, several fortified control samples were only partially thawed, then subsampled for analysis. Recoveries of both analytes were biased very high, and this observation was repeatable with other independent samples. Apparently, frozen AOT solutions are not homogeneous with respect to dissolved analytes; fractional crystallization during the freeze cycle is suspected.

Note 2: The developers of this method observed frequent cross-contamination of final sample extracts with malathion and, especially, diazinon. Generally, this problem is noticeable only with samples fortified at the limit of quantification when samples containing very high residues (100 X LOQ) have been previously analyzed using the same glassware or laboratory equipment. The vacuum manifold, especially the plastic SPE stopcocks and attached needles, are a primary source of this cross-contamination. **The entire vacuum manifold, including stopcocks and needles, should be scrupulously cleaned with hot, soapy water, rinsed with distilled water, then high-purity acetone prior to any subsequent use**. Stopcocks can be checked for retained residues by soaking them overnight in acetone, then analyzing the extract by gas chromatography (See Section D). If cross-contamination persists, replace the stopcocks. [The validation laboratory did not encounter frequent cross-contamination problems from the vacuum manifold or glassware, and rigorous cleaning of the vacuum manifold was not found to be necessary.]

Note 3: The analyst should note that low recoveries of diazinon from quality control samples may indicate a sample loading problem. Load flow rates may be a factor, but this has not been confirmed. Some analysts may wish to dilute the 0.01% AOT sample with water (e.g., 2X), but note that malathion and diazinon are sparingly soluble in water, and excessive dilution of the sample may cause loss of analyte due to precipitation.

Note 4: The hexane wash is initially very slow, and a full vacuum may be required to initiate flow. The hexane wash partitions some, but not all, of the retained AOT components from the column.

Excess hexane can elute diazinon and malathion from the column. Users of this method may find that, with field samples, the hexane wash can be deleted from the method.

Note 5: During developmental research, 8 mL of DCM quantitatively eluted both analytes from the C-18RP column. For the validation laboratory work, a total of up to 16 mL was used to obtain quantitative recovery. Subsequent work showed that

8 mL of 50:50 MeOH:DCM yielded excellent recoveries with no chromatographic problems. However, the analyst should note that this method has been optimized for analyte recoveries from samples prepared in the laboratory. Field samples may contain interferences which are also eluted with DCM and may compromise quantification of the analytes. In such cases, the DCM elution solvent should be modified to effect column resolution between the analytes and interferences (e.g., mixtures of DCM and hexane).

Each lot of C-18RP cartridges should be pre-calibrated with matrix prior to use. **This is a critical step in the assay, since AOT components can change the retention characteristics of the solid support.** An example procedure is as follows.

Prepare a C-18RP column and fortified-control AOT sample (100 μg both analytes/500 mL solution) as described in Sections C.2.a and C.2.b, respectively. Process the sample through the column as described in Sections C.2.c through C.2.g. Retain the load and hexane washes from C.2.c and C.2.e separately to this point. Dissolve the final dry residue in a 20 mL final volume. Analyze the sample by GC/FPD(P) (See Step D) against a 100 ng/mL diazinon/malathion standard prepared in 1.5% DEGDEE:acetone (Step E.1). At 100% recovery, the GC/FPD(P) detector responses for both compounds from the sample and standard injections should be equivalent.

If the recovery for either compound is biased low, vacuum-evaporate the hexane wash from C.2.e, dissolve the residue in 5 mL of 1.5% DEGDEE:acetone, then inject into the GC/FPD(P). Similarly, elute the column with additional DCM, vacuum-evaporate to just-dryness, dissolve the residue in 5 mL DEGDEE:acetone, then inject into the GC/FPD(P). Finally, dilute the retained load/water wash fraction with water (100X) and partition twice against 75 mL of DCM. Vacuum-evaporate the DCM to just-dryness, dissolve the residue in 5 mL of 1.5% DEGDEE:acetone, then analyze by GC/FPD(P).

As observed in Note 3 above, the presence of diazinon in the load/wash fraction from Step C.2.c may indicate a load flow rate problem or too high of an AOT concentration in the sample. Low-biased malathion recoveries are an indication that further elution of the C-18RP column with DCM is necessary; simply increase the elution volume from the recommended 8 mL to 10-16 mL, as indicated, or repeat the column profile work using a mixture of methanol and methylene chloride, such as 50:50 MeOH:DCM. If either analyte is present in the hexane wash fraction, reduce the volume of the hexane wash appropriately.

Note 6: Developmental research for this method demonstrated no losses of either analyte during vacuum-evaporation of methylene chloride, or during prolonged (up to 10 minutes) "dry" evaporation at ≤35°C (water bath) and 25" Hg vacuum. However, profound losses of diazinon (but not malathion) are observed if the sample contains droplets of water, and the water is evaporated to dryness.

Therefore, water **MUST** be removed from the C-18RP column prior to elution with methylene chloride (Step II.C.2.f). Profound losses of diazinon (but not malathion) are observed if the sample contains droplets of water, and the water is evaporated to dryness. This effect is poorly understood, but has attributes consistent with a diazinon/water azeotrope. No problems were encountered with the use of 50:50 MeOH:DCM provided the C-18RP columns were adequately dried.

The method developer could dry only 3 cartridges at a time to achieve proper drying. The validation laboratory was able to dry up to 12 cartridges at a time using a 45 min drying period at the maximum recommended operating vacuum for the vacuum manifold (20" Hg). This vacuum could only be achieved using a vacuum pump. During the drying period, the flow should be checked periodically through each cartridge by placing a finger over the top of the cartridge. A strong vacuum should be felt quickly (ca. 1-2 sec), and a sharp "popping" sound made when the finger is removed. The flow through all the columns should be checked and should be relatively uniform. As the columns dry, the flow characteristics of the columns will change, so it is necessary to moderate the vacuum and repeat the column flow check approximately every 10 min.

Note 7: Diazinon and malathion standards prepared in neat acetone give unacceptable chromatography; standard curves exhibit poor linearity (especially for malathion), reproducibility, and sensitivity. "Priming" the GC with extracts in and of itself does not correct the problem. Use of 1.5% DEGDEE in acetone solvent for GC standards and final sample extracts eliminates these problems and improves the signal/noise ratio for analyte detection at all concentrations. The mechanism of action for this effect is not known.

Even with the use of 1.5% DEGDEE in acetone, it was found that priming, or equilibrating, the GC with matrix extract was necessary prior to the analysis of a set of samples for hand wash matrix. In general, a minimum of two injections of matrix-laden extract is recommended immediately prior to initiation of a sample set. In addition, routine maintenance was found to be necessary due to buildup in the injector liner and at the front of the analytical column. Replacement of the injector liner and removal of approximately 15" from the front of the analytical column was necessary after approximately every 100 sample injections. It was

found that this maintenance was necessary to prevent a matrix effect (enhancement) on the malathion in matrix-laden samples.

If a high bias is observed with samples reconstituted in low volumes of 1.5% DEGDEE in acetone, it may be necessary to chill the evaporation flask prior to addition of the acetone-based solvent. This can be accomplished using an ice water bath.

V. SAFETY

The organic solvents utilized in this method represent both a general exposure and fire hazard. Provision must be made for working with these solvents for personnel safety.

VI. TABLES

Table 1. Standard Reference Materials.

STANDARD NAME	ABC STANDARD NUMBER	LOT NUMBER	PURITY:EXP. DATE	PHYSICAL CHARAC-TERISTICS
Diazinon, O,O-diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate, CAS #333-41-5.	PS-9824	95R-31-45C 09467	87.7%:9/14/98	Clear Yellow Liquid
Malathion, [(Dimethoxyphosphino-thioyl)thio]-butanedioic acid diethyl ester, CAS #121-75-5.	PS-9825	95R-31-44E CS030	95.0%:12/12/99	Clear Liquid

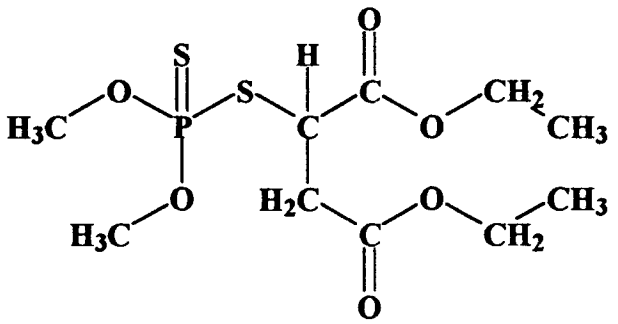
Table 2. Recovery of Diazinon and Malathion from Hand Wash Samples

ABC Sample ID	Sample Description	µg Diazinon/ sample found	% Recovery Diazinon	µg Malathion/ sample found	% Recovery Diazinon
43767-029	Control Hand Wash Solution	0	N/A	0	N/A
43767-030	Control + 0.992 µg Diazinon/1.02 µg Malathion	1.02	103	1.15	113
43767-031	Control + 0.992 µg Diazinon/1.02 µg Malathion	0.879	88.6	0.928	91.0
43767-032	Control + 9.92 µg Diazinon/10.2 µg Malathion	10.9	110	11.2	110
43767-033	Control + 9.92 µg Diazinon/10.2 µg Malathion	11.1	112	11.6	114
43767-034	Control + 992 µg Diazinon/1020 µg Malathion	1060	107	1150	113
43767-035	Control + 992 µg Diazinon/1020 µg Malathion	1020	103	1170	115
43767-036	Control Hand Wash Solution	0	N/A	0	N/A
43767-037	Control + 0.992 µg Diazinon/1.02 µg Malathion	0.897	90.4	0.941	92.3
43767-038	Control + 0.992 µg Diazinon/1.02 µg Malathion	0.784	79.0	0.952	93.3
43767-039	Control + 9.92 µg Diazinon/10.2 µg Malathion	9.17	92.4	9.98	97.8
43767-040	Control + 9.92 µg Diazinon/10.2 µg Malathion	9.53	96.1	10.4	102
43767-041	Control + 992 µg Diazinon/1020 µg Malathion	1030	104	1070	105
43767-042	Control + 992 µg Diazinon/1020 µg Malathion	1050	106	1140	112
	Average Overall % Recovery (n=12)		99.3		105
	Overall Standard Deviation (n=12)		9.97		9.23
	% Relative Standard Deviation		10.0		8.79

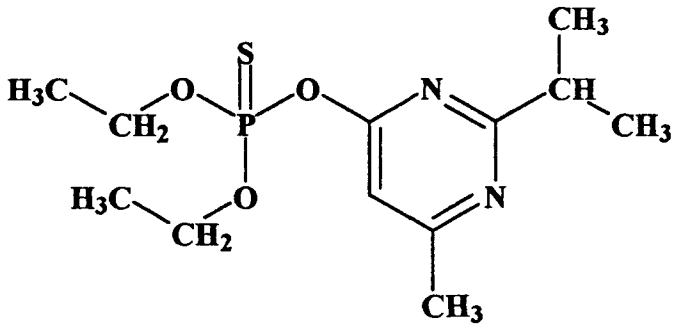
Recoveries corrected for the µg found in the respective controls of the sets.

VII. FIGURES

Figure 1. Chemical Structures of Diazinon and Malathion.



MALATHION
[(Dimethoxyphosphinothioyl)thio]-butanedioic acid diethyl ester



DIAZINON
O,O-Diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]-phosphorothioate

Figure 2. Representative Chromatogram of a 100 ng/mL Mixed External Standard

MCDO [43767] 29 767HWS9.2.1
GCMIX-1 NOMINAL 100 ng/mL
Acquired on 20-Jun-1997 at 16:16

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	95730	98.132
MALATHION	6.81	57607	102.321

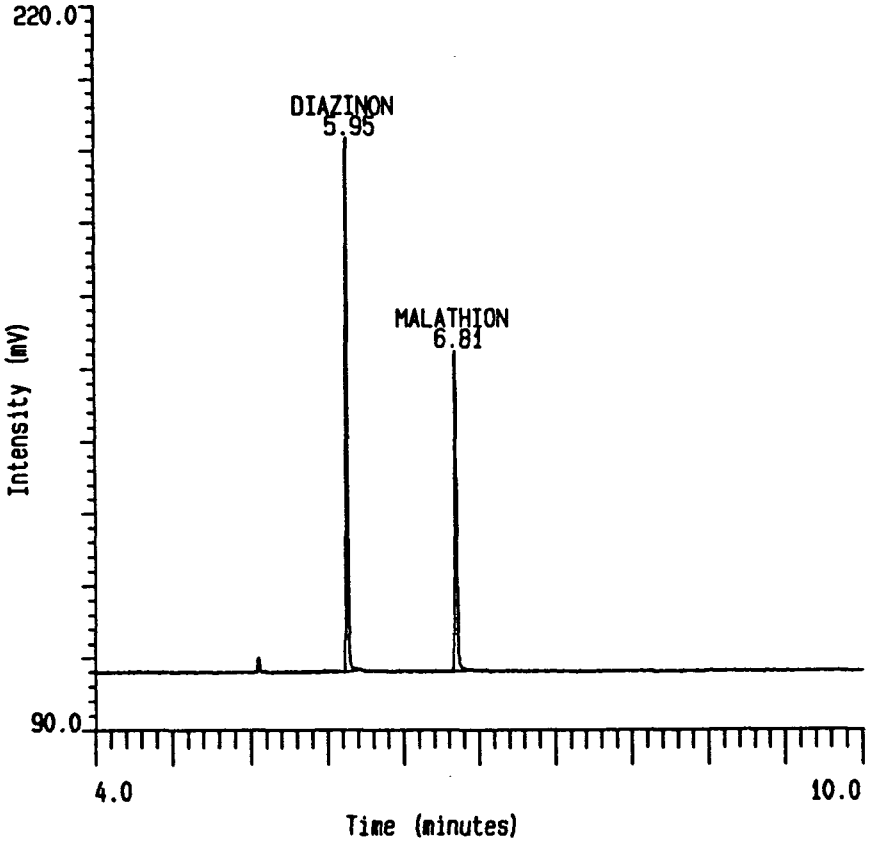


Figure 3. Representative Chromatogram of a 4.00 ng/mL Mixed External Standard

MCDO [43767] 29 767HWS9, 14, 1
GCMIX-6 NOMINAL 4 ng/mL
Acquired on 20-Jun-1997 at 20:21

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.96	4231	3.764
MALATHION	6.82	2450	3.866

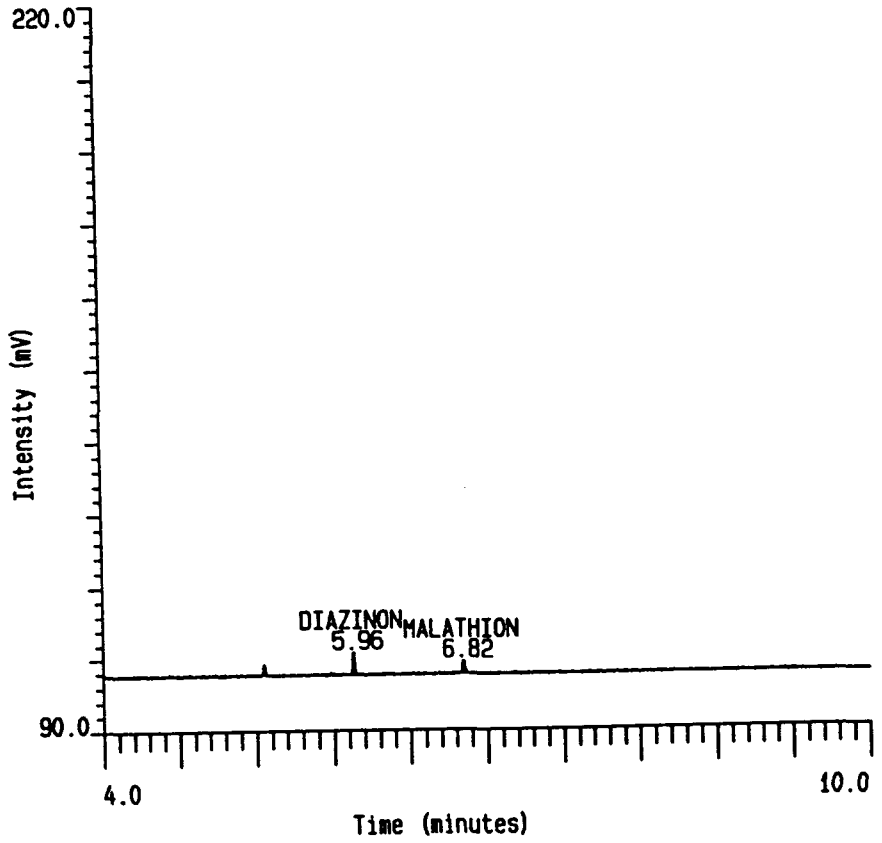


Figure 4. Representative Chromatogram of a Control Hand Wash Sample

MCDO [43767] 29 767HWS9, 4, 1
43767-029
Acquired on 20-Jun-1997 at 16:57

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	0.00	0	0
MALATHION	0.00	0	0

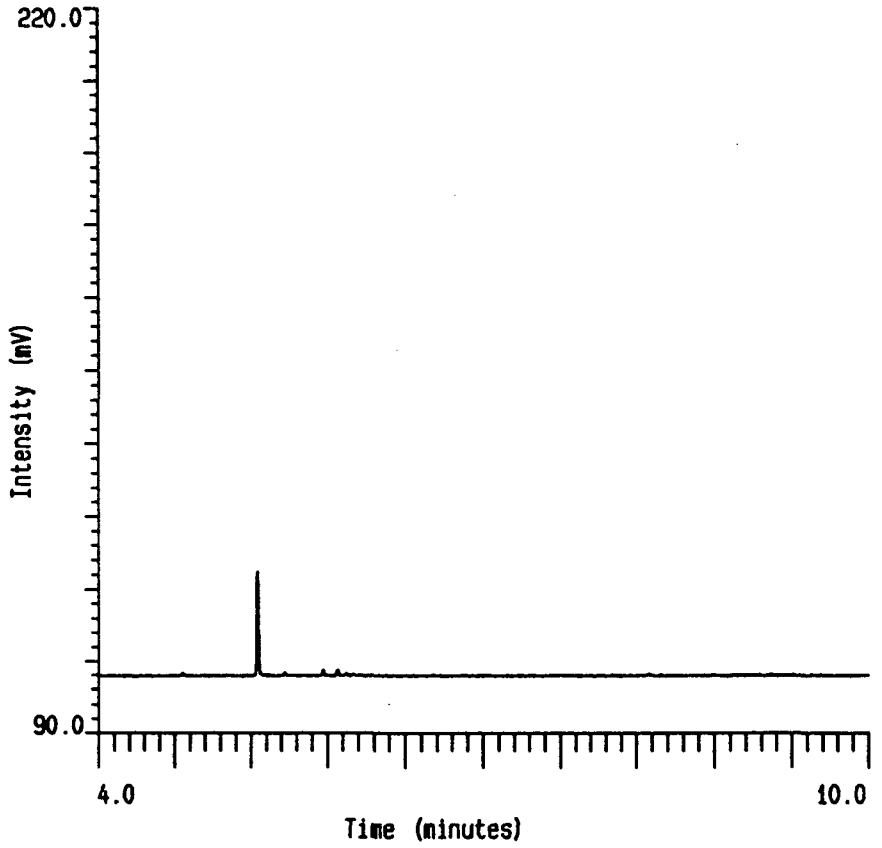
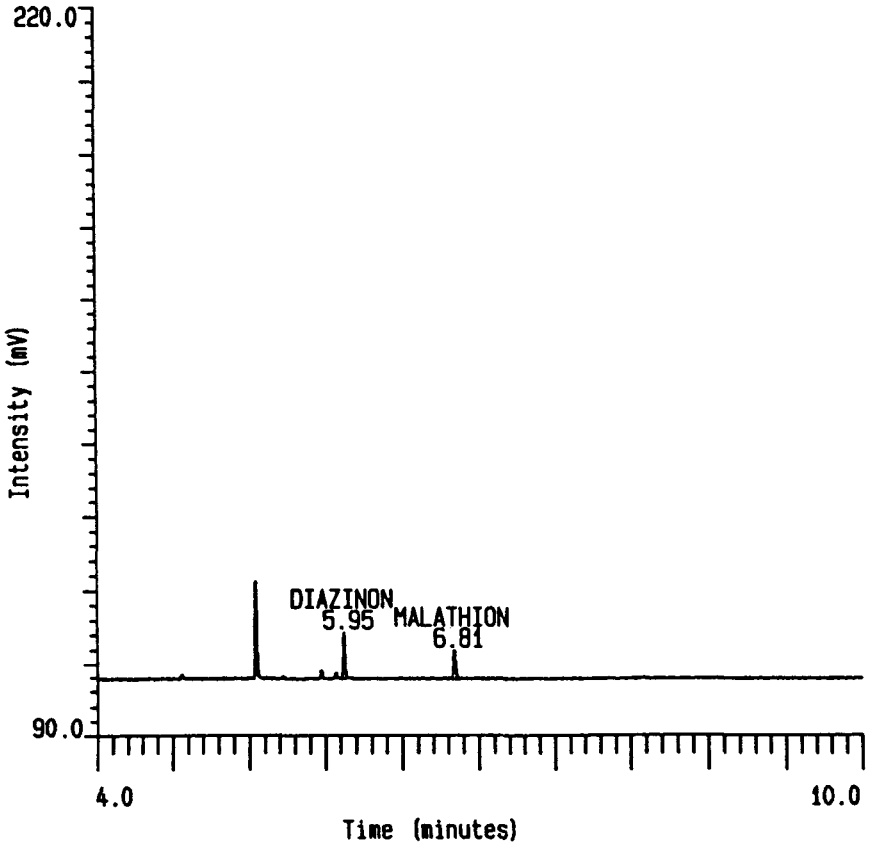


Figure 5. Representative Chromatogram of a 1 μg Hand Wash Fortification (LOQ) Sample

MCDO [43767] 29 767HWS9, 5, 1
43767-030
Acquired on 20-Jun-1997 at 17:18

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	8512	1.022
MALATHION	6.81	5441	1.151



Determination of Diazinon and Malathion in Leaf Wash Solutions

Method ARTF-AM-007

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Determination of Diazinon and Malathion in Leaf Wash Solutions

Method ARTF-AM-007

I. INTRODUCTION AND SUMMARY

A. Scope

Diazinon and malathion are organophosphate insecticides used for control of certain noxious insects on agriculturally important crops. To generate data which estimate human exposure to the insecticides during agricultural applications, a method of analysis is required for determination of diazinon and malathion residues in 0.01% Aerosol® OT (AOT) dislodging solutions from plant tissues.

B. Principle

Diazinon and malathion residues in AOT dislodging solution are retained on a conditioned C-18 reverse phase (C-18RP) column. The column is washed with water, then air-dried. Analytes are eluted from the column with methylene chloride which is evaporated to dryness. The residues are dissolved in acetone-based solvent, then quantified by gas chromatography (GC) with flame photometric detection in the phosphorous mode [FPD(P)]. The claimed limit of quantification (LOQ) for diazinon and malathion is 2.0 μg/sample[1].

Figure 1 presents the chemical structures of diazinon and malathion.

II. MATERIALS AND METHODS

A. Equipment

Equipment	Suggested Manufacturers:[2]
Analytical Balance	Ohaus GA110
C-18, Reverse Phase, SPE 1 gram, 6-mL	Varian Sample Preparation Products, Catalog #1225-6001

[1]This method analyzes diazinon and malathion residues in AOT dislodging solution samples. One sample equals 200 mL. The lowest limit of fortification during methods development research was 2.0 μg each of diazinon and malathion/200 mL sample.

[2]Equivalent sources of the listed equipment and reagents may be used.

Gas Chromatograph with a Flame Photometric Detector Phosphorous Mode Narrow-bore Capability Split-Splitless Injector	Hewlett-Packard Model 5890 Series II
Gas Chromatograph Column	J & W, DB-5, 30 m x 0.25 mm i.d., 0.25 μm film thickness
General Laboratory Glassware	Various
Rotary Evaporator	Fisher Scientific
Vacuum SPE Manifold	J & W Scientific

B. Reagents and Standards

AOT 75 Solution, 75% w:w Aqueous	Fisher Scientific Catalog #A345-500
0.01% Aqueous AOT 75	Dissolve 0.4 mL of 75% AOT Solution in 3800 mL (nominal 1 gallon) of water. Mix well. This solution is good for 48 hours at room temperature.
Di(ethylene glycol)diethylether: (i.e., DEGDEE), HPLC grade	Sigma/Aldrich Catalog #30,827-7
1.5% DEGDEE (w:v)	Dilute 7.5 g of DEGDEE to 500 mL with acetone. Mix and store at ambient temperatures.

Untreated Control Dislodging Solution (Spinach)

Prepare 3.8 L (1 gallon) of 0.01% aqueous AOT 75 solution. With a cork borer of appropriate size (eg., 2.54 cm), cut disks of untreated spinach leaves to yield one sample of 400 cm^2 surface area (includes both sides). Weigh the resulting disks to the nearest 0.1 g promptly to avoid evaporation of sample water. Calculate the mass

of leaves to yield 19 X 400 cm^2 samples. Cut this amount of fresh, intact, control leaves with scissors into ca. 2.5 cm squares, then immerse the cut leaves in 1.9 L of 0.01% AOT solution for 2 minutes with vigorous shaking. Decant the extract into a clean container, then add 1.9 L of fresh AOT solution to the leaves. Shake for 2 minutes and combine the extract with the original extract. Mix well and use immediately, or freeze pending analysis[3].

Methanol:	Fisher Optima Grade
Methylene Chloride (DCM):	Fisher Optima Grade
Water:	Distilled and/or deionized.

Diazinon, O,O-diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]-phosphorothioate, available from ARTF.

Malathion, [(Dimethoxyphosphinothioyl)thio]-butanedioic acid diethyl ester, available from ARTF.

C. 0.01% AOT Dislodging Solutions: Analytical Procedure

C.1 Sample Preparation

Freeze the field sample pending analysis. **IMPORTANT CRITICAL STEP!: Thaw the entire sample, then mix just prior to subsampling for analysis (See Note 1, page 12)**. Re-freeze the remainder of the sample.

C.2 C-18RP Clean-Up

a. Condition a 1 gram C-18RP SPE cartridge as follows: Place a cartridge on a clean vacuum manifold (See Note 2, page 12); the

[3]This procedure prepares untreated-control dislodging solution in bulk volume. The routine procedure for preparation of one dislodged sample is to extract 400 cm^2 of plant tissue with 100 mL of 0.01% AOT solution, decant the mother liquor, then repeat the extraction with a fresh 100 mL aliquot of 0.01% AOT solution. The extracts are combined to yield a single sample.

By example, HORIZON used a 2.1 cm diameter borer on spinach leaves for this development work. The surface area of one leaf disk was $2(\pi)(r^2) = 2(3.1416)(1.05^2) = 6.93$ cm^2. Hence, a single sample consisted of 400/6.93 = 58 leaf disks which weighed 10.74 grams. Hence, 204.1 g of spinach leaves extracted with 3.8 L of 0.01% AOT solution yielded 19 X 200 mL untreated-control dislodging samples.

vacuum should be sufficient to achieve eluate flows of only ca. 1 → 2 drops/second. Wash the cartridge successively with 2 x 5 mL of methanol, then 2 x 5 mL of water. **Do not allow the column to go dry at any point in this procedure unless specified otherwise.**

b. QC fortifications are made at this point as follows: Place 200 mL of untreated control 0.01% AOT dislodging solution (Section B) in a suitable glass beaker. Fortify the solution with an appropriate amount of diazinon and malathion in acetone (See Section E.1). Mix by stirring, then proceed as in C.2.c below (**IMPORTANT! See Note 1, p. 12**).

c. Pipet 5 mL of sample onto the C-18RP column. With very little vacuum, percolate the sample into the column at a maximum flow rate of ca. 1 → 2 drops/second. Wash the sample into the column with 10 mL of water, again observing the 1 - 2 drops/second flow rate through the column (Note 3, p. 13). Discard all eluates to this point.

d. With full vacuum (≥ 20" Hg) on the manifold, air-dry the column for at least 45 minutes. **This is a critical step in the procedure; all water must be removed from the column (Note 4, p. 13)!**

e. Elute diazinon and malathion from the column with 16 mL of DCM (maximum rate of ca. 1 → 2 drops/second, see Note 5, p. 14). Collect the eluate directly in a 125-mL evaporation flask, or in a culture tube of suitable size. Transfer the eluate from the culture tube to a 125-mL evaporation flask, and rinse the tube twice with ca. 2 mL DCM and add to the flask.

g. Vacuum-evaporate the sample to dryness (ca. 25" Hg, ≤35°C water bath). **Ensure that all DCM has been removed from the sample. Cautionary Note!: Discard and reanalyze any sample which contains droplets of water after complete evaporation of the DCM. Evaporation of the water to dryness will give profound losses of diazinon, but not malathion. (See Note 4, p. 13).**

h. Dissolve the dry residue in a known volume of 1.5% DEGDEE:acetone (generally 6.0 mL for LOQ residues, although 2.0 mL has been used, see Note 6, p. 15). Dilute with the same solvent as necessary to maintain analyte concentrations within the

standard curve range. Submit the sample for GC/FPD(P) analysis as described in Step D.

D. Gas Chromatographic Analysis

A gas chromatograph equipped with a Flame Photometric Detector (phosphorous mode) is required. Split-splitless injection and narrow-bore capabilities are recommended. The conditions described herein may be modified provided adequate performance of the analysis is demonstrated.

GC Column: J & W DB-5, 30 m length, 0.25 mm i.d., 0.25 μm film. Other columns may be substituted if they give satisfactory resolution between the analytes and any interferences.

Injector: 230°C

Detector: 220°C

Column:

Initial: 95°C, hold 1.0 min.
Ramp Rate 1: 30°C/min to 230°C, hold 4 minutes.
Ramp Rate 2: 40°C/min to 290°C, hold 5 minutes.

Carrier Gas: He, 1.7 mL/min at 95°C, head pressure = 20 psi. Constant flow off.

Septum Purge: He @ 3.0 mL/min.

Injector Liner: HP Liner, Deactivated, 4 mm i.d., with Deactivated Glass Wool Plug, Part #5062-3587, or
HP Liner, Deactivated, Double-tapered splitless, Part #5181-3315.

Split Vent: He @ 7.6 mL/min, on @ 0.75 min.

Detector Make-Up: N_2 @ 23 mL/min.

Detector Air: 95 mL/min.

Detector Hydrogen: 68 mL/min.

Injection: 2 μl, Split/Splitless.

E. Calibration Procedures

E.1 Preparation of Standard Solutions

Individual stock solutions of diazinon and malathion are prepared in acetone and stored in a freezer; primary stock concentrations are approximately 10.0 mg/mL. Stability of these stock solutions during prolonged storage has not been evaluated as part of this developmental and validation work.

Dilutions of diazinon and malathion are made at appropriate concentrations for fortification standards. These dilutions are made in acetone, stored in a freezer, and prepared as mixed or individual standards; that is, each solution may contain either or both diazinon and malathion. The concentration range for these fortification solutions will vary from study to study, but generally will range from 10 μg/mL to 5 mg/mL.

Dilutions of diazinon and malathion for GC standards are made in 1.5% DEGDEE in acetone (Note 6, p. 15) and are stored in a freezer. The standard concentrations suggested are 4, 10, 20, 40, 60, and 100 ng/mL for each analyte[4].

E.2 Detector Calibration

The sensitivity of the FPD(P) detector is monitored by injecting diazinon and malathion before, between, and after the samples. The suggested mass range is 8 pg to 200 pg injected.

Under the conditions of this assay, diazinon and malathion elute from the GC column at ca. 5.9 and 6.8 minutes, respectively. The GC/FPD(P) limit of detection for diazinon and malathion (injected as a pure standard in 1.5% DEGDEE:acetone) is ca. 2 pg injected for both analytes.

[4]The analyst should choose standard concentrations appropriate for the standard curve model (See footnote 5). For linear or quadratic standard curve models, the standard concentrations should be constructed in a linear manner; for logarithmic models, the concentrations should be arrayed geometrically.

F. Methods of Calculation

F.1 Injection Sequence

Analysis sequences are started and ended with one or two standards; standard injections are made throughout the run, generally with no more than three or four sample injections between each standard. A standard curve of analyte concentration (ng/mL) versus peak height or area is constructed using a method of curve generation appropriate for the GC/FPD(P) instrumentation. The construction may be linear, quadratic, or logarithmic[5]. It is recommended that the column be equilibrated with several injections of matrix-laden extract if a matrix effect is observed between samples and standards.

F.2 Calculations

Calculate μg/sample values for diazinon and malathion residues in AOT dislodging solutions using the following equation:

$$ug/Sample = \frac{(ng/mL\ Final\ Extract)\ X\ (mL\ Final\ Extract)}{} X \frac{200\ mL\ Sample\ Volume}{5\ mL\ C\text{-}18RP\ Aliquot\ Volume} X \frac{1\ ug}{1000\ ng}$$

For reference, the molecular weights of diazinon and malathion are 304.34 g/mole and 330.35 g/mole, respectively.

For fortified-control samples, use the following equation to calculate percent recovery:

$$\%\ Recovery = \left(\frac{(ug/Sample\ Found) - (ug/Sample\ Control)}{ug/Sample\ Fortified} \right) X\ 100$$

[5]The choice of the standard curve model is instrument/detector/laboratory specific, and should be based upon the precision of back-calculated standard responses against the various least squares curve models.

G. Interferences

G.1 Sample Matrices

Chromatographic interferences from AOT matrix are absent with this assay. GC parameters may require optimization to maximize resolution between the analytes and any other interferences that may be present in actual samples.

G.2 Other Pesticides

A specificity study has not been conducted for this method.

G.3 Solvents and Reagents

Solvents and reagents have contributed no interfering chromatographic peaks in this assay.

G.4 Glassware

There are no known interferences from labware at the stated LOQs. Extraction glassware is thoroughly washed with hot, soapy water, rinsed with acetone, air-dried, then placed in an oven at 150°C for at least 1 hour prior to use. Glass vessels are recommended for all steps without substitutions with plastic.

III. METHODS VERIFICATION

A. Experimental Design

The method for AOT dislodging matrix was tested by analysis of one unfortified control sample, three controls fortified at 2.0 µg/sample, three controls fortified at 20.0 µg/ sample, and three controls fortified at 2.0 mg/sample, duplicated over two days. The dislodging matrix was prepared from spinach leaves. This design was used by both the development and validation laboratories.

B. Analytical Reference Materials

Specific reference materials used during the conduct of the method development study are described in Table 1.

C. Untreated Control Dislodging Solution

Untreated control dislodging solution was prepared from fresh spinach leaves as noted in Section D of this method. Concentrated AOT was purchased from Fisher Scientific. Solutions at 0.01% were prepared as needed, and were assigned a 2-day expiration date.

D. Verification Results

Results from the AOT dislodging solution method validation study are presented in Table 2, and example chromatograms are presented in Figures 2 through 5.

The techniques outlined in this document are suitable for analysis of diazinon and malathion in AOT dislodging solution matrix from spinach leaves at fortification levels ranging from 2.0 μg/sample to 2 mg/sample. **Critical features of the method include: (a) complete thawing and mixing of the sample just prior to analysis, (b) proper drying of the C-18RP columns prior to elution, (c) ensuring that the C-18RP sorbent is adequately calibrated prior to use, and (d) scrupulously cleansed labware.**

IV. NOTES

Note 1: **The entire sample must be thawed, then mixed just prior to subsampling for analysis**. During methods development, several fortified-control samples were only partially thawed, then subsampled for analysis. Recoveries of both analytes were biased very high, and this observation was repeatable with other independent samples. Apparently, frozen AOT solutions are not homogeneous with respect to dissolved analytes; fractional crystallization during the freeze cycle is suspected.

In addition, there is evidence that diazinon, but not malathion, binds to extractable plant materials which precipitate during the freeze/thaw cycle. These precipitates are initially very fine, but they increase in size and amount with each freeze/thaw cycle. Sonication does not disperse the precipitate; instead, it promotes further precipitation and "clumping". Hence, stir the thawed samples vigorously with a glass stirring rod or magnetic bar, then quickly pipet (within 15 seconds) the suspension onto the C-18RP column.

This latter problem is noted only with LOQ or near-LOQ residue levels and, as mentioned, involves only diazinon.

Note 2: The developers of this method have observed frequent cross-contamination of final sample extracts with malathion and, especially, diazinon. Generally, this problem

is noticeable only with samples fortified at the limit of quantification when samples containing very high residues (100 X LOQ) have been previously analyzed using the same glassware or laboratory equipment. The vacuum manifold, especially the plastic SPE stopcocks and attached needles, are a primary source of this cross-contamination. **The entire vacuum manifold, including stopcocks and needles, should be scrupulously cleaned with hot, soapy water, rinsed with distilled water, then high-purity acetone prior to any subsequent use**. Stopcocks can be checked for retained residues by soaking them overnight in acetone, then analyzing the extract by gas chromatography (See Section D). If cross-contamination persists, replace the stopcocks. [The validation laboratory did not encounter frequent cross-contamination problems from the vacuum manifold or glassware, and the rigorous cleaning of the vacuum manifold was not found to be necessary.]

Note 3: The analyst should note that low recoveries of diazinon from quality control samples may indicate a sample loading problem. Load flow rates may be a factor, but this has not been confirmed. Some analysts may wish to dilute the 0.01% AOT sample with water (e.g., 2X), but note that malathion and diazinon are sparingly soluble in water, and excessive dilution of the sample may cause loss of analyte due to precipitation.

Note 4: Developmental research for this method demonstrated no losses of either analyte during vacuum-evaporation of methylene chloride, or during prolonged (up to 10 minutes) "dry" evaporation at ≤35°C (water bath) and 25" Hg vacuum. However, profound losses of diazinon (but not malathion) are observed if the sample contains droplets of water, and the water is evaporated to dryness.

Therefore, water MUST be removed from the C-18RP column prior to elution with methylene chloride (Step II.C.2.f). Profound losses of diazinon (but not malathion) are observed if the sample contains droplets of water, and the water is evaporated to dryness. This effect is poorly understood, but has attributes consistent with a diazinon/water azeotrope. No problems were encountered with the use of 50:50 MeOH:DCM provided the C-18RP columns were adequately dried.

The method developer could dry only 3 cartridges at a time to achieve proper drying. The validation laboratory was able to dry up to 12 cartridges at a time using a 45 min drying period at the maximum recommended operating vacuum for the vacuum manifold (20" Hg). This vacuum could only be achieved using a vacuum pump. During the drying period, the flow should be checked periodically through each cartridge by placing a finger over the top of the cartridge. A strong vacuum should be felt quickly (ca. 1-2 sec), and a sharp "popping" sound made when the finger is removed. The flow through all the columns should be checked

and should be relatively uniform. As the columns dry, the flow characteristics of the columns will change, so it is necessary to moderate the vacuum and repeat the column flow check approximately every 10 min.

Note 5: During developmental research, 8 mL of DCM quantitatively eluted both analytes from the C-18RP column. For the validation laboratory work, a total of up to 16 mL was used to obtain quantitative recovery. Subsequent work with a similar method showed that 8 mL of 50:50 MeOH:DCM yielded excellent recoveries with no chromatographic problems. However, the analyst should note that this method has been optimized for analyte recoveries from spinach samples prepared in the laboratory. No spinach field samples or other plant matrices have been tested with this method; other types of samples may contain interferences which are also eluted with DCM and may compromise quantification of the analytes. In such cases, the DCM elution solvent should be modified to effect column resolution between the analytes and interferences (e.g., mixtures of DCM and hexane).

Each lot of C-18RP cartridges should be pre-calibrated with matrix prior to use. **This is a critical step in the assay, since AOT components can change the retention characteristics of the solid support**. An example procedure is as follows.

Prepare a C-18RP column and fortified-control AOT dislodged sample (24 μg both analytes/200 mL solution) as described in Sections C.2.a and C.2.b, respectively. Process the sample through the column as described in Sections C.2.c through C.2.e. Retain the load and water washes from C.2.c to this point. Dissolve the final dry residue in a 6 mL final volume. Analyze the sample by GC/FPD(P) (See Step D) against a 100 ng/mL diazinon/malathion standard prepared in 1.5% DEGDEE:acetone (Step E.1). At 100% recovery, the GC/FPD(P) detector responses for both compounds from the sample and standard injections should be equivalent.

If the recovery for either compound is biased low, elute the column with additional DCM, vacuum-evaporate to just-dryness, dissolve the residue in 6 mL DEGDEE:acetone, then inject into the GC/FPD(P). Finally, dilute the retained load/water wash fraction with water (100X) and partition twice against 75 mL of DCM. Vacuum-evaporate the DCM to just-dryness, dissolve the residue in 6 mL of 1.5% DEGDEE:acetone, then analyze by GC/FPD(P).

As observed in Note 3 above, the presence of diazinon in the load/wash fraction from Step C.2.c may indicate a load flow rate problem or too high of an AOT concentration in the sample. Low-biased malathion recoveries are an indication that further elution of the C-18RP column with DCM is necessary; simply increase

the elution volume from the recommended 8 mL to 10-16 mL, as indicated, or repeat the column profile work with a mixture of methanol and DCM, such as 50:50 MeOH:DCM.

Note 6: Diazinon and malathion standards prepared in neat acetone give unacceptable chromatography; standard curves exhibit poor linearity (especially for malathion), reproducibility, and sensitivity. "Priming" the GC with extracts in and of itself does not correct the problem. Use of 1.5% DEGDEE in acetone solvent for GC standards and final sample extracts eliminates these problems and improves the signal/noise ratio for analyte detection at all concentrations. The mechanism of action for this effect is not known.

Even with the use of 1.5% DEGDEE in acetone, it was found that priming, or equilibrating, the GC with matrix extract was necessary prior to the analysis of a set of samples for hand wash matrix. In general, a minimum of two injections of matrix-laden extract is recommended immediately prior to initiation of a sample set. In addition, routine maintenance was found to be necessary due to buildup in the injector liner and at the front of the analytical column. Replacement of the injector liner and removal of approximately 15" from the front of the analytical column was necessary after approximately every 100 sample injections. It was found that this maintenance was necessary to prevent a matrix effect (enhancement) on the malathion in matrix-laden samples. If a high bias is observed with samples reconstituted in low volumes of 1.5% DEGDEE in acetone, it may be necessary to chill the evaporation flask prior to addition of the acetone-based solvent. This can be accomplished using an ice water bath.

Final extracts will range from colorless to light-green in color.

V. SAFETY

The organic solvents utilized in this method represent both a general exposure and fire hazard. Provision must be made for working with these solvents for personnel safety.

VI. TABLES

Table 1. Standard Reference Materials.

STANDARD NAME	ABC STANDARD NUMBER	LOT NUMBER	PURITY:EXP. DATE	PHYSICAL CHARAC-TERISTICS
Diazinon, O,O-diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate, CAS #333-41-5.	PS-9824	95R-31-45C 09467	87.7%:9/14/98	Clear Yellow Liquid
Malathion, [(Dimethoxyphosphino-thioyl)thio]-butanedioic acid diethyl ester, CAS #121-75-5.	PS-9825	95R-31-44E CS030	95.0%:12/12/99	Clear Liquid

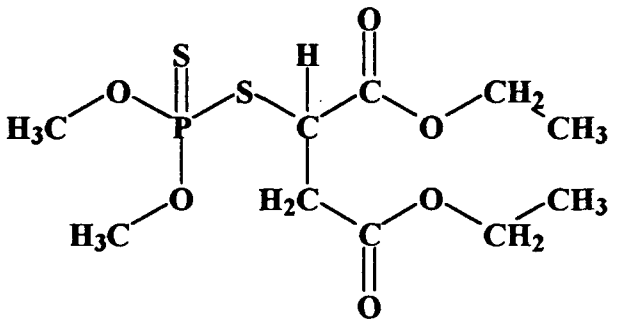
Table 2. Recovery of Diazinon and Malathion from Leaf Wash Samples

ABC Sample ID	Sample Description	µg Diazinon/ sample found	% Recovery Diazinon	µg Malathion/ sample found	% Recovery Diazinon
43767-043	Control Leaf Wash Solution	0	N/A	0	N/A
43767-044	Control + 1.98 µg Diazinon/2.04 µg Malathion	1.37	69.2	1.39	68.1
43767-045	Control + 1.98 µg Diazinon/2.04 µg Malathion	1.62	81.8	2.14	105
43767-046	Control + 19.8 µg Diazinon/20.4 µg Malathion	17.6	88.9	19.5	95.6
43767-047	Control + 19.8 µg Diazinon/20.4 µg Malathion	18.3	92.4	19.8	97.1
43767-048	Control + 1980 µg Diazinon/2040 µg Malathion	1870	94.4	2010	98.5
43767-049	Control + 1980 µg Diazinon/2040 µg Malathion	1800	90.9	1930	94.6
43767-050	Control Leaf Wash Solution	0	N/A	0	N/A
43767-051	Control + 1.98 µg Diazinon/2.04 µg Malathion	2.12	107	2.19	107
43767-052	Control + 1.98 µg Diazinon/2.04 µg Malathion	1.70	85.9	1.89	92.6
43767-053	Control + 19.8 µg Diazinon/20.4 µg Malathion	19.1	96.5	20.4	100
43767-054	Control + 19.8 µg Diazinon/20.4 µg Malathion	19.3	97.5	21.0	103
43767-055	Control + 1980 µg Diazinon/2040 µg Malathion	2010	102	2060	101
43767-056	Control + 1980 µg Diazinon/2040 µg Malathion	2030	103	2200	108
	Average Overall % Recovery (n=12)		92.5		97.5
	Overall Standard Deviation (n=12)		10.3		10.5
	% Relative Standard Deviation		11.1		10.8

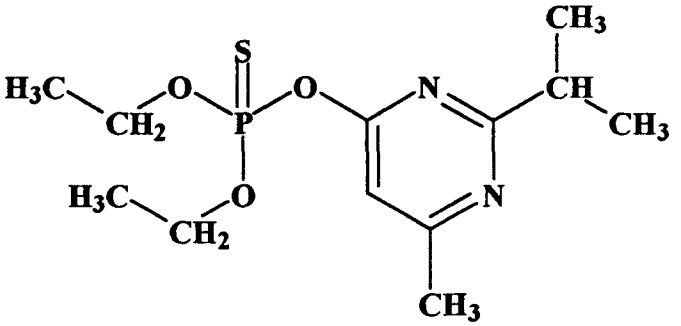
Recoveries corrected for the µg found in the respective controls of the sets.

VII. FIGURES

Figure 1. Chemical Structures of Diazinon and Malathion.



MALATHION
[(Dimethoxyphosphinothioyl)thio]-butanedioic acid diethyl ester



DIAZINON
O,O-Diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]-phosphorothioate

Figure 2. Representative Chromatogram of a 100 ng/mL Mixed External Standard

MCDO [43767] 29 767FDS2, 2, 1
GCMIX-1 NOMINAL 100 ng/mL
Acquired on 27-Jun-1997 at 16:15

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	109040	102.248
MALATHION	6.78	68102	106.210

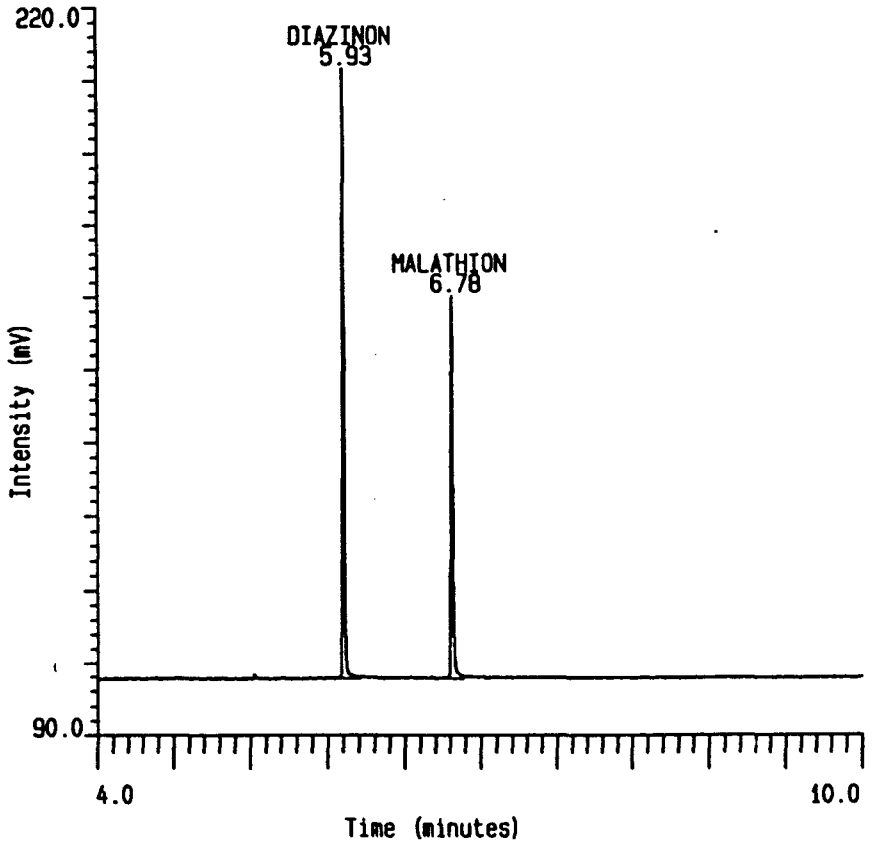


Figure 3. Representative Chromatogram of a 4.00 ng/mL Mixed External Standard

MCDO [43767] 29 767FDS2, 14, 1
GCMIX-6 NOMINAL 4 ng/mL
Acquired on 27-Jun-1997 at 20:19

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	4277	4.257
MALATHION	6.78	2625	4.381

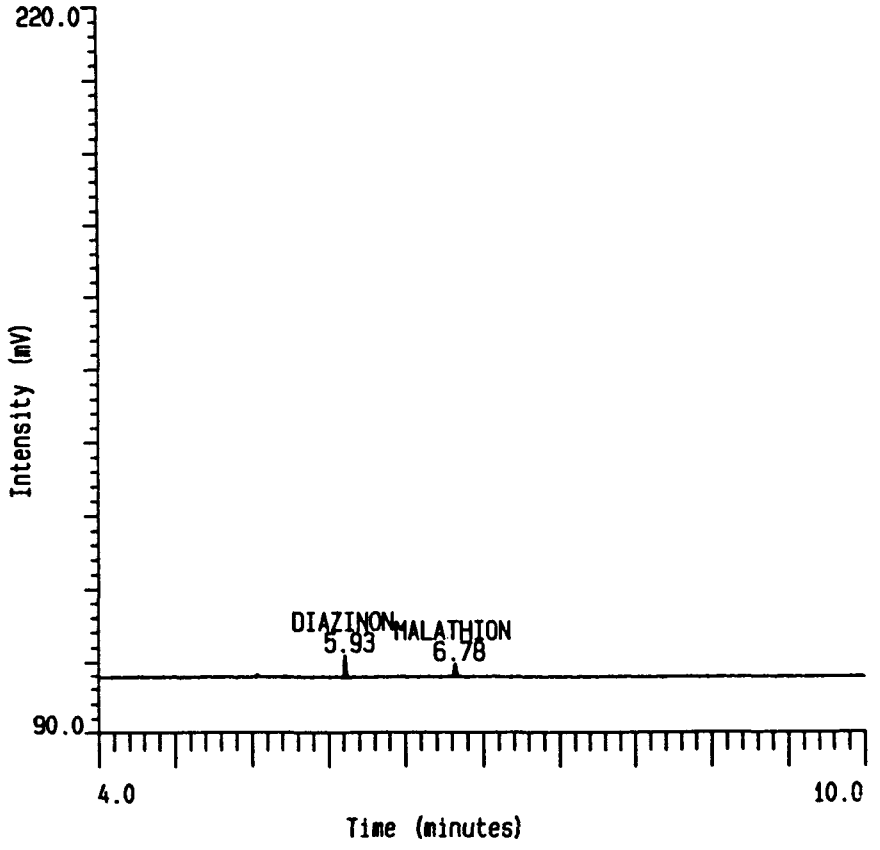


Figure 4. Representative Chromatogram of a Control Leaf Wash Sample

MCDO [43767] 29 767FDS2, 4, 1
43767-043
Acquired on 27-Jun-1997 at 16:55

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	0.00	0	0
MALATHION	0.00	0	0

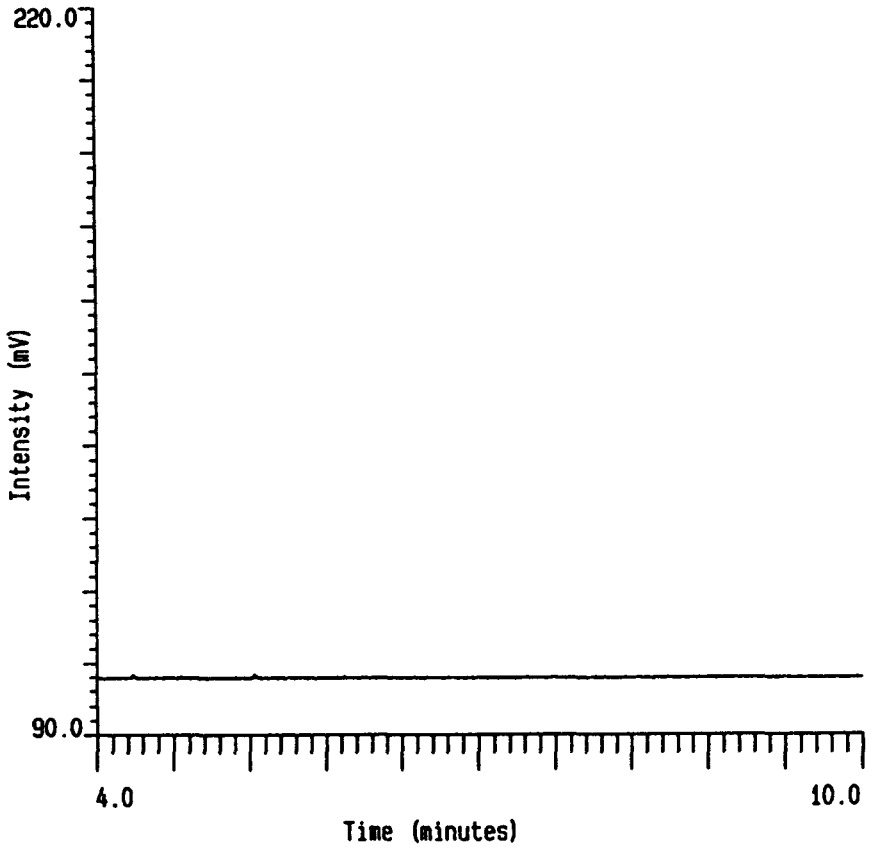
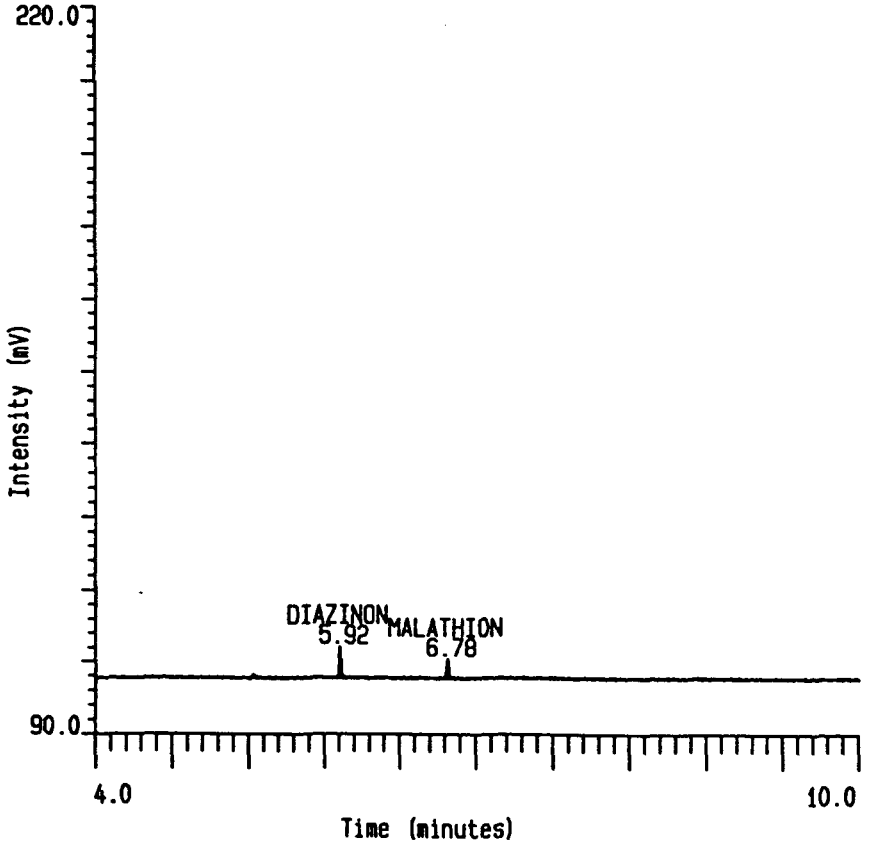


Figure 5. Representative Chromatogram of a 2 μg Leaf Wash Fortification (LOQ) Sample

MCDO [43767] 29 767FDS2, 5, 1
43767-044
Acquired on 27-Jun-1997 at 17:16

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.92	5840	1.372
MALATHION	6.78	3519	1.385



Determination of Diazinon and Malathion in Outer Dermal Dosimeters

Method ARTF-AM-008

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Determination of Diazinon and Malathion in Outer Dermal Dosimeters

Method ARTF-AM-008

I. INTRODUCTION AND SUMMARY

A. Scope

Diazinon and malathion are organophosphate insecticides used for control of certain noxious insects on agriculturally important crops. To generate data which estimate human exposure to the insecticides during agricultural applications, a method of analysis is required for determination of diazinon and malathion residues in/on cotton-based worker exposure fabrics such as outer whole body dosimeters (OWBD).

B. Principle

Diazinon and malathion residues in/on OWBD fabrics are extracted with acetone. Following evaporation of the solvent, the residues are suspended in water, then partitioned into 1:1 ethyl ether:hexane. Following evaporation of the 1:1 ethyl ether:hexane, the residues are suspended in 0.01% Aerosol® OT (AOT) solution. The residues in 0.01% AOT solution are retained on a conditioned C-18 reverse phase (C-18RP) column. The column is washed with water, then air-dried. Analytes are eluted from the column with methylene chloride, which is then evaporated to dryness. The residues are dissolved in an acetone-based solvent, then quantified by gas chromatography (GC) with flame photometric detection in the phosphorous mode [FPD(P)]. The claimed limit of quantification (LOQ) for diazinon and malathion is 5.0 μg/sample[1].

Figure 1 presents the chemical structures of diazinon and malathion.

[1]This method analyzes diazinon and malathion residues in/on segments cut from OWBD matrices (e.g., upper arms, lower legs, front torso, etc.; one segment = one sample). The lowest limit of fortification during methods development research and validation was 5.0 µg each of diazinon and malathion/sample.

II. MATERIALS AND METHODS

A. Equipment

Equipment	Suggested Manufacturers:[2]
Aluminum Foil	Local Grocery
Analytical Balance	Ohaus GA110
C-18, Reverse Phase, SPE 1 gram, 6-mL	Varian Sample Preparation Products, Catalog #1225-6001
Centrifuge, IEC Clinical	VWR Scientific
Centrifuge Tubes, 50 mL Round-bottomed with PTFE-Lined Screw Caps	Fisher Scientific, Catalog #05-558-5B
Gas Chromatograph with a Flame Photometric Detector Phosphorous Mode Narrow-bore Capability Split-Splitless Injector	Hewlett-Packard Model 5890 Series II
Gas Chromatograph Column	J & W Scientific, DB-5, 30 m x 0.25 mm i.d., 0.25 μm film thickness
General Laboratory Glassware	Various
Glass Jars, 1 Gallon, with PTFE or foil-lined Lids, Wide-Mouth	Fisher Scientific,
Glass Storage Jars, 4 ounce, with PTFE-Lined Lids	Fisher Scientific
Rotary Evaporator	Fisher Scientific

[2]Equivalent sources of the listed equipment and reagents may be used.

Shaker, Eberbach	VWR Scientific
Top-loading Balance	Ohaus E400
Vacuum SPE Manifold	J & W Scientific

B. Reagents and Standards

Acetone:	Fisher Optima Grade
AOT 75 Solution, 75% w:w Aqueous	Fisher Scientific Catalog #A345-500
0.01% Aqueous AOT 75	Dissolve 0.4 mL of 75% AOT Solution in 3800 mL (nominal 1 gallon) of water. Mix well. This solution is good for 48 hours at room temperature.
Di(ethylene glycol)diethylether: (i.e., DEGDEE), HPLC grade	Sigma/Aldrich Catalog #30,827-7
1.5% DEGDEE (w:v)	Dilute 7.5 g of DEGDEE to 500 mL with acetone. Mix and store at ambient temperatures.
Diethylether (EtOEt):	Fisher Pesticide Grade
Hexane:	Fisher Optima Grade
Methanol:	Fisher Optima Grade
Methylene Chloride (DCM):	Fisher Optima Grade
Water: Distilled and/or deionized.	Local
Cotton Untreated Control Outer Whole Body Dosimeters (OWBD).	Stewart Agricultural Research Services, Inc., P.O. Box 509, Macon, MO 63552.

Diazinon, O,O-diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]-phosphorothioate, available from ARTF.

Malathion, [(Dimethoxyphosphinothioyl)thio]-butanedioic acid diethyl ester, available from ARTF.

C. Cotton Outer Whole Body Dosimeters: Analytical Procedure

C.1 Sample Preparation

Freeze the field sample pending analysis. For analysis, cut an appropriate piece (e.g., upper arm, lower leg, front torso, etc.) from the OWBD as specified by protocol or appropriate SOP. Re-freeze the remainder of the sample.

C.2 Extraction

a. Place the field sample into a 1 gallon, wide-mouth glass jar. If sample is received in foil, rinse the foil with a minimum of 50 mL acetone and include this rinse as part of the 2.5 liter total extraction volume.

b. QC fortifications are made at this point as follows: Lay an untreated control OWBD sample onto a sheet of aluminum foil. Fortify the cloth with an appropriate amount of diazinon and malathion in acetone (Note 1, p. 15. Also see Section II.E.1). Fold or roll the sample, place the sample into a 1 gallon, wide-mouth glass jar, then proceed as in II.C.2.c below. Rinse the foil with a minimum of 50 mL acetone and include this rinse as part of the 2.5 liter total extraction volume. Discard the aluminum foil after a single use.

c. Add a total of 2.5 liters of acetone to the sample (including the foil rinse volume). Cap the sample tightly with a PTFE or aluminum foil-lined lid. Shake for 0.25 hr (ca. 2 excursions/sec, Note 2, p. 15).

d. Remove the sample jar from the shaker and allow loose particulate matter to settle (1-2 minutes). Pipet a 25-mL sample aliquot into a 125-mL evaporation flask; as a backup in the event of method failure, retain ca. 100 mL of the remaining extract in a labeled, PTFE-capped, glass bottle, and store in a freezer. Discard the OWBD sample.

e. Vacuum-evaporate the 25-mL aliquot to dryness (ca. 25" Hg, ≤35°C). **Ensure that all acetone has been removed from the sample** (Note 3, p. 15).

C.3 Partitioning

a. Add 20 mL of deionized water to the sample flask and sonicate for 2-5 minutes, tipping and rotating the flask to remove residue on the sides of the flask. (Note 4, p. 15). Pipet 7.5 mL of ethyl ether (EtOEt) onto the aqueous sample and mix well for 0.25 minutes.

b. Pipet 7.5 mL of hexane onto the EtOEt:aqueous sample and mix well for 0.25 minutes. Allow the phases to separate (Note 5, p. 16).

c. Transfer the entire sample (both layers; ethyl ether:hexane phase and aqueous phase) to a clean, dry, 50-mL centrifuge tube, cap, and vortex for 10-15 seconds, thoroughly mixing the two phases. Balance the tubes with deionized water. Centrifuge the sample for 5 minutes at approximately 1000 g (e.g., 15 cm rotation radius at 2400 rpm, Note 6, p. 16). Remove the top layer and place it in a 125-mL evaporation flask.

d. Rinse the original 125-mL evaporation flask with 15 mL of 50:50 EtOEt:hexane, transfer the solvent to the centrifuge tube, and vortex for 10-15 seconds, thoroughly mixing the two phases. Balance the tubes with deionized water. Centrifuge the sample for 2 - 5 minutes at approximately 1000 g. Remove the top layer and place it with the first partition fraction in the 125-mL evaporation flask.

e. Repeat II.C.3.d. once again and proceed to II.C.3.f.

f. Vacuum-evaporate the sample to dryness (ca. 25" Hg, ≤35°C).

C.4 C-18RP Clean-Up

a. Condition a 1 gram C-18RP SPE cartridge as follows: Place a cartridge on a clean vacuum manifold (See Note 7, page 16); the vacuum should be sufficient to achieve eluate flows of ca. 1 → 2 drops/second. Wash the cartridge successively with 2 x 5 mL of methanol, then 2 x 5 mL of water. **Do not allow the column to go dry at any point in this procedure unless specified otherwise.**

b. Place 15 mL of 0.01% AOT in the 125-mL evaporation flask (See Section II.C.3.f) and sonicate for approximately 5 minutes, tipping and rotating the flask to remove residue on the sides of the flask.

c. Pipet 5 mL of sample onto the C-18RP column. With a very low vacuum, percolate the sample into the column at a maximum flow rate of ca. 1 → 2 drops/second. Wash the column with 2 x 5 mL of water (Note 8, p. 16) at a maximum flow rate of ca. 1 → 2 drops/second. Discard all eluates to this point.

d. With full vacuum (≥ 20" Hg) on the manifold, air-dry the column for at least 45 minutes. **This is a critical step in the procedure; all water must be removed from the column (Note 9, p. 17)!**

e. Elute diazinon and malathion from the column with 16 mL of DCM (maximum of 1 → 2 drops/second, see Note 10, p. 17). Collect the eluate directly in a 125-mL evaporation flask, or in a culture tube of suitable size. Transfer the eluate from the culture tube to a 125-mL evaporation flask, and rinse the tube twice with ca. 2 mL DCM and add to the flask.

f. Vacuum-evaporate the sample to dryness (ca. 25" Hg, ≤35°C water bath). **Ensure that all DCM has been removed from the sample. Cautionary Note!: Discard and reanalyze any sample which contains droplets of water after complete evaporation of the DCM. Evaporation of the water to dryness will give profound losses of diazinon, but not malathion. (See Note 9, p. 17).**

g. Dissolve the dry residue in a known volume of 1.5% DEGDEE: acetone (generally 2.0 mL for LOQ residues, see Note 11, p. 18). Dilute with the same solvent as necessary to maintain analyte concentrations within the standard curve range. Submit the sample for GC/FPD(P) analysis as described in Step II.D.

D. Gas Chromatographic Analysis

A gas chromatograph equipped with a Flame Photometric Detector (phosphorous mode) is required. Split-splitless injection and narrow-bore capabilities are recommended. The conditions described herein may be modified provided adequate performance of the analysis is demonstrated.

GC Column: J & W DB-5, 30 M length, 0.25 mm i.d., 0.25 μM film. Other columns may be substituted if they give satisfactory resolution between the analytes and any interferences.

Injector: 230°C

Detector: 220°C

Column:

Initial: 95°C, hold 1.0 min.
Ramp Rate 1: 30°C/min to 230°C, hold 4 minutes.
Ramp Rate 2: 40°C/min to 290°C, hold 5 minutes.

Carrier Gas: He, 1.7 mL/min at 95°C, head pressure = 20 psi. Constant flow off.

Septum Purge: He @ 3.0 mL/min.

Injector Liner: HP Liner, Deactivated, 4 mm i.d., with Deactivated Glass Wool Plug, Part #5062-3587, or
HP Liner, Deactivated, Double-tapered splitless, Part #5181-3315.

Split Vent: He @ 7.6 mL/min, on @ 0.75 min.

Detector Make-Up: N_2 @ 23 mL/min.

Detector Air: 95 mL/min.

Detector Hydrogen: 68 mL/min.

Injection: 2 μl, Split/Splitless

E. Calibration Procedures

E.1 Preparation of Standard Solutions

Individual stock solutions of diazinon and malathion are prepared in acetone and stored in a freezer; primary stock concentrations are approximately 10.0 mg/mL. Stability of these stock solutions during prolonged storage has not been evaluated as part of this developmental and validation work.

Dilutions of diazinon and malathion are made at appropriate concentrations for fortification standards. These dilutions are made in acetone, stored in a freezer, and prepared as mixed or individual standards; that is, each solution may contain either or both diazinon and malathion. The concentration range for these fortification solutions will vary from study to study, but generally will range from 10 μg/mL to 5 mg/mL.

Dilutions of diazinon and malathion for GC standards are made in 1.5% DEGDEE in acetone (Note 11, p. 18) and are stored in a freezer. The standard concentrations suggested are 4, 10, 20, 40, 60, and 100 ng/mL for each analyte[3].

E.2 Detector Calibration

The sensitivity of the FPD(P) detector is monitored by injecting diazinon and malathion before, between, and after the samples. The suggested mass range is 8 pg to 200 pg injected.

Under the conditions of this assay, diazinon and malathion elute from the GC column at ca. 6.2 and 7.2 minutes, respectively. The GC/FPD(P) limit of detection for diazinon and malathion (injected as a pure standard in 1.5% DEGDEE:acetone) is ca. 2 pg injected for both analytes.

F. Methods of Calculation

F.1 Injection Sequence

Analysis sequences are started and ended with one or two standards; standard injections are made throughout the run, generally with no more than three or four sample injections between each standard. A standard curve of analyte concentration (ng/mL) versus peak height or area is constructed using a method of curve generation appropriate for the GC/FPD(P) instrumentation. The construction may be linear, quadratic,

[3]The analyst should choose standard concentrations appropriate for the standard curve model (See footnote 4). For linear or quadratic standard curve models, the standard concentrations should be constructed in a linear manner; for logarithmic models, the concentrations should be arrayed geometrically.

or logarithmic[4]. It is recommended that the column be equilibrated with several injections of matrix-laden extract if a matrix effect is observed between samples and standards.

F.2 Calculations

Calculate μg/sample values for diazinon and malathion residues in OWBD matrix using the following equation:

$$ug/Sample = \frac{(ng/mL\ Final\ Extract)\ X\ (mL\ Final\ Extract)}{} X \frac{15\ mL\ Pre\text{-}C\text{-}18\ SPE\ Total\ Volume}{5\ mL\ C\text{-}18\ SPE\ Aliquot\ Volume} X \frac{2500\ mL\ Acetone\ Extract\ Volume}{25\ mL\ Acetone\ Aliquot\ Volume} X \frac{1\ ug}{1000\ ng}$$

For reference, the molecular weights of diazinon and malathion are 304.34 g/mole and 330.35 g/mole, respectively.

For fortified control samples, use the following equation to calculate percent recovery:

$$\%\ Recovery = \left(\frac{(ug/Sample\ Found) - (ug/Sample\ Control)}{ug/Sample\ Fortified} \right) X\ 100$$

G. Interferences

G.1 Sample Matrices

Chromatographic interferences from pristine OWBD matrix are absent with this assay. The method has been successfully tested (see III.D.2) with soiled OWBD to mimic authentic field samples by the development laboratory, but interferences may vary under different conditions. GC parameters may require optimization to maximize resolution between

[4]The choice of the standard curve model is instrument/detector/laboratory specific, and should be based upon the precision of back-calculated standard responses against the various least squares curve models.

the analytes and any other interferences which may be present in actual samples.

G.2 Other Pesticides

A specificity study has not been conducted for this method.

G.3 Solvents and Reagents

Solvents and reagents have contributed no interfering chromatographic peaks in this assay. The developer of the method has noted that several (apparent) high-quality lots of EtOEt may contain interferences which are detected by GC/ECD, but no such interferences were detected by GC/FPD(P) in developmental research. If required, satisfactory purification of EtOEt is achieved by distilling (ca. 35°C) a stirred mixture of EtOEt (ca. 200 mL) and concentrated sulfuric acid (ca. 10 mL)[5].

G.4 Glassware

There are no known interferences from labware at the stated LOQs. Extraction glassware is thoroughly washed with hot, soapy water, rinsed with acetone, air-dried, then placed in an oven at 150°C for at least 1 hour prior to use. Glass vessels are recommended for all steps without substitutions with plastic.

III. METHODS VERIFICATION

A. Experimental Design

The method for OWBD matrix was tested by analysis of one unfortified control sample, three controls fortified at 5.0 µg/sample, three controls fortified at 50.0 µg/sample, and three controls fortified at 10.0 mg/sample, duplicated over two days. This design was used by the both the development and validation laboratory.

[5]**Caution: Do not store purified EtOEt for more than 1 week. Distillation removes antioxidants which prevent formation of explosive peroxides.**

B. Analytical Reference Materials

Specific reference materials used during the conduct of the method validation study are described in Table 1.

C. Control Matrix

Untreated control OWBD samples were provided by Stewart Agricultural Research Services, Inc., P.O. Box 509, Macon, MO 63552. OWBD samples were cut into various sections upon receipt, and were not pre-washed in detergent.

D. Verification Results

D.1 Outer Whole Body Dosimeters

Results from the lower and upper OWBD method validation study are presented in Table 2 and 3, respectively. Modifications were made to the original developer's method in order to obtain acceptable recoveries for both compounds. The method is technique sensitive, and may require a familiarization period before acceptable recoveries are obtained. Example chromatograms are presented in Figures 2 through 5.

D.2 "Soiled" Outer Whole Body Dosimeters

Examination of "soiled" OWBD matrix obtained from Stewart Agricultural Research Services and fortified at the method development laboratory confirmed method removal of potential interferences and achievement of acceptable compound recoveries. The overall mean recoveries for "soiled" OWBD (uppers and lowers) for diazinon and malathion considering all fortification levels (5 μg, 50 μg, and 10,000 μg) were 93.9% $\pm$ 12.5% (N=12) and 100.7% $\pm$ 7.77% (N=12), respectively.

D.3 Summary and Conclusions

The techniques outlined in this document are suitable for analysis of diazinon and malathion in OWBD matrix at fortification levels ranging from 5.0 μg/sample to 10 mg/sample. **Critical features of the OWBD method include: (a) ensuring that acetone is completely evaporated from the residues prior to EtOEt:hexane/water partitioning, (b) proper drying of the C-18RP columns prior to compound elution, (c) ensuring that the C-18RP sorbent is adequately calibrated prior to use, and (d) scrupulously cleansed labware. Interferences in the OWBD matrix**

can dramatically impact C-18RP retention of both analytes; if the calibration is not controlled, analyte recoveries will be biased low. In the validation lab, an emulsion was noted on some samples during the EtOEt:hexane/water partitioning step that did not break upon centrifuging (Note 6, p. 16).

IV. NOTES

Note 1: With a pipet, drizzle the fortification solution over the sample as uniformly as possible. **Do not apply the fortification solution to a single site on the sample; the solution will penetrate through the cloth onto the underlying aluminum foil, potentially resulting in low-biased recoveries.**

Note 2: The shaker speed will vary between laboratories and equipment. The analyst should visually ensure that shaking appears sufficiently vigorous to extract residues from all parts of the sample.

Note 3: OWBD cloth contains a "sizing" or "bluing" agent(s) which can interfere with this analysis. The interference(s) is likely a surfactant polymer and is at least partially soluble in a variety of solvents ranging from water to hexane. During vacuum evaporation, the acetone extract develops an oily, white haze, particles of which float on the liquid surface. Solvent "bumping" at ≤25" Hg is **not** observed during vacuum-evaporation. When dry, a thick, colorless, translucent film is deposited on the sides of the evaporation flask; no free-flowing liquid is evident.

Removing the acetone solvent is a critical step in this procedure; acetone will interfere with proper partitioning of residues into 50:50 ethyl ether:hexane during subsequent steps.

Developmental research for this method demonstrated no losses of either analyte during vacuum-evaporation of solvent, or during prolonged (up to 10 minutes) "dry" evaporation at ≤35°C and 25" Hg vacuum. However, **evaporation tests indicated significant losses of diazinon and, to a lesser extent, malathion when nitrogen blow down was used to remove solvent.**

Note 4: The sizing/bluing interferences are partially soluble in water, but most of the film (See Note 3 above) remains attached to the sides of the flask; the water appears hazy and may possess a surface foam. Sonication helps dislodge the majority of the film from the sides of the evaporation flask.

Do not use plastic stoppers to cap samples at any point in the method. Both compounds are absorbed to the plastic and slowly leach out, providing opportunity

for low compound residue recoveries and/or possible cross-contamination with subsequent samples.

Note 5: Addition of EtOEt, mixing, followed by the addition of hexane, then mixing again, destroys any foam on the surface of the aqueous extract (See Note 4 above), and solubilizes/detaches any remaining film from the sides of the flask. Phase separation is rapid and complete. Several oil-like droplets may appear around the neck of the flask; these are either insoluble, matrix-related materials, or simply a water/ EtOEt:hexane emulsion. In any event, these droplets are of no consequence to performance of the assay. After phase separation, the EtOEt:hexane layer is clear and colorless; the cloudy aqueous phase may contain white flakes.

Note 6: After centrifugation, the EtOEt:hexane layer is clear and colorless. The aqueous phase is colorless, but cloudy, and may contain particulates. A gelatinous-like emulsion interface has been observed with some samples which does not break upon centrifuging. It is important to remove only the clear EtOEt:hexane layer and not include the gelatinous emulsion in subsequent cleanup steps. The interface may be reduced by the addition of a small aliquot of deionized water, such as when balancing the centrifuge tubes.

Note 7: The developers of this method have observed frequent cross-contamination of final sample extracts with malathion and, especially, diazinon. Generally, this problem is noticeable only with samples fortified at the limit of quantification when samples containing very high residues (100 X LOQ) have been previously analyzed using the same glassware or laboratory equipment. The vacuum manifold, especially the plastic SPE stopcocks and attached needles, are a primary source of this cross-contamination. **The entire vacuum manifold, including stopcocks and needles, may need to be scrupulously cleaned with hot, soapy water, rinsed with distilled water, then high-purity acetone prior to any subsequent use.** Stopcocks and manifold needles can be checked for retained residues by soaking them overnight in acetone, then analyzing the extract by gas chromatography (See Section II.D, p. 9). If cross-contamination persists, replace the stopcocks and manifold needles. [The validation laboratory did not encounter frequent cross-contamination problems from the vacuum manifold or glassware, and rigorous cleaning of the vacuum manifold was not found to be necessary.]

Note 8: The analyst should note that low recoveries of diazinon from quality control samples may indicate a sample loading problem. Load flow rates may be a factor, but this has not been confirmed. Some analysts may wish to dilute the 0.01% AOT sample with water (e.g., 2X), but note that malathion and diazinon are sparingly soluble in water, and excessive dilution of the sample may cause loss of analyte due to precipitation.

Note 9: Water MUST be removed from the C-18RP column prior to elution with methylene chloride (Step II.C.4.e). Profound losses of diazinon (but not malathion) are observed if the sample contains droplets of water, and the water is evaporated to dryness. This effect is poorly understood, but has attributes consistent with a diazinon/water azeotrope. No problems were encountered with the use of 50:50 MeOH:DCM provided the C-18RP columns were adequately dried.

The method developer could dry only 3 cartridges at a time to achieve proper drying. The validation laboratory was able to dry up to 12 cartridges at a time using a 45 min drying period at the maximum recommended operating vacuum for the vacuum manifold (20" Hg). This vacuum could only be achieved using a vacuum pump. During the drying period, the flow should be checked periodically through each cartridge by placing a finger over the top of the cartridge. A strong vacuum should be felt quickly (ca. 1-2 sec), and a sharp "popping" sound made when the finger is removed. The flow through all the columns should be checked and should be relatively uniform. As the columns dry, the flow characteristics of the columns will change, so it is necessary to moderate the vacuum and repeat the column flow check approximately every 10 min.

Note 10: During developmental research, 8 mL of DCM quantitatively eluted both analytes from the C-18RP column. During the validation study, 16 mL of DCM was used based of column profile work. Subsequent work showed that 8 mL of 50:50 MeOH:DCM yielded excellent recoveries with no chromatographic problems. However, the analyst should note that this method must optimized for analyte recoveries from OWBD samples in the analyst's laboratory. Soiled OWBD samples have also been tested with this method, but other types of samples may contain interferences which are also eluted with DCM and may compromise quantification of the analytes. In such cases, the DCM elution solvent should be modified to effect column resolution between the analytes and interferences (e.g., mixtures of DCM and hexane).

Each lot of C-18RP cartridges should be pre-calibrated with matrix prior to use. **This is a critical step in the assay, since AOT components can change the retention characteristics of the solid support**. An example procedure is as follows.

Prepare a C-18RP column as described in Sections II.C.4.a. Process an untreated control OWBD sample through the method as described in steps II.C.1 through II.C.3.f. Pipet an acetone solution (e.g., 1.5 mL) containing 1.5 μg each of diazinon and malathion into the 125-mL evaporation flask containing the untreated control hexane:EtOEt extract in II.C.3.f.; vacuum-evaporate the solvent to just-

dryness. Process the sample through the column as described in Sections II.C.4.b through II.C.4.g. Retain the load and water washes from II.C.4.c to this point. Dissolve the final dry residue in a 5-mL final volume. Analyze the sample by GC/FPD(P) (See Step II.D) against a 100 ng/mL diazinon/malathion standard prepared in 1.5% DEGDEE:acetone (Step II.E.1). At 100% recovery, the GC/FPD(P) detector responses for both compounds from the sample and standard injections should be equivalent. The recommended minimum recovery for diazinon and malathion is 90%.

If the recovery for either compound is biased low, elute the column with additional DCM, vacuum-evaporate to just-dryness, dissolve the residue in 5 mL DEGDEE:acetone, then inject into the GC/FPD(P). Finally, dilute the retained load/water wash fraction with water (100x) and partition twice against 75 mL of DCM. Vacuum-evaporate the DCM to just-dryness, dissolve the residue in 5 mL of 1.5% DEGDEE:acetone, then analyze by GC/FPD(P).

As observed in Note 8 above, the presence of diazinon in the load/wash fraction from Step II.C.4.c may indicate a load flow rate problem or too high of an AOT concentration in the sample. Low-biased malathion recoveries are an indication that further elution of the C-18RP column with DCM is necessary; simply increase the elution volume from the recommended 8 mL to 10-12 mL, as indicated, or repeat the column profile work using a mixture of methanol and DCM, such as 50:50 MeOH:DCM.

It is recommended that the DCM elution be performed at a flow rate of no greater than 1-2 drops/sec. Water entrained in the C-18RP columns has been observed to be removed with the DCM if the column elution is performed at higher flow rates. The DCM eluate should be clear and show no appearances of the presence of water.

Note 11: Diazinon and malathion standards prepared in neat acetone give unacceptable chromatography; standard curves exhibit poor linearity (especially for malathion), reproducibility, and sensitivity. "Priming" the GC with extracts in and of itself does not correct the problem. Use of 1.5% DEGDEE in acetone solvent for GC standards and final sample extracts eliminates these problems and improves the signal/noise ratio for analyte detection at all concentrations. The mechanism of action for this effect is not known.

Even with the use of 1.5% DEGDEE in acetone, it was found that priming, or equilibrating, the GC with matrix extract was necessary prior to the analysis of a set of samples for OWBD. In general, a minimum of two injections of matrix-laden extract is recommended immediately prior to initiation of a sample set. In

addition, routine maintenance was found to be necessary due to buildup in the injector liner and at the front of the analytical column. Replacement of the injector liner and removal of approximately 15" from the front of the analytical column was necessary after approximately every 100 sample injections. It was found that this maintenance was necessary to prevent a matrix effect (enhancement) on the malathion in matrix-laden samples.

If a high bias is observed with samples reconstituted in low volumes of 1.5% DEGDEE in acetone, it may be necessary to chill the evaporation flask prior to addition of the acetone-based solvent. This can be accomplished using an ice water bath.

V. SAFETY

The organic solvents utilized in this method represent both a general exposure and fire hazard. Provision must be made for working with these solvents for personnel safety. In particular, it is recommended that diethyl ether only be worked with in a properly functioning fume hood away from potential ignition sources. Also, the prolonged storage of diethyl ether leads to a buildup of explosive peroxides, so care must be taken not to use diethyl ether beyond the manufacturer's recommended shelf life.

VI. TABLES

Table 1. Standard Reference Materials.

STANDARD NAME	ABC STANDARD NUMBER	LOT NUMBER	PURITY:EXP. DATE	PHYSICAL CHARAC-TERISTICS
Diazinon, O,O-diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate, CAS #333-41-5.	PS-9824	95R-31-45C 09467	87.7%:9/14/98	Clear Yellow Liquid
Malathion, [(Dimethoxyphosphino-thioyl)thio]-butanedioic acid diethyl ester, CAS #121-75-5.	PS-9825	95R-31-44E CS030	95.0%:12/12/99	Clear Liquid

Table 2. Recovery of Diazinon and Malathion from Lower Outer Whole Body Dosimeters

ABC Sample ID	Sample Description	µg Diazinon/ segment found	% Recovery Diazinon	µg Malathion/ segment found	% Recovery Diazinon
43767-098	Control Lower Legs	0.765	N/A	0	N/A
43767-099	Control Upper Legs + 5 µg both	6.07	106	5.73	115
43767-100	Control Lower Legs + 5 µg both	5.64	97.5	5.47	109
43767-101	Control Upper Legs + 50 µg both	47.1	92.7	51.6	103
43767-102	Control Lower Legs + 50 µg both	44.3	87.1	47.7	95.4
43767-103	Control Upper Legs + 10000 µg both	8290	82.9	9380	93.8
43767-104	Control Lower Legs + 10000 µg both	8620	86.2	9180	91.8
43767-105	Control Upper Legs	0.609	N/A	0	N/A
43767-106	Control Lower Legs + 5 µg both	5.44	96.6	5.30	106
43767-107	Control Upper Legs + 5 µg both	5.46	97.0	5.84	117
43767-108	Control Lower Legs + 50 µg both	44.7	88.2	52.5	105
43767-109	Control Upper Legs + 50 µg both	50.5	99.8	54.3	109
43767-110	Control Lower Legs + 10000 µg both	8530	85.3	9470	94.7
43767-111	Control Upper Legs + 10000 µg both	9250	92.5	10000	100
	Average Overall % Recovery (n=12)		92.7		103
	Overall Standard Deviation (n=12)		6.93		8.36
	% Relative Standard Deviation		7.48		8.12

Recoveries corrected for the µg found in the respective controls of the sets.

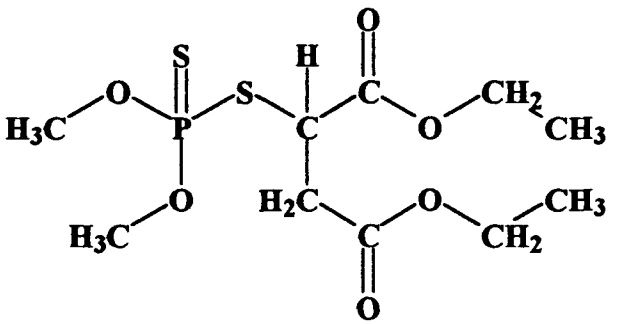
Table 3. Recovery of Diazinon and Malathion from Upper Outer Whole Body Dosimeters

ABC Sample ID	Sample Description	µg Diazinon/ segment found	% Recovery Diazinon	µg Malathion/ segment found	% Recovery Diazinon
43767-126	Control Back Torso	0.494	N/A	0.0464	N/A
43767-127	Control Upper Arm + 5 µg both	4.71	84.3	4.61	91.3
43767-128	Control Lower Arm + 5 µg both	3.75	65.1	4.30	85.3
43767-129	Control Front Torso + 50 µg both	44.6	88.2	47.4	94.7
43767-130	Control Back Torso + 50 µg both	40.5	80.0	39.8	79.5
43767-131	Control Upper Arm + 10000 µg both	7090	70.9	7840	78.4
43767-132	Control Lower Arm + 10000 µg both	7780	77.8	7500	75.0
43767-133	Control Front Torso	0.648	N/A	0	N/A
43767-134	Control Back Torso + 5 µg both	5.56	98.2	5.67	113
43767-135	Control Upper Arm + 5 µg both	5.30	93.0	5.21	104
43767-136	Control Lower Arm + 50 µg both	50.3	99.3	51.1	102
43767-137	Control Front Torso + 50 µg both	45.1	88.9	45.3	90.6
43767-138	Control Back Torso + 10000 µg both	9410	94.1	9380	93.8
43767-139	Control Upper Arm + 10000 µg both	8390	83.9	8830	88.3
43767-140	Control Back Torso	0	N/A	0	N/A
43767-141	Control Upper Arm + 5 µg both	5.08	102	5.15	103
43767-142	Control Lower Arm + 5 µg both	4.21	84.2	5.03	101
43767-143	Control Front Torso + 50 µg both	42.3	84.6	42.8	85.6
43767-144	Control Back Torso + 50 µg both	47.6	95.2	48.6	97.2
43767-145	Control Upper Arm + 10000 µg both	8790	87.9	9560	95.6
43767-146	Control Lower Arm + 10000 µg both	8320	83.2	8470	84.7
	Average Overall % Recovery (n=18)		86.7		92.4
	Overall Standard Deviation (n=18)		9.63		10.1
	% Relative Standard Deviation		11.1		10.9

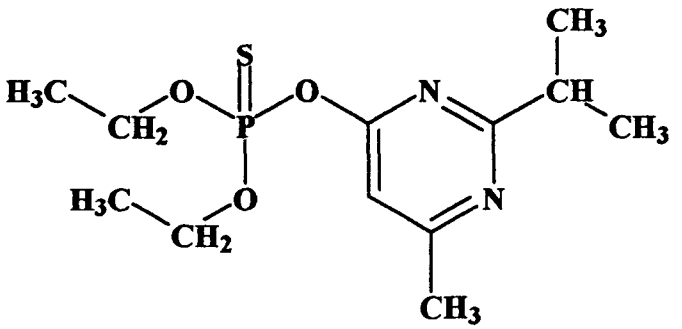
Recoveries corrected for the µg found in the respective controls of the sets.

VII. FIGURES

Figure 1. Chemical Structures of Diazinon and Malathion.



MALATHION
[(Dimethoxyphosphinothioyl)thio]-butanedioic acid diethyl ester



DIAZINON
O,O-Diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]-phosphorothioate

Figure 2. Representative Chromatogram of a 100 ng/mL Mixed External Standard

MCDO [43767] 29 PANTS15, 4, 1
GCMIX-G2 100 NG/ML STD
Acquired on 24-Aug-1997 at 17:51

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	6.26	95703	101.01320
MALATHION	7.21	58503	102.90988

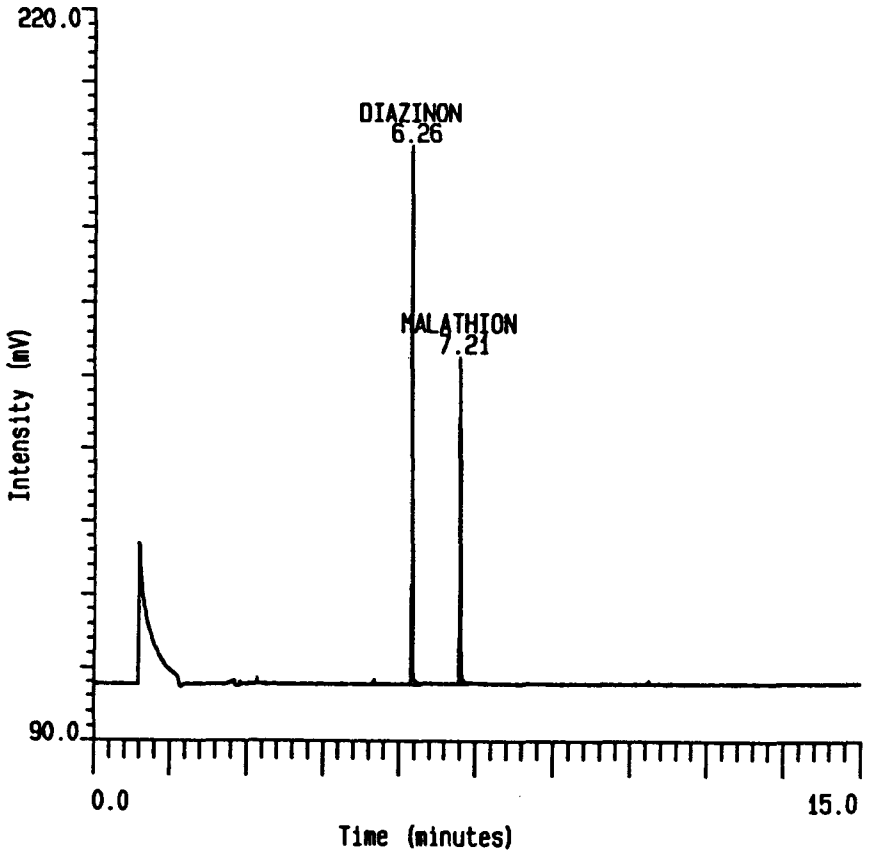


Figure 3. Representative Chromatogram of a 4.00 ng/mL Mixed External Standard

MCDO [43767] 29 PANTS15, 17, 1
GCMIX-H7 4.00 NG/ML STD
Acquired on 24-Aug-1997 at 22:12

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	6.26	3847	4.45816
MALATHION	7.21	2354	4.06990

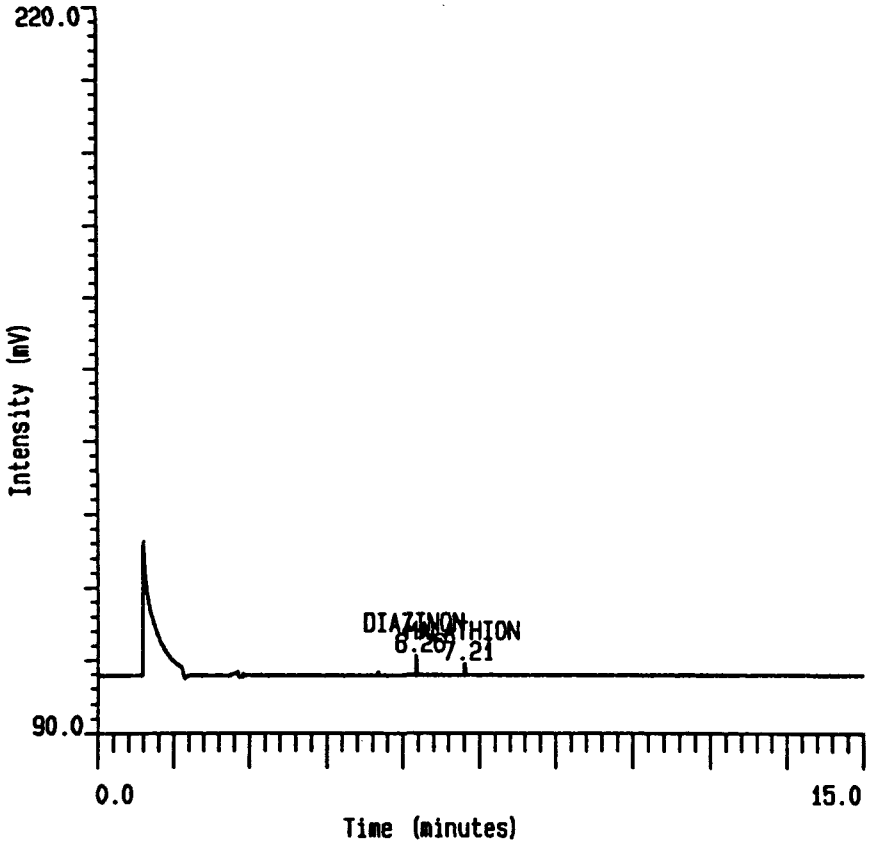


Figure 4. Representative Chromatogram of a Control Lower Outer Whole Body Dosimeter Sample

MCDO [43767] 29 PANTS15, 6, 1
43767-098
Acquired on 24-Aug-1997 at 18:31

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	6.25	818	0.76498
MALATHION	0.00	0	0

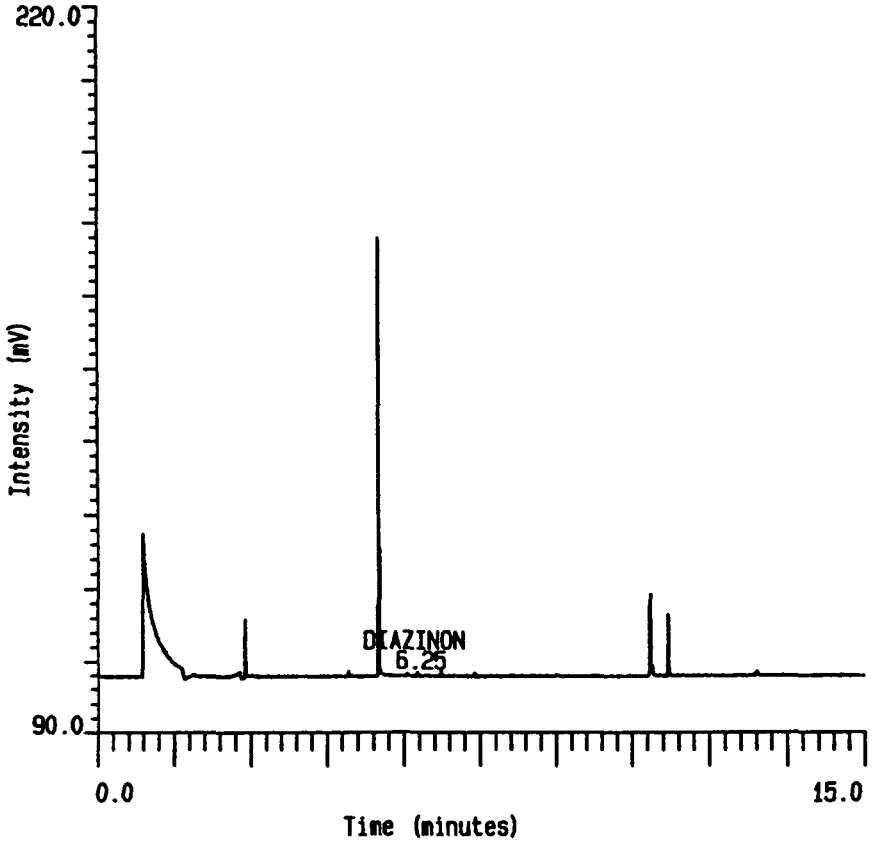


Figure 5. Representative Chromatogram of a 5 μg Lower Outer Whole Body Dosimeter Fortification (LOQ) Sample

MCDO [43767] 29 PANTS15, 7, 1
43767-099
Acquired on 24-Aug-1997 at 18:51

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	6.25	9226	6.06743
MALATHION	7.21	5463	5.72521

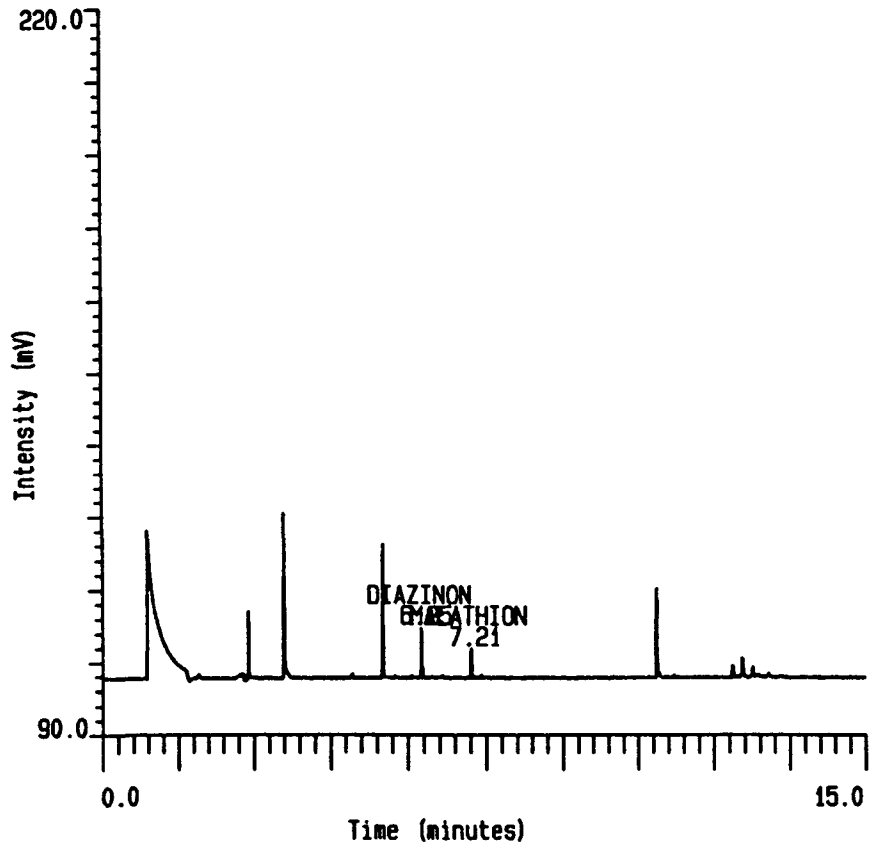
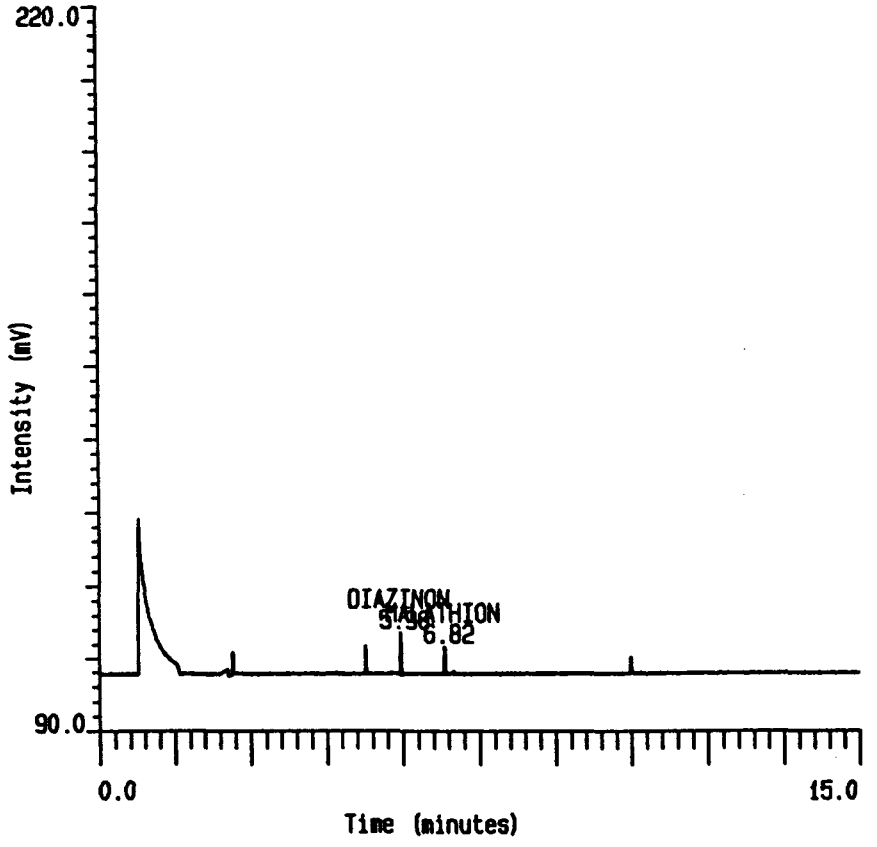


Figure 6. Representative Chromatogram of a 5 μg Upper Outer Whole Body Dosimeter Fortification (LOQ) Sample

MCDO [43767] 29 SHIRTS14, 7, 1
43767-127
Acquired on 30-Aug-1997 at 02:02

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.96	7854	4.70634
MALATHION	6.82	5365	4.60603



Determination of Diazinon and Malathion in OVS Air Sampling Tubes

Method ARTF-AM-009

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Determination of Diazinon and Malathion in OVS Air Sampling Tubes

Method ARTF-AM-009

I. INTRODUCTION AND SUMMARY

A. Scope

Diazinon and malathion are organophosphate insecticides used for control of certain noxious insects on agriculturally important crops. To generate data which estimate human exposure to the insecticides during agricultural applications, a method of analysis is required for determination of diazinon and malathion residues in air monitoring devices such as OVS (XAD-2) sorbent tubes.

B. Principle

Diazinon and malathion residues trapped in OVS sorbent tubes are extracted with acetone. Following evaporation of the solvent, the residues are dissolved in an acetone-based solvent. Quantification of both analytes in the final extract is performed by GC with flame photometric detection in the phosphorous mode [FPD(P)]. The claimed limit of quantification (LOQ) for diazinon and malathion is 0.010 μg/sample[1].

Figure 1 presents the chemical structures of diazinon and malathion.

II. MATERIALS AND METHODS

A. Equipment

Equipment	Suggested Manufacturers:[2]
Analytical Balance	Ohaus GA110

[1]This method analyzes diazinon and malathion residues in OVS sorbent tubes. One tube contains a front (270 mg) and back (140 mg) section of sorbent. The sorbents are held in the tube with a glass fiber disk and Teflon® o-ring in the front and a polyurethane foam plug on the back. The two sections are separated by a polyurethane foam plug. In this development research one sample = O-ring, fiber disk, front sorbent, and middle foam plug: final sample composition is defined by protocol. The lowest limit of fortification during methods development research was 10 ng each of diazinon and malathion/sample.

[2]Equivalent sources of the listed equipment and reagents may be used.

Gas Chromatograph with a Flame Photometric Detector Phosphorous Mode Narrow-bore Capability Split-Splitless Injector	Hewlett-Packard Model 5890 Series II
Gas Chromatograph Column	J & W, DB-5, 30 m x 0.25 mm i.d., 0.25 μm film thickness
General Laboratory Glassware	Various
Rotary Evaporator	Fisher Scientific

B. Reagents and Standards

Acetone:	Fisher Optima Grade
Di(ethylene glycol)diethylether: (i.e., DEGDEE), HPLC grade	Sigma/Aldrich Catalog #30,827-7
1.5% DEGDEE (w:v)	Dilute 7.5 g of DEGDEE to 500 mL with acetone. Mix and store at ambient temperatures.
OSHA Versatile Sampler (OVS) XAD-2 Sorbent Tubes:	SKC Inc., Eighty Four, PA, 800-752-8472, Cat. #226-30-16, or Stewart Agricultural Research Services, Inc., P.O. Box 509, Macon, MO 63552.

Diazinon, O,O-diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]-phosphorothioate, available from ARTF.

Malathion, [(Dimethoxyphosphinothioyl)thio]-butanedioic acid diethyl ester, available from ARTF.

C. OVS Sorbent Tubes: Analytical Procedure

C.1 Sample Preparation

Maintain field samples frozen pending analysis. For analysis, either separate the tubes into front and back sections, or combine front and back sections (follow protocol requirements). The front section will consist of the glass fiber disk, the front sorbent material (270 mg), and the foam divider. The back section will consist of the back sorbent material (140 mg) and the lower foam plug.

C.2 Extraction of Front and Back Tube Sections Separately

a. QC fortifications are made into the sorbent material prior to separation into front and back sections. Fortify the sorbent by injecting a small amount (10 μL recommended) of fortification solution just under the glass fiber disk into the center of the resin bed with a syringe if conduction breakthrough trials. Do not fortify along the glass tube walls. Allow the tubes to stand at ambient temperature (>0.5 hours) until all acetone has evaporated. If required for breakthrough evaluation, draw air through the sorbent tube for the prescribed time period (Note 1, p. 13). Separate the front and back sections as described above.

b. Place the sections of sorbent in individual culture tubes (15-mL or larger).

c. Add 10 mL of acetone to each sample. Cap the samples tightly with a PTFE-lined lid. Mix for 30 seconds on a vortex mixer.

d. Transfer the acetone into individual 125-mL evaporation flasks (Note 2, p. 13).

e. Repeat steps c. and d. two additional times, combining the extracts in their respective evaporation flask.

f. Vacuum-evaporate the samples to dryness (ca. 25" Hg, ≤35°C, Note 3, p. 13). Place the flasks into an ice-water bath to chill, and then dissolve the dry residues in a known volume of 1.5% DEGDEE in acetone (generally 1.00 mL for LOQ residues, see Note 4, p. 13). Dilute with the same solvent as needed to maintain

analyte concentrations within the standard curve range. Submit the samples for GC/FPD(P) analysis as described in Step D.

C.3 Extraction of Contents of Entire Tube as a Single Sample

a. QC fortifications are made into the sorbent material. Fortify the sorbent by injecting a small amount (10 μL recommended) of fortification solution just under the glass fiber disk into the center of the resin bed with a syringe. Do not fortify along the glass tube walls. Allow the tubes to stand at ambient temperature (>0.5 hours) until all acetone has evaporated. If required by protocol, draw air through the sorbent tube for the prescribed time period (Note 1, p. 13).

b. For field and laboratory fortification samples, transfer the entire contents of the tube, including the Teflon® retainer ring, to a 15-mL or larger culture tube. Rinse the inside of the empty tube twice with approximately 1-mL aliquots of acetone, and add the rinses to the culture tube.

c. For field samples, wet a cotton swab (e.g. Q-Tips) in acetone, a shake out excess solvent (swab should be relatively dry). Hold the sorbent tube vertically with the thin end upward, and carefully swab out the inside of the glass tube in front of the Teflon® retainer ring without touching or wetting the glass fiber filter. Repeat this step with a second cotton swab, and discard the swabs. Allow the glass tube to dry thoroughly. Remove and discard the Teflon® retainer ring, and transfer the entire remainder of the field sample to a 15-mL or larger culture tube. **Do not rinse the empty tube for the field samples.**

d. Add 10 mL of acetone to each sample. Cap the samples tightly with a PTFE-lined lid. Mix for 30 seconds on a vortex mixer.

e. Transfer the acetone into individual 125-mL evaporation flasks (Note 2, p. 13).

f. Repeat steps d. and e. two additional times, combining the extracts in their respective evaporation flask.

g. Vacuum-evaporate the samples to dryness (ca. 25" Hg, ≤35°C, Note 3, p. 13). Place the flasks into an ice-water bath to chill, and

then dissolve the dry residues in a known volume of 1.5% DEGDEE in acetone (generally 1.00 mL for LOQ residues, see Note 4, p. 13). Dilute with the same solvent as needed to maintain analyte concentrations within the standard curve range. Submit the samples for GC/FPD(P) analysis as described in Step D.

D. Gas Chromatographic Analysis

A gas chromatograph equipped with a Flame Photometric Detector (phosphorous mode) is required. Split-splitless injection and narrow-bore capabilities are recommended. The conditions described herein may be modified provided adequate performance of the analysis is demonstrated.

GC Column: J & W DB-5, 30 m length, 0.25 mm i.d., 0.25 μm film. Other columns may be substituted if they give satisfactory resolution between the analytes and any interferences.

Injector: 230°C

Detector: 220°C

Column:

Initial: 95°C, hold 1.0 min.
Ramp Rate 1: 30°C/min to 230°C, hold 4 minutes.
Ramp Rate 2: 40°C/min to 290°C, hold 5 minutes.

Carrier Gas: He, 1.7 mL/min at 95°C, head pressure = 20 psi. Constant flow off.

Septum Purge: He @ 3.0 mL/min.

Injector Liner: HP Liner, Deactivated, 4 mm i.d., with Deactivated Glass Wool Plug, Part #5062-3587, or
HP Liner, Deactivated, Double-tapered splitless, Part #5181-3315.

Split Vent: He @ 7.6 mL/min, on @ 0.75 min.

Detector Make-Up: N_2 @ 23 mL/min.

Detector Air: 95 mL/min.

Detector Hydrogen: 68 mL/min.

Injection: 2 μl, Split/Splitless

E. Calibration Procedures

E.1 Preparation of Standard Solutions

Individual stock solutions of diazinon and malathion are prepared in acetone and stored in a freezer; primary stock concentrations are approximately 10.0 mg/mL. Stability of these stock solutions during prolonged storage has not been evaluated as part of this developmental and validation work.

Dilutions of diazinon and malathion are made at appropriate concentrations for fortification standards. These dilutions are made in acetone, stored in a freezer, and prepared as mixed or individual standards; that is, each solution may contain either or both diazinon and malathion. The concentration range for these fortification solutions will vary from study to study, but generally will range from 10 μg/mL to 5 mg/mL.

Dilutions of diazinon and malathion for GC standards are made in 1.5% DEGDEE in acetone (Note 4, p. 13) and are stored in a freezer. The standard concentrations suggested are 4, 10, 20, 40, 60, and 100 ng/mL for each analyte[3].

E.2 Detector Calibration

The sensitivity of the FPD(P) detector is monitored by injecting diazinon and malathion before, between, and after the samples. The suggested mass range is 8 pg to 200 pg injected.

Under the conditions of this assay, diazinon and malathion elute from the GC column at ca. 5.9 and 6.8 minutes, respectively. The GC/FPD(P) limit of detection for diazinon and malathion (injected as a pure standard in 1.5% DEGDEE:acetone) is ca. 2 pg injected for both analytes.

[3]The analyst should choose standard concentrations appropriate for the standard curve model (See footnote 4). For linear or quadratic standard curve models, the standard concentrations should be constructed in a linear manner; for logarithmic models, the concentrations should be arrayed geometrically.

F. Methods of Calculation

F.1 Injection Sequence

Analysis sequences are started and ended with one or two standards; standard injections are made throughout the run, generally with no more than three or four sample injections between each standard. A standard curve of analyte concentration (ng/mL) versus peak height or area is constructed using a method of curve generation appropriate for the GC/FPD(P) instrumentation. The construction may be linear, quadratic, or logarithmic[4].

F.2 Calculations

Calculate μg/sample values for diazinon and malathion residues in OVS sorbent using the following equation:

$$ug/Sample = (ng/mL\ Final\ Extract)\ X\ (mL\ Final\ Extract)\ X\ \frac{1\ ug}{1000\ ng}$$

For reference, the molecular weights of diazinon and malathion are 304.34 g/mole and 330.35 g/mole, respectively.

For fortified-control samples, use the following equation to calculate percent recovery:

$$\%\ Recovery = \left(\frac{(ug/Sample\ Found) - (ug/Sample\ Control)}{ug/Sample\ Fortified} \right) X\ 100$$

[4]The choice of the standard curve model is instrument/ detector/laboratory specific, and should be based upon the precision of back-calculated standard responses against the various least squares curve models.

G. Interferences

G.1 Sample Matrices

Chromatographic interferences from pristine OVS sorbent are absent with this assay. GC parameters may require optimization to maximize resolution between the analytes and any other interferences that may be present in actual samples.

G.2 Other Pesticides

A specificity study has not been conducted for this method.

G.3 Solvents and Reagents

Solvents and reagents have contributed no interfering chromatographic peaks in this assay.

G.4 Glassware

There are no known interferences from labware at the stated LOQ. Extraction glassware is thoroughly washed with hot, soapy water, rinsed with acetone, air-dried, then placed in an oven at 150°C for at least 1 hour prior to use. Glass vessels are recommended for all steps without substitutions with plastic.

III. METHODS VERIFICATION

A. Experimental Design

The method for OVS sorbent was validated by analysis of one unfortified control sample, two controls fortified at 0.010 µg/sample, two controls fortified at 1.0 µg/sample, and two controls fortified at 100 µg/sample, on two separate days. Only the front portion of the tube was used for recovery determinations. The back portions were analyzed for breakthrough. This design was used by both the development and validation laboratories, except that the development lab only performed a single set of samples.

B. Analytical Reference Materials

Specific reference materials used during the conduct of the method validation study are described in Table 1.

C. Control Matrix

Untreated control OVS sorbent tubes were provided by Stewart Agricultural Research Services, Inc., P.O. Box 509, Macon, MO 63552.

D. Verification Results

D.1 OVS Sorbent Tubes

Results from the OVS sorbent tube method validation study are presented in Table 2, and example chromatograms are presented in Figures 2 through 5.

D.2 OVS Sorbent Tube Trapping Efficiency

To determine the trapping efficiency of the front portion (270 mg) of the XAD-2 sorbent under simulated field conditions, both test compounds were introduced into the sorbent in a gaseous form over an eight hour period by the development lab. A solution of both compounds in acetone (1 mg of diazinon and 5 mg of malathion) was placed in a 1-L sidearm flask and the solvent allowed to evaporate. A Teflon® inlet tube was placed through the sidearm and focused on the bottom of the flask. An OVS sorbent tube contained in a rubber stopper was placed on top of the flask. Air was then pulled through the inlet tube into the flask and out through the OVS tube for 8 hours at a rate of 1.5 L per minute with a calibrated pump. The average breakthrough of analyte into the back portion of the OVS tube was 0.10% and 0.14% of the total μg of compound (diazinon = 143 ug and malathion = 42.5 ug) trapped for diazinon and malathion, respectively.

D.3 Summary and Conclusions

The techniques outlined in this document are suitable for analysis of diazinon and malathion residues contained in a OVS sorbent tube at fortification levels ranging from 0.010 μg/sample to 100 μg/sample. **The critical feature of the OVS sorbent method is ensuring that the acetone from the fortification solution has completely evaporated from the OVS tube prior to drawing air through the system. Passing air through the sorbent before all acetone has evaporated results in high breakthrough of both analytes (especially diazinon) into the back portion of the tube.**

IV. NOTES

Note 1: With a syringe, inject an aliquot of fortification solution (recommended 10 μL) in the center of the sorbent tube, just under the glass fiber disk. Allow the acetone to evaporate at least 0.5 hours prior to drawing air through the sorbent. **Do not apply the fortification solution too deep in the sorbent or too close to the side of the tube. Do not draw air through the tube before all acetone has evaporated. In these situations, excess breakthrough will occur resulting in low-biased recoveries.**

Note 2: Care should be taken to exclude any sorbent in the evaporation flask. Sorbent particles in the flask will cause bumping during rotary evaporation of the acetone. If the tip of the transfer pipet is placed in the foam plug, it acts as a filter and eliminates the transfer of any sorbent with the solvent.

Note 3: Evaporation tests indicated significant losses of diazinon and, to a lesser extent, malathion when a stream of nitrogen has was used to remove the acetone solvent. However, no losses of either analyte are observed during vacuum-evaporation of solvent, or during prolonged (up to 10 minutes) "dry" evaporation at ≤35°C and 25" Hg vacuum.

Note 4: Diazinon and malathion standards prepared in neat acetone give unacceptable chromatography; standard curves exhibit poor linearity (especially for malathion), reproducibility, and sensitivity. "Priming" the GC with extracts in and of itself does not correct the problem. Use of 1.5% DEGDEE in acetone solvent for GC standards and final sample extracts eliminates these problems and improves the signal/noise ratio for analyte detection at all concentrations. The mechanism of action for this effect is not known.

Even with the use of 1.5% DEGDEE in acetone, it was found that priming, or equilibrating, the GC with matrix extract was necessary prior to the analysis of a set of samples for hand wash matrix. In general, a minimum of two injections of matrix-laden extract is recommended immediately prior to initiation of a sample set. In addition, routine maintenance was found to be necessary due to buildup in the injector liner and at the front of the analytical column. Replacement of the injector liner and removal of approximately 15" from the front of the analytical column was necessary after approximately every 100 sample injections. It was found that this maintenance was necessary to prevent a matrix effect (enhancement) of the malathion in matrix-laden samples.

V. SAFETY

The organic solvents utilized in this method represent both a general exposure and fire hazard. Provision must be made for working with these solvents for personnel safety.

VI. TABLES

Table 1. Standard Reference Materials.

STANDARD NAME	ABC STANDARD NUMBER	LOT NUMBER	PURITY:EXP. DATE	PHYSICAL CHARAC-TERISTICS
Diazinon, O,O-diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate, CAS #333-41-5.	PS-9824	95R-31-45C 09467	87.7%:9/14/98	Clear Yellow Liquid
Malathion, [(Dimethoxyphosphino-thioyl)thio]-butanedioic acid diethyl ester, CAS #121-75-5.	PS-9825	95R-31-44E CS030	95.0%:12/12/99	Clear Liquid

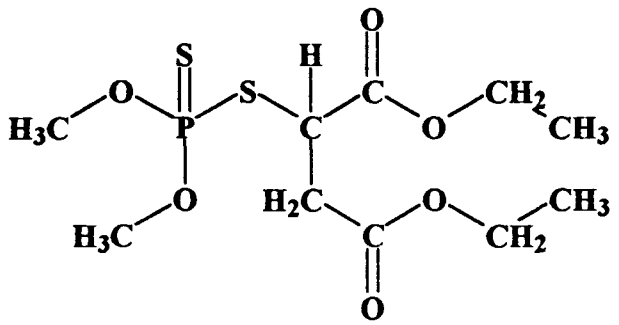
Table 2. Recovery of Diazinon and Malathion from OVS Air Sampling Tubes

ABC Sample ID	Sample Description	µg Diazinon/ sample found	% Recovery Diazinon	µg Malathion/ sample found	% Recovery Diazinon
43767-057	Control Air Sampling Tube	0.00096	N/A	0	N/A
43767-058	Control + 0.00992 µg Diazinon/0.0102 µg Malathion	0.0125	Data Not Used	0.0118	Data Not Used
43767-059	Control + 0.00992 µg Diazinon/0.0102 µg Malathion	0.0138	Data Not Used	0.0135	Data Not Used
43767-060	Control + 0.992 µg Diazinon/1.02 µg Malathion	1.01	102	1.09	107
43767-061	Control + 0.992 µg Diazinon/1.02 µg Malathion	0.994	100	1.05	103
43767-062	Control + 99.2 µg Diazinon/102 µg Malathion	77.8	78.4	104	102
43767-063	Control + 99.2 µg Diazinon/102 µg Malathion	101	102	105	103
43767-074	Control Air Sampling Tube	0	N/A	0	NA
43767-075	Control + 0.00992 µg Diazinon/0.0102 µg Malathion	0.0101	102	0.0108	106
43767-076	Control + 0.00992 µg Diazinon/0.0102 µg Malathion	0.0103	104	0.0104	102
43767-077	Control + 0.992 µg Diazinon/1.02 µg Malathion	0.898	90.5	1.10	108
43767-078	Control + 0.992 µg Diazinon/1.02 µg Malathion	1.01	102	1.13	111
43767-079	Control + 99.2 µg Diazinon/102 µg Malathion	92.3	93.0	103	101
43767-080	Control + 99.2 µg Diazinon/102 µg Malathion	92.9	93.6	102	100
43767-088	Control Air Sampling Tube	0	N/A	0	N/A
43767-089	Control + 0.00992 µg Diazinon/0.0102 µg Malathion	0.00953	96.1	0.0101	99.0
43767-090	Control + 0.00992 µg Diazinon/0.0102 µg Malathion	0.00944	95.2	0.00952	93.3
	Average Overall % Recovery (n=12)		96.6		103
	Overall Standard Deviation (n=12)		7.23		4.66
	% Relative Standard Deviation		7.48		4.52

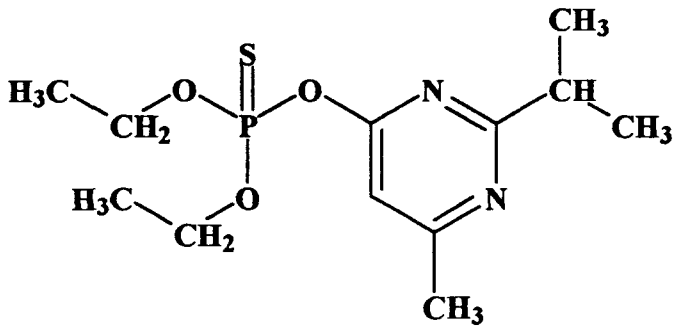
Recoveries corrected for the µg found in the respective controls of the sets.

VII. FIGURES

Figure 1. Chemical Structures of Diazinon and Malathion.



MALATHION
[(Dimethoxyphosphinothioyl)thio]-butanedioic acid diethyl ester



DIAZINON
O,O-Diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]-phosphorothioate

Figure 2. Representative Chromatogram of a 100 ng/mL Mixed External Standard

MCDO [43767] 29 767XAD5, 2, 1
GCMIX-1 NOMINAL 100 ng/mL
Acquired on 18-Jul-1997 at 09:11

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	104085	97.74555
MALATHION	6.79	65280	100.40713

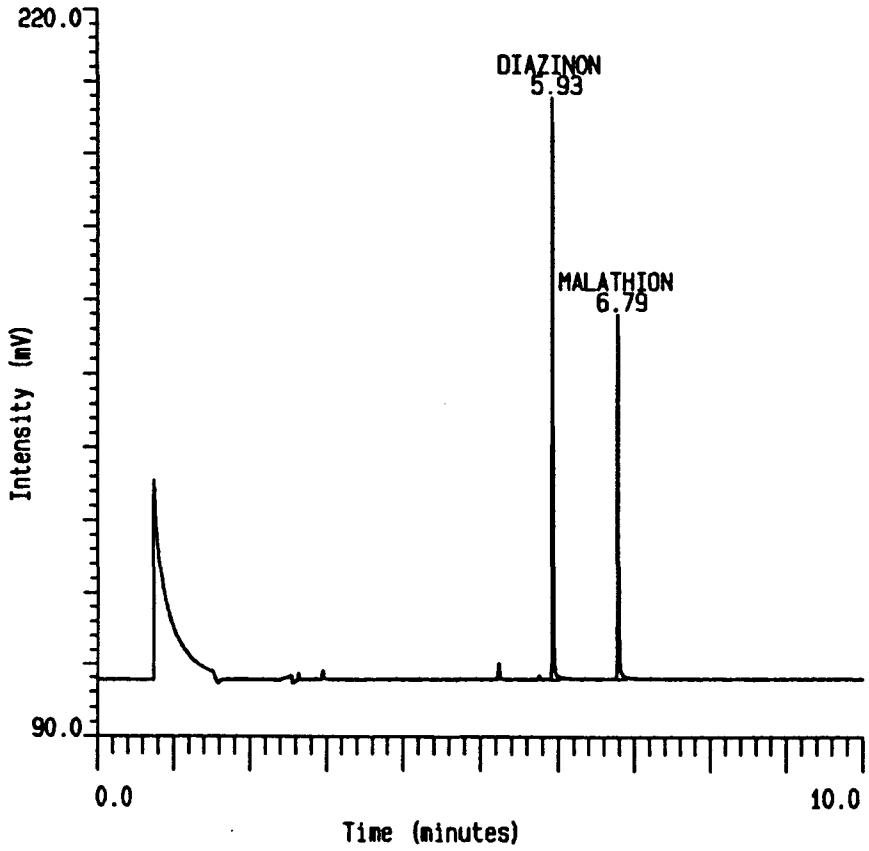


Figure 3. Representative Chromatogram of a 4.00 ng/mL Mixed External Standard

MCDO [43767] 29 767XAD5, 14, 1
6CMIX-6 NOMINAL 4 ng/mL
Acquired on 18-Jul-1997 at 13:16

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	4555	3.94325
MALATHION	6.79	2739	4.02103

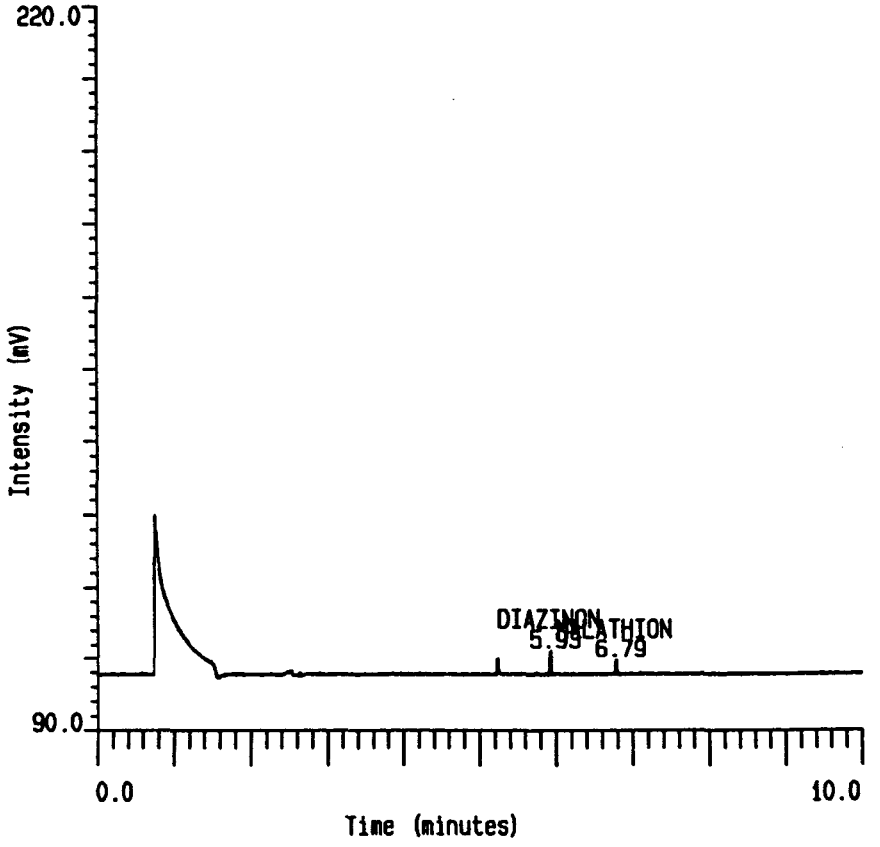


Figure 4. Representative Chromatogram of a Control Air Sampling Tube Extract

MCDO [43767] 29 767XAD5, 4, 1
43767-074
Acquired on 18-Jul-1997 at 09:52

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	0.00	0	0
MALATHION	0.00	0	0

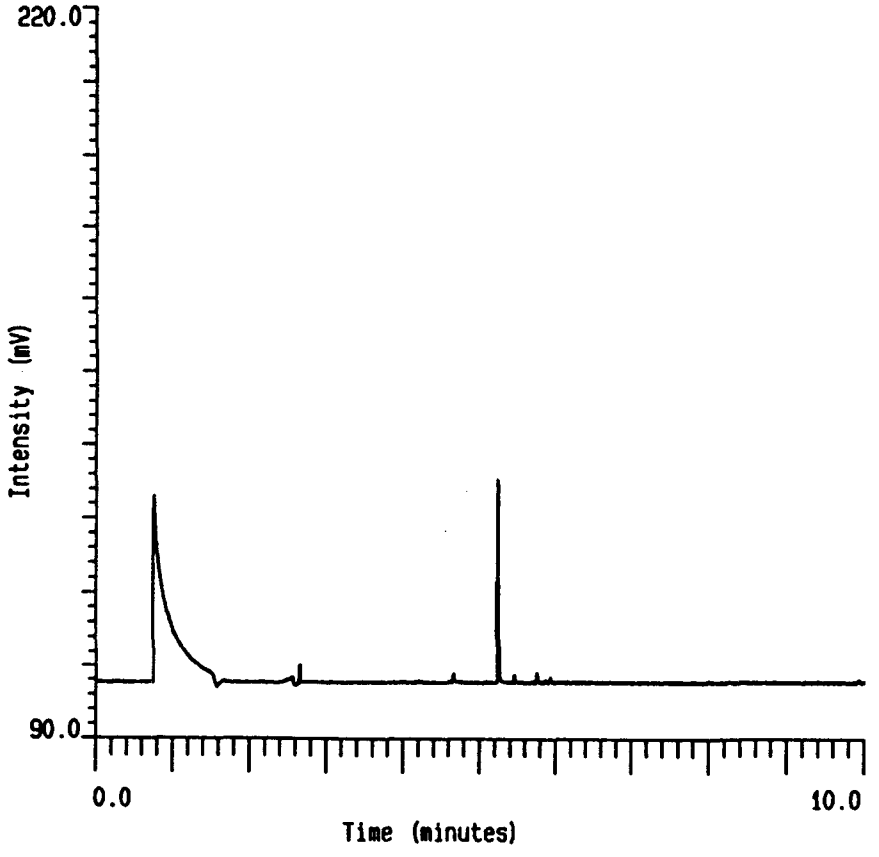
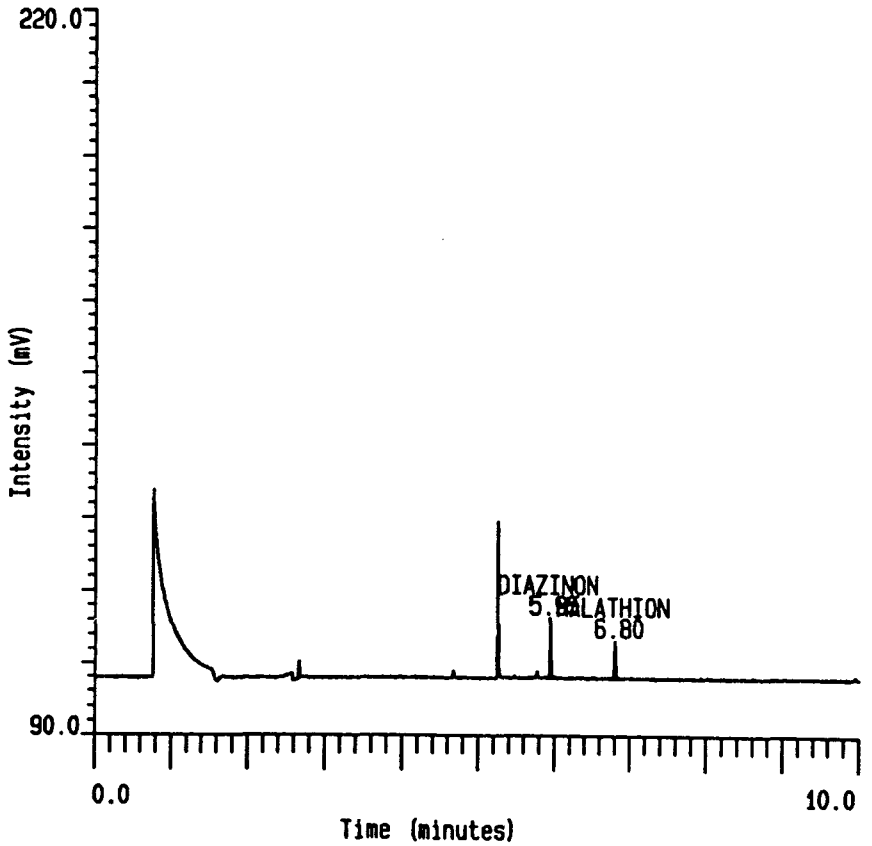


Figure 5. Representative Chromatogram of a 0.010 μg Air Sampling Tube Fortification (LOQ) Sample

MCDO [43767] 29 767XAD5, 5, 1
43767-075
Acquired on 18-Jul-1997 at 10:13

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	11111	0.01012
MALATHION	6.80	7155	0.01083



Determination of Diazinon and Malathion in Facial/Neck Wipes

Method ARTF-AM-010

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Determination of Diazinon and Malathion in Facial/Neck Wipes

Method ARTF-AM-010

I. INTRODUCTION AND SUMMARY

A. Scope

Diazinon and malathion are organophosphate insecticides used for control of certain noxious insects on agriculturally important crops. To generate data which estimate human exposure to the insecticides during agricultural applications, a method of analysis is required for determination of diazinon and malathion residues in/on cotton-based worker exposure fabrics such as gauze facial/neck wipes.

B. Principle

Diazinon and malathion residues in/on gauze wipes are extracted with an aqueous AOT solution, and are retained on a conditioned C-18 reverse phase (C-18RP) column. The column is washed with water, air-dried, and the analytes are eluted from the column with 50:50 methylene chloride:methanol which is evaporated to dryness. The residues are dissolved in acetone-based solvent, then quantified by gas chromatography (GC) with flame photometric detection in the phosphorous mode [FPD(P)]. The claimed limit of quantification (LOQ) for diazinon and malathion is 1.0 μg/ sample[1].

Figure 1 presents the chemical structures of diazinon and malathion.

II. MATERIALS AND METHODS

A.

Equipment	Suggested Manufacturers:[2]
Aluminum Foil	Local Grocery
Analytical Balance	Ohaus GA110

[1]This method analyzes diazinon and malathion residues in/on gauze neck/face wipe samples. One sample equals two gauze pads. The lowest limit of fortification during methods development research was 1.0 μg each of diazinon and malathion/gauze sample.

[2]Equivalent sources of the listed equipment and reagents may be used.

Gas Chromatograph with a Flame Photometric Detector Phosphorous Mode Narrow-bore Capability Split-Splitless Injector	Hewlett-Packard Model 5890 Series II
Gas Chromatograph Column	J & W Scientific, DB-5, 30 m x 0.25 mm i.d., 0.25 μm film thickness
General Laboratory Glassware	Various
Glass Jars, 0.25 Gallon, with PTFE or foil-lined Lids, Wide-Mouth	Fisher Scientific
Glass Storage Jars, 100 mL, with PTFE-Lined Lids	Fisher Scientific
Rotary Evaporator	Fisher Scientific
C-18, Reverse Phase, SPE 1 gram, 6-mL	Varian Sample Preparation Products, Catalog #1225-6001
Vacuum SPE Manifold	J & W Scientific
Shaker, Eberbach	VWR Scientific

B. Reagents and Standards

Acetone:	Fisher Optima Grade
AOT 75 Solution, 75% w:w Aqueous	Fisher Scientific Catalog #A345-500
0.01% Aqueous AOT 75	Dissolve 0.4 mL of 75% AOT in 3800 mL (nominal 1 gallon) of water. Mix well. This solution is good for 48 hours at room temperature.

Di(ethyleneglycol)diethylether: (i.e., DEGDEE), HPLC grade)	Sigma/Aldrich Catalog #30,827-7
1.5% DEGDEE (w:v)	Dilute 7.5 g of DEGDEE to 500 mL with acetone. Mix and store at ambient temperature.
Methylene Chloride (DCM):	Fisher Optima Grade
Methanol:	Fisher Optima Grade
50:50 methylene chloride:methanol	Combine 50 mL of methylene chloride with 50 mL of methanol. Mix well.
Water:	Distilled and/or deionized.
Untreated Control Facial Gauze Wipes, Cotton:	Stewart Agricultural Research Services, Inc., P.O. Box 509, Macon, MO 63552.

Diazinon, O,O-diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]-phosphorothioate, available from ARTF.

Malathion, [(Dimethoxyphosphinothioyl)thio]-butanedioic acid diethyl ester, available from ARTF.

C. Gauze Facial/Neck Wipes: Analytical Procedure

C.1 Sample Preparation

Freeze the field sample pending analysis. Allow the sample to thaw completely prior to transfer of the gauze and rinsing the sample container. No further preparation is required prior to analysis.

a. Transfer the field sample into a 0.25 gallon, wide-mouth glass jar. Rinse the container with a minimum of 50 mL 0.01% AOT solution and include this rinse as part of the 0.5 L total extraction volume.

b. QC fortifications are made at this point as follows: Place a untreated control gauze sample into a 0.25 gallon, wide-mouth glass jar. Pipet 8 mL of 0.01% AOT solution onto the gauze (Note 1,

p. 12), fortify the cloth with an appropriate amount of diazinon and malathion in acetone (Note 2, p. 13). For the companion unfortified QC sample, add 8 mL of 0.01% AOT solution to the gauze, but do not fortify with diazinon or malathion.

c. Add a total of 0.5 liter of 0.01% AOT solution to the sample (including the field sample container rinse volume). Cap the sample tightly with a PTFE or aluminum foil-lined lid. Shake for 0.25 hr (ca. 2 excursions/sec, Note 3, p. 13).

C.2 C-18RP Clean-Up

a. Condition a 1 gram C-18RP SPE cartridge as follows: Place a cartridge on a clean vacuum manifold (See Note 4, page 13); the vacuum should be sufficient to achieve eluate flows of only ca. 1 → 2 drops/second. Wash the cartridge successively with 2 x 5 mL of 50:50 DCM:methanol, 2 x 5 mL of methanol, and 2 x 5 mL of water (See Note 5, p. 13). **Do not allow the column to go dry at any point in this procedure unless specified otherwise.**

b. Pipet 10 mL of sample onto the C-18RP column. With very little vacuum, percolate the sample into the column at a maximum flow rate of ca. 1 → 2 drops/second. Wash the column with 5 mL of water, again observing the 1 - 2 drops/second flow rate (Note 6, p. 13). Discard all eluates to this point.

d. With full vacuum (≥ 20" Hg) on the manifold, air-dry the column for at least 45 minutes. **This is a critical step in the procedure; all water must be removed from the column!**

e. Elute diazinon and malathion from the column with 8 mL of 50:50 DCM:methanol (maximum rate of ca. 1 → 2 drops/second, see Note 7, p. 13). Collect the eluate directly in a 125-mL evaporation flask, or in a culture tube of suitable size. Transfer the eluate from the culture tube to a 125-mL evaporation flask, and rinse the tube twice with ca. 2 mL of 50:50 DCM:methanol and add to the flask.

f. Vacuum-evaporate the sample to dryness (ca. 25" Hg, ≤35°C water bath). **Ensure that all solvent has been removed from the sample. Cautionary Note!: Discard and reanalyze any sample which contains droplets of water after complete evaporation of**

the solvent. Evaporation of the water to dryness will give profound losses of diazinon, but not malathion. (See Note 8, p. 14).

h. Dissolve the dry residue in a known volume of 1.5% DEGDEE:acetone (generally 2.0 mL for LOQ residues, see Note 9, p. 15). Dilute with the same solvent as necessary to maintain analyte concentrations within the standard curve range. Submit the sample for GC/FPD(P) analysis as described in Step D.

D. Gas Chromatographic Analysis

A gas chromatograph equipped with a Flame Photometric Detector (phosphorous mode) is required. Split-splitless injection and narrow-bore capabilities are recommended. The conditions described herein may be modified provided adequate performance of the analysis is demonstrated.

GC Column: J & W DB-5, 30 m length, 0.25 mm i.d., 0.25 μm film. Other columns may be substituted if they give satisfactory resolution between the analytes and any interferences.

Injector: 230°C

Detector: 220°C

Column:

Initial: 95°C, hold 1.0 min.
Ramp Rate 1: 30°C/min to 230°C, hold 4 minutes.
Ramp Rate 2: 40°C/min to 290°C, hold 5 minutes.

Carrier Gas: He, 1.7 mL/min at 95°C, head pressure = 20 psi. Constant flow off.

Septum Purge: He @ 3.0 mL/min.

Injector Liner: HP Liner, Deactivated, 4 mm i.d., with Deactivated Glass Wool Plug, Part #5062-3587, or
HP Liner, Deactivated, Double-tapered splitless, Part #5181-3315.

Split Vent: He @ 7.6 mL/min, on @ 0.75 min.

Detector Make-Up: N_2 @ 23 mL/min.

Detector Air: 95 mL/min.

Detector Hydrogen: 68 mL/min.

Injection: 2 μl, Split/Splitless

E. Calibration Procedures

E.1 Preparation of Standard Solutions

Individual stock solutions of diazinon and malathion are prepared in acetone and stored in a freezer; primary stock concentrations are approximately 10.0 mg/mL. Stability of these stock solutions during prolonged storage has not been evaluated as part of this developmental and validation work.

Dilutions of diazinon and malathion are made at appropriate concentrations for fortification standards. These dilutions are made in acetone, stored in a freezer, and prepared as mixed or individual standards; that is, each solution may contain either or both diazinon and malathion. The concentration range for these fortification solutions will vary from study to study, but generally will range from 10 μg/mL to 5 mg/mL.

Dilutions of diazinon and malathion for GC standards are made in 1.5% DEGDEE in acetone (Note 9, p. 15) and are stored in a freezer. The standard concentrations suggested are 4, 10, 20, 40, 60, and 100 ng/mL for each analyte[3].

E.2 Detector Calibration

The sensitivity of the FPD(P) detector is monitored by injecting diazinon and malathion before, between, and after the samples. The suggested mass range is 8 pg to 200 pg injected.

[3]The analyst should choose standard concentrations appropriate for the standard curve model (See footnote 4). For linear or quadratic standard curve models, the standard concentrations should be constructed in a linear manner; for logarithmic models, the concentrations should be arrayed geometrically.

Under the conditions of this assay, diazinon and malathion elute from the GC column at ca. 5.4 and 6.1 minutes, respectively. The GC/FPD(P) limit of detection for diazinon and malathion (injected as a pure standard in 1.5% DEGDEE:acetone) is ca. 2 pg injected for both analytes.

F. Methods of Calculation

F.1 Injection Sequence

Analysis sequences are started and ended with one or two standards; standard injections are made throughout the run, generally with no more than three or four sample injections between each standard. A standard curve of analyte concentration (ng/mL) versus peak height or area is constructed using a method of curve generation appropriate for the GC/FPD(P) instrumentation. The construction may be linear, quadratic, or logarithmic[4]. It is recommended that the column be equilibrated with several injections of matrix-laden extract if a matrix effect is observed between samples and standards.

F.2 Calculations

Calculate μg/sample values for diazinon and malathion residues in gauze neck/face wipe samples using the following equation:

$$ug/Sample = \frac{(ng/mL\ Final\ Extract)\ X\ (mL\ Final\ Extract)}{} X \frac{500\ mL\ Sample\ Volume}{10\ mL\ C\text{-}18RP\ Aliquot\ Volume} X \frac{1\ ug}{1000\ ng}$$

For reference, the molecular weights of diazinon and malathion are 304.34 g/mole and 330.35 g/mole, respectively.

For fortified-control samples, use the following equation to calculate percent recovery:

[4]The choice of the standard curve model is instrument/detector/laboratory specific, and should be based upon the precision of back-calculated standard responses against the various least squares curve models.

$$\%\ Recovery = \left(\frac{(ug/Sample\ Found) - (ug/Sample\ Control)}{ug/Sample\ Fortified} \right) X\ 100$$

G. Interferences

G.1 Sample Matrices

Chromatographic interferences from pristine gauze facial wipe matrix are absent with this assay. GC parameters may require optimization to maximize resolution between the analytes and any other interferences which may be present in actual samples.

G.2 Other Pesticides

A specificity study has not been conducted for this method.

G.3 Solvents and Reagents

Solvents and reagents have contributed no interfering chromatographic peaks in this assay.

G.4 Glassware

There are no known interferences from labware at the stated LOQs. Extraction glassware is thoroughly washed with hot, soapy water, rinsed with acetone, air-dried, then placed in an oven at 150°C for at least 1 hour prior to use. Glass vessels are recommended for all steps without substitutions with plastic.

III. METHODS VERIFICATION

A. Experimental Design

The gauze facial wipe matrix was originally tested and validated using the inner whole body dosimeter method described in ARTF Method ARTF-AM-005. The method failed to produce acceptable results on both lab and field fortification samples during subsequent work, however, so the C18 method described herein was adapted for use with the gauze facial wipes. This matrix was validated by analysis of one unfortified control sample, two controls fortified at 1.0 μg/sample, two controls fortified at 10.0 μg/sample, and two controls fortified at

1000 μg/sample, duplicated over two days. The development lab did not perform this method with this matrix, although it is a modification of the hand wash method, ARTF Method ARTF-AM-006.

B. Analytical Reference Materials

Specific reference materials used during the conduct of the method validation study are described in Table 1.

C. Control Matrix

Untreated control gauze facial wipe samples were provided by Stewart Agricultural Research Services, Inc., P.O. Box 509, Macon, MO 63552.

D. Verification Results

D.1 Gauze facial/neck wipes

Results from the C18 cleanup gauze facial/neck wipe method validation study are presented in Table 2. Example chromatograms are presented in Figures 2 through 5.

D.2 Summary and Conclusions

The techniques outlined in this document are suitable for analysis of diazinon and malathion in gauze facial/neck wipe matrices at fortification levels ranging from 1.0 μg/sample to 1 mg/sample. **Critical features of the gauze facial/neck wipe method include: (a) proper drying of the C-18RP columns prior to elution, and (b) ensuring that the C-18RP sorbent is adequately calibrated prior to use, and (c) scrupulously cleansed labware. Interferences from AOT reagent can dramatically impact retention of both analytes onto C-18RP adsorbent; if the calibration is not controlled, analyte recoveries will be biased low.**

IV. NOTES

Note 1: In the field, pristine gauze facial/neck wipes are pre-wetted with 8 mL of 0.01% aqueous AOT solution. The surfactant facilitates removal of residues from the facial/neck surfaces of field personnel.

Note 2: With a pipet, drizzle the fortification solution over the sample as uniformly as possible.

Note 3: The shaker speed will vary between laboratories and equipment. The analyst should visually ensure that shaking appears sufficiently vigorous to extract residues from all parts of the sample.

Note 4: The developers of this method observed frequent cross-contamination of final sample extracts with malathion and, especially, diazinon. Generally, this problem is noticeable only with samples fortified at the limit of quantification when samples containing very high residues (100 X LOQ) have been previously analyzed using the same glassware or laboratory equipment. The vacuum manifold, especially the plastic SPE stopcocks and attached needles, are a primary source of this cross-contamination. **The entire vacuum manifold, including stopcocks and needles, should be scrupulously cleaned with hot, soapy water, rinsed with distilled water, then high-purity acetone prior to any subsequent use.** Stopcocks can be checked for retained residues by soaking them overnight in acetone, then analyzing the extract by gas chromatography (See Section D). If cross-contamination persists, replace the stopcocks. [The validation laboratory did not encounter frequent cross-contamination problems from the vacuum manifold or glassware, and the rigorous cleaning of the vacuum manifold was not found to be necessary.]

Note 5: If necessary to improve cleanup, a hexane wash can be performed after drying the C18 column but prior to elution of the compounds with DCM:methanol. If a hexane wash is used, the C18 column should be conditioned with 2 x 5 mL hexane prior to rinsing with the 50:50 DCM:methanol.

After drying the column, the hexane wash may be initially very slow, and a full vacuum may be required to initiate flow. The hexane wash partitions some, but not all, of the retained AOT components from the column. Excess hexane <u>can</u> elute diazinon and malathion from the column.

Note 6: The analyst should note that low recoveries of diazinon from quality control samples may indicate a sample loading problem. Load flow rates may be a factor, but this has not been confirmed. Some analysts may wish to dilute the 0.01% AOT sample with water (e.g., 2X), but note that malathion and diazinon are sparingly soluble in water, and excessive dilution of the sample may cause loss of analyte due to precipitation.

Note 7: During developmental research (performed by the validation lab), 8 mL of 50:50 DCM:methanol quantitatively eluted both analytes from the C-18RP column. Work on similar methods used 100% DCM as the elution solvent, with volumes ranging from 8-16 mL.

Each lot of C-18RP cartridges should be pre-calibrated with matrix prior to use. **This is a critical step in the assay, since AOT components can change the retention characteristics of the solid support**. An example procedure is as follows.

Prepare a C-18RP column and fortified-control gauze AOT extract (100 μg both analytes/500 mL solution) as described in Sections C.1.b and C.1.c, respectively. Process the sample through the column as described in Sections C.2.b through C.2.g. Retain the load and hexane washes from C.2.c and C.2.e separately to this point. Dissolve the final dry residue in a 20 mL final volume. Analyze the sample by GC/FPD(P) (See Step D) against a 100 ng/mL diazinon/malathion standard prepared in 1.5% DEGDEE:acetone (Step E.1). At 100% recovery, the GC/FPD(P) detector responses for both compounds from the sample and standard injections should be equivalent.

If the recovery for either compound is biased low, vacuum-evaporate the hexane wash from C.2.e, dissolve the residue in 5 mL of 1.5% DEGDEE:acetone, then inject into the GC/FPD(P). Similarly, elute the column with additional 50:50 DCM:methanol, vacuum-evaporate to just-dryness, dissolve the residue in 5 mL DEGDEE:acetone, then inject into the GC/FPD(P). Finally, dilute the retained load/water wash fraction with water (100X) and partition twice against 75 mL of DCM. Vacuum-evaporate the DCM to just-dryness, dissolve the residue in 5 mL of 1.5% DEGDEE:acetone, then analyze by GC/FPD(P).

As observed in Note 6 above, the presence of diazinon in the load/wash fraction from Step C.2.c may indicate a load flow rate problem or too high of an AOT concentration in the sample. Low-biased malathion recoveries are an indication that further elution of the C-18RP column with 50:50 DCM:methanol is necessary; simply increase the elution volume from the recommended 8 mL to 10-12 mL, as indicated, or increase the ratio of methanol to DCM. If either analyte is present in the hexane wash fraction (if used, see Note 5), reduce the volume of the hexane wash appropriately, or do not include the hexane wash as part of the procedure.

Note 8: Developmental research for this method demonstrated no losses of either analyte during vacuum-evaporation of methylene chloride, or during prolonged (up to 10 minutes) "dry" evaporation at ≤35°C (water bath) and 25" Hg vacuum. However, profound losses of diazinon (but not malathion) are observed if the sample contains droplets of water, and the water is evaporated to dryness.

Therefore, water **MUST** be removed from the C-18RP column prior to elution with 50:50 DCM:methanol (Step II.C.2.e). Profound losses of diazinon (but not malathion) are observed if the sample contains droplets of water, and the water is

evaporated to dryness. This effect is poorly understood, but has attributes consistent with a diazinon/water azeotrope.

The method developer could dry only 3 cartridges at a time to achieve proper drying. The validation laboratory was able to dry and entire bank of up to 12 cartridges at a time using a 45 min drying period at the maximum recommended operating vacuum for the vacuum manifold (20" Hg). This vacuum could only be achieved using a vacuum pump. During the drying period, the flow should be checked periodically through each cartridge by placing a finger over the top of the cartridge. A strong vacuum should be felt quickly (ca. 1-2 sec), and a sharp "popping" sound made when the finger is removed. The flow through all the columns should be checked and should be relatively uniform. As the columns dry, the flow characteristics of the columns will change, so it is necessary to moderate the vacuum and repeat the column flow check approximately every 10 min.

Note 9: Diazinon and malathion standards prepared in neat acetone give unacceptable chromatography; standard curves exhibit poor linearity (especially for malathion), reproducibility, and sensitivity. "Priming" the GC with untreated control extracts in and of itself does not correct the problem. Use of 1.5% DEGDEE in acetone solvent for GC standards and final sample extracts eliminates these problems and improves the signal/noise ratio for analyte detection at all concentrations. The mechanism of action for this effect is not known.

Even with the use of 1.5% DEGDEE in acetone, it was found that priming, or equilibrating, the GC with matrix extract was necessary prior to the analysis of a set of samples for gauze neck/face wipes. In general, a minimum of two injections of matrix-laden extract is recommended immediately prior to initiation of a sample set. In addition, routine maintenance was found to be necessary due to buildup in the injector liner and at the front of the analytical column. Replacement of the injector liner and removal of approximately 15" from the front of the analytical column was necessary after approximately every 100 sample injections. It was found that this maintenance was necessary to prevent a matrix effect (enhancement) on the malathion in matrix-laden samples. If a high bias is observed with samples reconstituted in low volumes of 1.5% DEGDEE in acetone, it may be necessary to chill the evaporation flask prior to addition of the acetone-based solvent. This can be accomplished using an ice water bath.

V. SAFETY

The organic solvents utilized in this method represent both a general exposure and fire hazard. Provision must be made for working with these solvents for personnel safety.

VI. TABLES

Table 1. Standard Reference Materials.

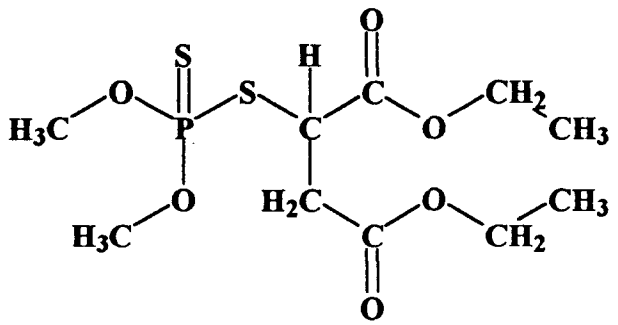
STANDARD NAME	ABC STANDARD NUMBER	LOT NUMBER	PURITY:EXP. DATE	PHYSICAL CHARAC-TERISTICS
Diazinon, O,O-diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate, CAS #333-41-5.	PS-9824	95R-31-45C 09467	87.7%:9/14/98	Clear Yellow Liquid
Malathion, [(Dimethoxyphosphino-thioyl)thio]-butanedioic acid diethyl ester, CAS #121-75-5.	PS-9825	95R-31-44E CS030	95.0%:12/12/99	Clear Liquid

Table 2. Recovery of Diazinon and Malathion from Gauze Neck/Face Wipes

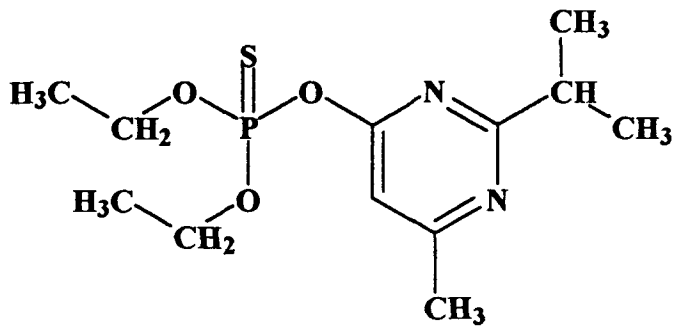
ABC Sample ID	Sample Description	µg Diazinon/ segment found	% Recovery Diazinon	µg Malathion/ segment found	% Recovery Diazinon
43767-147	Control Neck Wipe	0	N/A	0	N/A
43767-148	Control Neck Wipe + 1.00 µg Diazinon and Malathion	0.935	93.5	1.05	105
43767-149	Control Neck Wipe + 1.00 µg Diazinon and Malathion	0.961	96.1	1.07	107
43767-150	Control Neck Wipe + 10.0 µg Diazinon and Malathion	8.80	88.0	9.95	99.5
43767-151	Control Neck Wipe + 10.0 µg Diazinon and Malathion	9.20	92.0	9.94	99.4
43767-152	Control Neck Wipe + 1000 µg Diazinon and Malathion	848	84.8	769	76.9
43767-153	Control Neck Wipe + 1000 µg Diazinon and Malathion	841	84.1	754	75.4
43767-154	Control Neck Wipe	0	N/A	0	N/A
43767-155	Control Neck Wipe + 1.00 µg Diazinon and Malathion	1.05	105	1.21	121
43767-156	Control Neck Wipe + 1.00 µg Diazinon and Malathion	1.03	103	1.14	114
43767-157	Control Neck Wipe + 10.0 µg Diazinon and Malathion	8.98	89.8	9.25	92.5
43767-158	Control Neck Wipe + 10.0 µg Diazinon and Malathion	9.31	93.1	9.77	97.7
43767-159	Control Neck Wipe + 1000 µg Diazinon and Malathion	873	87.3	789	78.9
43767-160	Control Neck Wipe + 1000 µg Diazinon and Malathion	904	90.4	880	88.0
	Average Overall % Recovery (n=12)		92.3		96.3
	Overall Standard Deviation (n=12)		6.53		14.6
	% Relative Standard Deviation		7.07		15.2

VII. FIGURES

Figure 1. Chemical Structures of Diazinon and Malathion.



MALATHION
[(Dimethoxyphosphinothioyl)thio]-butanedioic acid diethyl ester



DIAZINON
O,O-Diethyl-O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]-phosphorothioate

Figure 2. Representative Chromatogram of a Nominal 100 ng/mL Mixed External Standard

MCDO [43767] 29 C18NWMV1, 4, 1
GCMIX-G2 100 NG/ML STD
Acquired on 27-Oct-1997 at 17:48

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.40	95406	102.35741
MALATHION	6.10	57965	104.17831

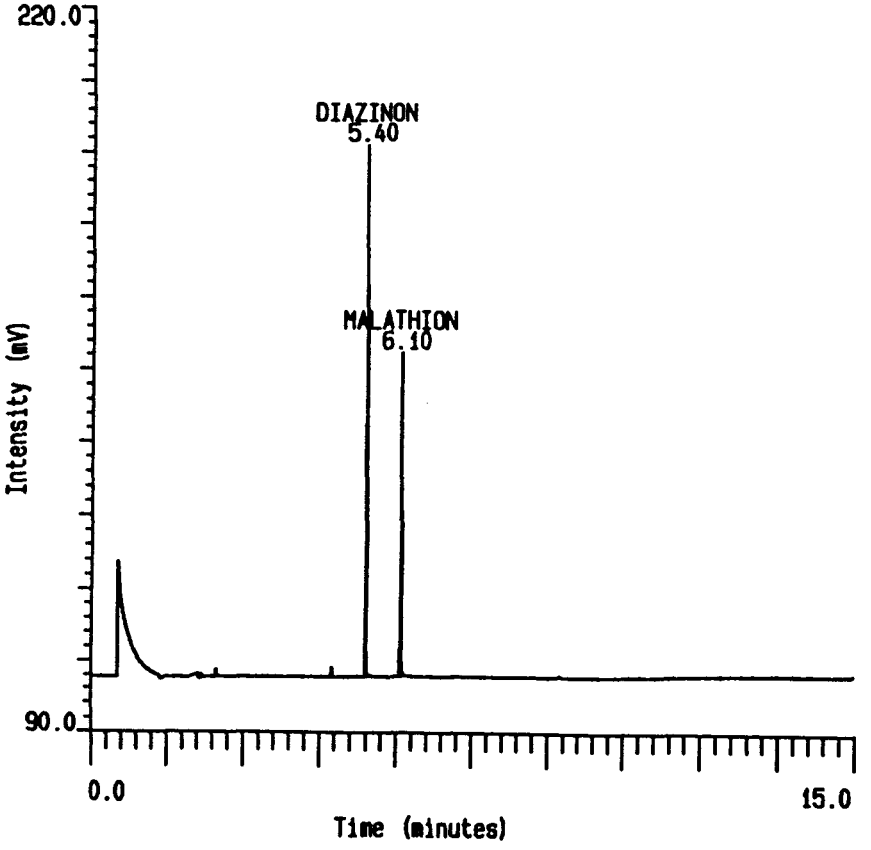


Figure 3. Representative Chromatogram of a Nominal 4.00 ng/mL Mixed External Standard

MCDO [43767] 29 C18NWMV1, 16, 1
GCMIX-H7 4.00 NG/ML STD
Acquired on 27-Oct-1997 at 21:49

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.39	3890	4.09209
MALATHION	6.08	2177	4.07318

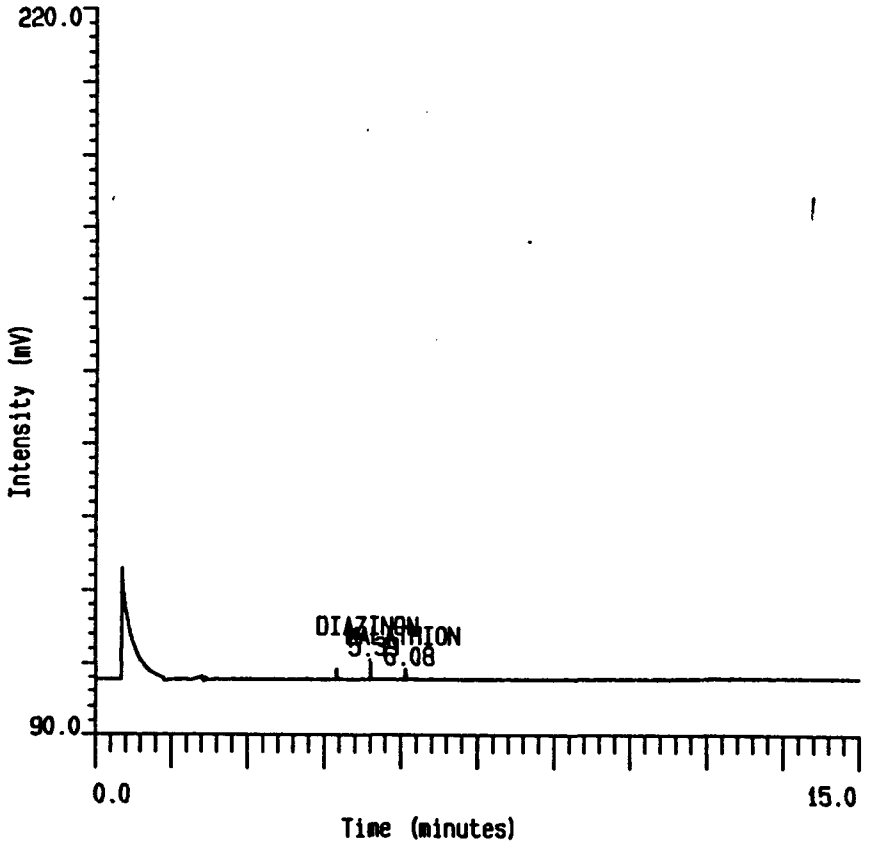


Figure 4. Representative Chromatogram of a Control Gauze Face/Neck Wipe Sample

MCDO [43767] 29 C18NWMV1, 6, 1
43767-147 CONTROL
Acquired on 27-Oct-1997 at 18:28

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	0.00	0	0
MALATHION	0.00	0	0

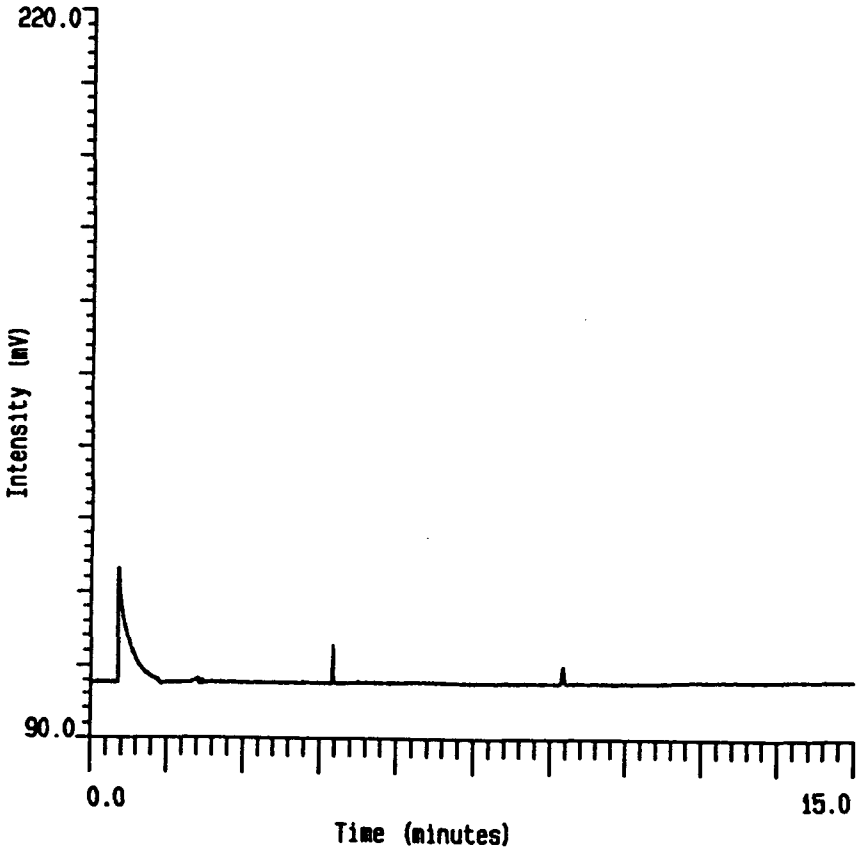
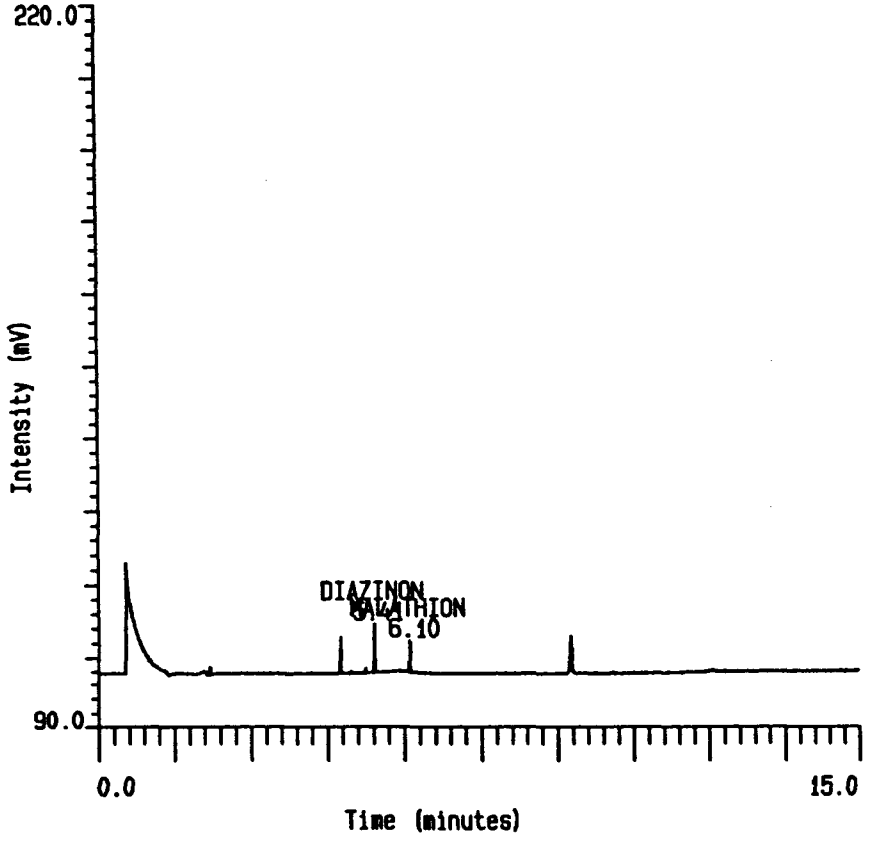


Figure 5. Representative Chromatogram of a Nominal 1 μg Gauze Face/Neck Wipe Fortification (LOQ) Sample

MCDO [43767] 29 C18NWMV1, 7, 1
43767-148 CONTROL + 1 UG EACH
Acquired on 27-Oct-1997 at 18:48

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.41	8785	0.93480
MALATHION	6.10	5753	1.04886



Attachment 2. Validation Data for Inner Dermal Dosimeter Method ARTF-AM-005

Summary Results for Inner Whole Body Dosimeters Method Validation - Malathion
Reference Multichrom files 767IWBD3 and 767IWBD7

Sample ID	Sample Description	Malathion Fortification Level (ug/dosimeter)	Malathion Recovery (ug/dosimeter)	% Recovery
43767-001R	Control Upper Arms	NA	Not Detected	
43767-002R	Upper Arms + nominal 1 ug each	1.02	1.05	103%
43767-003R	Front Torso + nominal 1 ug each	1.02	1.07	105%
43767-004R	Lower Arms + nominal 10 ug each	10.2	9.00	88.2%
43767-005R	Reat Torso + nominal 10 ug each	10.2	10.0	98.0%
43767-006R	Lower Legs + nominal 1000 ug each	1020	947	92.8%
43767-007R	Upper Legs + nominal 1000 ug each	1020	888	87.1%
43767-008	Control Lower Legs	NA	Not Detected	
43767-009	Upper Arms + nominal 1 ug each	1.02	0.836	82.0%
43767-010	Front Torso + nominal 1 ug each	1.02	1.19	117%
43767-011	Rear Torso + nominal 10 ug each	10.2	10.4	102%
43767-012	Lower Arms + nominal 10 ug each	10.2	11.0	108%
43767-013	Lower Legs + nominal 1000 ug each	1020	1040	102%
43767-014	Upper Legs + nominal 1000 ug each	1020	990	97.1%
			Average % Recovery (n=12)	98.5%
			Standard Deviation (n=12)	9.83%
			Avg. + 2 Std. Dev.	118%
			Avg. - 2 Std. Dev.	78.8%

Prepared by: [illegible] 24 Apr 97

Checked by: [illegible] 4-25-97

Summary Results for Inner Whole Body Dosimeters Method Validation - Diazinon
Reference Multichrom files 767IWBD3 and 767IWBD7

Sample ID	Sample Description	Diazinon Fortification Level (ug/dosimeter)	Diazinon Recovery (ug/dosimeter)	% Recovery
43767-001R	Control Upper Arms	NA	Not Detected	
43767-002R	Upper Arms + nominal 1 ug each	0.992	1.10	111%
43767-003R	Front Torso + nominal 1 ug each	0.992	1.12	113%
43767-004R	Lower Arms + nominal 10 ug each	9.92	9.51	95.9%
43767-005R	Reat Torso + nominal 10 ug each	9.92	9.94	100%
43767-006R	Lower Legs + nominal 1000 ug each	992	924	93.1%
43767-007R	Upper Legs + nominal 1000 ug each	992	867	87.4%
43767-008	Control Lower Legs	NA	Not Detected	
43767-009	Upper Arms + nominal 1 ug each	0.992	0.932	94.0%
43767-010	Front Torso + nominal 1 ug each	0.992	1.11	112%
43767-011	Rear Torso + nominal 10 ug each	9.92	9.70	97.8%
43767-012	Lower Arms + nominal 10 ug each	9.92	10.4	105%
43767-013	Lower Legs + nominal 1000 ug each	992	982	99.0%
43767-014	Upper Legs + nominal 1000 ug each	992	896	90.3%
			Average % Recovery (n=12)	99.9%
			Standard Deviation (n=12)	8.62%
			Avg. + 2 Std. Dev.	117%
			Avg. - 2 Std. Dev.	82.7%

Prepared by: [illegible] 24 Apr 97

Checked by: [illegible] [illegible] 4-25-97

SAMPLE TRACKING FORM

Customer Name: ARTF	Study Director: Loren C. Schrier	Test Material: Diazinon and Malathion	Matrix: IWBD
ARTF Protocol: ARF003	ABC Study Number: 43767	Inner Cotton Whole Body Dosimeters Method Validation Set 2	

Extraction (Section II.C.1, C.2)	Partitioning (Section II.C.3)	Florisil Cleanup (Section II.C.4)	Vial	GC/FPD Analysis (Section II.E)	Chromatography review:
[illegible], CYG 4-7-97 [illegible] 4-9-97	[illegible], CYG 4-7-97 [illegible] 4-9-97 ①	[illegible], CYG 4-7-97 [illegible] 4-10-97	[illegible] 4-7-97 [illegible] 4-10-97	[illegible] 4-8-97 [illegible] 4-10-97	21 Apr 97
					Spreadsheet entry by: 21 Apr 97

ABC Lab Number	Sample Identification (Designate Part of IWBD; e.g. "Upper Arms")	Extraction Volume	Aliquot Taken	Hexane Volume, Aliquot Taken for Florisil Cleanup	Final Volume and Dilutions	Fortified by: [illegible] 4-7-97 Witnessed by: CYG 4-7-97
43767-008	Control lower legs	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	2.50 mL	
43767-009	Control + nominal 1 ug Each upper arms	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	2.50 mL	Fortify with 1.0 mL of 0.992 ug/mL diazinon and 1.02 ug/mL malathion mixed fortification solution (Fort-3)
43767-010	Control + nominal 1 ug Each Front Torso	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	2.50 mL	Fortify with 1.0 mL of 0.992 ug/mL diazinon and 1.02 ug/mL malathion mixed fortification solution (Fort-3)
43767-011	Control + nominal 10 ug Each Rear Torso	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	4.00 mL	Fortify with 1.0 mL of 9.92 ug/mL diazinon and 10.2 ug/mL malathion mixed fortification solution (Fort-2)
43767-012	Control + nominal 10 ug Each Lower arms	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	4.00 mL	Fortify with 1.0 mL of 9.92 ug/mL diazinon and 10.2 ug/mL malathion mixed fortification solution (Fort-2)
43767-013	Control + nominal 1000 ug Each Lower Legs	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	10.0 mL, then dilute 0.50 mL to 15.5 mL	Fortify with 1.0 mL of 992 ug/mL diazinon and 1020 ug/mL malathion mixed fortification solution (Fort-1)
43767-014	Control + nominal 1000 ug Each Upper legs	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	10.0 mL, then dilute 0.50 mL to 15.5 mL	Fortify with 1.0 mL of 992 ug/mL diazinon and 1020 ug/mL malathion mixed fortification solution (Fort-1)

Remarks: Dilution factor for the high fortification level is 31.

① A second 50mL aliquot was taken from the extracted sample. [illegible] 4-9-97 ② [illegible] 4-14-97

Acetone: BO512 BJJ
Hexane: BN237 BJJ
Ethyl Ether: BM863 BJJ
Florisil: Fisher Lot 964720
Water: Labconco DI

Checked by [illegible] 24 Apr 97 Approved by [illegible] 24 Apr 97

[43767] 29 767IWBD3
Reported on 11-APR-1997 at 09:39
Modified on 10-APR-1997 at 11:41

Page 1

List Run Sequence File

ANALYST NAME..... Heidi Anderson
43767 INNER WHOLE BODY DOSIMETERS SET 3

ANALYSIS INFORMATION

Analysis name..... 767IWBD3
Method name..... 767IWBD3
Calibration name..... 767IWBD3
Calibration sequence..... Average Standard
User parameter 1 name..... FINAL VOLUME
User parameter 2 name..... FACTOR 1
User parameter 3 name..... FACTOR 2

SAMPLE SUMMARY

SAMPLE NUMBER	LIMS ID	SAMPLE NAME
1	----------	SOLVENT BLANK
2	----------	GCMIX-1 NOMINAL 100 NG/ML
3	----------	GCMIX-2 NOMINAL 60 NG/ML
4	----------	43767-008
5	----------	43767-009
6	----------	43767-010
7	----------	GCMIX-3 NOMINAL 40 NG/ML STD
8	----------	43767-011
9	----------	43767-012
10	----------	GCMIX-4 NOMINAL 20 NG/ML
11	----------	43767-013
12	----------	43767-014
13	----------	GCMIX-5 NOMINAL 10 NG/ML
14	----------	GCMIX-6 NOMINAL 4 NG/ML

[43767] 29 767IWBD3 Page 2
Reported on 11-APR-1997 at 09:39
Modified on 10-APR-1997 at 11:41

SAMPLE INFORMATION

SAMPLE NUMBER	TYPE	CALIB LEVEL	UPDATE RT	UPDATE RF	AMOUNT	NUM INJ	BOT NUM
1	Sa	--	-	-	1.00000	1	1
2	St	01	N	I	1.00000	1	1
3	St	02	N	I	1.00000	1	2
4	Sa	--	-	-	1.00000	1	3
5	Sa	--	-	-	1.00000	1	5
6	Sa	--	-	-	1.00000	1	6
7	St	03	N	I	1.00000	1	7
8	Sa	--	-	-	1.00000	1	8
9	Sa	--	-	-	1.00000	1	9
10	St	04	N	I	1.00000	1	10
11	Sa	--	-	-	1.00000	1	11
12	Sa	--	-	-	1.00000	1	12
13	St	05	N	I	1.00000	1	13
14	St	06	N	I	1.00000	1	14

USER PARAMETER VALUES

SAMPLE	FINAL VOLUME	FACTOR 1	FACTOR 2
1	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000
4	2.50000	20.00000	400.00000
5	2.50000	20.00000	400.00000
6	2.50000	20.00000	400.00000
7	1.00000	1.00000	1.00000
8	4.00000	20.00000	400.00000
9	4.00000	20.00000	400.00000
10	1.00000	1.00000	1.00000
11	10.00000	310.00000	200.00000
12	10.00000	310.00000	200.00000
13	1.00000	1.00000	1.00000
14	1.00000	1.00000	1.00000

[43767] 29 7671WBD3 Page 3
Reported on 11-APR-1997 at 09:39
Modified on 10-APR-1997 at 11:41

INTERNAL/DILUTION STANDARDS

SAMPLE NUMBER	ISTD1 AMOUNT	ISTD2 AMOUNT	ISTD3 AMOUNT	DIL1 AMOUNT	DIL2 AMOUNT
1	1.00000	1.00000	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000	1.00000	1.00000
4	1.00000	1.00000	1.00000	1.00000	1.00000
5	1.00000	1.00000	1.00000	1.00000	1.00000
6	1.00000	1.00000	1.00000	1.00000	1.00000
7	1.00000	1.00000	1.00000	1.00000	1.00000
8	1.00000	1.00000	1.00000	1.00000	1.00000
9	1.00000	1.00000	1.00000	1.00000	1.00000
10	1.00000	1.00000	1.00000	1.00000	1.00000
11	1.00000	1.00000	1.00000	1.00000	1.00000
12	1.00000	1.00000	1.00000	1.00000	1.00000
13	1.00000	1.00000	1.00000	1.00000	1.00000
14	1.00000	1.00000	1.00000	1.00000	1.00000

PROCESSING ORDER

SAMPLE NUMBER	TYPE
2	Standard
3	Standard
7	Standard
10	Standard
13	Standard
14	Standard
1	Sample
4	Sample
5	Sample
6	Sample
8	Sample
9	Sample
11	Sample
12	Sample

Gas Chromatographic Instrument Parameters Form

ABC Laboratory Study Number: 43767
Customer Identification: ARTF

Instrument: HP 5890 Series II Material ID# 1652-0120
Autoinjector: HP 7673B Material ID# 1625-802A

Column: HP-5MS, 30 M X 0.25 mm, 0.25 μm film thickness
Serial#: 56253614

Detector Type: FPD/P

Electrometer: Range 4; Attenuation 0

Temperatures:
- Injector (°C): 230
- Detector (°C): 230
- Column:
  - Initial Temp.(°C): 95
  - Initial Time: 1.0 min.
  - Program Rate 1: 30 °C/min to 230 °C, hold 4 min
  - Program Rate 2: 40 °C/min to 290 °C, hold 4 min
  - Equilibration Time: 1 min

Carrier Gas Flow Rate: He 1.6 mL/min
Air Flow Rate: 100 mL/min.
Hydrogen Flow Rate: 75 mL/min.
Purge Valve: Off at 0 min, on at 0.75 min

Injection Volume: 2 μL

Run Sequence File: 7671WB1D3

Quantitation Standards: GCMIX- 1→6 inclusive

Prepared By: [signature] Date: 4-10-97

Checked By: [signature] Date: 24Apr97
1E 4-10-97

MCDO [43767] 29 767IWBD3

ABC Laboratories, Inc.
Sample Information Report ver 3.3

Report Date: 21 APR 97 at 10:00:58
Page 1

Sample Name	No.	Type	Level	User Parameter 1 FINAL VOLUME	User Parameter 2 FACTOR 1	User Parameter 3 FACTOR 2
SOLVENT BLANK	1	SA		1.00000	1.00000	1.00000
GCMIX-1 NOMINAL 100 NG/ML	2	ST	01	1.00000	1.00000	1.00000
GCMIX-2 NOMINAL 60 NG/ML	3	ST	02	1.00000	1.00000	1.00000
43767-008	4	SA		2.50000	20.00000	400.00000
43767-009	5	SA		2.50000	20.00000	400.00000
43767-010	6	SA		2.50000	20.00000	400.00000
GCMIX-3 NOMINAL 40 NG/ML STD	7	ST	03	1.00000	1.00000	1.00000
43767-011	8	SA		4.00000	20.00000	400.00000
43767-012	9	SA		4.00000	20.00000	400.00000
GCMIX-4 NOMINAL 20 NG/ML	10	ST	04	1.00000	1.00000	1.00000
43767-013	11	SA		10.00000	310.00000	200.00000
43767-014	12	SA		10.00000	310.00000	200.00000
GCMIX-5 NOMINAL 10 NG/ML	13	ST	05	1.00000	1.00000	1.00000
GCMIX-6 NOMINAL 4 NG/ML	14	ST	06	1.00000	1.00000	1.00000

MCDO [43767] 29 767IWBD3

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: DIAZINON

Report Date: 21 APR 97
Time: 10:00:58
Page: 1

Sample Name	SMP #	INJ #	RT(mins)	Area	NG/ML OR UG	CAL. RANG	Peak Type	Bad INJ
SOLVENT BLANK	1	1	0.00	0	0.000	UNDR		---
GCMIX-1 NOMINAL 100 NG/ML	2	1	6.43	59993	97.667		B	---
GCMIX-2 NOMINAL 60 NG/ML	3	1	6.44	35522	57.520		B	---
43767-008	4	1	0.00	0	0.000	UNDR		---
43767-009	5	1	6.43	5008	0.932		F	---
43767-010	6	1	6.42	5859	1.107		B	---
GCMIX-3 NOMINAL 40 NG/ML STD	7	1	6.43	26348	42.468		B	---
43767-011	8	1	6.43	30017	9.698		B	---
43767-012	9	1	6.43	32032	10.359		OB	---
GCMIX-4 NOMINAL 20 NG/ML	10	1	6.43	13111	20.752		OB	---
43767-013	11	1	6.43	39078	981.976		B	---
43767-014	12	1	6.43	35712	896.382		B	---
GCMIX-5 NOMINAL 10 NG/ML	13	1	6.42	6954	10.650		OB	---
GCMIX-6 NOMINAL 4 NG/ML	14	1	6.43	2567	3.453		BF	---

MCDO [43767] 29 767IWBD3

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: MALATHION

Report Date: 21 APR 97
Time: 10:00:58
Page: 1

Sample Name	SMP #	INJ #	RT(mins)	Area	NG/ML OR UG	CAL. RANG	Peak Type	Bad INJ
SOLVENT BLANK	1	1	0.00	0	0.000	UNDR	B	---
GCMIX-1 NOMINAL 100 NG/ML	2	1	7.44	50100	99.684		OB	---
GCMIX-2 NOMINAL 60 NG/ML	3	1	7.46	30010	59.330		OB	---
43767-008	4	1	0.00	0	0.000	UNDR		---
43767-009	5	1	7.44	3800	0.836		B	---
43767-010	6	1	7.44	5210	1.190		B	---
GCMIX-3 NOMINAL 40 NG/ML STD	7	1	7.44	22375	43.995		B	---
43767-011	8	1	7.45	26395	10.414		BF	---
43767-012	9	1	7.44	27836	10.993		B	---
GCMIX-4 NOMINAL 20 NG/ML	10	1	7.44	11472	22.096		B	---
43767-013	11	1	7.44	33866	1039.686		B	---
43767-014	12	1	7.45	32266	989.862		BF	---
GCMIX-5 NOMINAL 10 NG/ML	13	1	7.44	5750	10.603		O	---
GCMIX-6 NOMINAL 4 NG/ML	14	1	7.45	2223	3.519		OB	---

Acquisition and Peak Processing Parameters Report Print Date and Time : 21 APR 97 10:03:23
Page : 1

MCDO [43767] 29 767IWBD3 Based on Sample Number : 1 Injection Number : 1

ACQUISITION PARAMETERS

Data Collection :

Length of Run..... 14.97 mins
Post Injection Delay..... 0.00 mins
Sampling Rate..... 15.00 Hz

PEAK PROCESSING PARAMETERS

Auto Process Parameters :

Peak Threshold..... 6.00
Baseline Test..... 2
Peak Trend..... 2

Separation Parameters :

Shoulder Sensitivity..... 0.10
Rider Sensitivity..... 0.05

Rejection Parameters :

Minimum Peak Width..... 0.00 secs
Minimum Peak Height..... 0.00 uV
Minimum Peak Area..... 1000.00 uVs
Ignore Flat Top Peak..... No

User Imposed Action Control :

Forced Baseline..... No
Suppress Integration..... Yes
Tangent Skimming..... No
Shoulder Detection..... No
Data Bunching..... No
Negative Detection..... No

Integration Modes :

Retention Time Integration..... No
Square Root Area and Height..... No

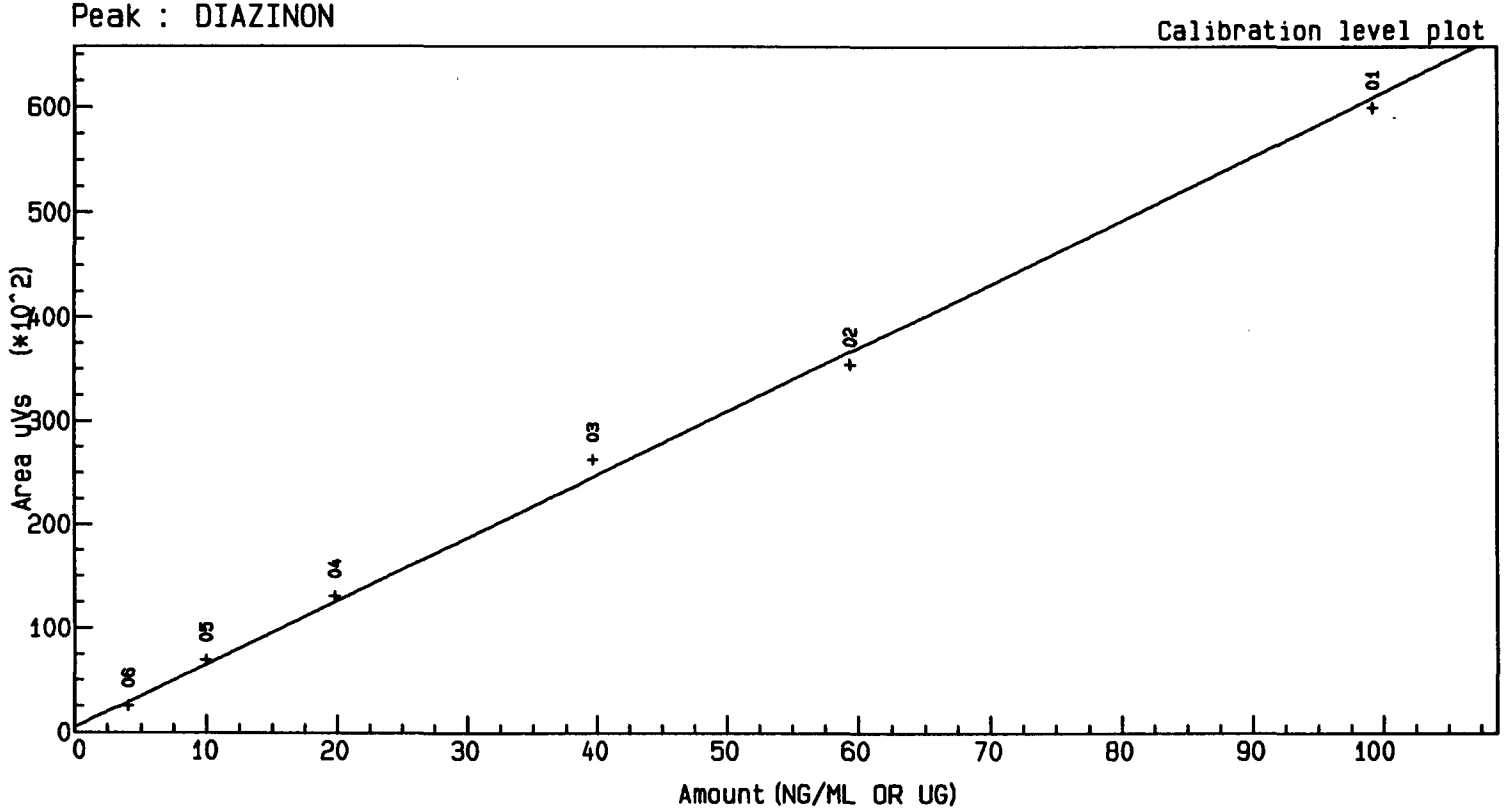
PROCESSING ACTIONS

Time (mins)	Force Baseline	Integrate Suppress	Tangent Skim	Bunch Size	Shoulder Detect	Negative Detect
0.00	--	SI	_	0	--	--
6.35	--	ES	_	0	--	--
6.50	--	SI	_	0	--	--
7.37	--	ES	_	0	--	--
7.55	--	SI	_	0	--	--

These parameters apply to all injections of set 767IWBD3 with no exceptions

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767IWBD3.
43767 INNER WHOLE BODY DOSIMETERS SET 3
Peak : DIAZINON



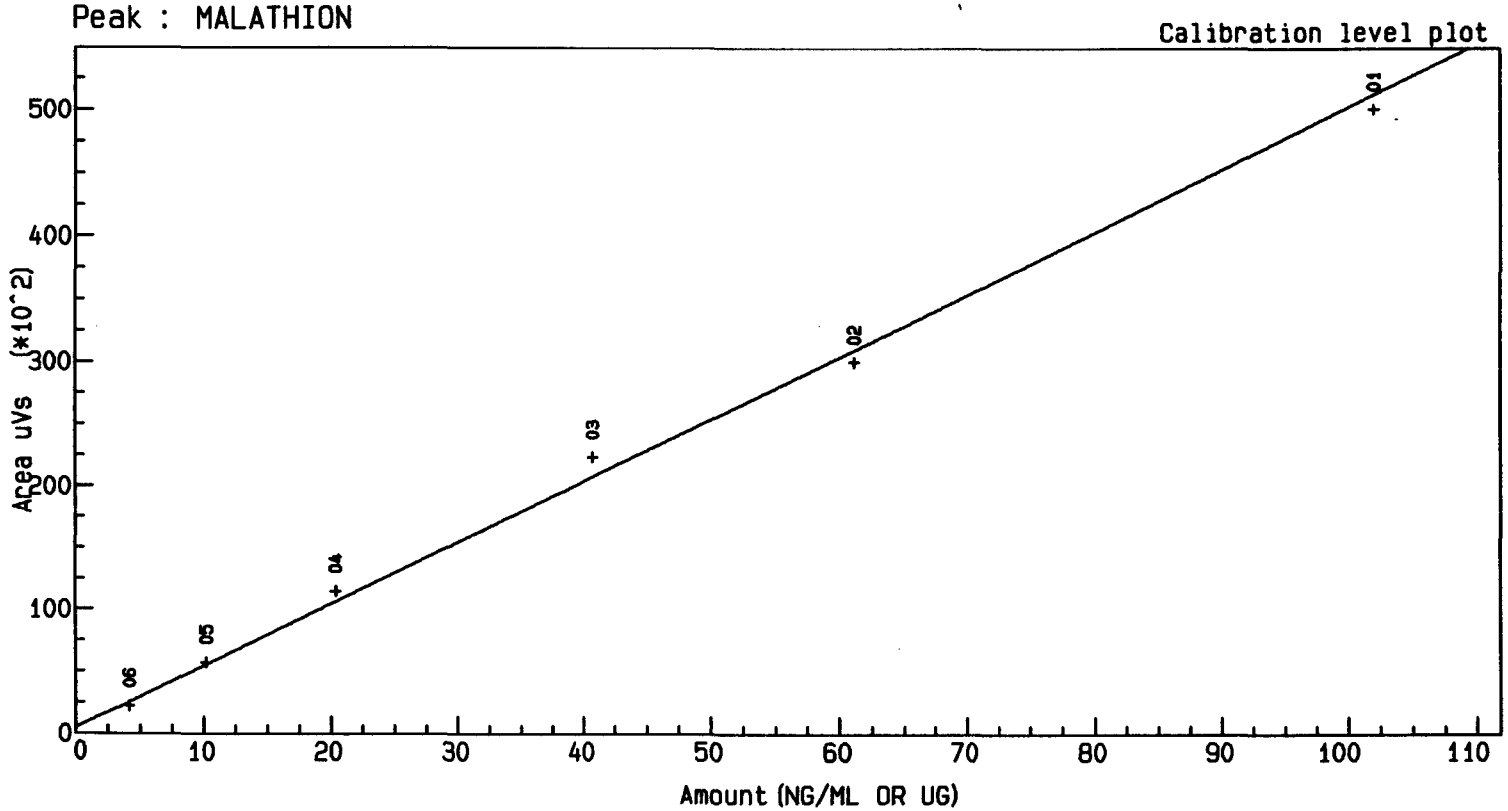
Constant : 4.62428E+2
1st degree : 6.09521E+2

Curve fit : Linear
Correlation coefficient : 0.99874
Standard error : 1.20524E+3

Reported on 21-APR-1997 at 10:03

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767IWBD3.
43767 INNER WHOLE BODY DOSIMETERS SET 3
Peak : MALATHION



Constant : 4.71318E+2
1st degree : 4.97859E+2

Curve fit : Linear
Correlation coefficient : 0.99827
Standard error : 1.17869E+3

Reported on 21-APR-1997 at 10:04

ABC Laboratories, Inc.

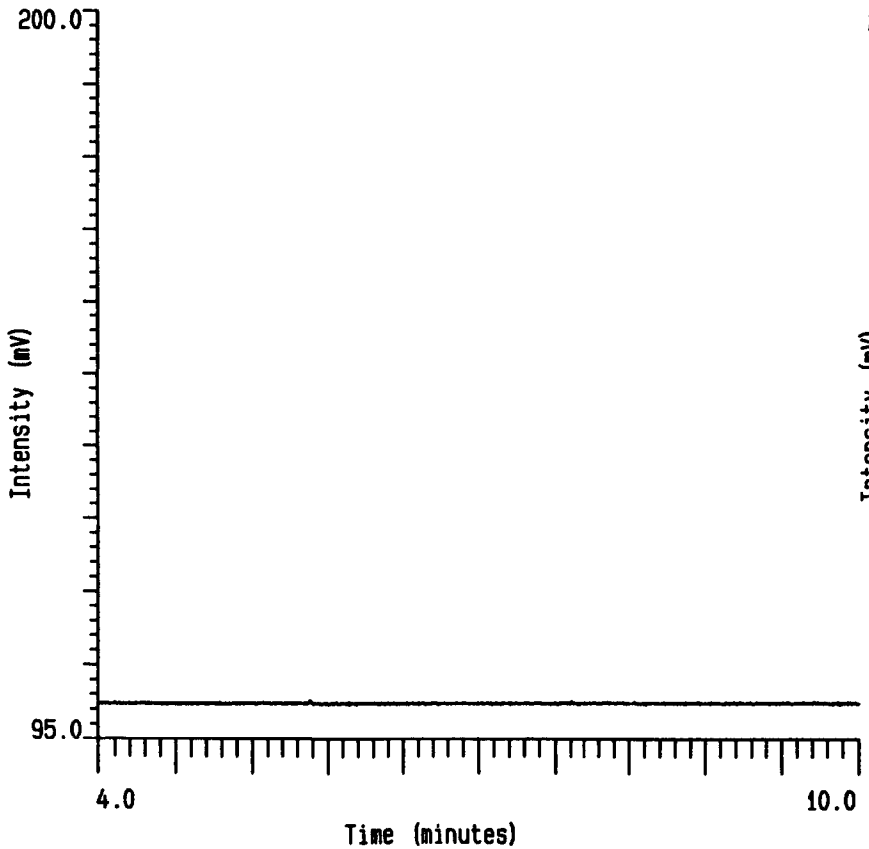
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS SET 3

Date of Report: 21 APR 97 at 10:05:12

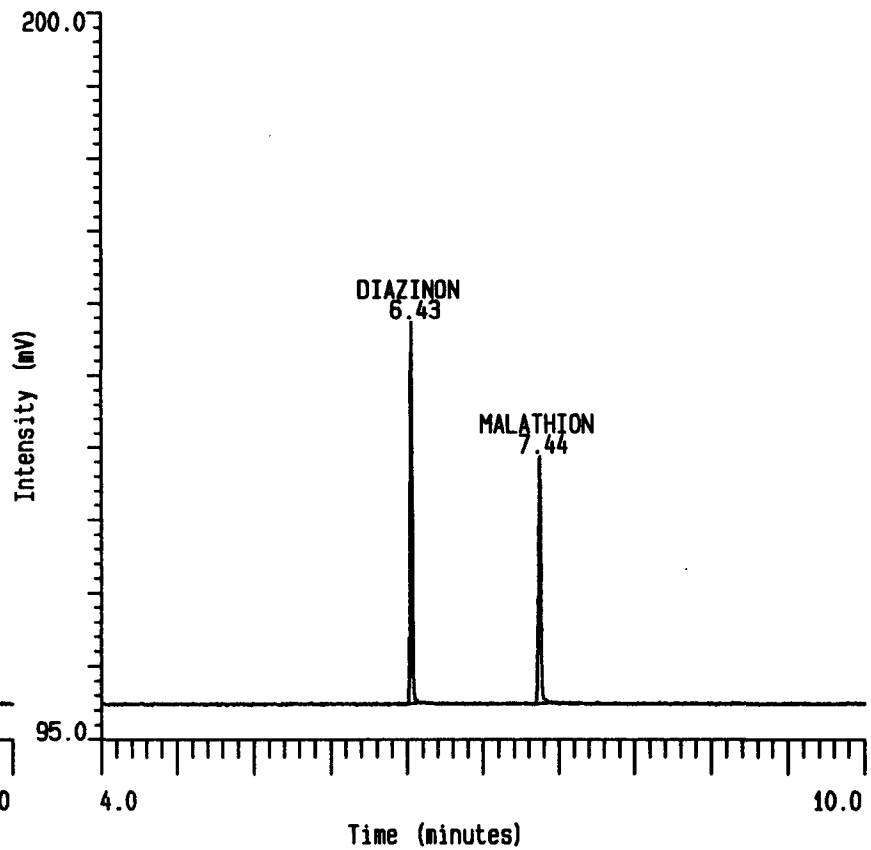
MCDO [43767] 29 767IWBD3, 1, 1
SOLVENT BLANK
Acquired on 10-Apr-1997 at 17:03

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	0.00	0	0
MALATHION	0.00	0	0



MCDO [43767] 29 767IWBD3, 2, 1
GCMIX-1 NOMINAL 100 NG/ML
Acquired on 10-Apr-1997 at 17:23

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.43	59993	97.667
MALATHION	7.44	50100	99.684



ABC Laboratories, Inc.

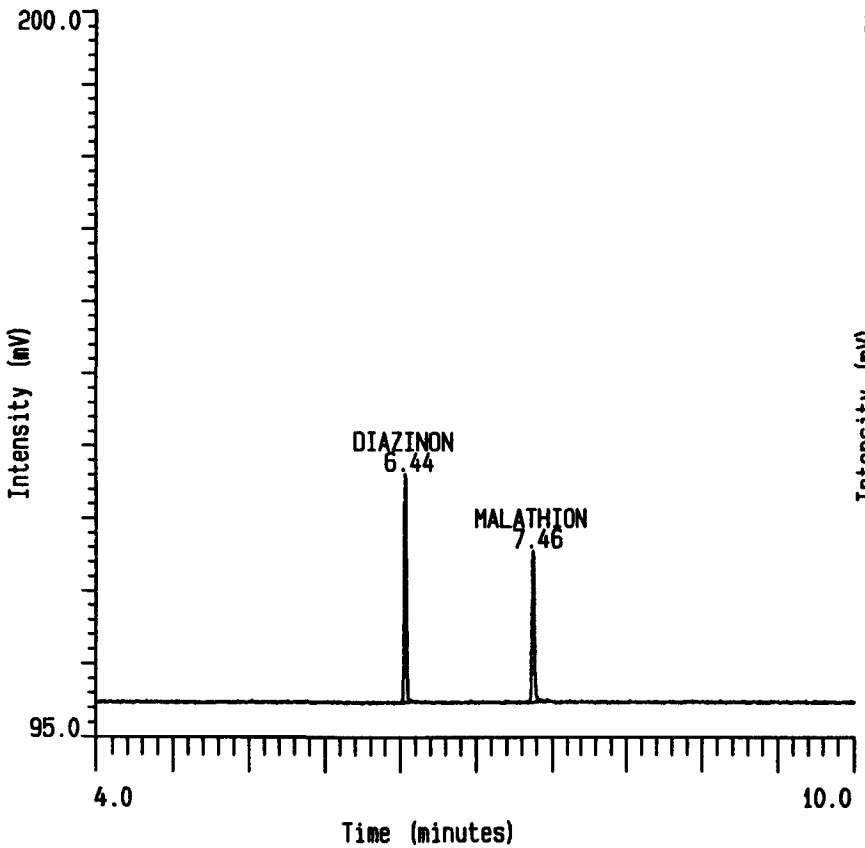
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS SET 3

Date of Report: 21 APR 97 at 10:05:12

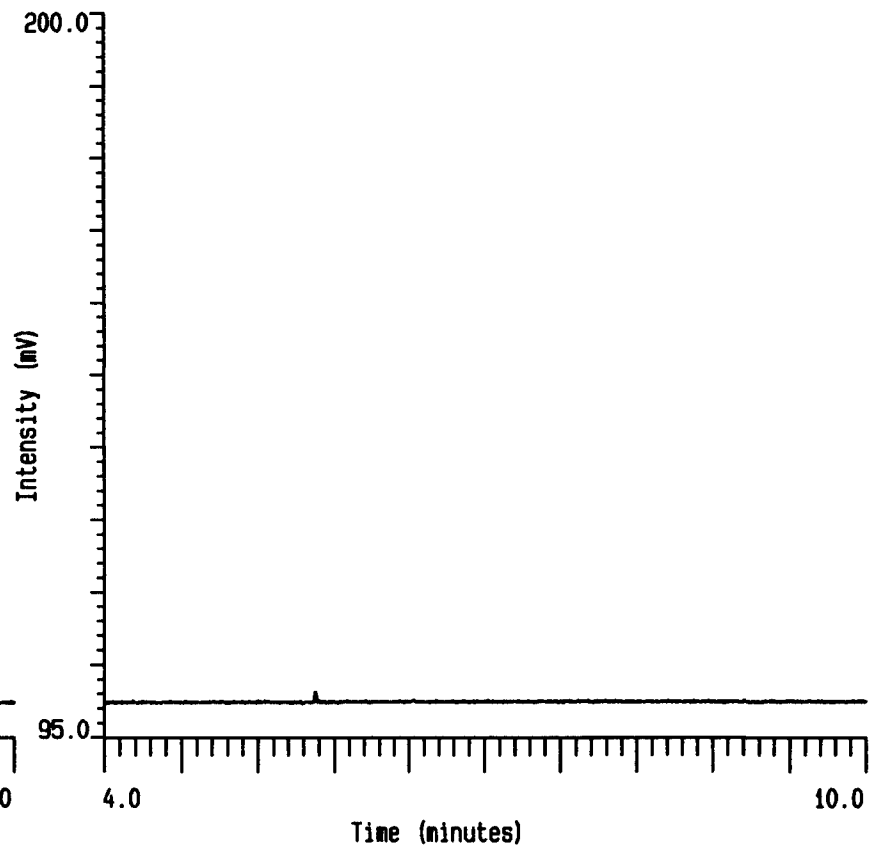
MCDO [43767] 29 767IWBD3, 3, 1
GCMIX-2 NOMINAL 60 NG/ML
Acquired on 10-Apr-1997 at 17:43

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.44	35522	57.520
MALATHION	7.46	30010	59.330



MCDO [43767] 29 767IWBD3, 4, 1
43767-008
Acquired on 10-Apr-1997 at 18:03

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	0.00	0	0
MALATHION	0.00	0	0



ABC Laboratories, Inc.

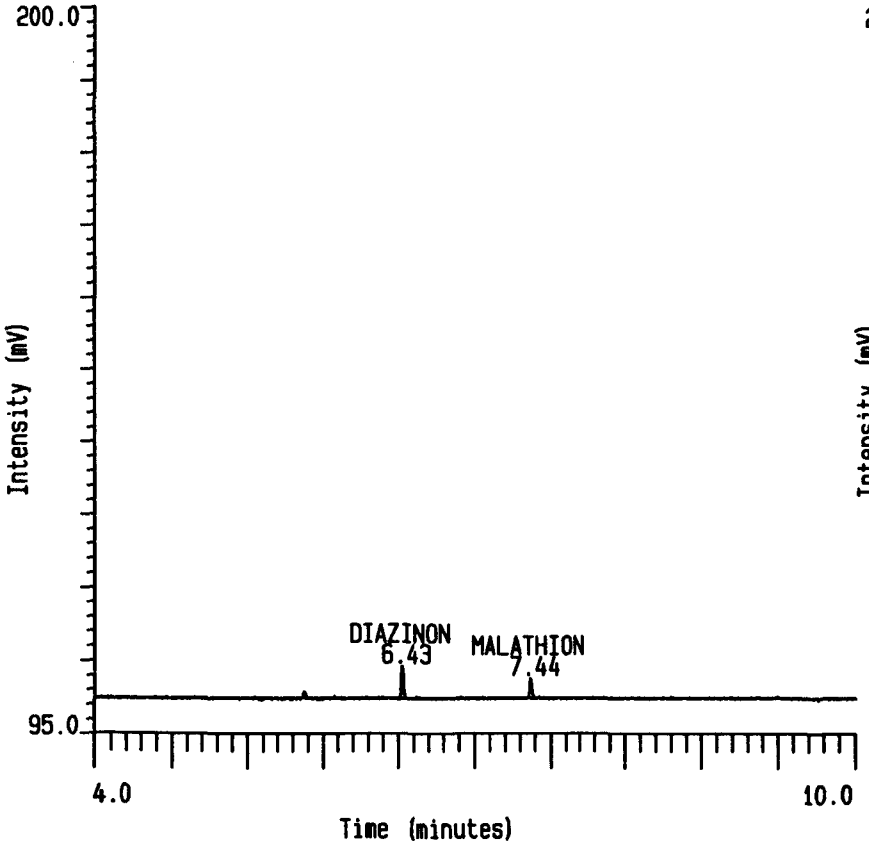
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS SET 3

Date of Report: 21 APR 97 at 10:05:12

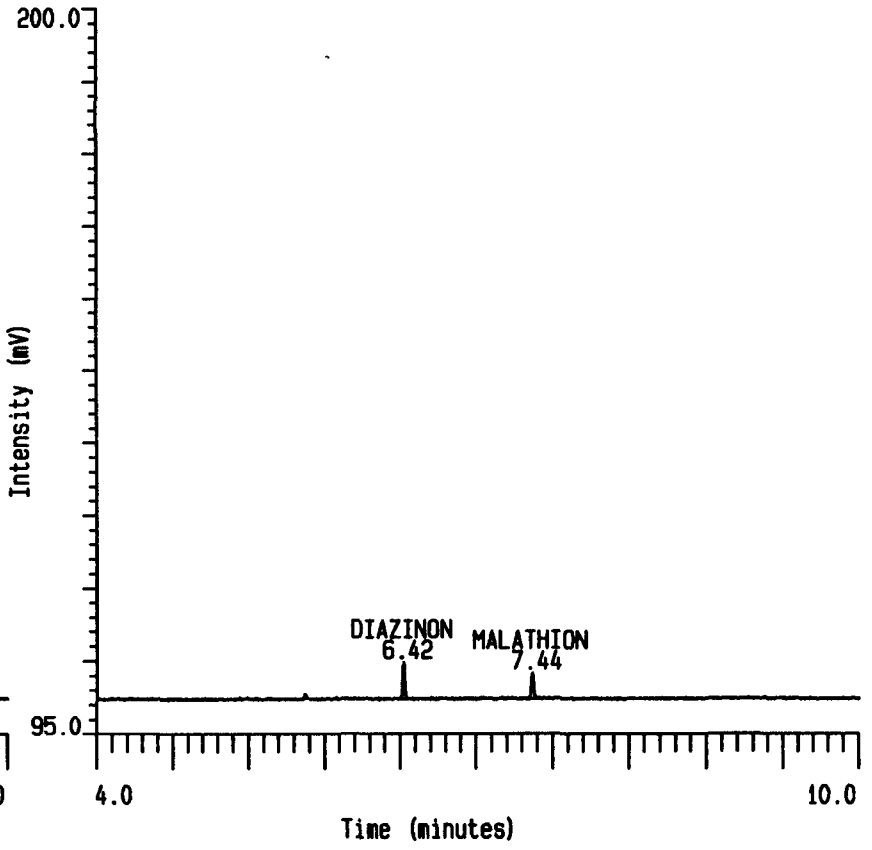
MCDO [43767] 29 767IWBD3,5,1
43767-009
Acquired on 10-Apr-1997 at 18:24

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.43	5008	0.932
MALATHION	7.44	3800	0.836



MCDO [43767] 29 767IWBD3,6,1
43767-010
Acquired on 10-Apr-1997 at 18:44

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.42	5859	1.107
MALATHION	7.44	5210	1.190



ABC Laboratories, Inc.

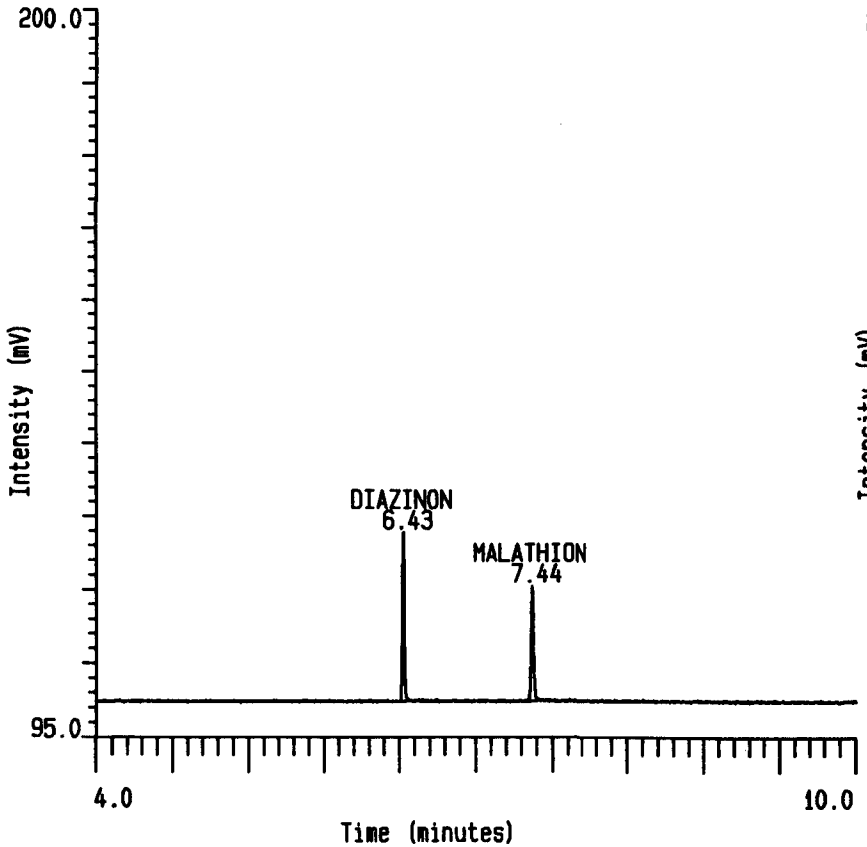
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS SET 3

Date of Report: 21 APR 97 at 10:05:12

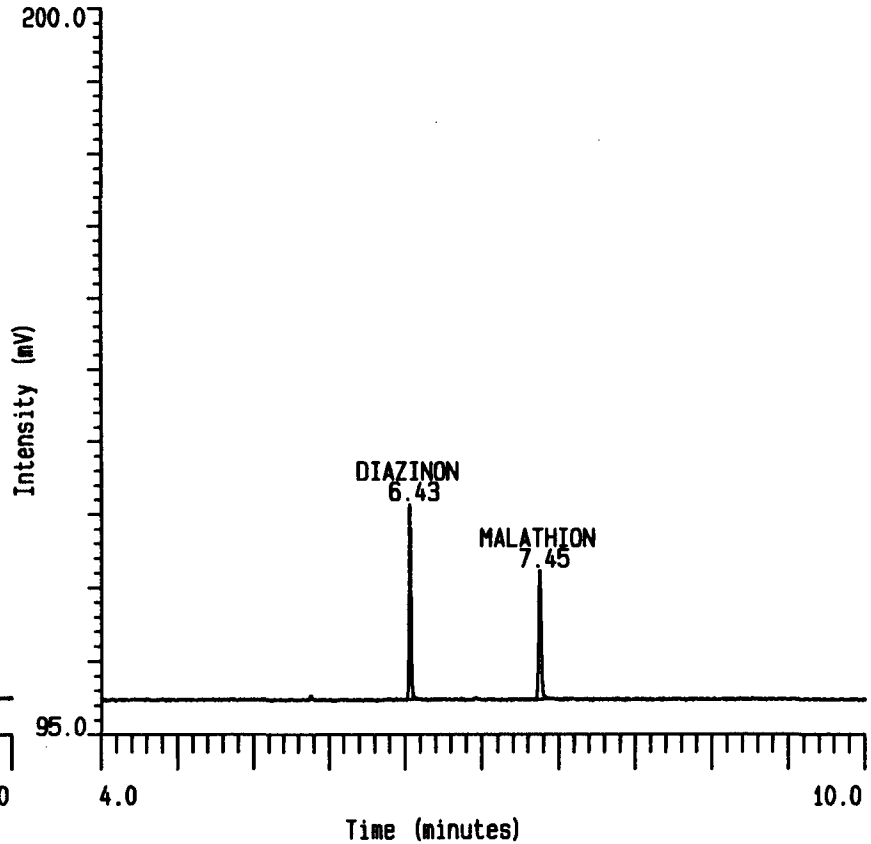
MCDO [43767] 29 767IWBD3,7,1
GCMIX-3 NOMINAL 40 NG/ML STD
Acquired on 10-Apr-1997 at 19:04

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.43	26348	42.468
MALATHION	7.44	22375	43.995



MCDO [43767] 29 767IWBD3,8,1
43767-011
Acquired on 10-Apr-1997 at 19:24

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.43	30017	9.698
MALATHION	7.45	26395	10.414



ABC Laboratories, Inc.

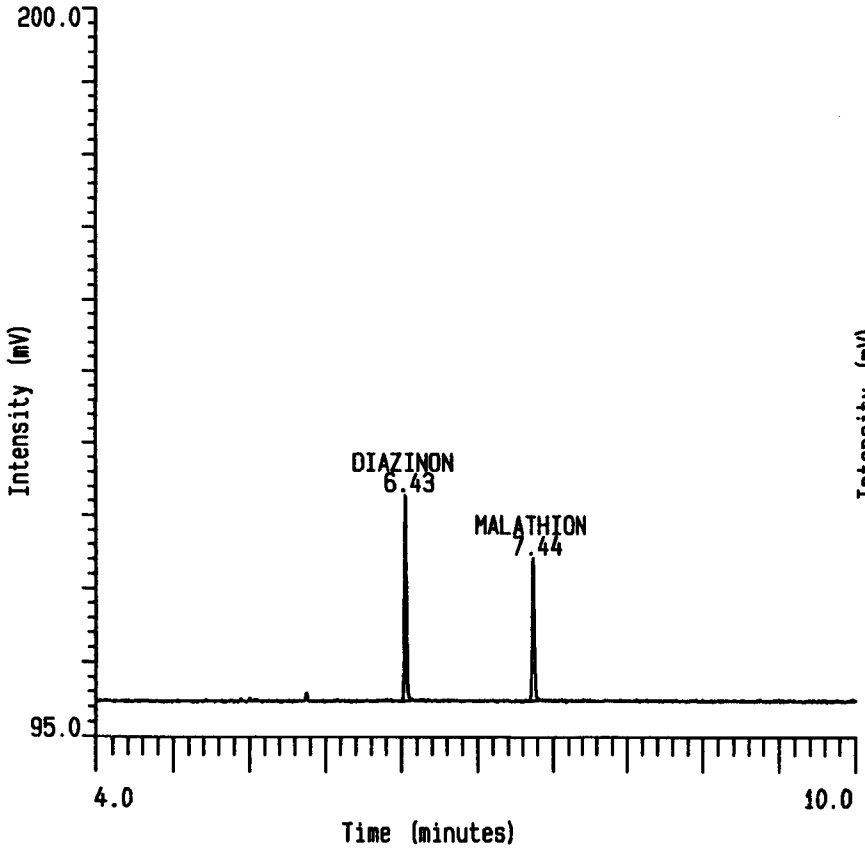
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS SET 3

Date of Report: 21 APR 97 at 10:05:12

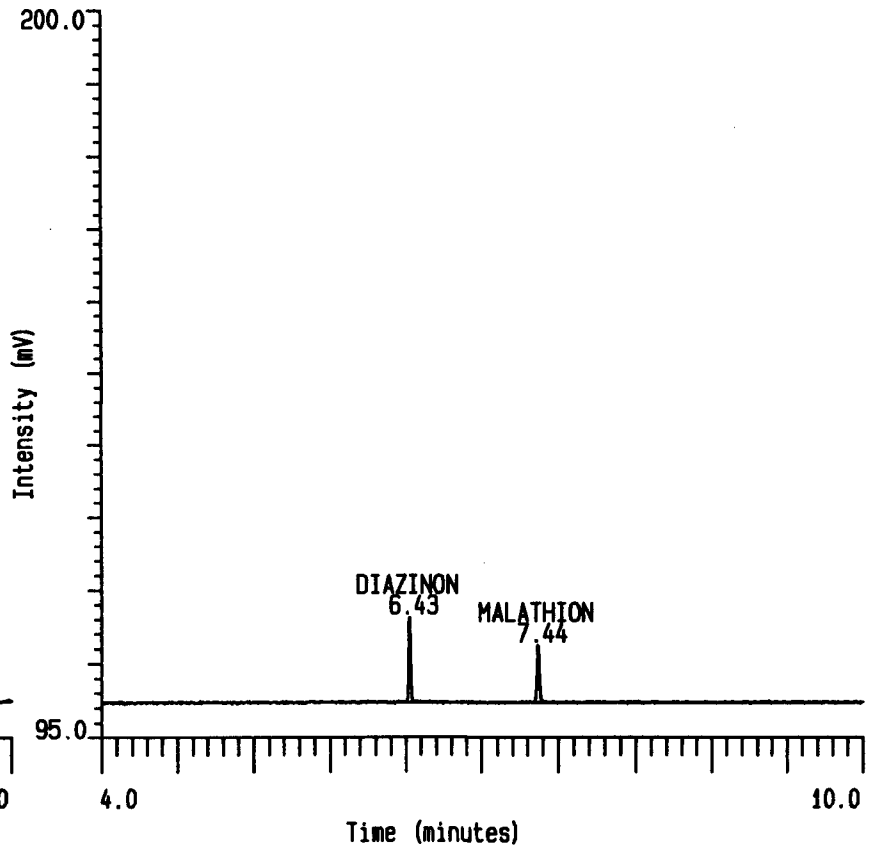
MCDO [43767] 29 767IWBD3, 9, 1
43767-012
Acquired on 10-Apr-1997 at 19:45

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.43	32032	10.359
MALATHION	7.44	27836	10.993



MCDO [43767] 29 767IWBD3, 10, 1
GCMIX-4 NOMINAL 20 NG/ML
Acquired on 10-Apr-1997 at 20:05

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.43	13111	20.752
MALATHION	7.44	11472	22.096



ABC Laboratories, Inc.

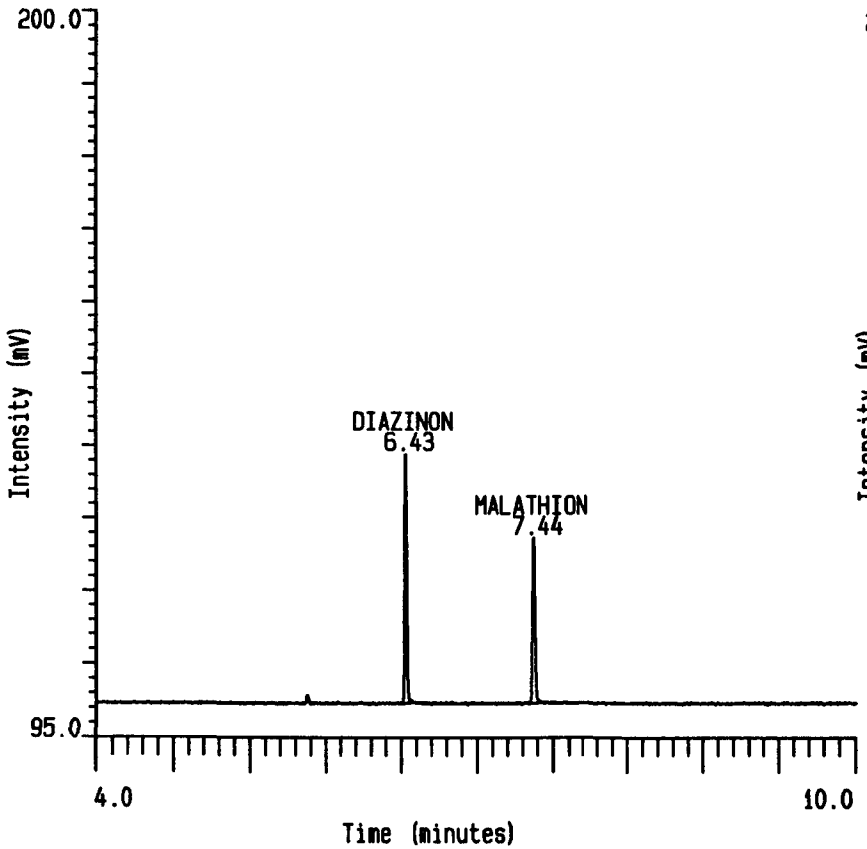
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS SET 3

Date of Report: 21 APR 97 at 10:05:12

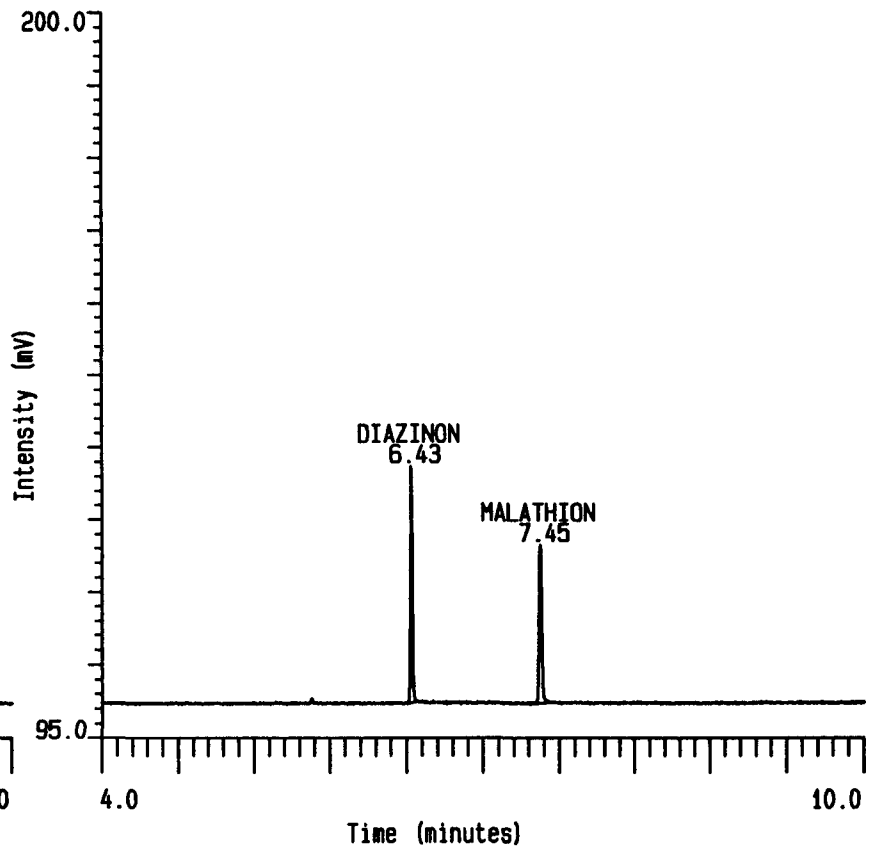
MCDO [43767] 29 767IWBD3, 11, 1
43767-013
Acquired on 10-Apr-1997 at 20:25

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.43	39078	981.976
MALATHION	7.44	33866	1039.686



MCDO [43767] 29 767IWBD3, 12, 1
43767-014
Acquired on 10-Apr-1997 at 20:45

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.43	35712	896.382
MALATHION	7.45	32266	989.862



ABC Laboratories, Inc.

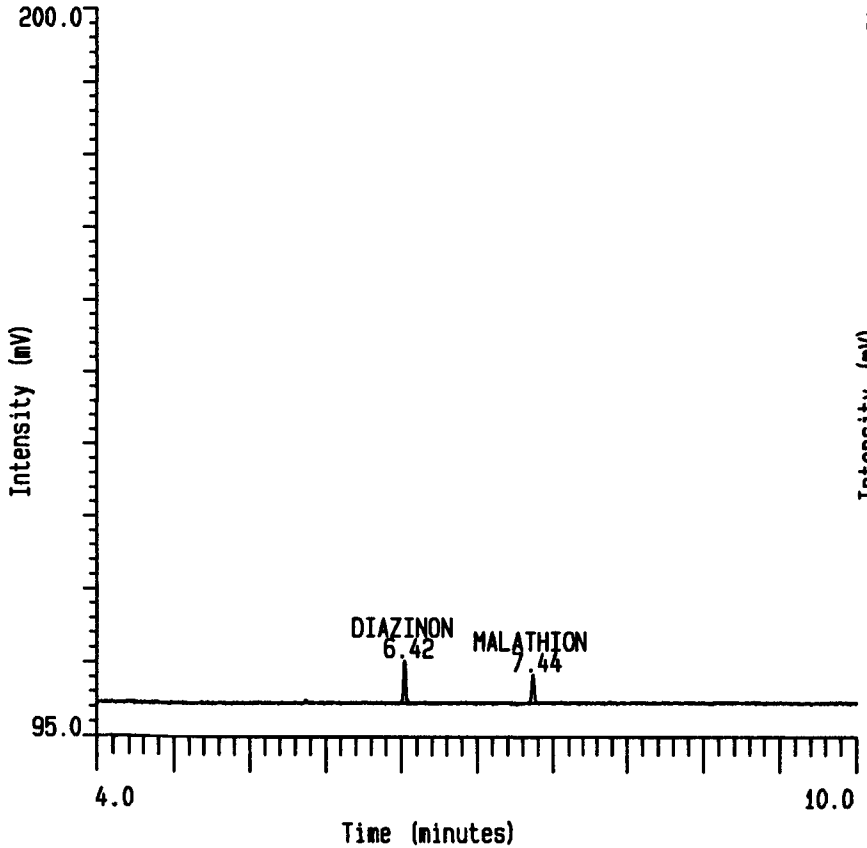
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS SET 3

Date of Report: 21 APR 97 at 10:05:12

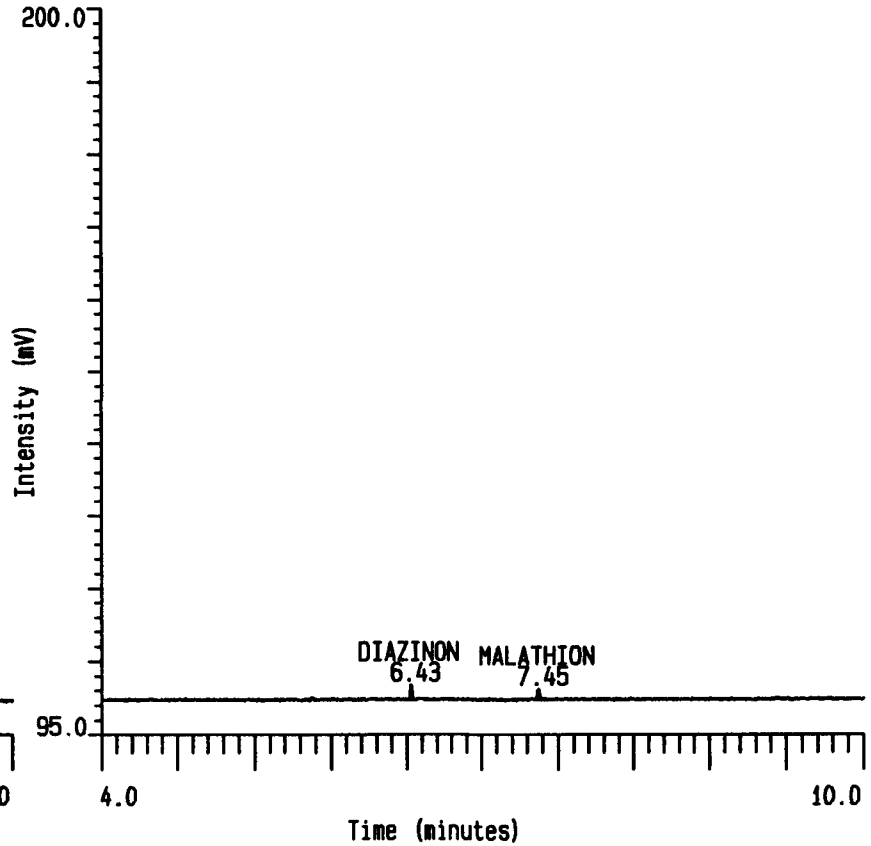
MCDO [43767] 29 767IWBD3, 13, 1
GCMIX-5 NOMINAL 10 NG/ML
Acquired on 10-Apr-1997 at 21:05

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.42	6954	10.650
MALATHION	7.44	5750	10.603



MCDO [43767] 29 767IWBD3, 14, 1
GCMIX-6 NOMINAL 4 NG/ML
Acquired on 10-Apr-1997 at 21:26

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.43	2567	3.453
MALATHION	7.45	2223	3.519



[43767] 29 767IWBD3 Page 1
Reported on 21-APR-1997 at 15:13
Modified on 21-APR-1997 at 09:57

List Calibration File

CALIBRATION HEADER INFORMATION

Calibration Title : 43767 INNER WHOLE BODY DOSIMETERS SET 3
General :
Calibration type..... External standard
Units..... NG/ML OR UG
Calibration base..... Area
Reference Peak Identification :
Reference window..... 5.0 %
Minimum window..... 0.50 mins
Peak threshold..... 0.0 %
Uncalibrated Peaks Response Factor :
Response factor source..... User set response factor
Response factor..... 0.0000
Additional Information :
Source library..... None
Initialise on 1st standard..... No
Variation tolerance..... 100.00 %
Calibrant Peak Identification :
Calibrant window..... 0.20 mins
Calibrant threshold..... 0.0 %
Response Factor Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... 1 / Y
Retention Value Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... 1 / Y
Timed Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... 1 / Y
No group information entered.

[43767] 29 767IWBD3 Page 2
Reported on 21-APR-1997 at 15:13
Modified on 21-APR-1997 at 09:57

Peak name : DIAZINON
Expected retention time : 6.45 mins (RT range : 6.35 - 6.55 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	3.9700	646.6168	1
05	9.9200	701.0217	1
04	19.8000	662.1805	1
03	39.7000	663.6697	1
02	59.5000	597.0080	1
01	99.2000	604.7667	1

Peak name : MALATHION
Expected retention time : 7.47 mins (RT range : 7.37 - 7.57 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	4.0800	544.9572	1
05	10.2000	563.7379	1
04	20.4000	562.3483	1
03	40.8000	548.3993	1
02	61.2000	490.3516	1
01	102.0000	491.1755	1

SAMPLE TRACKING FORM

Customer Name: ARTF	Study Director: Loren C. Schrier	Test Material: Diazinon and Malathion	Matrix: IWBD
ARTF Protocol: ARF003	ABC Study Number: 43767	Inner Cotton Whole Body Dosimeters Method Validation Set 1R	

Extraction (Section II.C.1, C.2)	Partitioning (Section II.C.3)	Florisil Cleanup (Section II.C.4)	Vial	GC/FPD Analysis (Section II.E)	Chromatography review:
4-23-97	4-23-97	4-23-97	4-23-97	4-23-97 24 Apr 97	24 Apr 97
					Spreadsheet entry by: 24 Apr 97

ABC Lab Number	Sample Identification (Designate Part of IWBD; e.g. "Upper Arms")	Extraction Volume	Aliquot Taken	Hexane Volume, Aliquot Taken for Florisil Cleanup	Final Volume and Dilutions	Fortified by: 4-23-97 Witnessed by: 23 Apr 97
43767-001R	Control upper arms	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	2.50 mL	
43767-002R	Control + nominal 1 ug Each upper arms	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	2.50 mL	Fortify with 1.0 mL of 0.992 ug/mL diazinon and 1.02 ug/mL malathion mixed fortification solution (Fort-3)
43767-003R	Control + nominal 1 ug Each front torso	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	2.50 mL	Fortify with 1.0 mL of 0.992 ug/mL diazinon and 1.02 ug/mL malathion mixed fortification solution (Fort-3)
43767-004R	Control + nominal 10 ug Each lower arms	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	4.00 mL	Fortify with 1.0 mL of 9.92 ug/mL diazinon and 10.2 ug/mL malathion mixed fortification solution (Fort-2)
43767-005R	Control + nominal 10 ug Each rear torso	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	4.00 mL	Fortify with 1.0 mL of 9.92 ug/mL diazinon and 10.2 ug/mL malathion mixed fortification solution (Fort-2)
43767-006R	Control + nominal 1000 ug Each lower legs	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	10.0 mL, then dilute 0.50 mL to 15.5 mL	Fortify with 1.0 mL of 992 ug/mL diazinon and 1020 ug/mL malathion mixed fortification solution (Fort-1)
43767-007R	Control + nominal 1000 ug Each upper legs	1000 mL	50.0 mL	20.0 mL, then 8.00 mL	10.0 mL, then dilute 0.50 mL to 15.5 mL	Fortify with 1.0 mL of 992 ug/mL diazinon and 1020 ug/mL malathion mixed fortification solution (Fort-1)

Remarks: Dilution factor for the high fortification level is 31. 4-23-97

Acetone: B0369
Hexane: BN 237
Ethyl Ether: BM 863
Florisil: Fisher Lot 964720
Water: Labconco DI

Checked by 4-24-97 Approved by 25 Apr 97

[43767] 29 767IWBD7 Page 1
Reported on 24-APR-1997 at 14:30
Modified on 24-APR-1997 at 09:15

List Run Sequence File

ANALYST NAME..... HEIDI ANDERSON
43767 INNER WHOLE BODY DOSIMETERS REPEATED SET

ANALYSIS INFORMATION

Analysis name..... 767IWBD7
Method name..... 767IWBD7
Calibration name..... 767IWBD7
Calibration sequence..... Average Standard
User parameter 1 name..... FINAL VOLUME
User parameter 2 name..... FACTOR 1
User parameter 3 name..... FACTOR 2

SAMPLE SUMMARY

SAMPLE NUMBER	LIMS ID	SAMPLE NAME
1	----------	SOLVENT BLANK
2	----------	GCMIX-1 NOMINAL 100 NG/ML
3	----------	GCMIX-2 NOMINAL 60 NG/ML
4	----------	43767-001R
5	----------	43767-002R
6	----------	43767-003R
7	----------	GCMIX-3 NOMINAL 40 NG/ML STD
8	----------	43767-004R
9	----------	43767-005R
10	----------	GCMIX-4 NOMINAL 20 NG/ML
11	----------	43767-006R
12	----------	43767-007R
13	----------	GCMIX-5 NOMINAL 10 NG/ML
14	----------	GCMIX-6 NOMINAL 4 NG/ML

[43767] 29 767IWBD7 Page 2
Reported on 24-APR-1997 at 14:30
Modified on 24-APR-1997 at 09:15

SAMPLE INFORMATION

SAMPLE NUMBER	TYPE	CALIB LEVEL	UPDATE RT	UPDATE RF	AMOUNT	NUM INJ	BOT NUM
1	Sa	--	-	-	1.00000	1	1
2	St	01	N	I	1.00000	1	2
3	St	02	N	I	1.00000	1	2
4	Sa	--	-	-	1.00000	1	3
5	Sa	--	-	-	1.00000	1	5
6	Sa	--	-	-	1.00000	1	5
7	St	03	N	I	1.00000	1	7
8	Sa	--	-	-	1.00000	1	8
9	Sa	--	-	-	1.00000	1	9
10	St	04	N	I	1.00000	1	10
11	Sa	--	-	-	1.00000	1	11
12	Sa	--	-	-	1.00000	1	12
13	St	05	N	I	1.00000	1	13
14	St	06	N	I	1.00000	1	14

USER PARAMETER VALUES

SAMPLE	FINAL VOLUME	FACTOR 1	FACTOR 2
1	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000
4	2.50000	20.00000	400.00000
5	2.50000	20.00000	400.00000
6	2.50000	20.00000	400.00000
7	1.00000	1.00000	1.00000
8	4.00000	20.00000	400.00000
9	4.00000	20.00000	400.00000
10	1.00000	1.00000	1.00000
11	10.00000	310.00000	200.00000
12	10.00000	310.00000	200.00000
13	1.00000	1.00000	1.00000
14	1.00000	1.00000	1.00000

[43767] 29 767IWBD7 Page 3
Reported on 24-APR-1997 at 14:30
Modified on 24-APR-1997 at 09:15

INTERNAL/DILUTION STANDARDS

SAMPLE NUMBER	ISTD1 AMOUNT	ISTD2 AMOUNT	ISTD3 AMOUNT	DIL1 AMOUNT	DIL2 AMOUNT
1	1.00000	1.00000	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000	1.00000	1.00000
4	1.00000	1.00000	1.00000	1.00000	1.00000
5	1.00000	1.00000	1.00000	1.00000	1.00000
6	1.00000	1.00000	1.00000	1.00000	1.00000
7	1.00000	1.00000	1.00000	1.00000	1.00000
8	1.00000	1.00000	1.00000	1.00000	1.00000
9	1.00000	1.00000	1.00000	1.00000	1.00000
10	1.00000	1.00000	1.00000	1.00000	1.00000
11	1.00000	1.00000	1.00000	1.00000	1.00000
12	1.00000	1.00000	1.00000	1.00000	1.00000
13	1.00000	1.00000	1.00000	1.00000	1.00000
14	1.00000	1.00000	1.00000	1.00000	1.00000

PROCESSING ORDER

SAMPLE NUMBER	TYPE
2	Standard
3	Standard
7	Standard
10	Standard
13	Standard
14	Standard
1	Sample
4	Sample
5	Sample
6	Sample
8	Sample
9	Sample
11	Sample
12	Sample

Gas Chromatographic Instrument Parameters Form

ABC Laboratory Study Number: 43767
Customer Identification: ARTF

Instrument: HP 5890 Series II Material ID# 1652-0120
Autoinjector: HP 7673B Material ID# 1625-802A

Column: HP-5MS, 30 M X 0.25 mm, 0.25 μm film thickness
Serial#: 56253614

Detector Type: FPD/P

Electrometer: Range 4; Attenuation 0

Temperatures:
- Injector (°C): 230
- Detector (°C): 230
- Column:
  - Initial Temp.(°C): 95
  - Initial Time: 1.0 min.
  - Program Rate 1: 30 °C/min to 230 °C, hold 4 min
  - Program Rate 2: 40 °C/min to 290 °C, hold 4 min
  - Equilibration Time: 1 min

Carrier Gas Flow Rate: He 1.6 mL/min
Air Flow Rate: 100 mL/min.
Hydrogen Flow Rate: 75 mL/min.
Purge Valve: Off at 0 min, on at 0.75 min

Injection Volume: 2 μL

Run Sequence File: 767IW8D7

Quantitation Standards: GC mix - 1 → 6 Inclusive

Prepared By: [signature] Date: 24 Apr 97

Checked By: CY Guo Date: 24 Apr 97

MCDO [43767] 29 767IWBD7

ABC Laboratories, Inc.
Sample Information Report ver 3.3

Report Date: 24 APR 97 at 14:57:25
Page 1

Sample Name	No.	Type	Level	User Parameter 1 FINAL VOLUME	User Parameter 2 FACTOR 1	User Parameter 3 FACTOR 2
SOLVENT BLANK	1	SA		1.00000	1.00000	1.00000
GCMIX-1 NOMINAL 100 NG/ML	2	ST	01	1.00000	1.00000	1.00000
GCMIX-2 NOMINAL 60 NG/ML	3	ST	02	1.00000	1.00000	1.00000
43767-001R	4	SA		2.50000	20.00000	400.00000
43767-002R	5	SA		2.50000	20.00000	400.00000
43767-003R	6	SA		2.50000	20.00000	400.00000
GCMIX-3 NOMINAL 40 NG/ML STD	7	ST	03	1.00000	1.00000	1.00000
43767-004R	8	SA		4.00000	20.00000	400.00000
43767-005R	9	SA		4.00000	20.00000	400.00000
GCMIX-4 NOMINAL 20 NG/ML	10	ST	04	1.00000	1.00000	1.00000
43767-006R	11	SA		10.00000	310.00000	200.00000
43767-007R	12	SA		10.00000	310.00000	200.00000
GCMIX-5 NOMINAL 10 NG/ML	13	ST	05	1.00000	1.00000	1.00000
GCMIX-6 NOMINAL 4 NG/ML	14	ST	06	1.00000	1.00000	1.00000

MCDO [43767] 29 7671WBD7

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: DIAZINON

Report Date: 24 APR 97
Time: 14:57:25
Page: 1

Sample Name	SMP #	INJ #	RT(mins)	Area	NG/ML OR UG	CAL. RANG	Peak Type	Bad INJ
SOLVENT BLANK	1	1	0.00	0	0.000	UNDR	B	---
GCMIX-1 NOMINAL 100 NG/ML	2	1	6.39	86228	104.961		OBF	---
GCMIX-2 NOMINAL 60 NG/ML	3	1	6.38	46846	57.027		OB	---
43767-001R	4	1	0.00	0	0.000	UNDR	BF	---
43767-002R	5	1	6.38	7245	1.103		OB	---
43767-003R	6	1	6.38	7332	1.116		OBF	---
GCMIX-3 NOMINAL 40 NG/ML STD	7	1	6.38	30743	37.426		OB	---
43767-004R	8	1	6.38	39053	9.508		OB	---
43767-005R	9	1	6.38	40821	9.939		OB	---
GCMIX-4 NOMINAL 20 NG/ML	10	1	6.38	15928	19.394		OBF	---
43767-006R	11	1	6.38	48994	924.434		OB	---
43767-007R	12	1	6.40	45956	867.113		OB	---
GCMIX-5 NOMINAL 10 NG/ML	13	1	6.39	7734	9.420		OB	---
GCMIX-6 NOMINAL 4 NG/ML	14	1	6.37	3714	4.527		OB	---

MCDO [43767] 29 767IWBD7

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: MALATHION

Report Date: 24 APR 97
Time: 14:57:25
Page: 1

Sample Name	SMP #	INJ #	RT(mins)	Area	NG/ML OR UG	CAL. RANG	Peak Type	Bad INJ
SOLVENT BLANK	1	1	0.00	0	0.000	UNDR	O	---
GCMIX-1 NOMINAL 100 NG/ML	2	1	7.38	74387	108.330		OB	---
GCMIX-2 NOMINAL 60 NG/ML	3	1	7.37	40028	58.340		OB	---
43767-001R	4	1	0.00	0	0.000	UNDR	OB	---
43767-002R	5	1	7.38	5717	1.052		OBF	---
43767-003R	6	1	7.37	5807	1.069		O	---
GCMIX-3 NOMINAL 40 NG/ML STD	7	1	7.38	26724	38.983		OB	---
43767-004R	8	1	7.37	30860	9.000		OB	---
43767-005R	9	1	7.38	34414	10.034		OBF	---
GCMIX-4 NOMINAL 20 NG/ML	10	1	7.37	13175	19.269		OB	---
43767-006R	11	1	7.38	41939	947.368		OB	---
43767-007R	12	1	7.39	39324	888.393		OBF	---
GCMIX-5 NOMINAL 10 NG/ML	13	1	7.39	6677	9.815		OB	---
GCMIX-6 NOMINAL 4 NG/ML	14	1	7.37	3166	4.707		OBF	---

Acquisition and Peak Processing Parameters Report Print Date and Time : 24 APR 97 15:01:17
Page : 1

MCDO [43767] 29 767IWBD7 Based on Sample Number : 1 Injection Number : 1

ACQUISITION PARAMETERS

Data Collection :

Length of Run..... 14.99 mins
Post Injection Delay..... 0.00 mins
Sampling Rate..... 15.00 Hz

PEAK PROCESSING PARAMETERS

Auto Process Parameters :

Peak Threshold..... 2.00
Baseline Test..... 2
Peak Trend..... 2

Separation Parameters :

Shoulder Sensitivity..... 0.10
Rider Sensitivity..... 0.05

Rejection Parameters :

Minimum Peak Width..... 0.00 secs
Minimum Peak Height..... 0.00 uV
Minimum Peak Area..... 1000.00 uVs
Ignore Flat Top Peak..... No

User Imposed Action Control :

Forced Baseline..... No
Suppress Integration..... Yes
Tangent Skimming..... No
Shoulder Detection..... No
Data Bunching..... No
Negative Detection..... No

Integration Modes :

Retention Time Integration..... No
Square Root Area and Height..... No

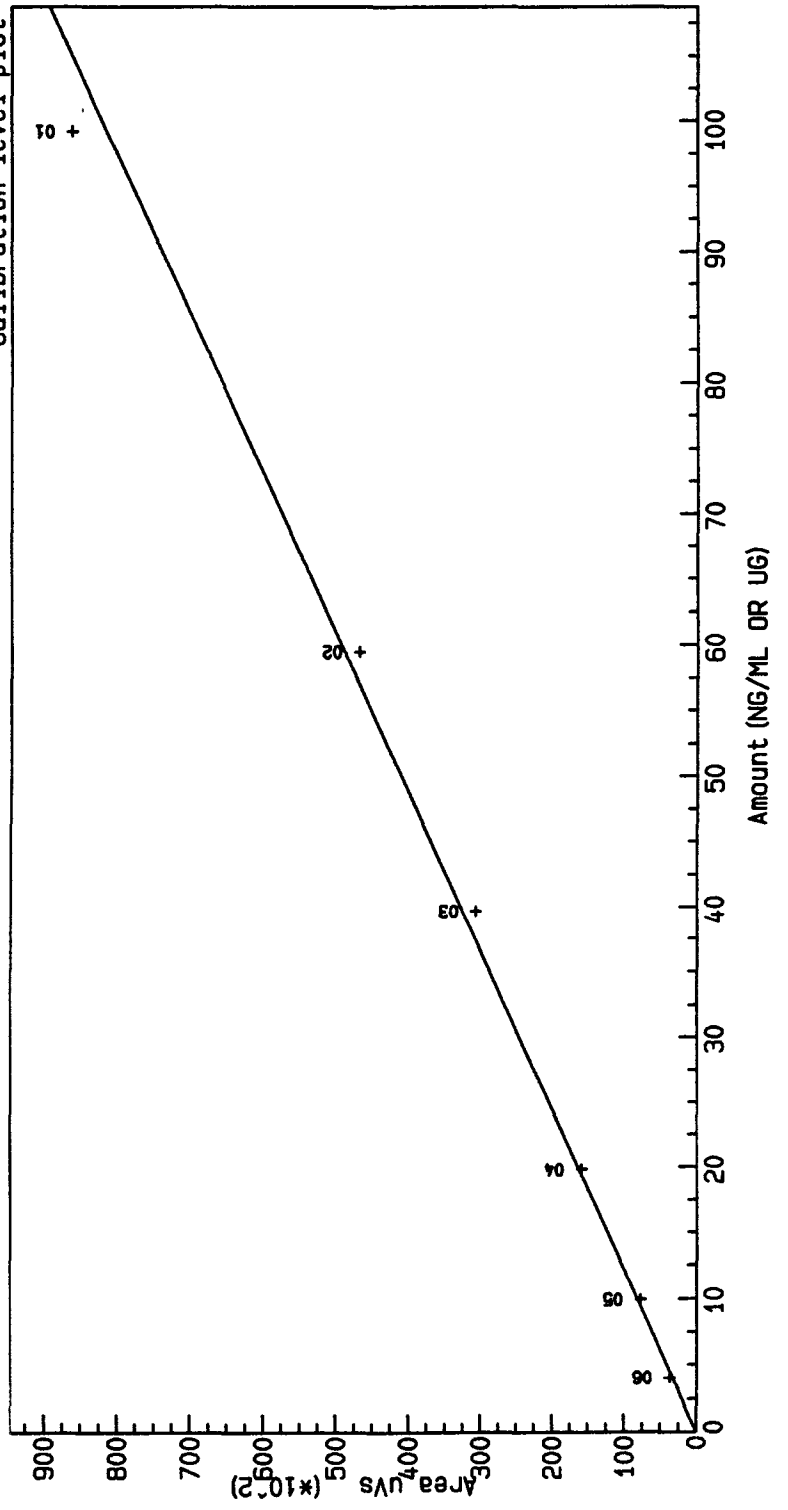
PROCESSING ACTIONS

Time (mins)	Force Baseline	Integrate Suppress	Tangent Skim	Bunch Size	Shoulder Detect	Negative Detect
0.00	--	SI	_	0	--	--
6.30	--	ES	_	0	--	--
6.55	--	SI	_	0	--	--
7.30	--	ES	_	0	--	--
7.60	--	SI	_	0	--	--

These parameters apply to all injections of set 767IWBD7 with no exceptions

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767IWBD7.
43767 INNER WHOLE BODY DOSIMETERS REPEATED SET
Peak : DIAZINON



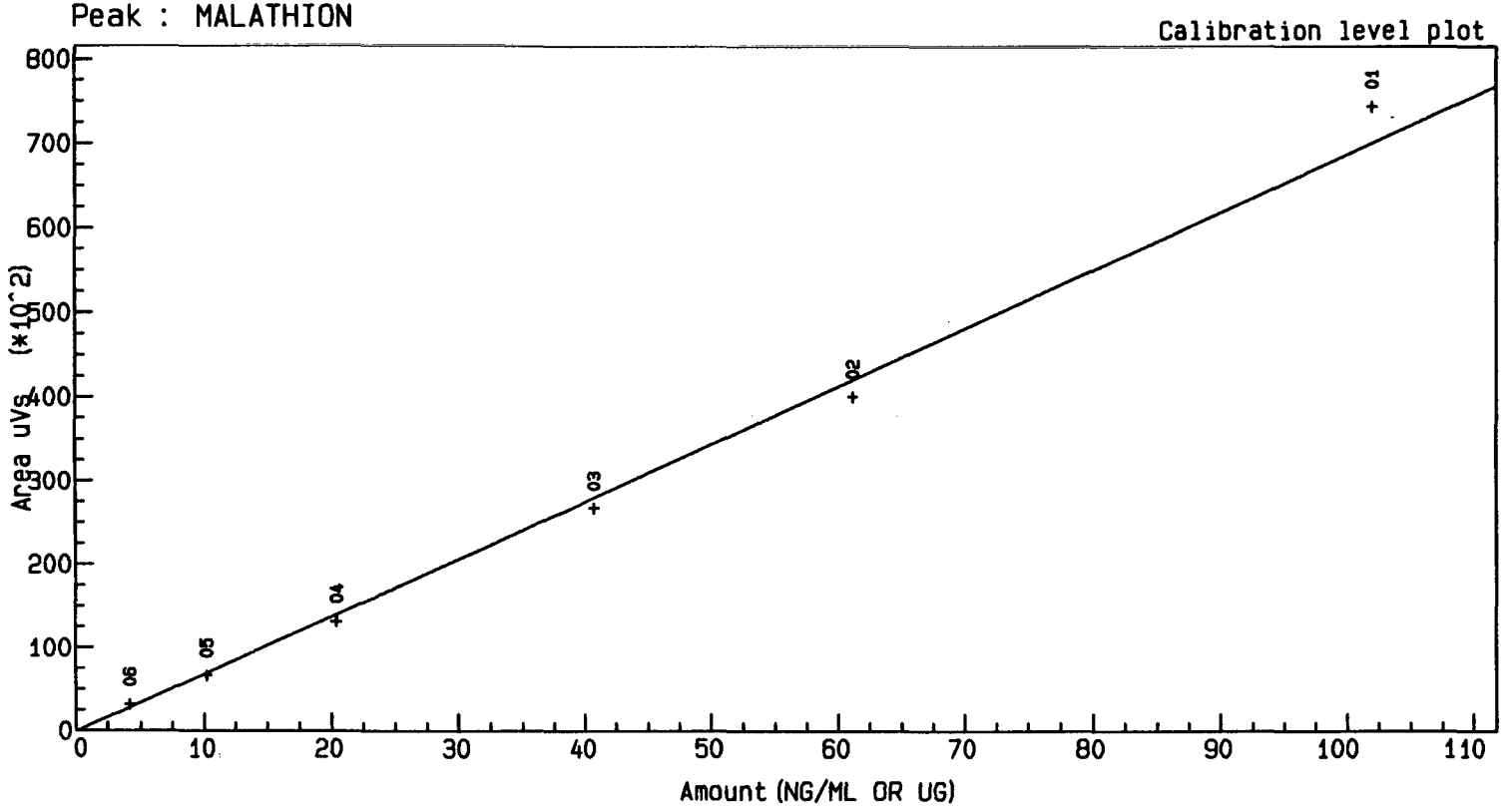
Constant : -5.18765
1st degree : 8.21570E+2

Curve fit : Linear
Correlation coefficient : 0.99682
Standard error : 2.76188E+3

Reported on 24-APR-1997 at 15:01

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767IWBD7.
43767 INNER WHOLE BODY DOSIMETERS REPEATED SET
Peak : MALATHION



Constant : -6.902827E+1
1st degree : 6.87304E+2

Curve fit : Linear
Correlation coefficient : 0.99648
Standard error : 2.51058E+3

Reported on 24-APR-1997 at 15:01

ABC Laboratories, Inc.

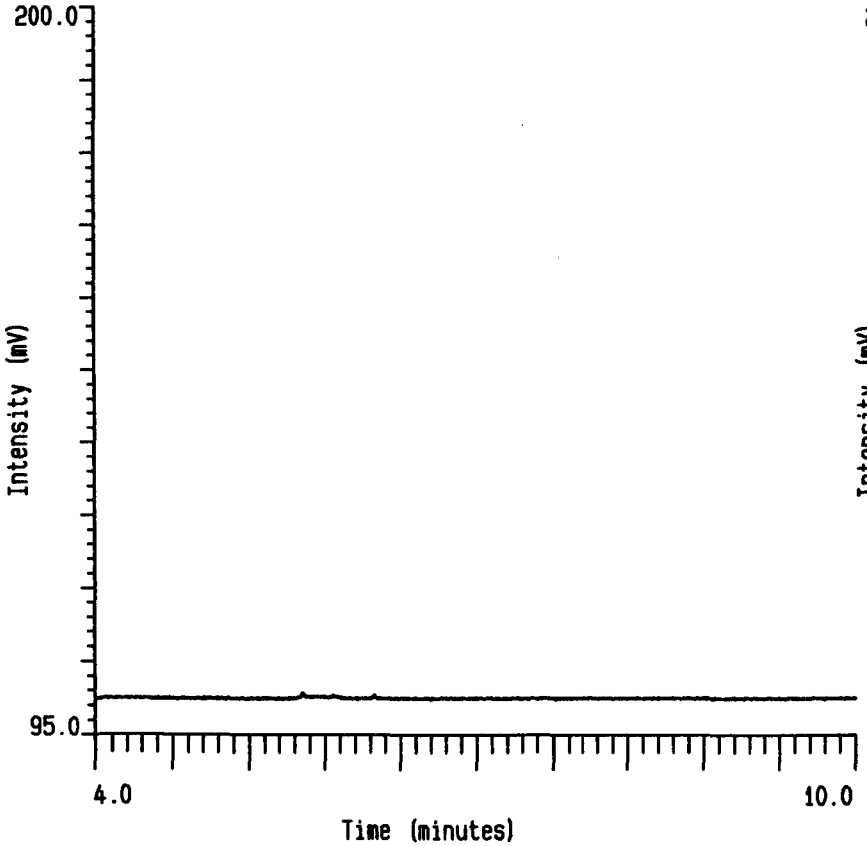
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS REPEATED SET

Date of Report: 24 APR 97 at 15:02:47

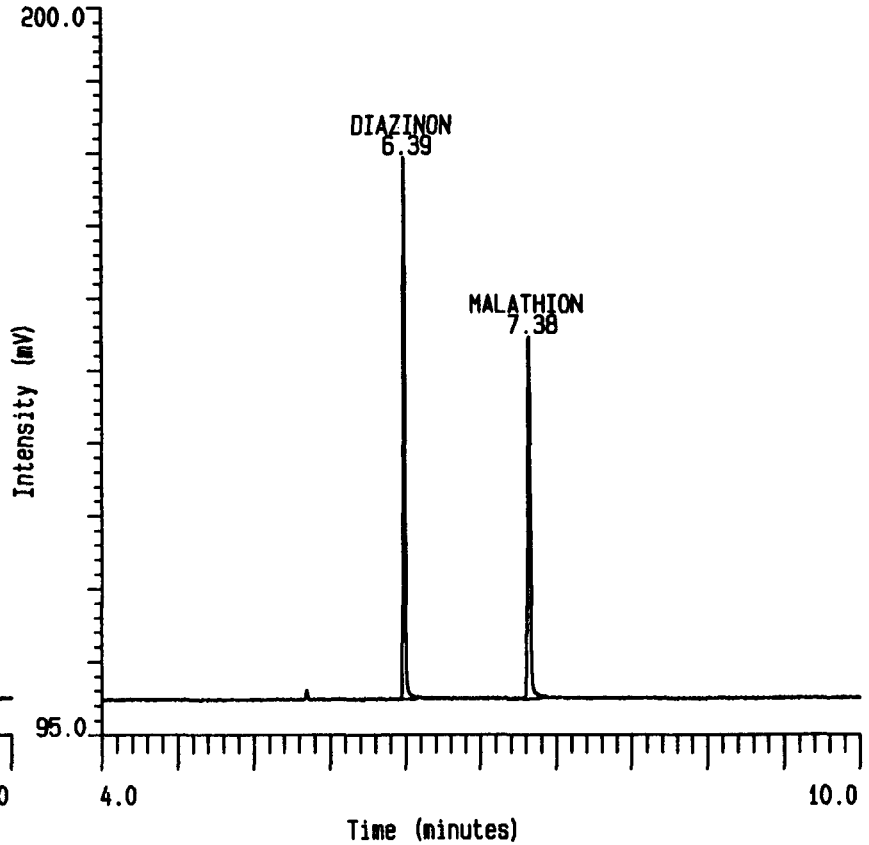
MCDO [43767] 29 767IWBD7,1,1
SOLVENT BLANK
Acquired on 24-Apr-1997 at 09:46

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	0.00	0	0
MALATHION	0.00	0	0



MCDO [43767] 29 767IWBD7,2,1
GCMIX-1 NOMINAL 100 NG/ML
Acquired on 24-Apr-1997 at 10:06

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.39	86228	104.961
MALATHION	7.38	74387	108.330



ABC Laboratories, Inc.

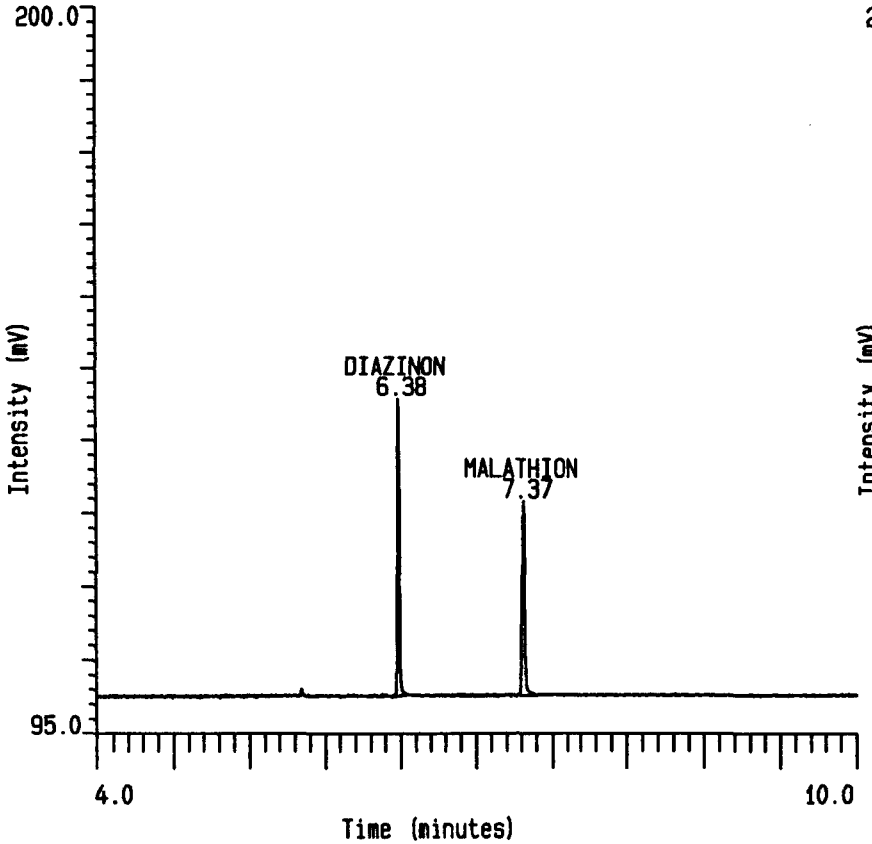
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS REPEATED SET

Date of Report: 24 APR 97 at 15:02:47

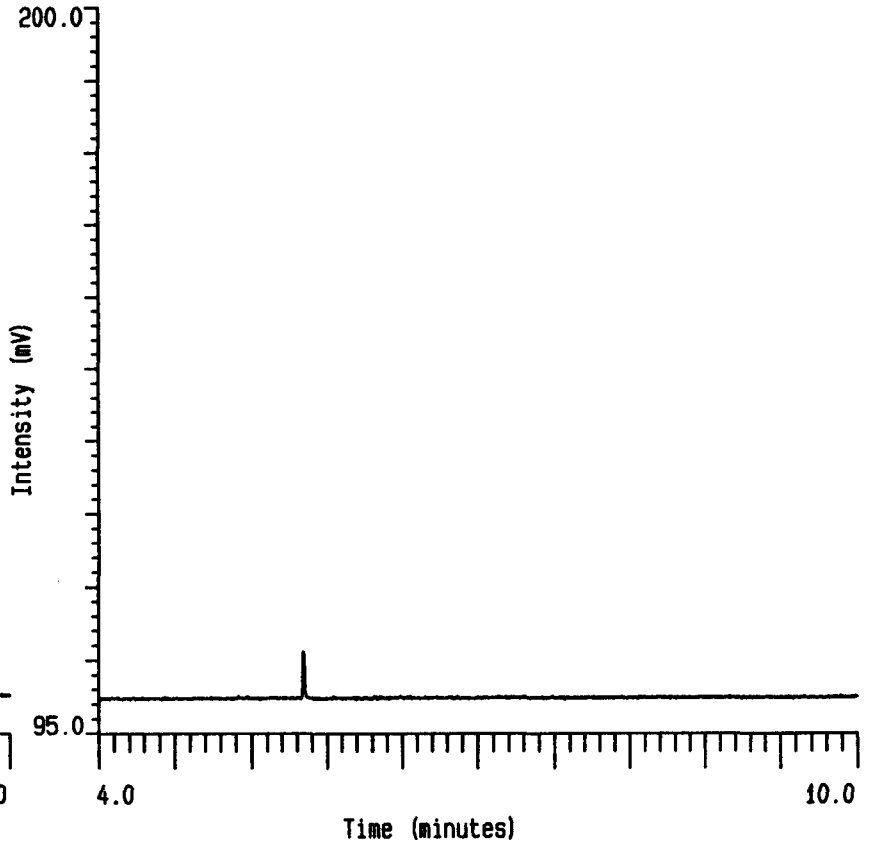
MCDO [43767] 29 767IWBD7,3,1
GCMIX-2 NOMINAL 60 NG/ML
Acquired on 24-Apr-1997 at 10:26

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.38	46846	57.027
MALATHION	7.37	40028	58.340



MCDO [43767] 29 767IWBD7,4,1
43767-001R
Acquired on 24-Apr-1997 at 10:46

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	0.00	0	0
MALATHION	0.00	0	0



ABC Laboratories, Inc.

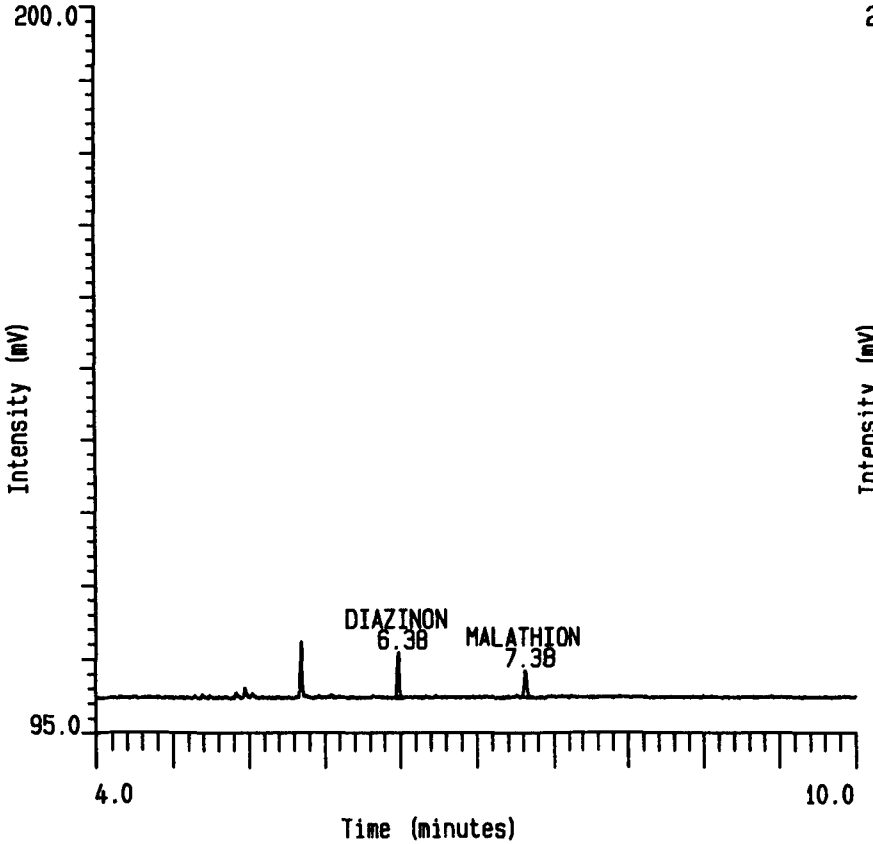
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS REPEATED SET

Date of Report: 24 APR 97 at 15:02:47

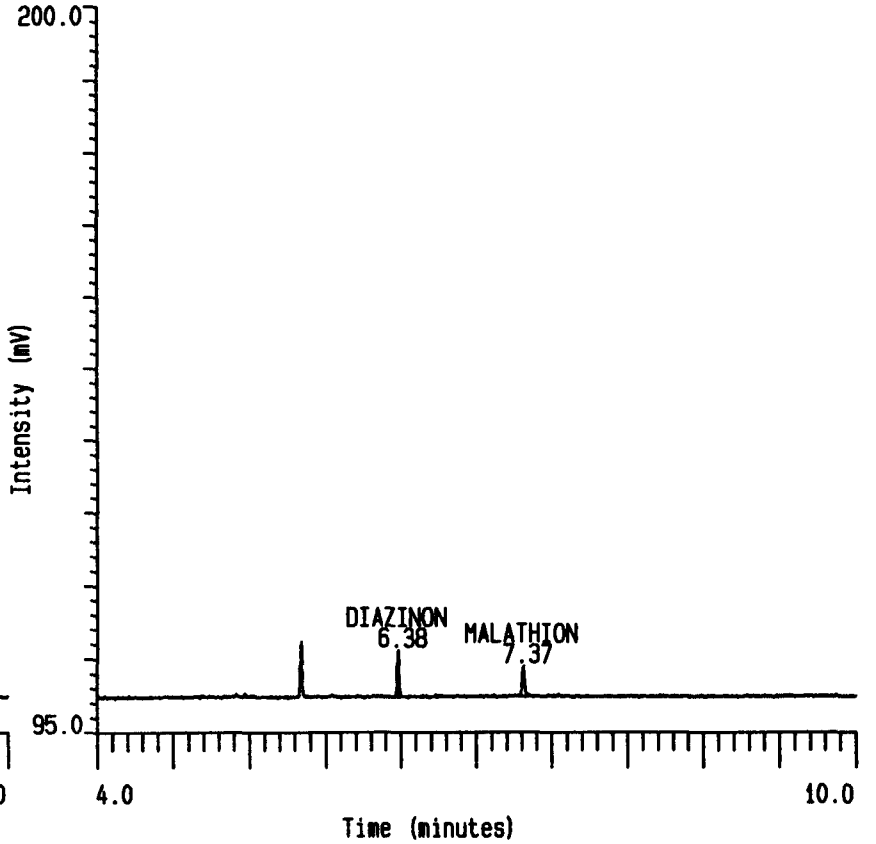
MCDO [43767] 29 767IWBD7,5,1
43767-002R
Acquired on 24-Apr-1997 at 11:07

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.38	7245	1.103
MALATHION	7.38	5717	1.052



MCDO [43767] 29 767IWBD7,6,1
43767-003R
Acquired on 24-Apr-1997 at 11:27

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.38	7332	1.116
MALATHION	7.37	5807	1.069



ABC Laboratories, Inc.

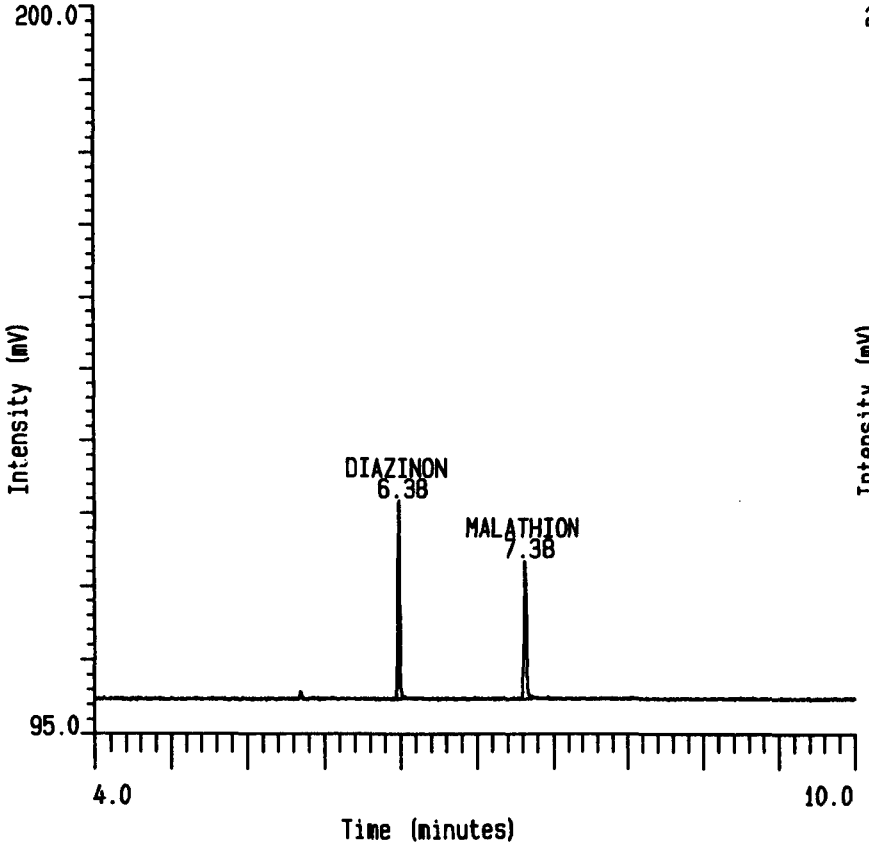
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS REPEATED SET

Date of Report: 24 APR 97 at 15:02:47

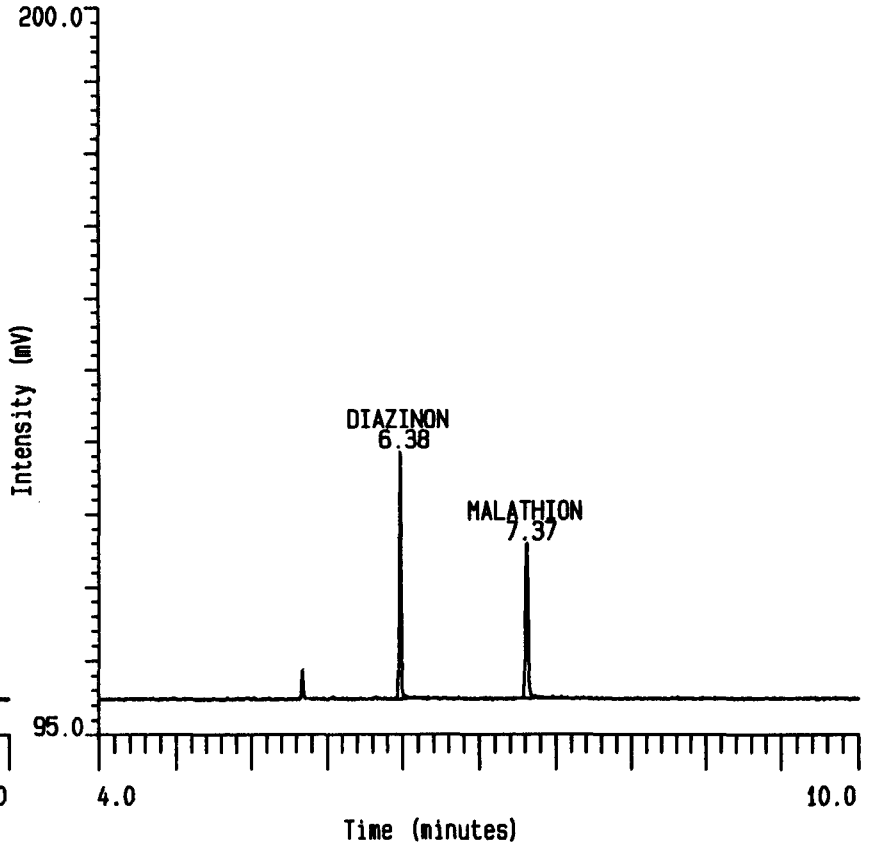
MCDO [43767] 29 767IWBD7,7,1
GCMIX-3 NOMINAL 40 NG/ML STD
Acquired on 24-Apr-1997 at 11:47

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.38	30743	37.426
MALATHION	7.38	26724	38.983



MCDO [43767] 29 767IWBD7,8,1
43767-004R
Acquired on 24-Apr-1997 at 12:08

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.38	39053	9.508
MALATHION	7.37	30860	9.000



ABC Laboratories, Inc.

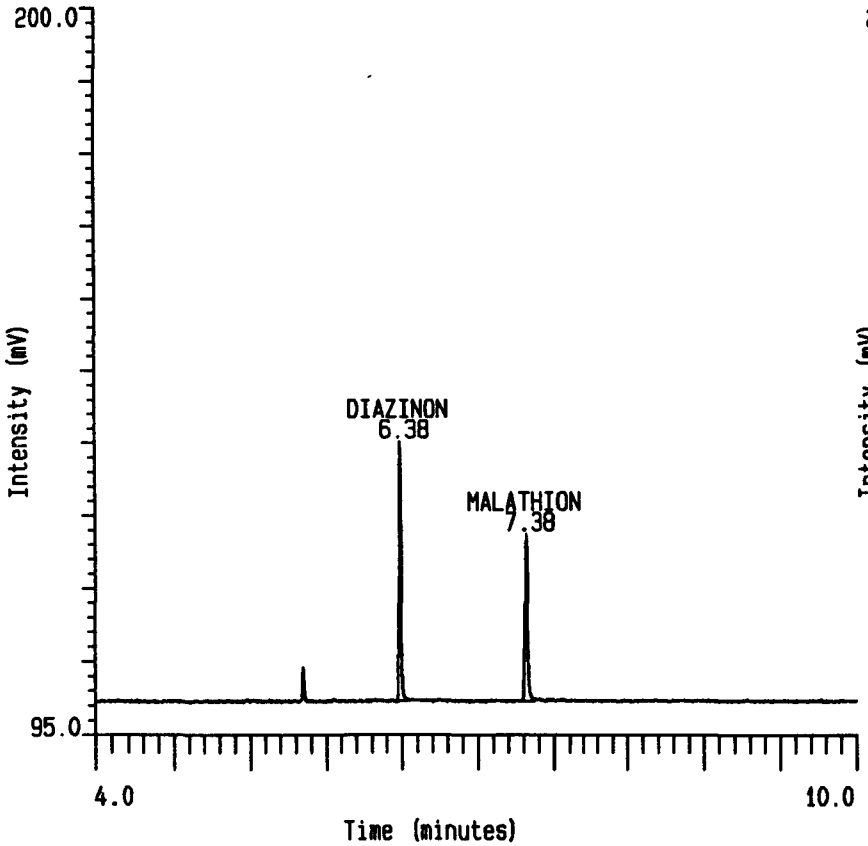
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS REPEATED SET

Date of Report: 24 APR 97 at 15:02:47

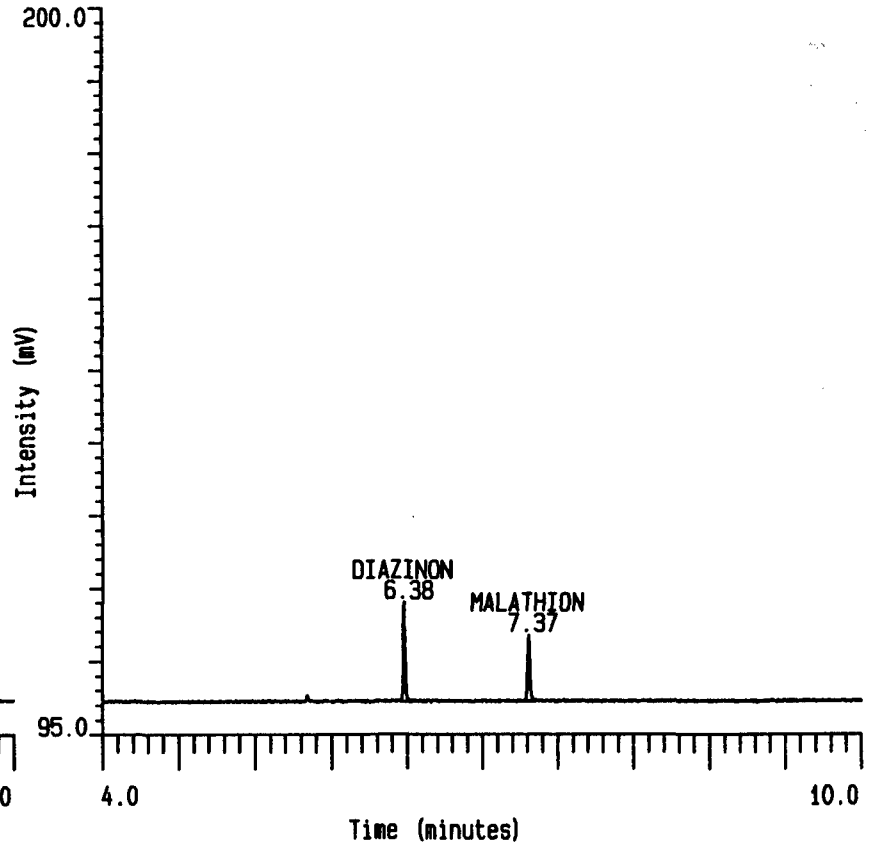
MCDO [43767] 29 767IWBD7, 9, 1
43767-005R
Acquired on 24-Apr-1997 at 12:28

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.38	40821	9.939
MALATHION	7.38	34414	10.034



MCDO [43767] 29 767IWBD7, 10, 1
GCMIX-4 NOMINAL 20 NG/ML
Acquired on 24-Apr-1997 at 12:48

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.38	15928	19.394
MALATHION	7.37	13175	19.269



ABC Laboratories, Inc.

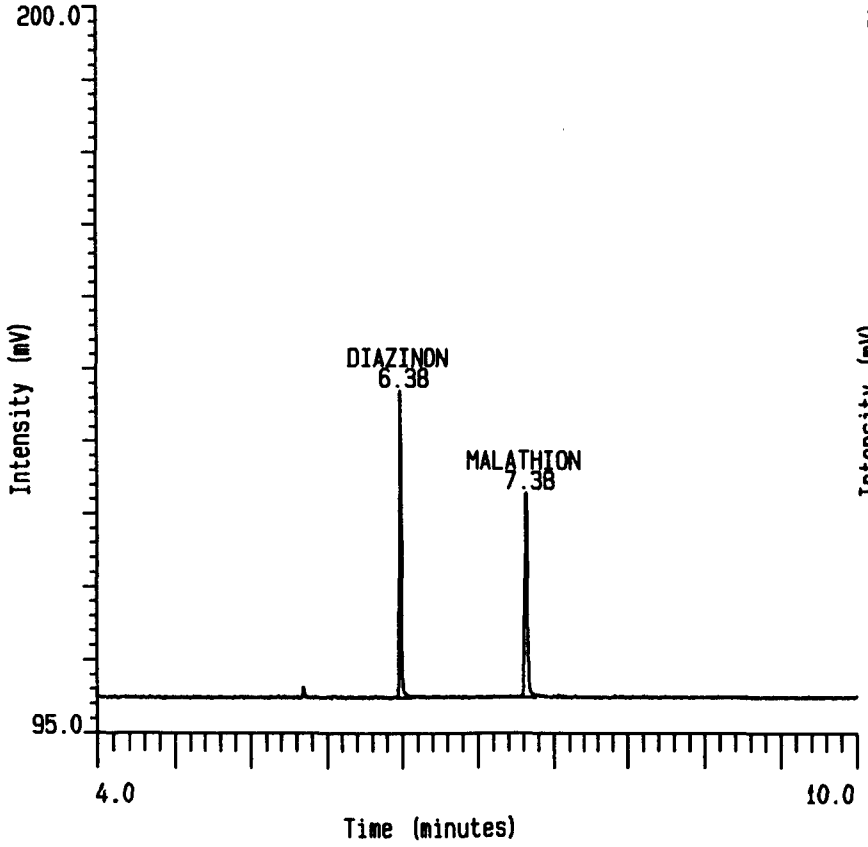
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS REPEATED SET

Date of Report: 24 APR 97 at 15:02:47

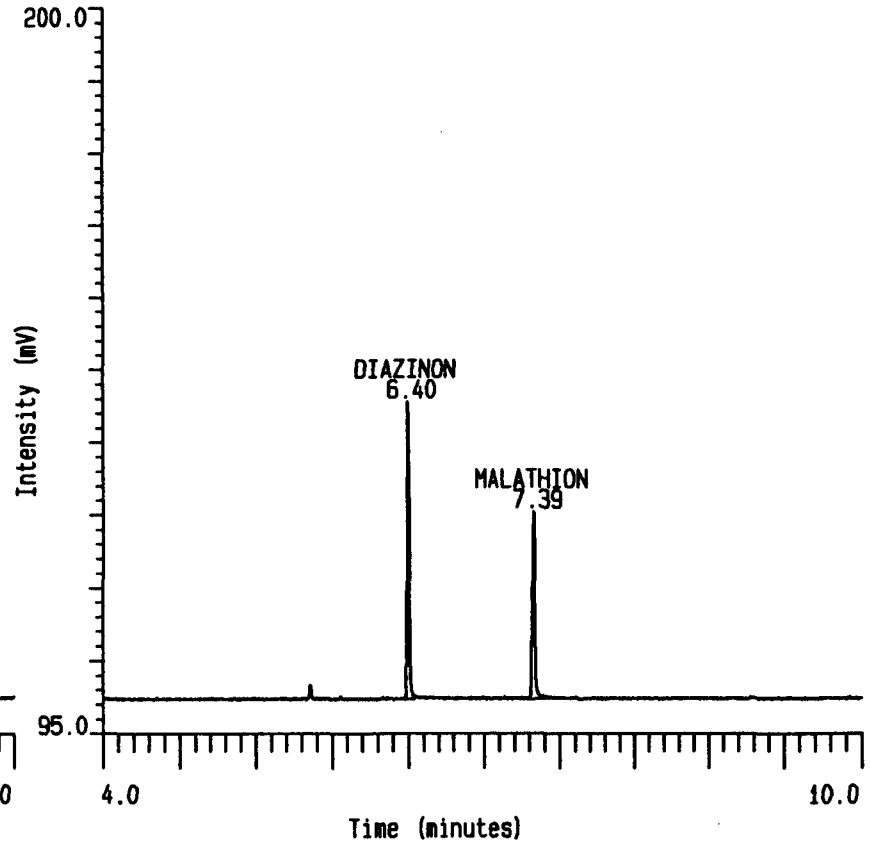
MCDO [43767] 29 767IWBD7, 11, 1
43767-006R
Acquired on 24-Apr-1997 at 13:09

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.38	48994	924.434
MALATHION	7.38	41939	947.368



MCDO [43767] 29 767IWBD7, 12, 1
43767-007R
Acquired on 24-Apr-1997 at 13:29

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.40	45956	867.113
MALATHION	7.39	39324	888.393



ABC Laboratories, Inc.

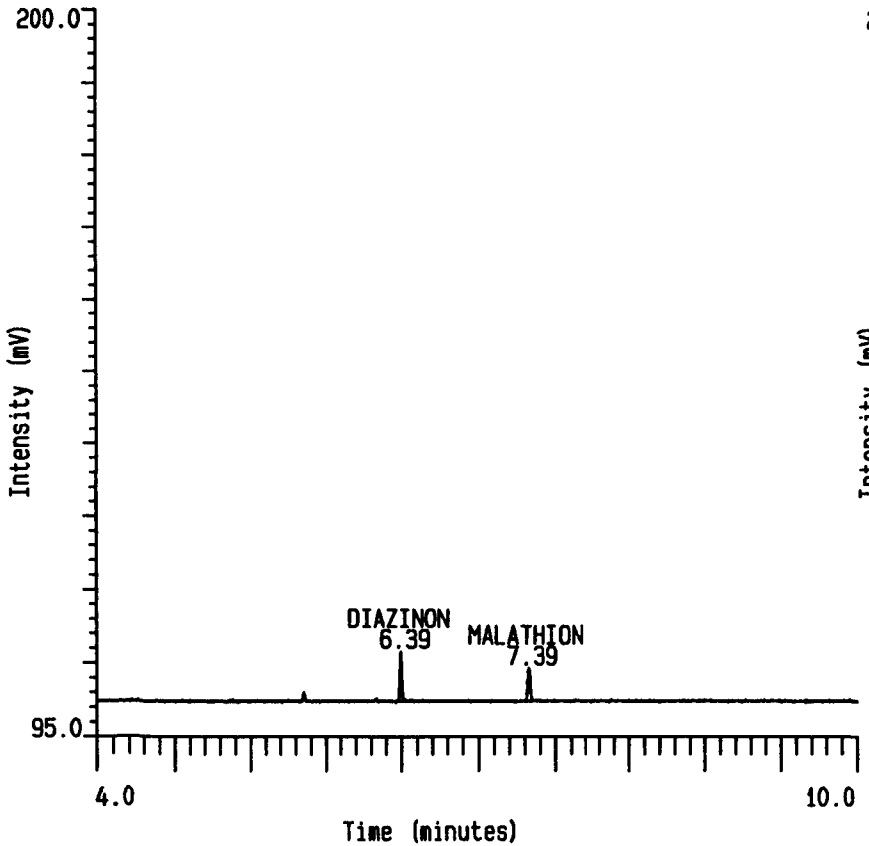
MCPP ver 2.3

43767 INNER WHOLE BODY DOSIMETERS REPEATED SET

Date of Report: 24 APR 97 at 15:02:47

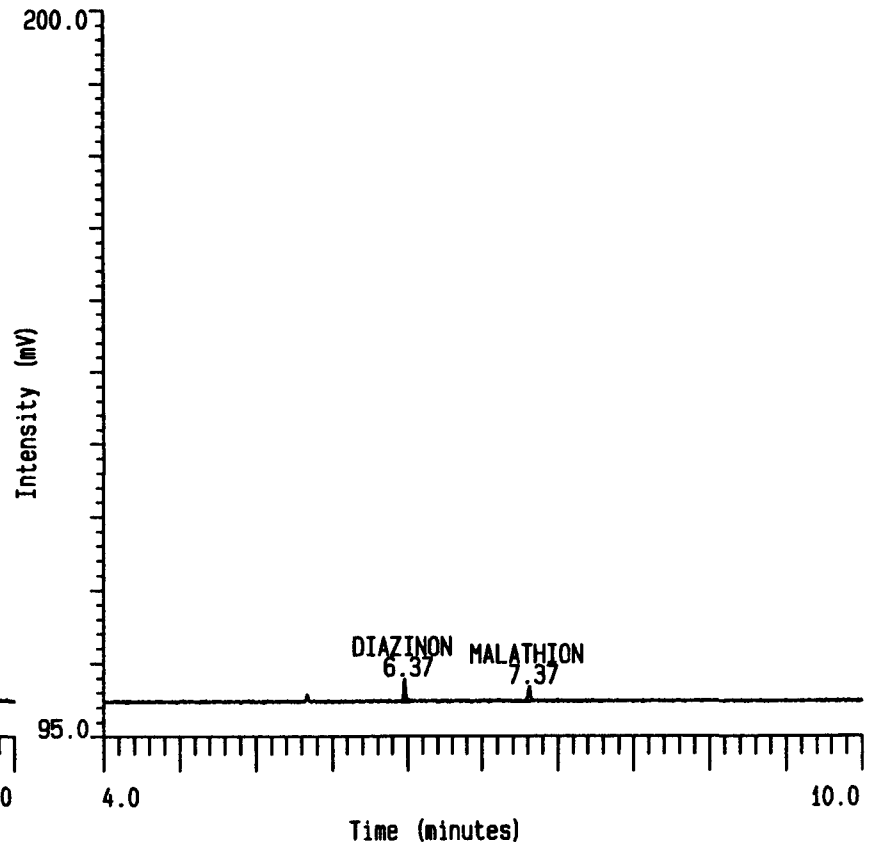
MCDO [43767] 29 767IWBD7, 13, 1
GCMIX-5 NOMINAL 10 NG/ML
Acquired on 24-Apr-1997 at 13:49

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.39	7734	9.420
MALATHION	7.39	6677	9.815



MCDO [43767] 29 767IWBD7, 14, 1
GCMIX-6 NOMINAL 4 NG/ML
Acquired on 24-Apr-1997 at 14:09

Peak Name	RT (mins)	Area	NG/ML OR UG
DIAZINON	6.37	3714	4.527
MALATHION	7.37	3166	4.707



[43767] 29 767IWBD7 Page 1
Reported on 24-APR-1997 at 16:17
Modified on 24-APR-1997 at 14:50

List Calibration File

CALIBRATION HEADER INFORMATION

Calibration Title : 43767 INNER WHOLE BODY DOSIMETERS REPEATED SET
General :
Calibration type..... External standard
Units..... NG/ML OR UG
Calibration base..... Area
Reference Peak Identification :
Reference window..... 5.0 %
Minimum window..... 0.50 mins
Peak threshold..... 0.0 %
Uncalibrated Peaks Response Factor :
Response factor source..... User set response factor
Response factor..... 0.0000
Additional Information :
Source library..... None
Initialise on 1st standard..... No
Variation tolerance..... 100.00 %
Calibrant Peak Identification :
Calibrant window..... 0.20 mins
Calibrant threshold..... 0.0 %
Response Factor Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... 1 / Y
Retention Value Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... 1 / Y
Timed Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... 1 / Y
No group information entered.

[43767] 29 767IWBD7 Page 2
Reported on 24-APR-1997 at 16:17
Modified on 24-APR-1997 at 14:50

Peak name : DIAZINON
Expected retention time : 6.39 mins (RT range : 6.29 - 6.49 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	3.9700	935.6293	1
05	9.9200	779.6395	1
04	19.8000	804.4630	1
03	39.7000	774.3768	1
02	59.5000	787.3345	1
01	99.2000	869.2311	1

Peak name : MALATHION
Expected retention time : 7.38 mins (RT range : 7.28 - 7.48 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	4.0800	775.9359	1
05	10.2000	654.5717	1
04	20.4000	645.8136	1
03	40.8000	654.9990	1
02	61.2000	654.0553	1
01	102.0000	729.2800	1

Attachment 3. Validation Data for Hand Wash Method ARTF-AM-006

Summary Results for AOT Handwash Method Validation - Diazinon
Reference Multichrom files 767HWS9 and 767HWS10

Sample ID	Sample Description	Diazinon Fortification Level (ug/sample)	Diazinon Recovery (ug/sample)	% Recovery
43767-029	Control	NA	Not Detected	
43767-030	Control + nominal 1 ug each	0.992	1.02	103%
43767-031	Control + nominal 1 ug each	0.992	0.879	88.6%
43767-032-1	Control + nominal 10 ug each	9.92	10.9	110%
43767-033-2	Control + nominal 10 ug each	9.92	11.1	112%
43767-034	Control + nominal 1000 ug each	992	1060	107%
43767-035	Control + nominal 1000 ug each	992	1020	103%
43767-036	Control	NA	Not Detected	
43767-037	Control + nominal 1 ug each	0.992	0.897	90.4%
43767-038	Control + nominal 1 ug each	0.992	0.784	79.0%
43767-039	Control + nominal 10 ug each	9.92	9.17	92.4%
43767-040	Control + nominal 10 ug each	9.92	9.53	96.1%
43767-041	Control + nominal 1000 ug each	992	1030	104%
43767-042	Control + nominal 1000 ug each	992	1050	106%
			Average % Recovery (n=12)	99.3%
			Standard Deviation (n=12)	9.97%
			Avg. + 2 Std. Dev.	119%
			Avg. - 2 Std. Dev.	79.4%

Prepared by: 24 June 97

Checked by: Barbara J Bryant 24 Jun 1997

Summary Results for AOT Handwash Method Validation - Malathion
Reference Multichrom files 767HWS9 and 767HWS10

Sample ID	Sample Description	Malathion Fortification Level (ug/sample)	Malathion Recovery (ug/sample)	% Recovery
43767-029	Control	NA	Not Detected	
43767-030	Control + nominal 1 ug each	1.02	1.15	113%
43767-031	Control + nominal 1 ug each	1.02	0.928	91.0%
43767-032-1	Control + nominal 10 ug each	10.2	11.2	110%
43767-033-2	Control + nominal 10 ug each	10.2	11.6	114%
43767-034	Control + nominal 1000 ug each	1020	1150	113%
43767-035	Control + nominal 1000 ug each	1020	1170	115%
43767-036	Control	NA	Not Detected	
43767-037	Control + nominal 1 ug each	1.02	0.941	92.3%
43767-038	Control + nominal 1 ug each	1.02	0.952	93.3%
43767-039	Control + nominal 10 ug each	10.2	9.98	97.8%
43767-040	Control + nominal 10 ug each	10.2	10.4	102%
43767-041	Control + nominal 1000 ug each	1020	1070	105%
43767-042	Control + nominal 1000 ug each	1020	1140	112%
			Average % Recovery (n=12)	105%
			Standard Deviation (n=12)	9.23%
			Avg. + 2 Std. Dev.	123%
			Avg. - 2 Std. Dev.	86.5%

Prepared by: 24 Jun 97

Checked by: Barbara J Bryant 24 Jun 1997

SAMPLE TRACKING FORM

Customer Name: ARTF	Study Director: Loren C. Schrier	Test Material: Diazinon and Malathion	Matrix: 0.01%AOT
ARTF Protocol: ARF003	ABC Study Number: 43767	0.01% AOT Handwash Solution Method Validation Set 1	

C-18RP Column Cleanup (Section II. C.2) CYG 6-16-97					GC/FPD Analysis (Section II. D.) CYG 6-16-97 (3)	Chromatography review: 23 June 97 Spreadsheet entry by: 24 June 97
ABC Lab Number	Sample Identification	Sample Volume	Sample Volume for Cleanup	Eluent Volume (Methylene Chloride)	Final Volume and Dilutions	Fortified by: CYG 6-16-97 Witnessed by: (1)
43767-029	Control	500 mL	10 mL	8 mL	2.50 mL	
43767-030	Control + nominal 1 ug Each	500 mL	10 mL	8 mL	2.50 mL	Fortify with 1.0 mL of 0.992 ug/mL diazinon and 1.02 ug/mL malathion mixed fortification solution (Fort-3)
43767-031	Control + nominal 1 ug Each	500 mL	10 mL	8 mL	2.50 mL	Fortify with 1.0 mL of 0.992 ug/mL diazinon and 1.02 ug/mL malathion mixed fortification solution (Fort-3)
43767-032	Control + nominal 10 ug Each	500 mL	10 mL	8 mL	2.50 mL (2)	Fortify with 1.0 mL of 9.92 ug/mL diazinon and 10.2 ug/mL malathion mixed fortification solution (Fort-2)
43767-033	Control + nominal 10 ug Each	500 mL	10 mL	8 mL	2.50 mL (2)	Fortify with 1.0 mL of 9.92 ug/mL diazinon and 10.2 ug/mL malathion mixed fortification solution (Fort-2)
43767-034	Control + nominal 1000 ug Each	500 mL	10 mL	8 mL	10.0 mL, then dilute 0.50 mL to 15.5 mL	Fortify with 1.0 mL of 992 ug/mL diazinon and 1020 ug/mL malathion mixed fortification solution (Fort-1)
43767-35	Control + nominal 1000 ug Each	500 mL	10 mL	8 mL	10.0 mL, then dilute 0.50 mL to 15.5 mL	Fortify with 1.0 mL of 992 ug/mL diazinon and 1020 ug/mL malathion mixed fortification solution (Fort-1)

Remarks: (1) No Witness CYG 6-19-97

Methylene Chloride: Burdick & Jackson, Lot# BN794 CYG 6-16-97

Acetone: Burdick & Jackson. Lot# BO920 CYG 6-16-97

Hexane: Burdick & Jackson. Lot# BN936 CYG 6-16-97

Alcohol: Burdick & Jackson, Lot# BO820 CYG 6-16-97

Aerosol OT Solution (75% w/w Aqueous), Fisher, Lot Number 963392

Water: Labconco DI

(2) Diluted 0.50 mL to 1.0 mL for final set 767HWS9. 23 June 97

(3) Final set 767HWS9 injected on 20 June 97 by CYG no. 23 June 97

Checked by: Barbara J Bryant 24 June 1997

Approved by: 24 June 97

Observations and Remarks	
Test Material: Diazinon and Malathion Study Sponsor: ARTF Matrices: Various Study Number: 43767	Form AC72A (5/4/93) ABC Laboratories, Inc. 7200 E. ABC Lane Columbia, MO 65202
	Study Director: Loren C. Schrier

COMMENTS

0.50 mL of sample # 032 (from Handwash Solution set 1) was added to 0.50 mL 1.5% DEGDEE.
Labeled: 032-1.

0.50 mL of Sample # 033 (from Handwash Solution set 1) was added to 0.50 mL 1.5% DEGDEE.
Labeled: 033-1.

Glass pipets: A, Fisher brand. 0.50 mL.

Entered by: CY Guo Date: 6-20-97

Checked by: [signature] Date: 23 June 97

Approved by: [signature] Date: 23 June 97

[43767] 29 767HWS9 Page 1
Reported on 23-JUN-1997 at 07:44 CYG
Modified on 20-JUN-1997 at 11:50

List Run Sequence File

ANALYST NAME..... CY Guo
43767 Hand Wash Solution SET 1

ANALYSIS INFORMATION

Analysis name..... 767HWS9
Method name..... 767HWS9
Calibration name..... 767HWS9
Calibration sequence..... Average Standard
User parameter 1 name..... Final Volume
User parameter 2 name..... ~~Factro~~ 1 (2)
User parameter 3 name..... Factor 2

SAMPLE SUMMARY

SAMPLE NUMBER	LIMS ID	SAMPLE NAME
1	----------	Solvent Blank
2	----------	GCMIX-1 NOMINAL 100 ng/mL
3	----------	GCMIX-2 NOMINAL 60 ng/mL
4	----------	43~~676~~-029 (1)
5	----------	43~~676~~-030
6	----------	43~~676~~-031
7	----------	GCMIX-3 NOMINAL 40 ng/mL
8	----------	43~~676~~-032-1 (1)
9	----------	43~~676~~-033-1
10	----------	GCMIX-4 NOMINAL 20 ng/mL
11	----------	43~~676~~-034 (1)
12	----------	43~~676~~-035
13	----------	GCMIX-5 NOMINAL 10 ng/mL
14	----------	GCMIX-6 NOMINAL 4 ng/mL

(1) Entry Error - 43767.
JCY 23 June 97

(2) Spelling Error - Factor
JCY 23 June 97

[43767] 29 767HWS9 Page 2
Reported on 23-JUN-1997 at 07:44
Modified on 20-JUN-1997 at 11:50

SAMPLE INFORMATION

SAMPLE NUMBER	TYPE	CALIB LEVEL	UPDATE RT	UPDATE RF	AMOUNT	NUM INJ	BOT NUM
1	Sa	--	-	-	1.00000	1	1
2	St	01	N	I	1.00000	1	2
3	St	02	N	I	1.00000	1	3
4	Sa	--	-	-	1.00000	1	4
5	Sa	--	-	-	1.00000	1	5
6	Sa	--	-	-	1.00000	1	6
7	St	03	N	I	1.00000	1	7
8	Sa	--	-	-	1.00000	1	8
9	Sa	--	-	-	1.00000	1	9
10	St	04	N	I	1.00000	1	10
11	Sa	--	-	-	1.00000	1	11
12	Sa	--	-	-	1.00000	1	12
13	St	05	N	I	1.00000	1	13
14	St	06	N	I	1.00000	1	14

USER PARAMETER VALUES

SAMPLE	FINAL VOLUME	FACTRO 1	FACTOR 2
1	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000
4	1.00000	1.00000	1.00000
5	2.50000	500.00000	10000.00000
6	2.50000	500.00000	10000.00000
7	1.00000	1.00000	1.00000
8	5.00000	500.00000	10000.00000
9	5.00000	500.00000	10000.00000
10	1.00000	1.00000	1.00000
11	10.00000	7750.00000	5000.00000
12	10.00000	7750.00000	5000.00000
13	1.00000	1.00000	1.00000
14	1.00000	1.00000	1.00000

[43767] 29 767HWS9 Page 3
Reported on 23-JUN-1997 at 07:44
Modified on 20-JUN-1997 at 11:50

INTERNAL/DILUTION STANDARDS

SAMPLE NUMBER	ISTD1 AMOUNT	ISTD2 AMOUNT	ISTD3 AMOUNT	DIL1 AMOUNT	DIL2 AMOUNT
1	1.00000	1.00000	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000	1.00000	1.00000
4	1.00000	1.00000	1.00000	1.00000	1.00000
5	1.00000	1.00000	1.00000	1.00000	1.00000
6	1.00000	1.00000	1.00000	1.00000	1.00000
7	1.00000	1.00000	1.00000	1.00000	1.00000
8	1.00000	1.00000	1.00000	1.00000	1.00000
9	1.00000	1.00000	1.00000	1.00000	1.00000
10	1.00000	1.00000	1.00000	1.00000	1.00000
11	1.00000	1.00000	1.00000	1.00000	1.00000
12	1.00000	1.00000	1.00000	1.00000	1.00000
13	1.00000	1.00000	1.00000	1.00000	1.00000
14	1.00000	1.00000	1.00000	1.00000	1.00000

PROCESSING ORDER

SAMPLE NUMBER	TYPE
2	Standard
3	Standard
7	Standard
10	Standard
13	Standard
14	Standard
1	Sample
4	Sample
5	Sample
6	Sample
8	Sample
9	Sample
11	Sample
12	Sample

Gas Chromatographic Instrument Parameters Form

ABC Laboratory Study Number: 43767
Customer Identification: ARTF

Instrument: HP 5890 Series II Material ID# 1652-0120
Autoinjector: HP 7673B Material ID# 1652-802A

Column: HP-5MS, 30 M X 0.25 mm, 0.25 μm film thickness
Serial#: 56253614

Detector Type: FPD/P

Electrometer: Range 4

Temperatures: Injector (°C): 230
Detector(°C): 230
Column:
Initial Temp. (°C): 95
Initial Time: 1.0 min.
Program Rate 1: 30 °C/min to 230 °C, hold 4 min
Program Rate 2: 40 °C/min to 290 °C, hold 4 min

Carrier Gas Flow Rate: He 1.6 mL/min
Septum Purge: He 2.0 mL/min
Make Up Gas: N_2 21 mL/min
Air Flow Rate: 98 mL/min
Hydrogen Flow Rate: 69 mL/min
Purge Valve: Off at 0 min, on at 0.75 min

Injection Volume: 2 μL

Quantitation Standard ID(s) # GCMIX-1,-2,-3,-4,-5,-6

Run Sequence File 767HWS9

Prepared by CY Guo Date: 6-20-97

Checked by [illegible] Date: 23 June 97

MCDO [43767] 29 767HWS9

ABC Laboratories, Inc.
Sample Information Report ver 3.3

Report Date: 23 JUN 97 at 13:35:43
Page 1

Sample Name	No.	Type	Level	User Parameter 1 Final Volume	User Parameter 2 Factor 1	User Parameter 3 Factor 2
Solvent Blank	1	SA		1.00000	1.00000	1.00000
GCMIX-1 NOMINAL 100 ng/mL	2	ST	01	1.00000	1.00000	1.00000
GCMIX-2 NOMINAL 60 ng/mL	3	ST	02	1.00000	1.00000	1.00000
43767-029	4	SA		1.00000	1.00000	1.00000
43767-030	5	SA		2.50000	500.00000	10000.00000
43767-031	6	SA		2.50000	500.00000	10000.00000
GCMIX-3 NOMINAL 40 ng/mL	7	ST	03	1.00000	1.00000	1.00000
43767-032-1	8	SA		5.00000	500.00000	10000.00000
43767-033-1	9	SA		5.00000	500.00000	10000.00000
GCMIX-4 NOMINAL 20 ng/mL	10	ST	04	1.00000	1.00000	1.00000
43767-034	11	SA		10.00000	7750.00000	5000.00000
43767-035	12	SA		10.00000	7750.00000	5000.00000
GCMIX-5 NOMINAL 10 ng/mL	13	ST	05	1.00000	1.00000	1.00000
GCMIX-6 NOMINAL 4 ng/mL	14	ST	06	1.00000	1.00000	1.00000

MCDO [43767] 29 767HWS9

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: DIAZINON

Report Date: 23 JUN 97
Time: 13:35:43
Page: 1

Sample Name	SMP #	INJ #	RT(mins)	Height	ng/mL or ug	CAL. RANG	Peak Type	Bad INJ
Solvent Blank	1	1	0.00	0	0.000	UNDR	B	---
GCMIX-1 NOMINAL 100 ng/mL	2	1	5.95	95730	98.132		B	---
GCMIX-2 NOMINAL 60 ng/mL	3	1	5.95	59006	60.256		BF	---
43767-029	4	1	0.00	0	0.000	UNDR	BF	---
43767-030	5	1	5.95	8512	1.022		B	---
43767-031	6	1	5.95	7399	0.879		B	---
GCMIX-3 NOMINAL 40 ng/mL	7	1	5.95	38434	39.039		B	---
43767-032-1	8	1	5.94	42798	10.885		B	---
43767-033-1	9	1	5.94	43770	11.136		F	---
GCMIX-4 NOMINAL 20 ng/mL	10	1	5.95	20979	21.038		B	---
43767-034	11	1	5.95	66797	1058.523		B	---
43767-035	12	1	5.95	64564	1022.832		B	---
GCMIX-5 NOMINAL 10 ng/mL	13	1	5.94	10252	9.974		B	---
GCMIX-6 NOMINAL 4 ng/mL	14	1	5.96	4231	3.764		BF	---

MCDO [43767] 29 767HWS9

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: MALATHION

Report Date: 23 JUN 97
Time: 13:35:43
Page: 1

Sample Name	SMP #	INJ #	RT(mins)	Height	ng/mL or ug	CAL. RANG	Peak Type	Bad INJ
Solvent Blank	1	1	0.00	0	0.000	UNDR		---
GCMIX-1 NOMINAL 100 ng/mL	2	1	6.81	57607	102.321		B	---
GCMIX-2 NOMINAL 60 ng/mL	3	1	6.81	33244	58.834		B	---
43767-029	4	1	0.00	0	0.000	UNDR	B	---
43767-030	5	1	6.81	5441	1.151		B	---
43767-031	6	1	6.81	4441	0.928			---
GCMIX-3 NOMINAL 40 ng/mL	7	1	6.81	23806	41.987		B	---
43767-032-1	8	1	6.80	25340	11.181		B	---
43767-033-1	9	1	6.80	26207	11.568		B	---
GCMIX-4 NOMINAL 20 ng/mL	10	1	6.81	12436	21.692		B	---
43767-034	11	1	6.81	41898	1151.359		B	---
43767-035	12	1	6.81	42524	1168.666		B	---
GCMIX-5 NOMINAL 10 ng/mL	13	1	6.80	5995	10.194		B	---
GCMIX-6 NOMINAL 4 ng/mL	14	1	6.82	2450	3.866		B	---

Acquisition and Peak Processing Parameters Report Print Date and Time : 23 JUN 97 13:38:28
Page : 1

MCDO [43767] 29 767HWS9 Based on Sample Number : 1 Injection Number : 1

ACQUISITION PARAMETERS

Data Collection :

Length of Run..... 14.96 mins
Post Injection Delay..... 0.00 mins
Sampling Rate..... 15.00 Hz

PEAK PROCESSING PARAMETERS

Auto Process Parameters :

Peak Threshold..... 0.50
Baseline Test..... 4
Peak Trend..... 4

Separation Parameters :

Shoulder Sensitivity..... 0.10
Rider Sensitivity..... 0.05

Rejection Parameters :

Minimum Peak Width..... 0.00 secs
Minimum Peak Height..... 0.00 uV
Minimum Peak Area..... 2000.00 uVs
Ignore Flat Top Peak..... No

User Imposed Action Control :

Forced Baseline..... Yes
Suppress Integration..... Yes
Tangent Skimming..... No
Shoulder Detection..... No
Data Bunching..... No
Negative Detection..... No

Integration Modes :

Retention Time Integration..... No
Square Root Area and Height..... Yes

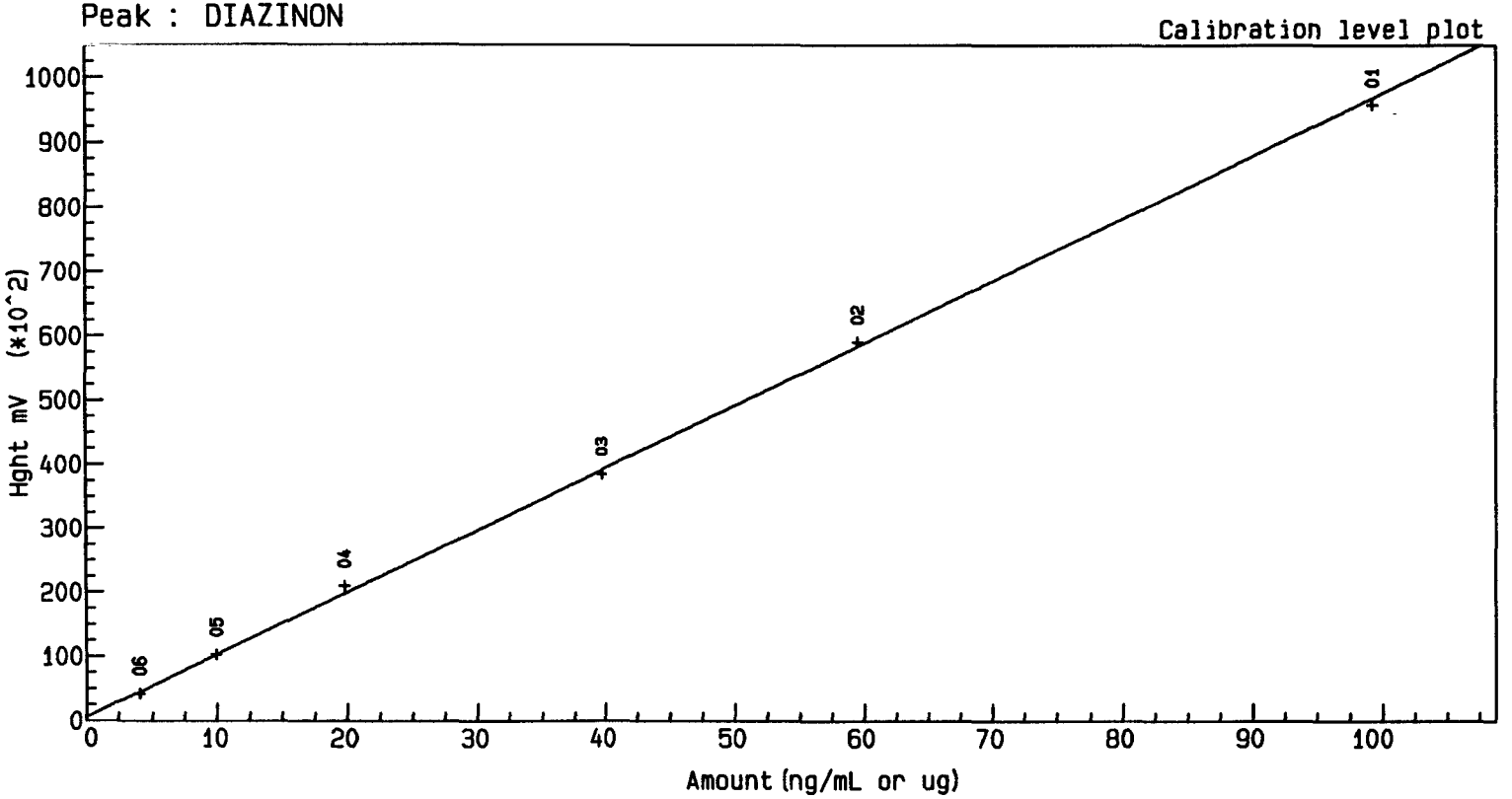
PROCESSING ACTIONS

Time (mins)	Force Baseline	Integrate Suppress	Tangent Skim	Bunch Size	Shoulder Detect	Negative Detect
0.00	--	SS	_	0	--	--
5.80	--	ES	_	0	--	--
5.90	SF	--	_	0	--	--
6.10	EF	--	_	0	--	--
6.15	--	SI	_	0	--	--
6.70	--	ES	_	0	--	--
6.75	SF	--	_	0	--	--
7.00	EF	--	_	0	--	--
7.10	--	SI	_	0	--	--

These parameters apply to all injections of set 767HWS9 with no exceptions

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767HWS9.
43767 Hand Wash Solution Set 1
Peak : DIAZINON



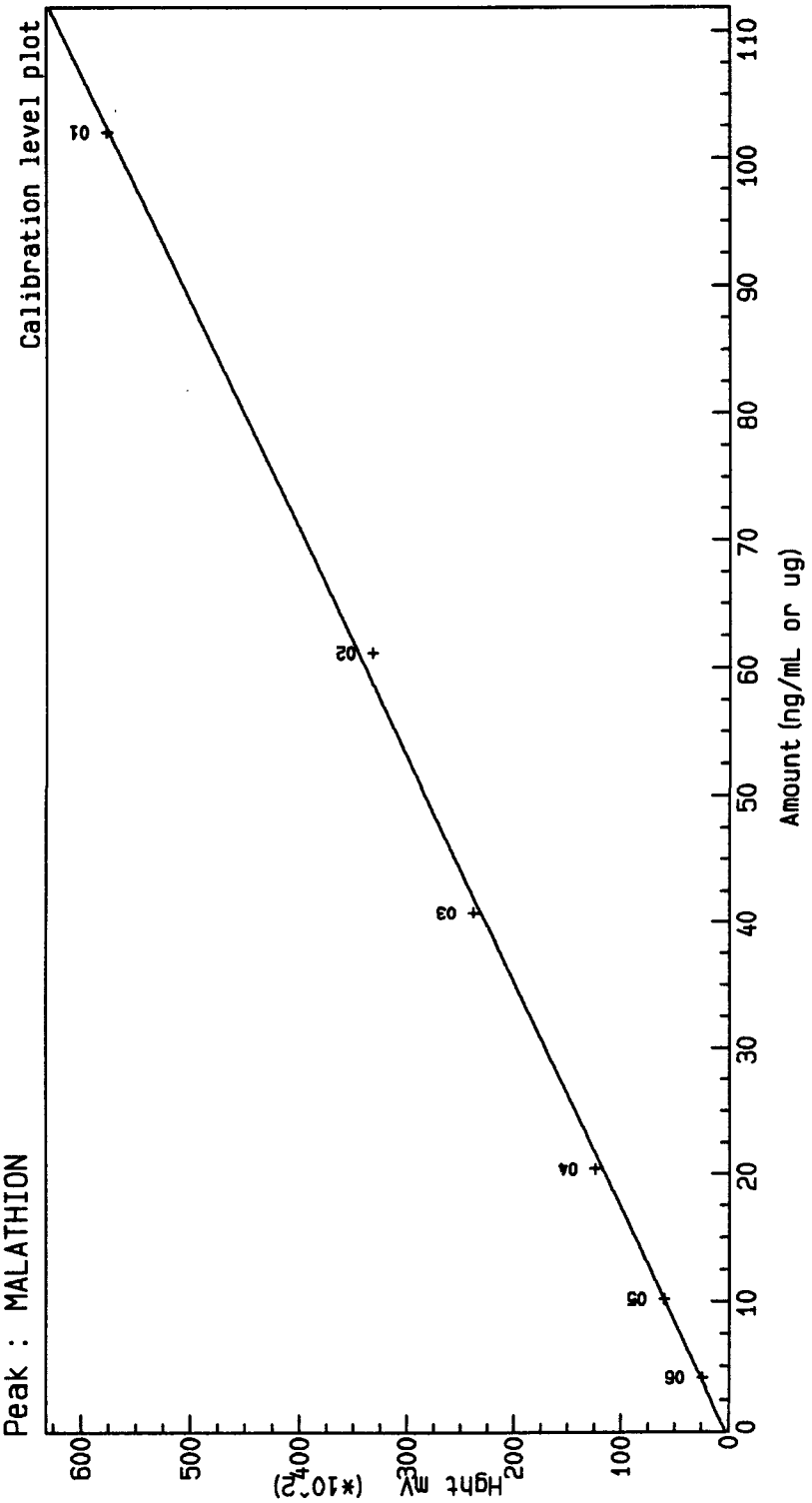
Constant : 5.81162E+2
1st degree : 9.69602E+2

Curve fit : Linear
Correlation coefficient : 0.99971
Standard error : 9.35822E+2

Reported on 23-JUN-1997 at 13:39

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767HWS9.
43767 Hand Wash Solution Set 1
Peak : MALATHION



Constant : 2.83734E+2
1st degree : 5.60229E+2

Curve fit : Linear
Correlation coefficient : 0.99935
Standard error : 8.32201E+2

Reported on 23-JUN-1997 at 13:39

ABC Laboratories, Inc.

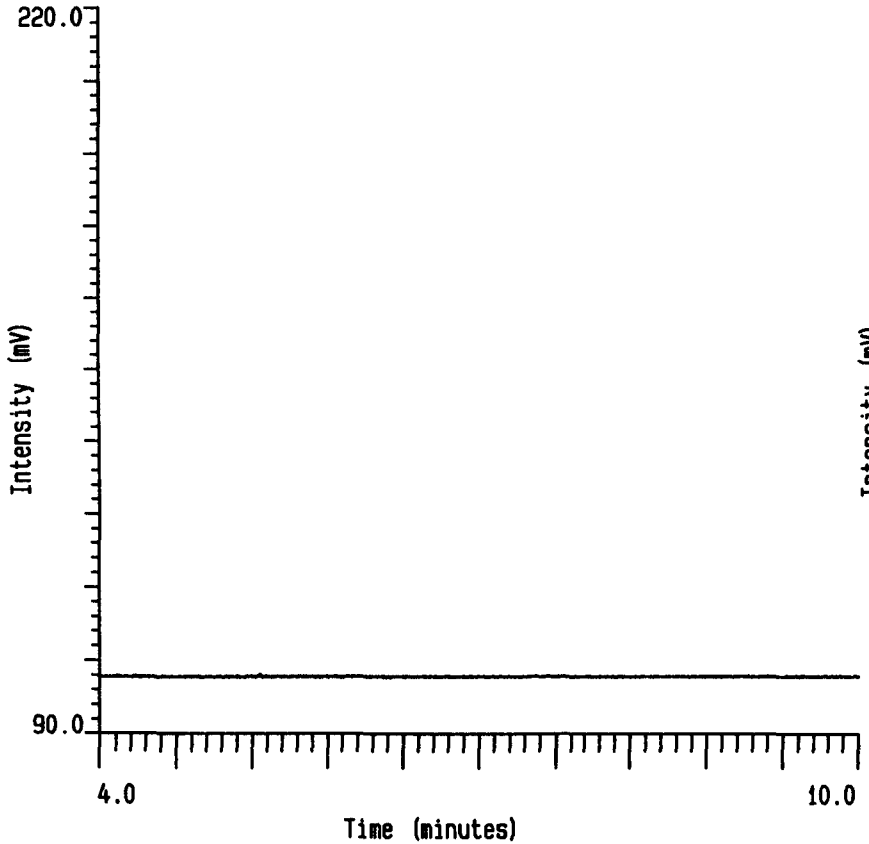
MCPP ver 2.3

43767 Hand Wash Solution SET 1

Date of Report: 23 JUN 97 at 13:39:56

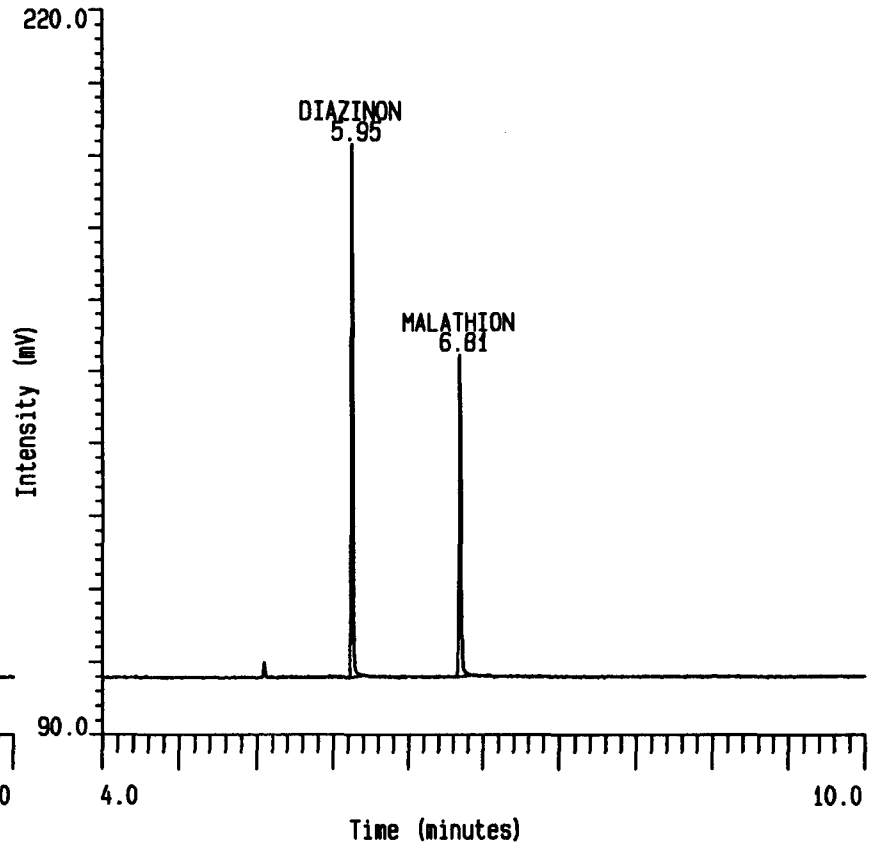
MCDO [43767] 29 767HWS9, 1, 1
Solvent Blank
Acquired on 20-Jun-1997 at 15:56

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	0.00	0	0
MALATHION	0.00	0	0



MCDO [43767] 29 767HWS9, 2, 1
GCMIX-1 NOMINAL 100 ng/mL
Acquired on 20-Jun-1997 at 16:16

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	95730	98.132
MALATHION	6.81	57607	102.321



ABC Laboratories, Inc.

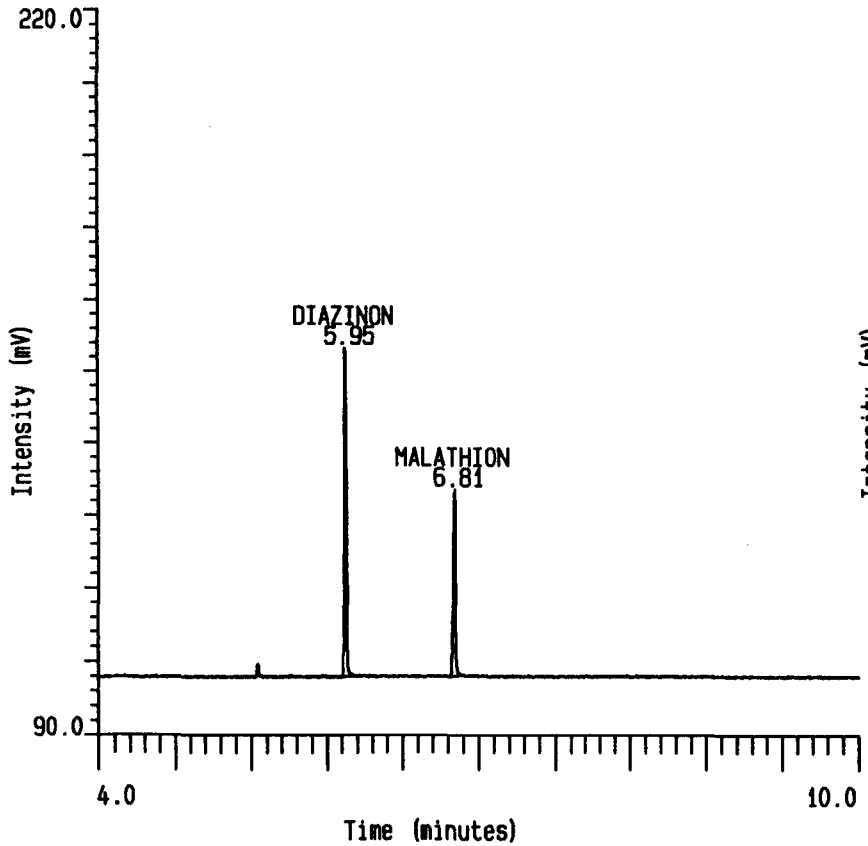
MCPP ver 2.3

43767 Hand Wash Solution SET 1

Date of Report: 23 JUN 97 at 13:39:56

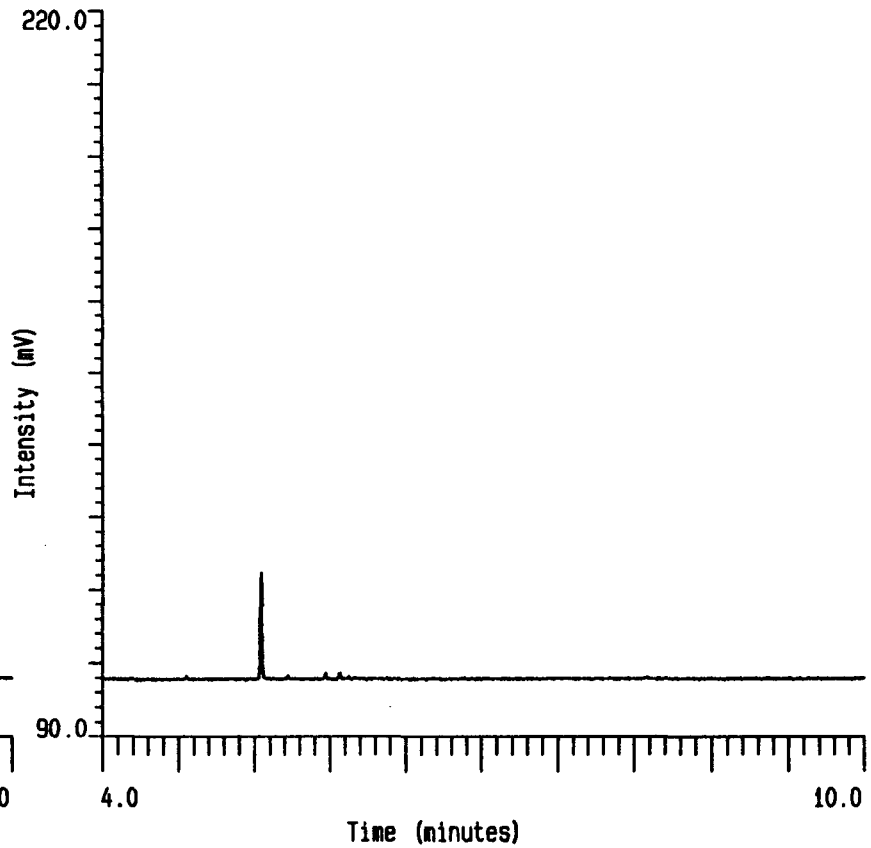
MCDO [43767] 29 767HWS9, 3, 1
GCMIX-2 NOMINAL 60 ng/mL
Acquired on 20-Jun-1997 at 16:37

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	59006	60.256
MALATHION	6.81	33244	58.834



MCDO [43767] 29 767HWS9, 4, 1
43767-029
Acquired on 20-Jun-1997 at 16:57

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	0.00	0	0
MALATHION	0.00	0	0



ABC Laboratories, Inc.

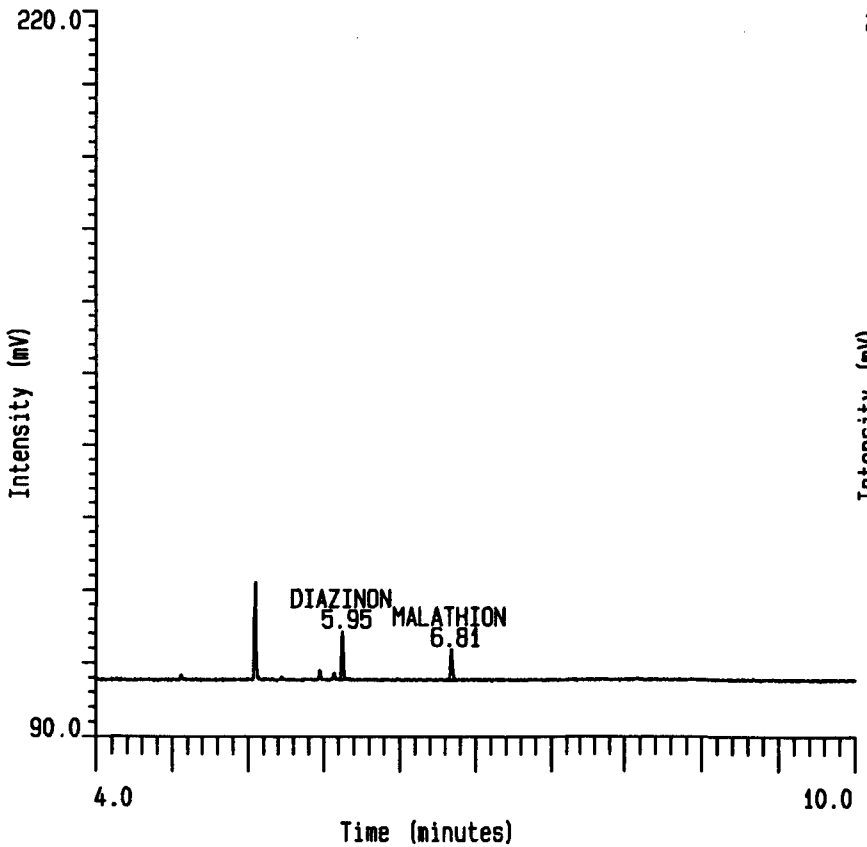
MCPP ver 2.3

43767 Hand Wash Solution SET 1

Date of Report: 23 JUN 97 at 13:39:56

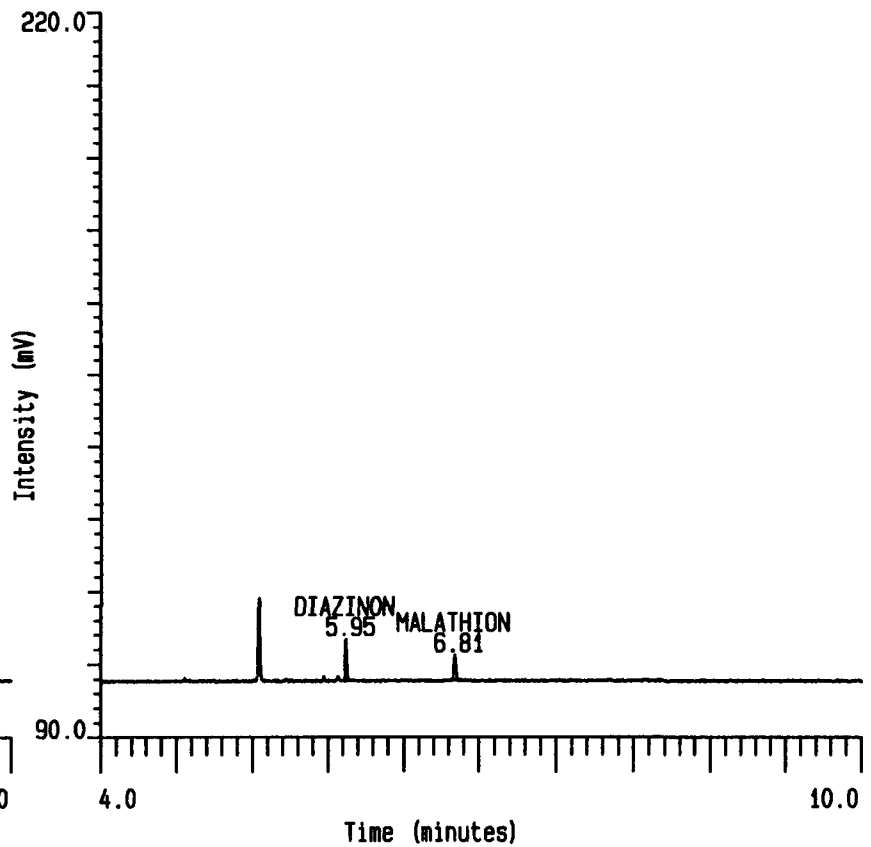
MCDO [43767] 29 767HWS9,5,1
43767-030
Acquired on 20-Jun-1997 at 17:18

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	8512	1.022
MALATHION	6.81	5441	1.151



MCDO [43767] 29 767HWS9,6,1
43767-031
Acquired on 20-Jun-1997 at 17:38

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	7399	0.879
MALATHION	6.81	4441	0.928



ABC Laboratories, Inc.

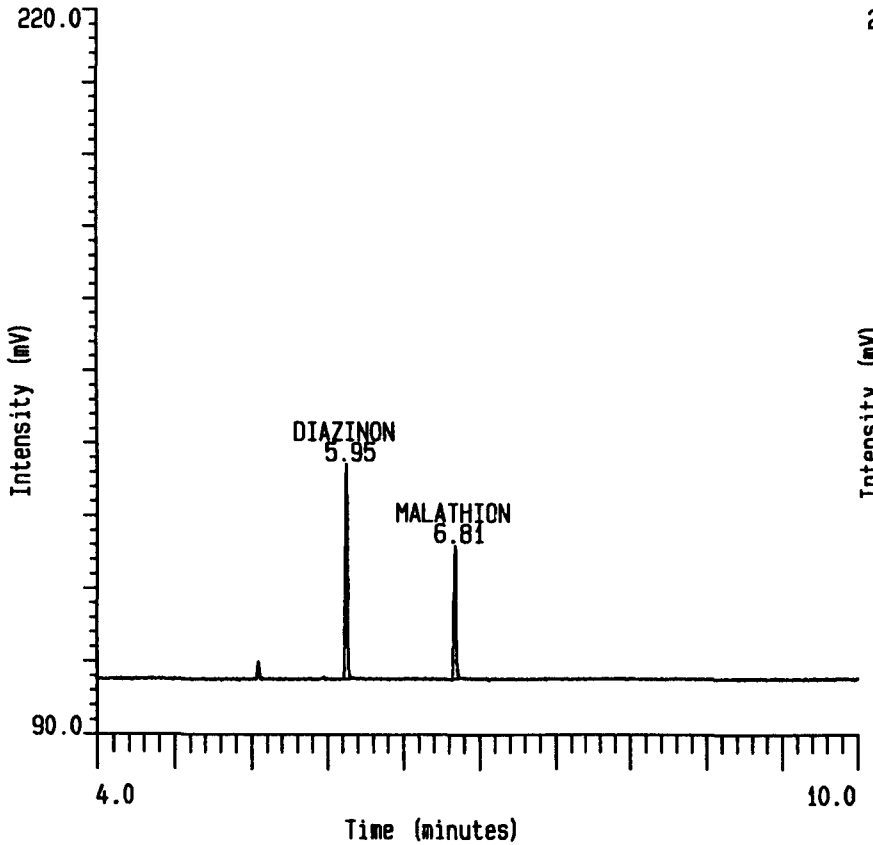
MCPP ver 2.3

43767 Hand Wash Solution SET 1

Date of Report: 23 JUN 97 at 13:39:56

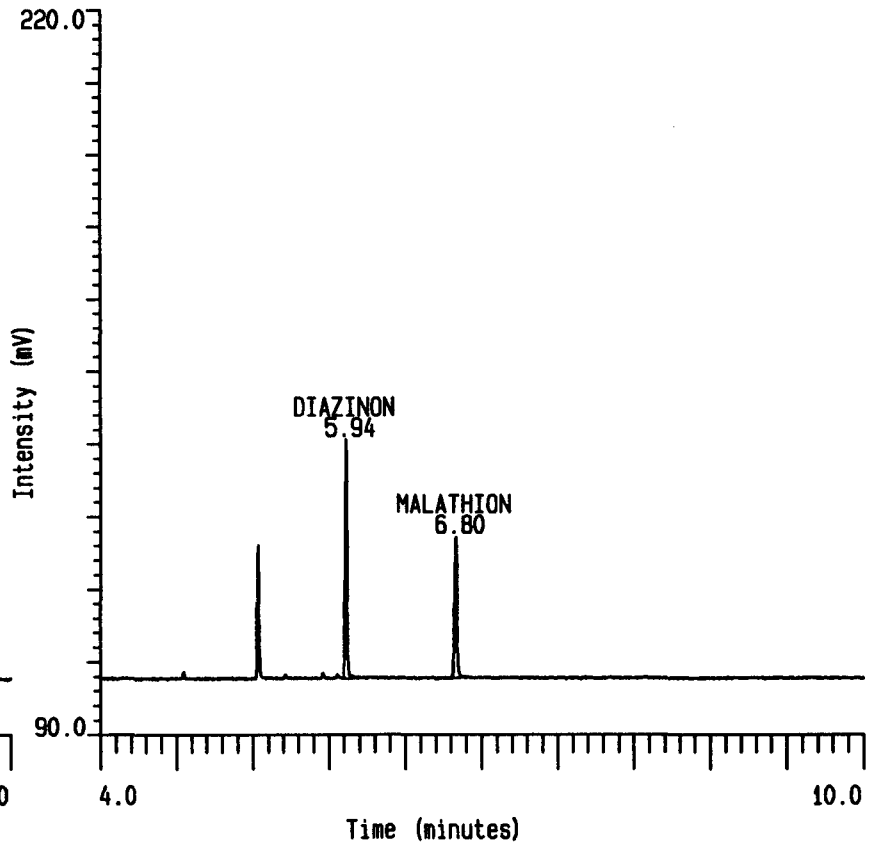
MCDO [43767] 29 767HWS9,7,1
GCMIX-3 NOMINAL 40 ng/mL
Acquired on 20-Jun-1997 at 17:58

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	38434	39.039
MALATHION	6.81	23806	41.987



MCDO [43767] 29 767HWS9,8,1
43767-032-1
Acquired on 20-Jun-1997 at 18:19

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.94	42798	10.885
MALATHION	6.80	25340	11.181



ABC Laboratories, Inc.

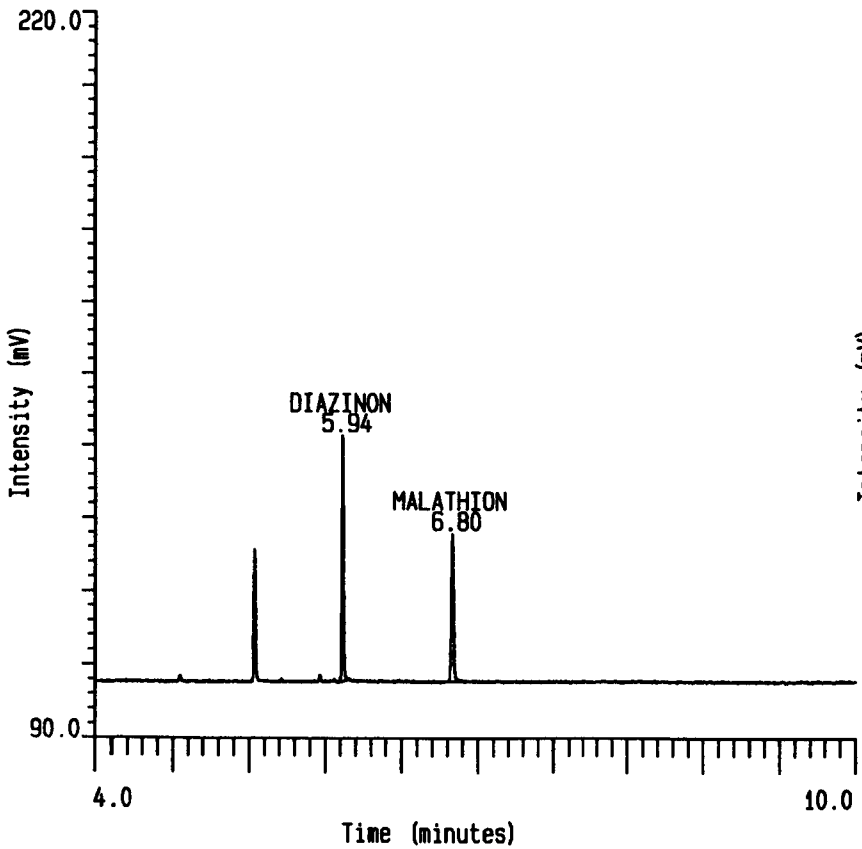
MCPP ver 2.3

43767 Hand Wash Solution SET 1

Date of Report: 23 JUN 97 at 13:39:56

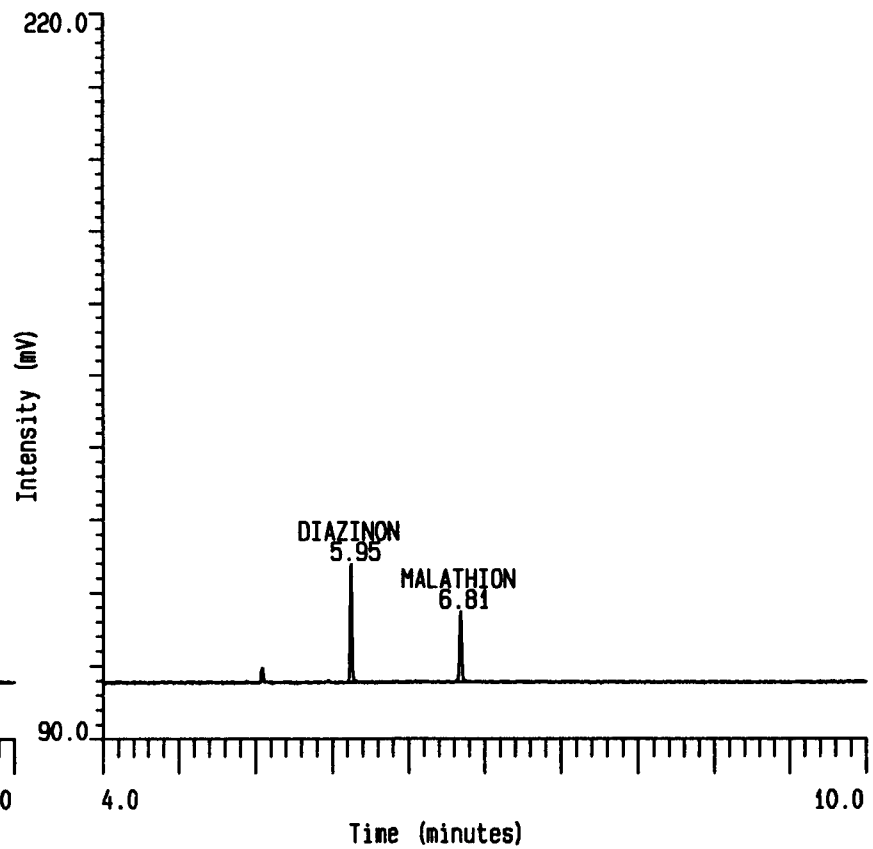
MCDO [43767] 29 767HWS9, 9, 1
43767-033-1
Acquired on 20-Jun-1997 at 18:39

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.94	43770	11.136
MALATHION	6.80	26207	11.568



MCDO [43767] 29 767HWS9, 10, 1
GCMIX-4 NOMINAL 20 ng/mL
Acquired on 20-Jun-1997 at 19:00

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	20979	21.038
MALATHION	6.81	12436	21.692



ABC Laboratories, Inc.

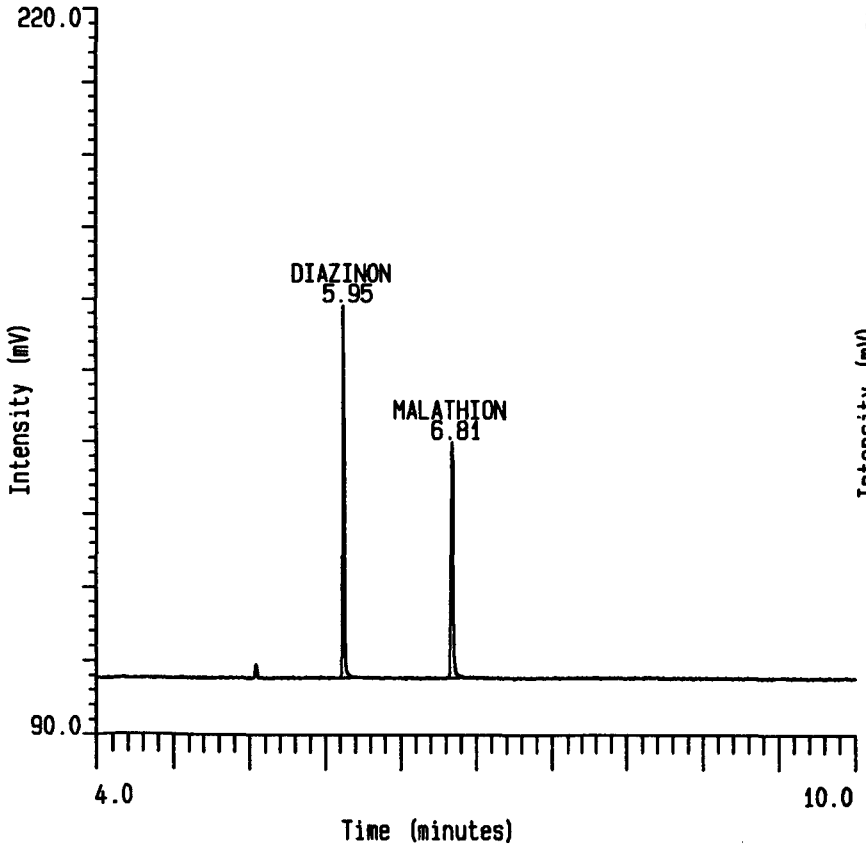
MCPP ver 2.3

43767 Hand Wash Solution SET 1

Date of Report: 23 JUN 97 at 13:39:56

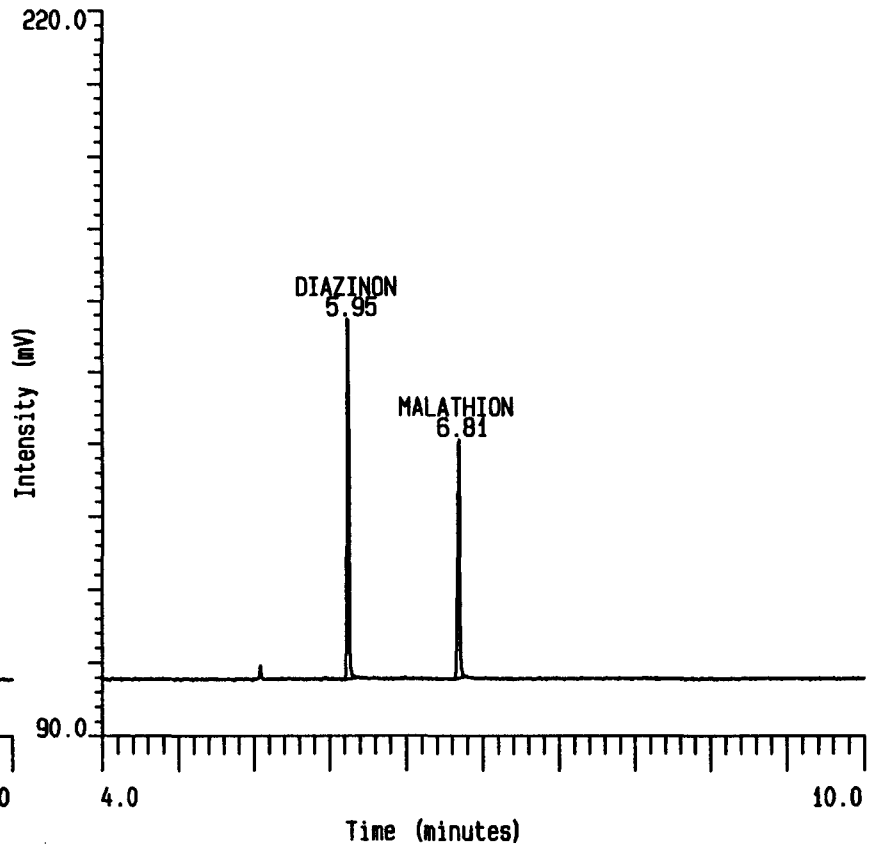
MCDO [43767] 29 767HWS9, 11, 1
43767-034
Acquired on 20-Jun-1997 at 19:20

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	66797	1058.523
MALATHION	6.81	41898	1151.359



MCDO [43767] 29 767HWS9, 12, 1
43767-035
Acquired on 20-Jun-1997 at 19:41

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	64564	1022.832
MALATHION	6.81	42524	1168.666



ABC Laboratories, Inc.

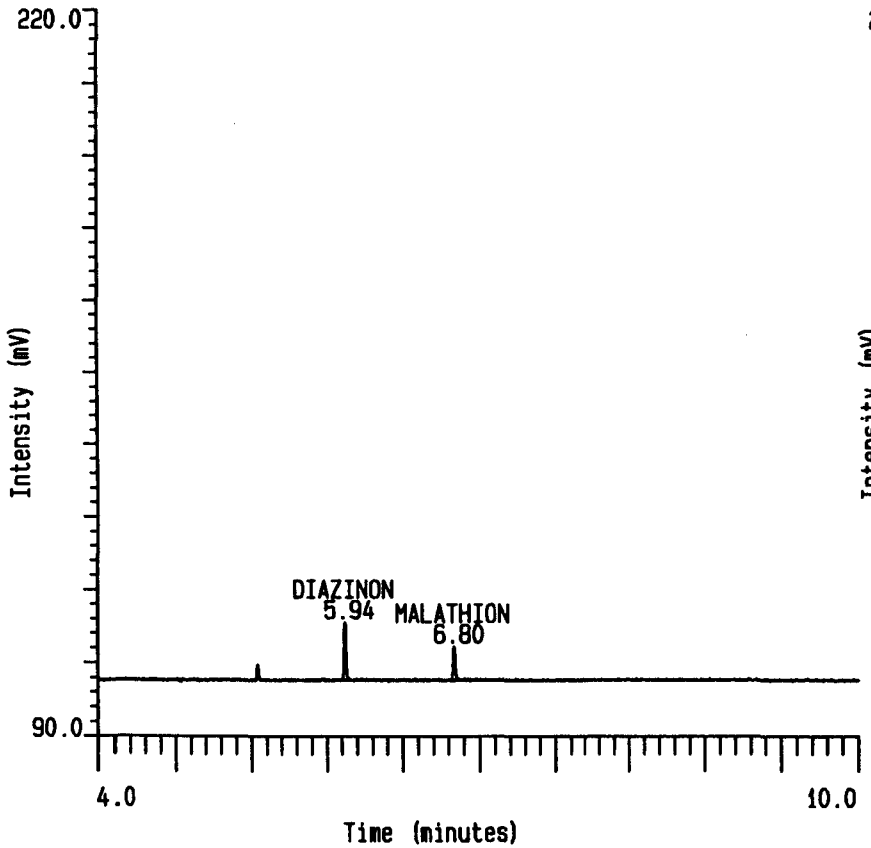
MCPP ver 2.3

43767 Hand Wash Solution SET 1

Date of Report: 23 JUN 97 at 13:39:56

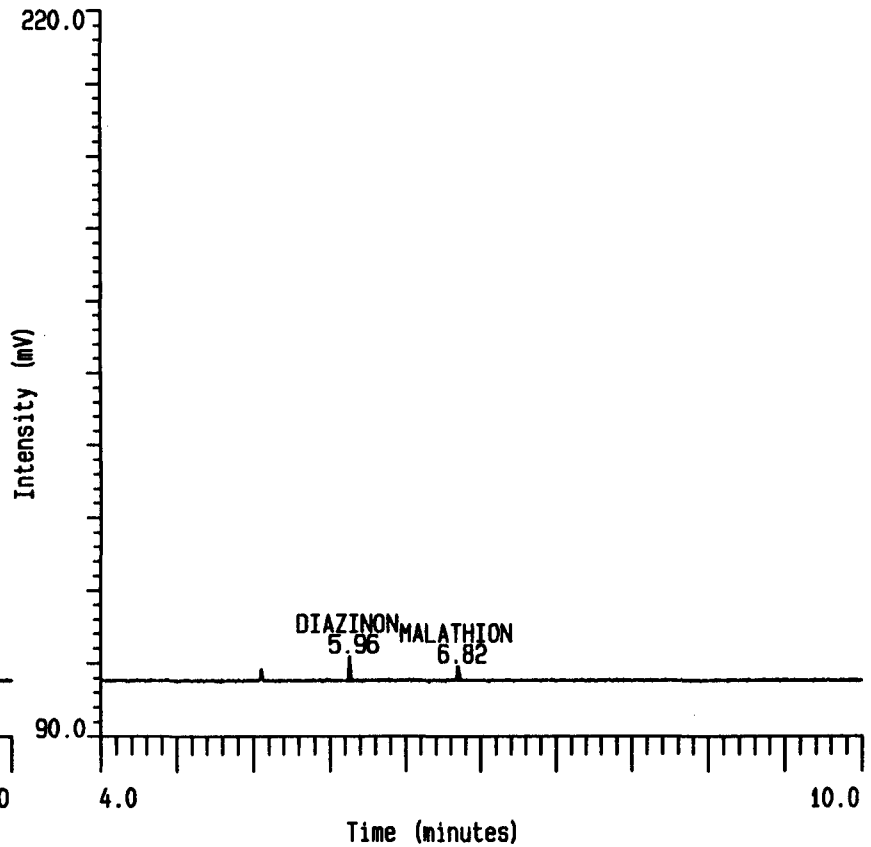
MCDO [43767] 29 767HWS9, 13, 1
GCMIX-5 NOMINAL 10 ng/mL
Acquired on 20-Jun-1997 at 20:01

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.94	10252	9.974
MALATHION	6.80	5995	10.194



MCDO [43767] 29 767HWS9, 14, 1
GCMIX-6 NOMINAL 4 ng/mL
Acquired on 20-Jun-1997 at 20:21

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.96	4231	3.764
MALATHION	6.82	2450	3.866



[43767] 29 767HWS9 Page 1
Reported on 24-JUN-1997 at 09:02
Modified on 23-JUN-1997 at 13:34

List Calibration File

CALIBRATION HEADER INFORMATION

Calibration Title : 43767 Hand Wash Solution Set 1
General :
Calibration type..... External standard
Units..... ng/mL or ug
Calibration base..... Height
Reference Peak Identification :
Reference window..... 5.0 %
Minimum window..... 0.50 mins
Peak threshold..... 0.0 %
Uncalibrated Peaks Response Factor :
Response factor source..... User set response factor
Response factor..... 0.0000
Additional Information :
Source library..... None
Initialise on 1st standard..... No
Variation tolerance..... 100.00 %
Calibrant Peak Identification :
Calibrant window..... 0.10 mins
Calibrant threshold..... 0.0 %
Response Factor Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... 1 / Y
Retention Value Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... None
Timed Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... None
No group information entered.

[43767] 29 767HWS9 Page 2
Reported on 24-JUN-1997 at 09:02
Modified on 23-JUN-1997 at 13:34

Peak name : DIAZINON
Expected retention time : 5.95 mins (RT range : 5.90 - 6.00 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	3.9700	1065.6582	1
05	9.9200	1033.4496	1
04	19.8000	1059.5610	1
03	39.7000	968.1014	1
02	59.5000	991.6909	1
01	99.2000	965.0215	1

Peak name : MALATHION
Expected retention time : 6.81 mins (RT range : 6.76 - 6.86 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	4.0800	600.4419	1
05	10.2000	587.7274	1
04	20.4000	609.6240	1
03	40.8000	583.4824	1
02	61.2000	543.2039	1
01	102.0000	564.7709	1

SAMPLE TRACKING FORM

Customer Name: ARTF	Study Director: Loren C. Schrier	Test Material: Diazinon and Malathion	Matrix: 0.01%AOT
ARTF Protocol: ARF003	ABC Study Number: 43767	0.01% AOT Handwash Solution Method Validation Set 2	

C-18RP Column Cleanup (Section II. C.2) CYG 6-23-97

GC/FPD Analysis (Section II. D.) CYG 6-23-97

Chromatography review: 24 June 97

Spreadsheet entry by: 24 June 97

Fortified by: CYG 6-23-97

Witnessed by: Barbara Bryant 23 Jun 1997

ABC Lab Number	Sample Identification	Sample Volume	Sample Volume for Cleanup	Eluent Volume (Methylene Chloride)	Final Volume and Dilutions	
43767-036	Control	500 mL	10 mL	8 mL	2.50 mL	
43767-037	Control + nominal 1 ug Each	500 mL	10 mL	8 mL	2.50 mL	Fortify with 1.0 mL of 0.992 ug/mL diazinon and 1.02 ug/mL malathion mixed fortification solution (Fort-3)
43767-038	Control + nominal 1 ug Each	500 mL	10 mL	8 mL	2.50 mL	Fortify with 1.0 mL of 0.992 ug/mL diazinon and 1.02 ug/mL malathion mixed fortification solution (Fort-3)
43767-039	Control + nominal 10 ug Each	500 mL	10 mL	8 mL	5.00 ① ~~2.50~~ mL	Fortify with 1.0 mL of 9.92 ug/mL diazinon and 10.2 ug/mL malathion mixed fortification solution (Fort-2)
43767-040	Control + nominal 10 ug Each	500 mL	10 mL	8 mL	5.00 ① ~~2.50~~ mL	Fortify with 1.0 mL of 9.92 ug/mL diazinon and 10.2 ug/mL malathion mixed fortification solution (Fort-2)
43767-041	Control + nominal 1000 ug Each	500 mL	10 mL	8 mL	10.0 mL, then dilute 0.50 mL to 15.5 mL	Fortify with 1.0 mL of 992 ug/mL diazinon and 1020 ug/mL malathion mixed fortification solution (Fort-1)
43767-042	Control + nominal 1000 ug Each	500 mL	10 mL	8 mL	10.0 mL, then dilute 0.50 mL to 15.5 mL	Fortify with 1.0 mL of 992 ug/mL diazinon and 1020 ug/mL malathion mixed fortification solution (Fort-1)

Remarks: ① F CYG 6-23-97

Methylene Chloride Burdick & Jackson, BN 794 CYG 6-23-97

Acetone: Burdick & Jackson, Lot # B0920 CYG 6-23-97

Hexane: Burdick & Jackson, Lot # BN936 CYG 6-23-97

Methanol: Burdick & Jackson, Lot # B0320 CYG 6-23-97

Aerosol OT Solution (75% w/w Aqueous), Fisher, Lot Number 963392

Water: Labconco DI

Checked by: BCB 24 Jun 1997

Approved by: 24 June 97

[43767] 29 767HWS10 Page 1
Reported on 24-JUN-1997 at 06:53
Modified on 23-JUN-1997 at 13:25

List Run Sequence File

ANALYST NAME..... CY Guo
43767 Hand Wash Solution SET 2

ANALYSIS INFORMATION

Analysis name..... 767HWS10
Method name..... 767HWS10
Calibration name..... 767HWS10
Calibration sequence..... Average Standard
User parameter 1 name..... Final Volume
User parameter 2 name..... Factor 1
User parameter 3 name..... Factor 2

SAMPLE SUMMARY

SAMPLE NUMBER	LIMS ID	SAMPLE NAME
1	----------	Solvent Blank
2	----------	GCMIX-1 NOMINAL 100 ng/mL
3	----------	GCMIX-2 NOMINAL 60 ng/mL
4	----------	43767-036
5	----------	43767-037
6	----------	43767-038
7	----------	GCMIX-3 NOMINAL 40 ng/mL
8	----------	43767-039
9	----------	43767-040
10	----------	GCMIX-4 NOMINAL 20 ng/mL
11	----------	43767-041
12	----------	43767-042
13	----------	GCMIX-5 NOMINAL 10 ng/mL
14	----------	GCMIX-6 NOMINAL 4 ng/mL

[43767] 29 767HWS10 Page 2
Reported on 24-JUN-1997 at 06:53
Modified on 23-JUN-1997 at 13:25

SAMPLE INFORMATION

SAMPLE NUMBER	TYPE	CALIB LEVEL	UPDATE RT	UPDATE RF	AMOUNT	NUM INJ	BOT NUM
1	Sa	--	-	-	1.00000	1	1
2	St	01	N	I	1.00000	1	2
3	St	02	N	I	1.00000	1	3
4	Sa	--	-	-	1.00000	1	4
5	Sa	--	-	-	1.00000	1	5
6	Sa	--	-	-	1.00000	1	6
7	St	03	N	I	1.00000	1	7
8	Sa	--	-	-	1.00000	1	8
9	Sa	--	-	-	1.00000	1	9
10	St	04	N	I	1.00000	1	10
11	Sa	--	-	-	1.00000	1	11
12	Sa	--	-	-	1.00000	1	12
13	St	05	N	I	1.00000	1	13
14	St	06	N	I	1.00000	1	14

USER PARAMETER VALUES

SAMPLE	FINAL VOLUME	FACTOR 1	FACTOR 2
1	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000
4	1.00000	1.00000	1.00000
5	2.50000	500.00000	10000.00000
6	2.50000	500.00000	10000.00000
7	1.00000	1.00000	1.00000
8	5.00000	500.00000	10000.00000
9	5.00000	500.00000	10000.00000
10	1.00000	1.00000	1.00000
11	10.00000	7750.00000	5000.00000
12	10.00000	7750.00000	5000.00000
13	1.00000	1.00000	1.00000
14	1.00000	1.00000	1.00000

[43767] 29 767HWS10 Page 3
Reported on 24-JUN-1997 at 06:53
Modified on 23-JUN-1997 at 13:25

INTERNAL/DILUTION STANDARDS

SAMPLE NUMBER	ISTD1 AMOUNT	ISTD2 AMOUNT	ISTD3 AMOUNT	DIL1 AMOUNT	DIL2 AMOUNT
1	1.00000	1.00000	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000	1.00000	1.00000
4	1.00000	1.00000	1.00000	1.00000	1.00000
5	1.00000	1.00000	1.00000	1.00000	1.00000
6	1.00000	1.00000	1.00000	1.00000	1.00000
7	1.00000	1.00000	1.00000	1.00000	1.00000
8	1.00000	1.00000	1.00000	1.00000	1.00000
9	1.00000	1.00000	1.00000	1.00000	1.00000
10	1.00000	1.00000	1.00000	1.00000	1.00000
11	1.00000	1.00000	1.00000	1.00000	1.00000
12	1.00000	1.00000	1.00000	1.00000	1.00000
13	1.00000	1.00000	1.00000	1.00000	1.00000
14	1.00000	1.00000	1.00000	1.00000	1.00000

PROCESSING ORDER

SAMPLE NUMBER	TYPE
2	Standard
3	Standard
7	Standard
10	Standard
13	Standard
14	Standard
1	Sample
4	Sample
5	Sample
6	Sample
8	Sample
9	Sample
11	Sample
12	Sample

Gas Chromatographic Instrument Parameters Form

ABC Laboratory Study Number: 43767
Customer Identification: ARTF

Instrument: HP 5890 Series II Material ID# 1652-0120
Autoinjector: HP 7673B Material ID# 1652-802A

Column: HP-5MS, 30 M X 0.25 mm, 0.25 μm film thickness
Serial#: 56253614

Detector Type: FPD/P

Electrometer: Range 4

Temperatures: Injector (°C): 230
Detector(°C): 230
Column:
Initial Temp. (°C): 95
Initial Time: 1.0 min.
Program Rate 1: 30 °C/min to 230 °C, hold 4 min
Program Rate 2: 40 °C/min to 290 °C, hold 4 min

Carrier Gas Flow Rate: He 1.6 mL/min
Septum Purge: He 2.0 mL/min
Make Up Gas: N_2 21 mL/min
Air Flow Rate: 98 mL/min
Hydrogen Flow Rate: 69 mL/min
Purge Valve: Off at 0 min, on at 0.75 min

Injection Volume: 2 μL

Quantitation Standard ID(s) # GCMIX-1,-2,-3,-4,-5,-6

Run Sequence File 767HWS10

Prepared by CY Guo Date: 6-23-97

Checked by [illegible] Date: 24 June 97

MCDO [43767] 29 767HWS10

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: DIAZINON

Report Date: 24 JUN 97
Time: 07:00:07
Page: 1

Sample Name	SMP #	INJ #	RT(mins)	Height	ng/mL or ug	CAL. RANG	Peak Type	Bad INJ
Solvent Blank	1	1	0.00	0	0.000	UNDR	OBF	---
GCMIX-1 NOMINAL 100 ng/mL	2	1	5.95	97919	99.272		OB	---
GCMIX-2 NOMINAL 60 ng/mL	3	1	5.96	56454	56.908		OB	---
43767-036	4	1	0.00	0	0.000	UNDR	OF	---
43767-037	5	1	5.95	7776	0.897		OB	---
43767-038	6	1	5.94	6890	0.784		OB	---
GCMIX-3 NOMINAL 40 ng/mL	7	1	5.94	42275	42.423		OBF	---
43767-039	8	1	5.95	36654	9.170		OB	---
43767-040	9	1	5.95	38065	9.530		OB	---
GCMIX-4 NOMINAL 20 ng/mL	10	1	5.96	20111	19.778		O	---
43767-041	11	1	5.96	65723	1028.862		OBF	---
43767-042	12	1	5.95	67127	1051.092		OBF	---
GCMIX-5 NOMINAL 10 ng/mL	13	1	5.95	10812	10.277		O	---
GCMIX-6 NOMINAL 4 ng/mL	14	1	5.95	4418	3.744		O	---

MCDO [43767] 29 767HWS10

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: MALATHION

Report Date: 24 JUN 97
Time: 07:00:07
Page: 1

Sample Name	SMP #	INJ #	RT(mins)	Height	ng/mL or ug	CAL. RANG	Peak Type	Bad INJ
Solvent Blank	1	1	0.00	0	0.000	UNDR	O	---
GCMIX-1 NOMINAL 100 ng/mL	2	1	6.81	60590	102.095		OB	---
GCMIX-2 NOMINAL 60 ng/mL	3	1	6.82	34661	58.067		OB	---
43767-036	4	1	0.00	0	0.000	UNDR	OB	---
43767-037	5	1	6.81	4898	0.941		OB	---
43767-038	6	1	6.80	4951	0.952		OB	---
GCMIX-3 NOMINAL 40 ng/mL	7	1	6.80	26707	44.561		OB	---
43767-039	8	1	6.81	23961	9.975		OB	---
43767-040	9	1	6.81	24910	10.377		OB	---
GCMIX-4 NOMINAL 20 ng/mL	10	1	6.82	12317	20.127		OB	---
43767-041	11	1	6.82	41026	1067.548		OB	---
43767-042	12	1	6.81	43822	1141.146		OB	---
GCMIX-5 NOMINAL 10 ng/mL	13	1	6.81	6598	10.416		OBF	---
GCMIX-6 NOMINAL 4 ng/mL	14	1	6.81	2765	3.907		O	---

Acquisition and Peak Processing Parameters Report Print Date and Time : 24 JUN 97 07:03:01
Page : 1

MCDO [43767] 29 767HWS10 Based on Sample Number : 1 Injection Number : 1

ACQUISITION PARAMETERS

Data Collection :

Length of Run..... 14.95 mins
Post Injection Delay..... 0.00 mins
Sampling Rate..... 15.00 Hz

PEAK PROCESSING PARAMETERS

Auto Process Parameters :

Peak Threshold..... 0.50
Baseline Test..... 4
Peak Trend..... 4

Separation Parameters :

Shoulder Sensitivity..... 0.10
Rider Sensitivity..... 0.05

Rejection Parameters :

Minimum Peak Width..... 0.00 secs
Minimum Peak Height..... 0.00 uV
Minimum Peak Area..... 2000.00 uVs
Ignore Flat Top Peak..... No

User Imposed Action Control :

Forced Baseline..... No
Suppress Integration..... Yes
Tangent Skimming..... No
Shoulder Detection..... No
Data Bunching..... No
Negative Detection..... No

Integration Modes :

Retention Time Integration..... No
Square Root Area and Height..... Yes

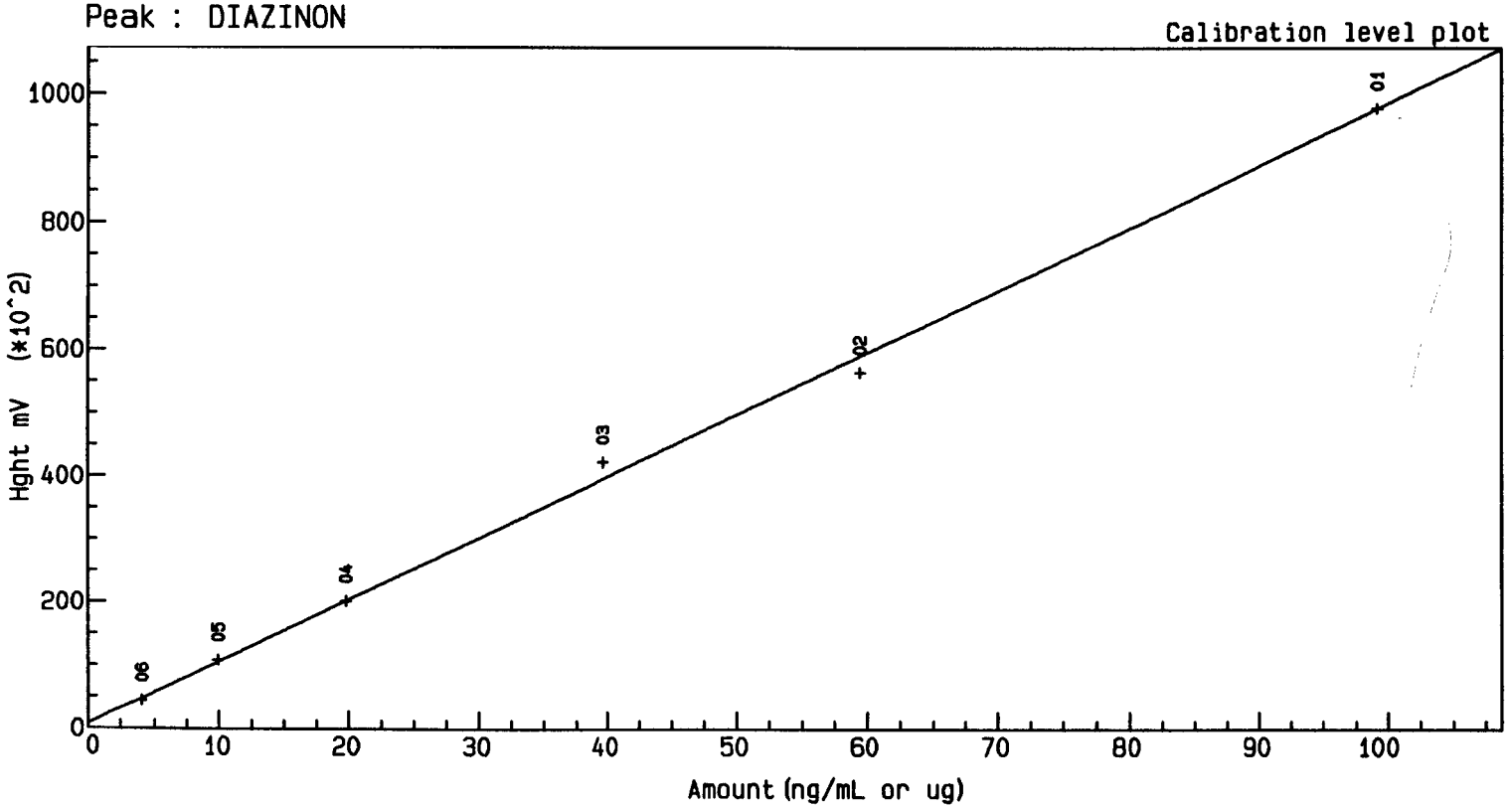
PROCESSING ACTIONS

Time (mins)	Force Baseline	Integrate Suppress	Tangent Skim	Bunch Size	Shoulder Detect	Negative Detect
0.00	--	SS	_	0	--	--
5.60	--	ES	_	0	--	--
7.10	--	SI	_	0	--	--

These parameters apply to all injections of set 767HWS10 with no exceptions

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767HWS10.
43767 Hand Wash Solution Set 2
Peak : DIAZINON



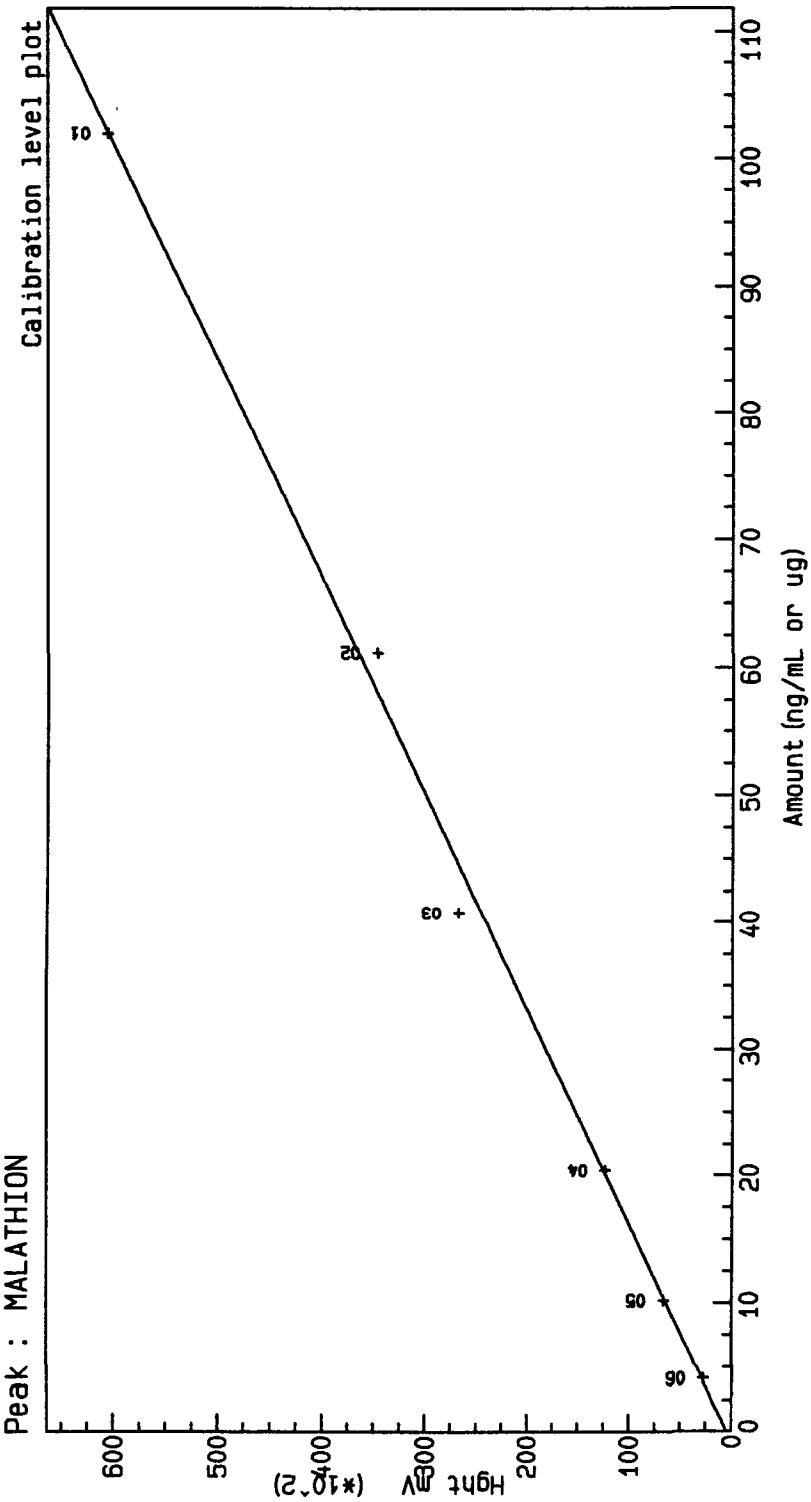
Constant : 7.52761E+2
1st degree : 9.78788E+2

Curve fit : Linear
Correlation coefficient : 0.99888
Standard error : 1.85155E+3

Reported on 24-JUN-1997 at 07:03

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767HWS10.
43767 Hand Wash Solution Set 2
Peak : MALATHION



Constant : 4.63858E+2
1st degree : 5.88927E+2

Curve fit : Linear
Correlation coefficient : 0.99822
Standard error : 1.44634E+3

Reported on 24-JUN-1997 at 07:03

ABC Laboratories, Inc.

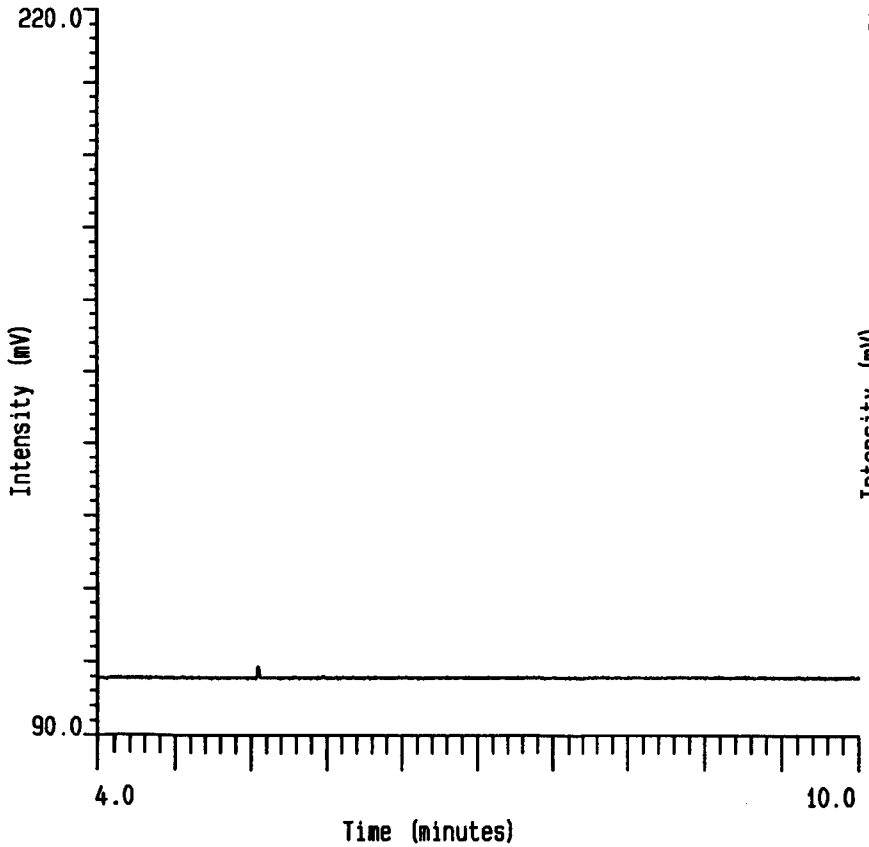
MCPP ver 2.3

43767 Hand Wash Solution SET 2

Date of Report: 24 JUN 97 at 07:04:20

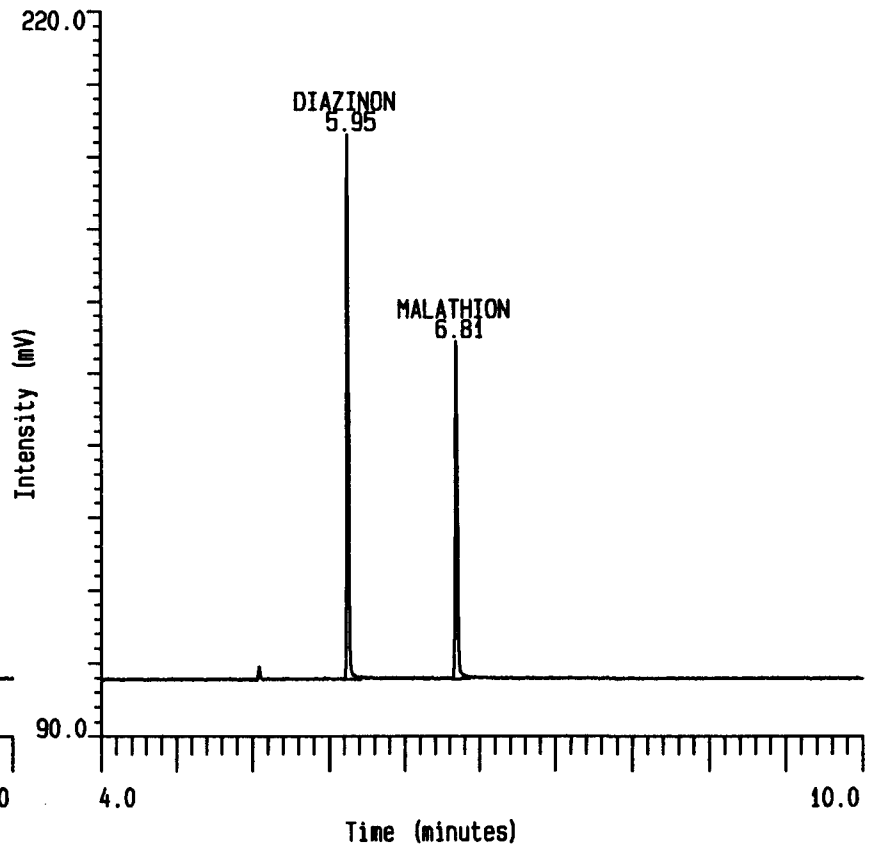
MCDO [43767] 29 767HWS10, 1, 1
Solvent Blank
Acquired on 23-Jun-1997 at 17:25

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	0.00	0	0
MALATHION	0.00	0	0



MCDO [43767] 29 767HWS10, 2, 1
GCMIX-1 NOMINAL 100 ng/mL
Acquired on 23-Jun-1997 at 17:46

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	97919	99.272
MALATHION	6.81	60590	102.095



ABC Laboratories, Inc.

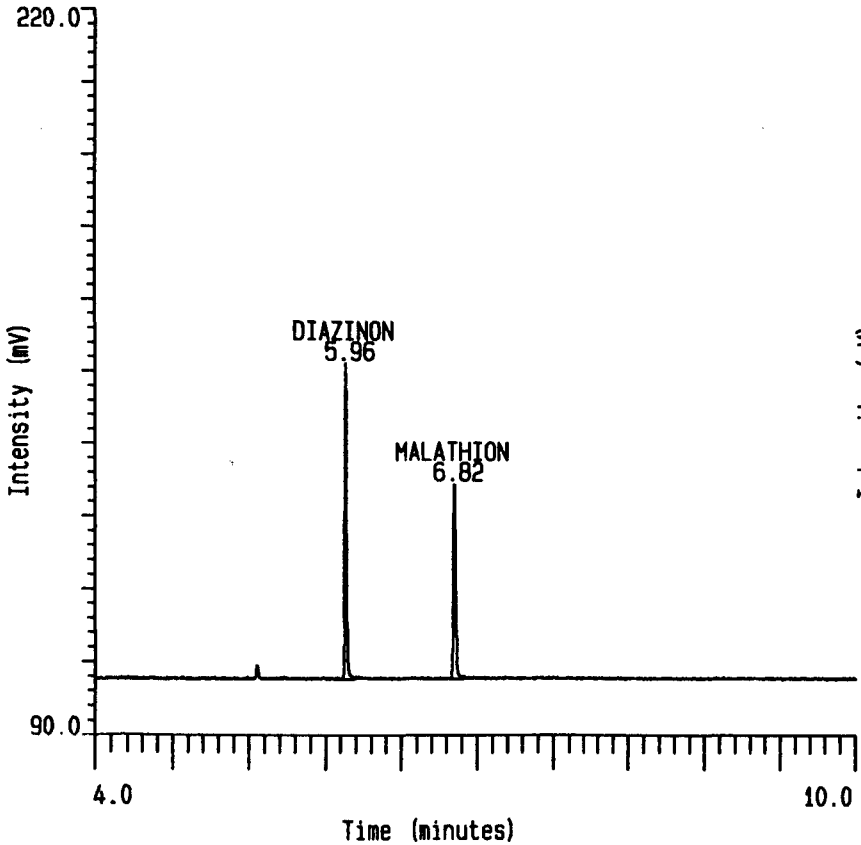
MCPP ver 2.3

43767 Hand Wash Solution SET 2

Date of Report: 24 JUN 97 at 07:04:20

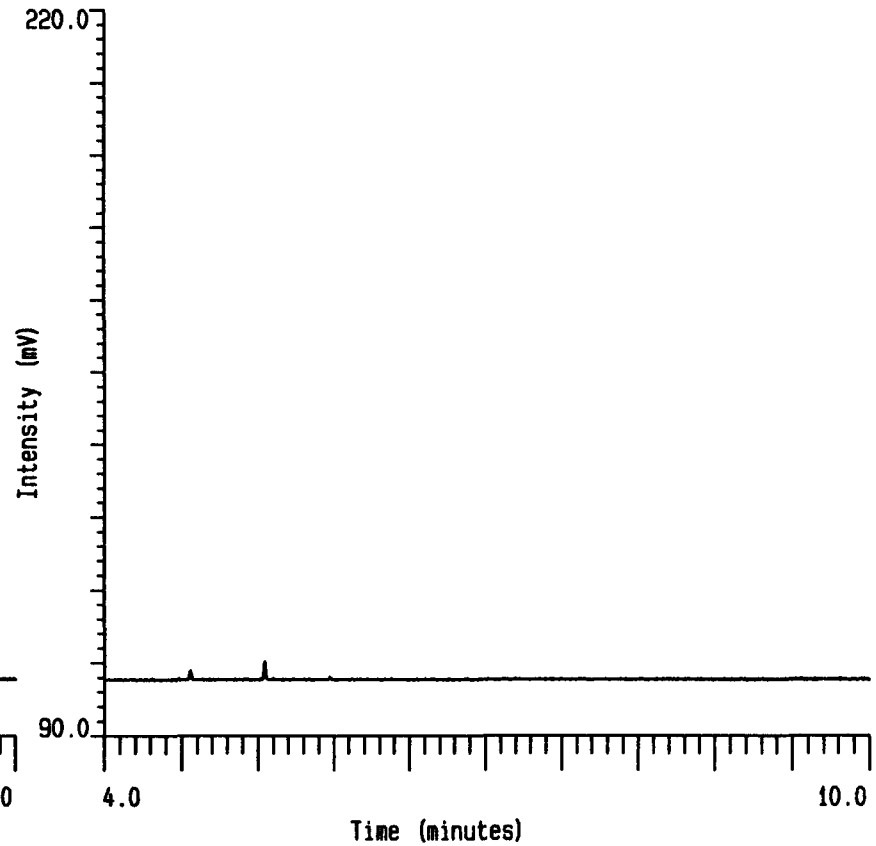
MCDO [43767] 29 767HWS10,3,1
GCMIX-2 NOMINAL 60 ng/mL
Acquired on 23-Jun-1997 at 18:06

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.96	56454	56.908
MALATHION	6.82	34661	58.067



MCDO [43767] 29 767HWS10,4,1
43767-036
Acquired on 23-Jun-1997 at 18:26

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	0.00	0	0
MALATHION	0.00	0	0



ABC Laboratories, Inc.

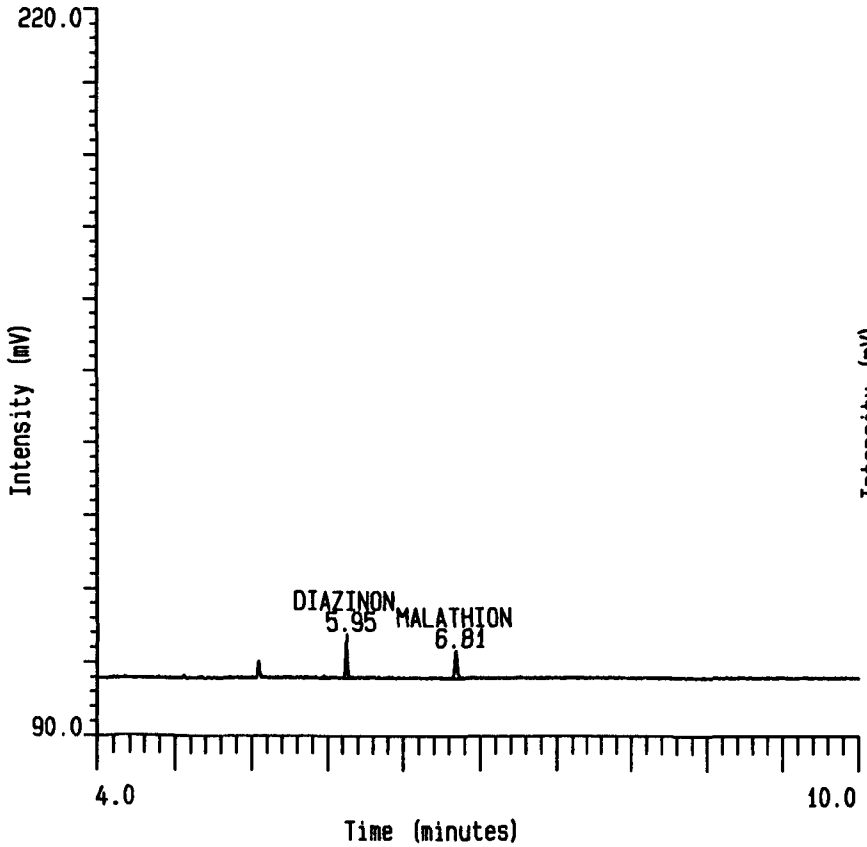
MCPP ver 2.3

43767 Hand Wash Solution SET 2

Date of Report: 24 JUN 97 at 07:04:20

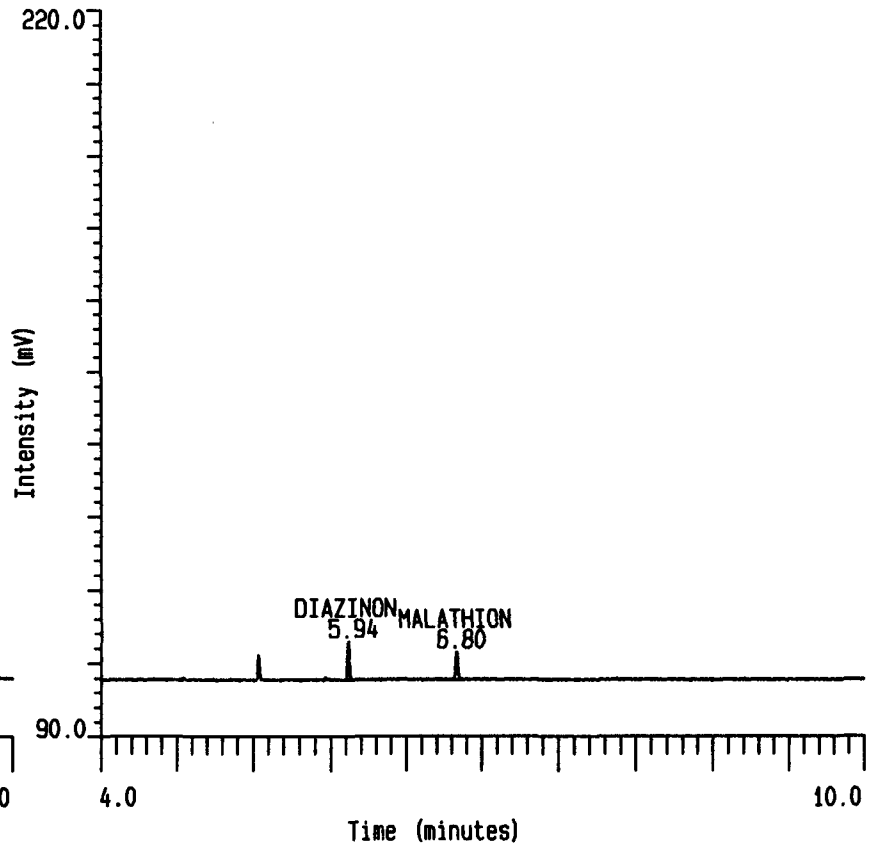
MCDO [43767] 29 767HWS10,5,1
43767-037
Acquired on 23-Jun-1997 at 18:47

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	7776	0.897
MALATHION	6.81	4898	0.941



MCDO [43767] 29 767HWS10,6,1
43767-038
Acquired on 23-Jun-1997 at 19:07

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.94	6890	0.784
MALATHION	6.80	4951	0.952



ABC Laboratories, Inc.

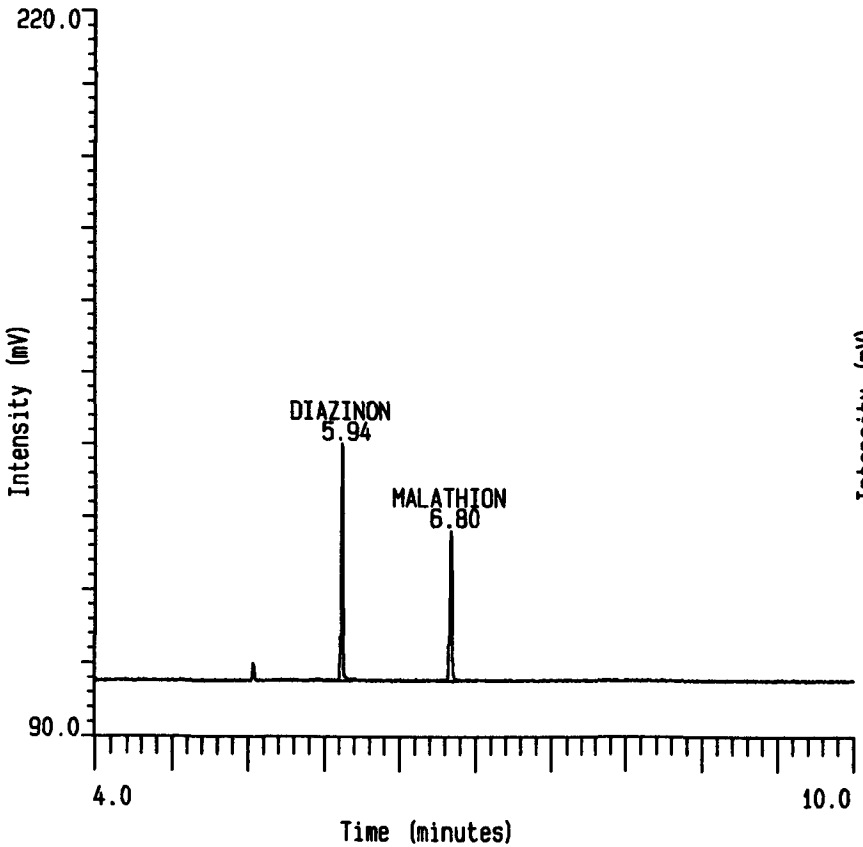
MCPP ver 2.3

43767 Hand Wash Solution SET 2

Date of Report: 24 JUN 97 at 07:04:20

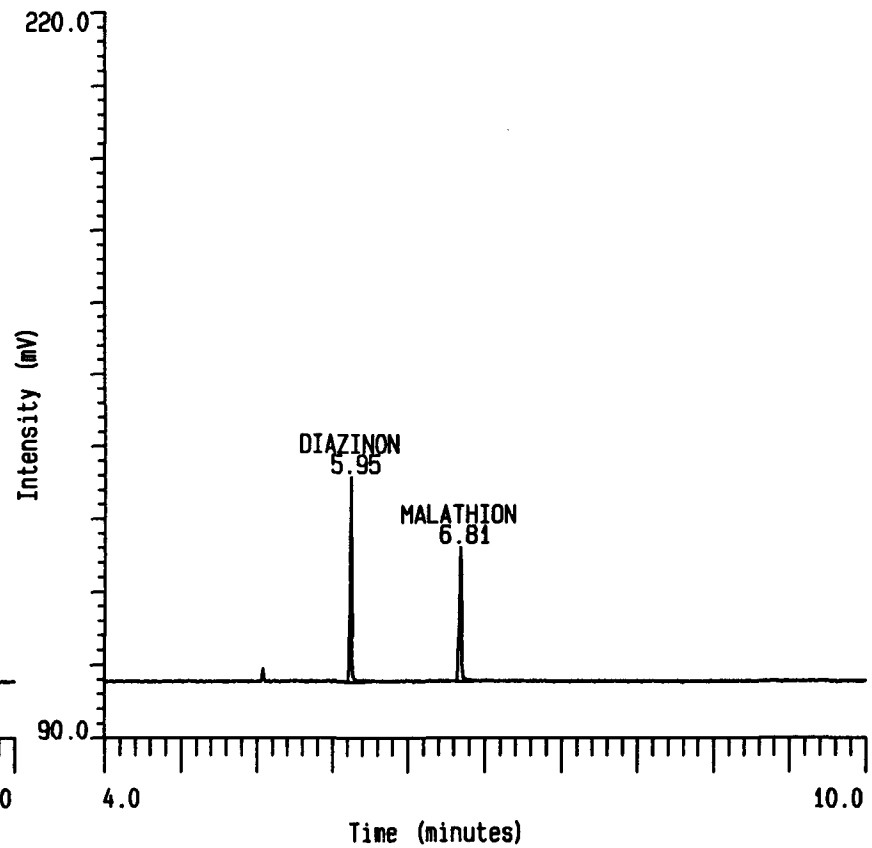
MCDO [43767] 29 767HWS10,7,1
GCMIX-3 NOMINAL 40 ng/mL
Acquired on 23-Jun-1997 at 19:27

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.94	42275	42.423
MALATHION	6.80	26707	44.561



MCDO [43767] 29 767HWS10,8,1
43767-039
Acquired on 23-Jun-1997 at 19:48

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	36654	9.170
MALATHION	6.81	23961	9.975



ABC Laboratories, Inc.

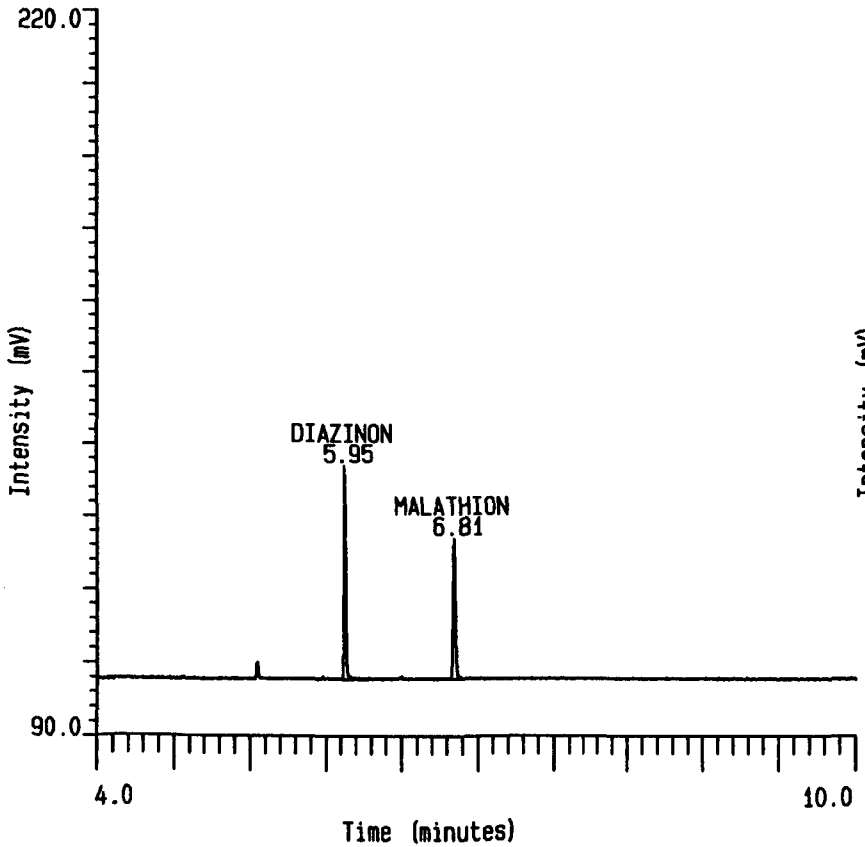
MCPP ver 2.3

43767 Hand Wash Solution SET 2

Date of Report: 24 JUN 97 at 07:04:20

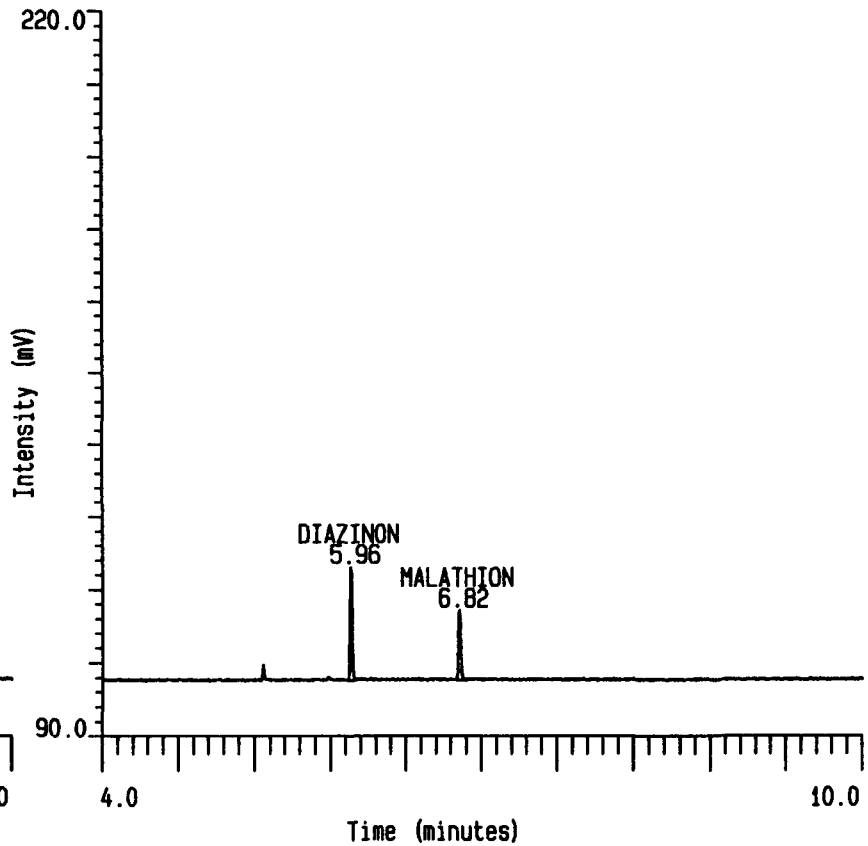
MCDO [43767] 29 767HWS10, 9, 1
43767-040
Acquired on 23-Jun-1997 at 20:08

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	38065	9.530
MALATHION	6.81	24910	10.377



MCDO [43767] 29 767HWS10, 10, 1
GCMIX-4 NOMINAL 20 ng/mL
Acquired on 23-Jun-1997 at 20:28

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.96	20111	19.778
MALATHION	6.82	12317	20.127



ABC Laboratories, Inc.

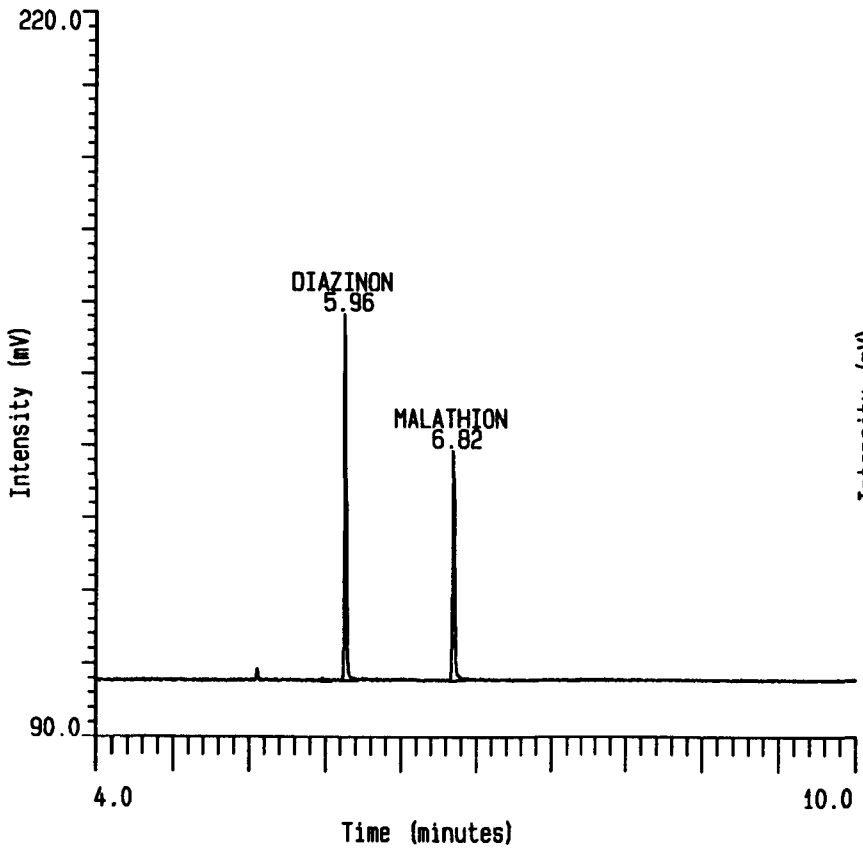
MCPP ver 2.3

43767 Hand Wash Solution SET 2

Date of Report: 24 JUN 97 at 07:04:20

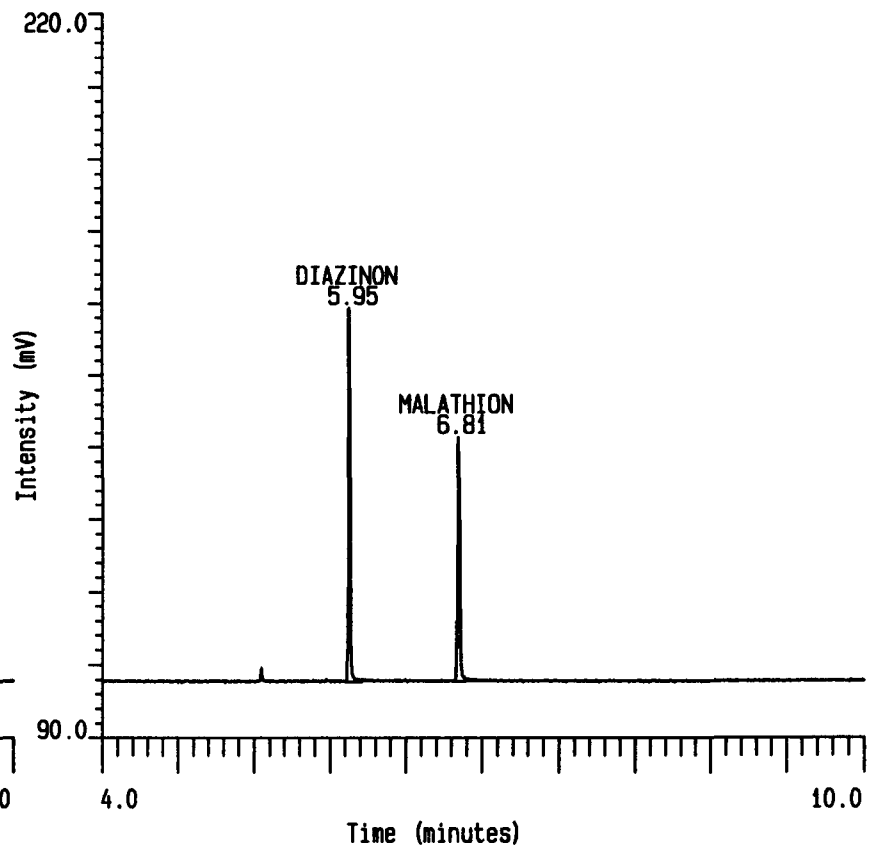
MCDO [43767] 29 767HWS10, 11, 1
43767-041
Acquired on 23-Jun-1997 at 20:49

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.96	65723	1028.862
MALATHION	6.82	41026	1067.548



MCDO [43767] 29 767HWS10, 12, 1
43767-042
Acquired on 23-Jun-1997 at 21:09

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	67127	1051.092
MALATHION	6.81	43822	1141.146



ABC Laboratories, Inc.

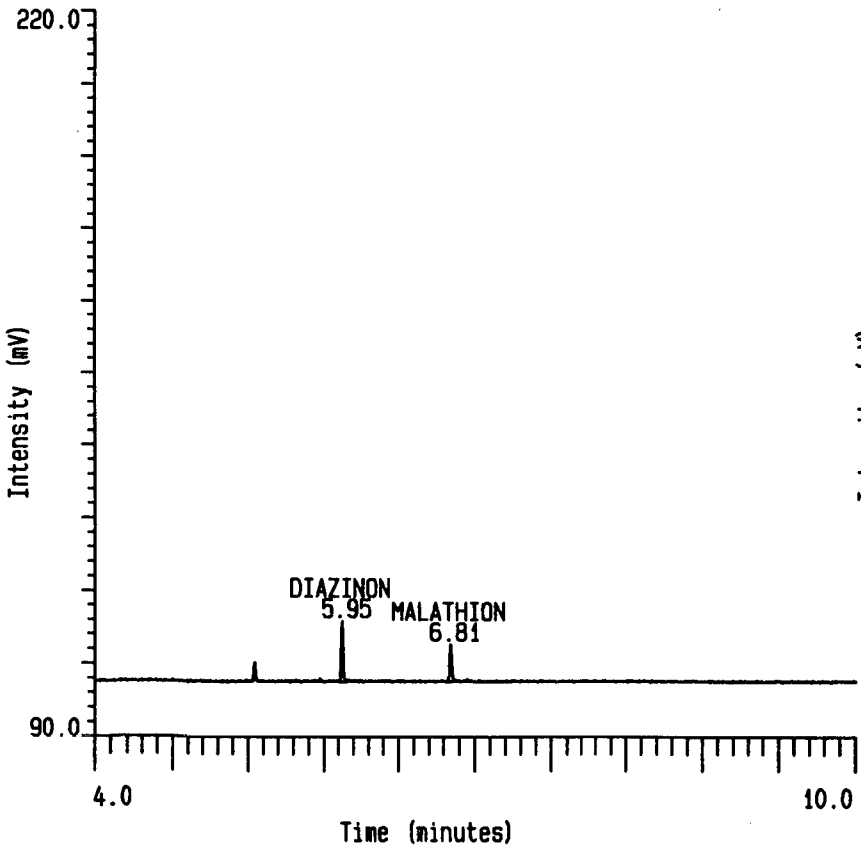
MCPP ver 2.3

43767 Hand Wash Solution SET 2

Date of Report: 24 JUN 97 at 07:04:20

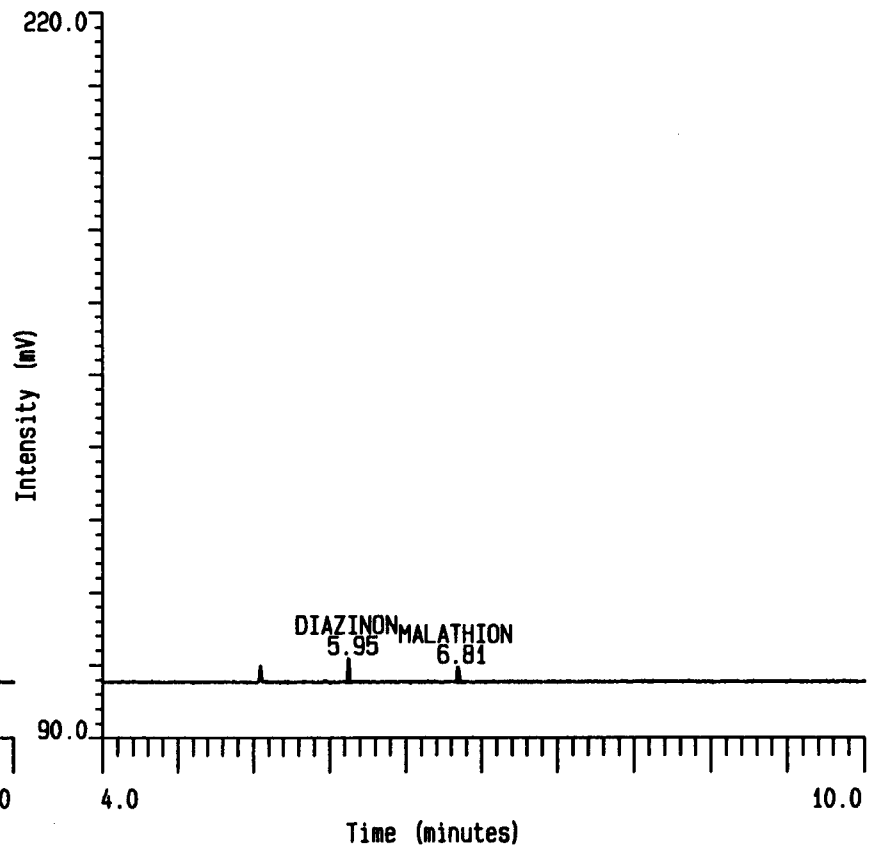
MCDO [43767] 29 767HWS10, 13, 1
GCMIX-5 NOMINAL 10 ng/mL
Acquired on 23-Jun-1997 at 21:29

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	10812	10.277
MALATHION	6.81	6598	10.416



MCDO [43767] 29 767HWS10, 14, 1
GCMIX-6 NOMINAL 4 ng/mL
Acquired on 23-Jun-1997 at 21:50

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	4418	3.744
MALATHION	6.81	2765	3.907



[43767] 29 767HWS10 Page 1
Reported on 24-JUN-1997 at 09:03
Modified on 24-JUN-1997 at 06:56

List Calibration File

CALIBRATION HEADER INFORMATION

Calibration Title : 43767 Hand Wash Solution Set 2
General :
Calibration type..... External standard
Units..... ng/mL or ug
Calibration base..... Height
Reference Peak Identification :
Reference window..... 5.0 %
Minimum window..... 0.50 mins
Peak threshold..... 0.0 %
Uncalibrated Peaks Response Factor :
Response factor source..... User set response factor
Response factor..... 0.0000
Additional Information :
Source library..... None
Initialise on 1st standard..... No
Variation tolerance..... 100.00 %
Calibrant Peak Identification :
Calibrant window..... 0.10 mins
Calibrant threshold..... 0.0 %
Response Factor Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... 1 / Y
Retention Value Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... None
Timed Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... None
No group information entered.

[43767] 29 767HWS10 Page 2
Reported on 24-JUN-1997 at 09:03
Modified on 24-JUN-1997 at 06:56

Peak name : DIAZINON
Expected retention time : 5.93 mins (RT range : 5.88 - 5.98 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	3.9700	1112.7357	1
05	9.9200	1089.8757	1
04	19.8000	1015.6985	1
03	39.7000	1064.8729	1
02	59.5000	948.8038	1
01	99.2000	987.0828	1

Peak name : MALATHION
Expected retention time : 6.80 mins (RT range : 6.75 - 6.85 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	4.0800	677.6139	1
05	10.2000	646.9003	1
04	20.4000	603.7921	1
03	40.8000	654.5894	1
02	61.2000	566.3546	1
01	102.0000	594.0206	1

Attachment 4. Validation Data for Leaf Wash Method ARTF-AM-007

Summary Results for AOT Leaf Wash Method Validation - Diazinon
Reference Multichrom files 767FDS2 and 767FDS3

Sample ID	Sample Description	Diazinon Fortification Level (ug/sample)	Diazinon Recovery (ug/sample)	% Recovery
43767-043	Control	NA	Not Detected	
43767-044	Control + nominal 2 ug each	1.98	1.37	69.2%
43767-045	Control + nominal 2 ug each	1.98	1.62	81.8%
43767-046	Control + nominal 20 ug each	19.8	17.6	88.9%
43767-047	Control + nominal 20 ug each	19.8	18.3	92.4%
43767-048	Control + nominal 2000 ug each	1980	1870	94.4%
43767-049	Control + nominal 2000 ug each	1980	1800	90.9%
43767-050	Control	NA	Not Detected	
43767-051	Control + nominal 2 ug each	1.98	2.12	107%
43767-052	Control + nominal 2 ug each	1.98	1.70	85.9%
43767-053	Control + nominal 20 ug each	19.8	19.1	96.5%
43767-054	Control + nominal 20 ug each	19.8	19.3	97.5%
43767-055	Control + nominal 2000 ug each	1980	2010	102%
43767-056	Control + nominal 2000 ug each	1980	2030	103%
			Average % Recovery (n=12)	92.5%
			Standard Deviation (n=12)	10.3%
			Avg. + 2 Std. Dev.	113%
			Avg. - 2 Std. Dev.	71.9%

Prepared by: [illegible] 2 July 97

Checked by: Barbara J Bryant 02 Jul 1997

Summary Results for AOT Leaf Wash Method Validation - Malathion
Reference Multichrom files 767FDS2 and 767FDS3

Sample ID	Sample Description	Malathion Fortification Level (ug/sample)	Malathion Recovery (ug/sample)	% Recovery
43767-043	Control	NA	Not Detected	
43767-044	Control + nominal 2 ug each	2.04	1.39	68.1%
43767-045	Control + nominal 2 ug each	2.04	2.14	105%
43767-046	Control + nominal 20 ug each	20.4	19.5	95.6%
43767-047	Control + nominal 20 ug each	20.4	19.8	97.1%
43767-048	Control + nominal 2000 ug each	2040	2010	98.5%
43767-049	Control + nominal 2000 ug each	2040	1930	94.6%
43767-050	Control	NA	Not Detected	
43767-051	Control + nominal 2 ug each	2.04	2.19	107%
43767-052	Control + nominal 2 ug each	2.04	1.89	92.6%
43767-053	Control + nominal 20 ug each	20.4	20.4	100%
43767-054	Control + nominal 20 ug each	20.4	21.0	103%
43767-055	Control + nominal 2000 ug each	2040	2060	101%
43767-056	Control + nominal 2000 ug each	2040	2200	108%
			Average % Recovery (n=12)	97.5%
			Standard Deviation (n=12)	10.5%
			Avg. + 2 Std. Dev.	119%
			Avg. - 2 Std. Dev.	76.5%

Prepared by: 2 Jul 97

Checked by: Barbara J Bryant 02 Jul 1997

Observations and Remarks

Test Material: Diazinon and Malathion Study Sponsor: ARTF Matrices: Various Study Number: 43767	Form AC72A (5/4/93) ABC Laboratories, Inc. 7200 E. ABC Lane Columbia, MO 65202
	Study Director: Loren C. Schrier

COMMENTS

prep. of 0.01% Aqueous AOT 75 solution

0.4 mL of 75% AOT was dissolved in 1 gallon Labconco water.

prep. of UTC Dislodging solution:

2.1 cm diameter borer was used on spinach, the surface area of one leaf disk was

$2\pi r^2 = 2(3.1416)(1.05)^2 = 6.93\ cm^2$;

A single sample: $400\ cm^2 / 6.93\ cm^2 = 58$ leaf disks

Aerosol OT Solution 75% w/w Aqueous, Fisher, Lot # 963372
A345-500

Entered by: CY Guo Date: 6-25-97

Checked by: Barbara J Bryant Date: 02 Jul 1997

Approved by: [signature] Date: 2 Jul 97

Observations and Remarks

Test Material: Diazinon and Malathion Study Sponsor: ARTF Matrices: Various Study Number: 43767	Form AC72A (5/4/93) ABC Laboratories, Inc. 7200 E. ABC Lane Columbia, MO 65202
	Study Director: Loren C. Schrier

COMMENTS

the weight of 59 leaf disks: 5.7g.

19 samples x 5.7g = 108.3g.

108.3g leaf disks was immersed in 1.9L of 0.01% AOT solution. ~~shaked~~ shaken 2min vigorously. The extract was decanted into a clean container, then 1.9L of 0.01% AOT solution was added, shaked 2min. Combined the extract with the original extract. Total 3.8L, stored in Refrigerator #1715745

Balance: 1622-172

DE CYG 6-25-97

Entered by: CY Guo Date: 6-25-97

Checked by: Barbara J Bryant Date: 02 Jul 1997

Approved by: [illegible] Date: 2 Jul 97

SAMPLE TRACKING FORM

Customer Name: ARTF	Study Director: Loren C. Schrier	Test Material: Diazinon and Malathion	Matrix: 0.01% AOT (Spinach)
ARTF Protocol: ARF003	ABC Study Number: 43767	0.01% AOT Dislodging Solution Method Validation Set 1	

C-18RP Column Cleanup (Section II. C.2)					GC/FPD Analysis (Section II. D.)	Sequence File	Chromatography review: 2 Jul 97
CYG 6-27-97					CYG 6-27-97	CYG 6-27-97	Spreadsheet entry by: 2 Jul 97

ABC Lab Number	Sample Identification	Sample Volume	Sample Volume for Cleanup	Eluent Volume (Methylene Chloride)	Final Volume and Dilutions	Fortified by: CYG 6-27-97 Witnessed by: Barbara Bryant 27 Jun 1997
43767-043	Control	200 mL	5 mL	8 mL	6.00 mL	
43767-044	Control + nominal 2 ug Each	200 mL	5 mL	8 mL	6.00 mL	Fortify with 1.0 mL of 1.98 ug/mL diazinon and 2.04 ug/mL malathion mixed fortification solution (Fort-7)
43767-045	Control + nominal 2 ug Each	200 mL	5 mL	8 mL	6.00 mL	Fortify with 1.0 mL of 1.98 ug/mL diazinon and 2.04 ug/mL malathion mixed fortification solution (Fort-7)
43767-046	Control + nominal 20 ug Each	200 mL	5 mL	8 mL	10.0 mL	Fortify with 1.0 mL of 19.8 ug/mL diazinon and 20.4 ug/mL malathion mixed fortification solution (Fort-6)
43767-047	Control + nominal 20 ug Each	200 mL	5 mL	8 mL	10.0 mL	Fortify with 1.0 mL of 19.8 ug/mL diazinon and 20.4 ug/mL malathion mixed fortification solution (Fort-6)
43767-048	Control + nominal 2000 ug Each	200 mL	5 mL	8 mL	25.0 mL, then dilute 0.50 mL to 15.5 mL	Fortify with 1.0 mL of 1980 ug/mL diazinon and 2040 ug/mL malathion mixed fortification solution (Fort-5)
43767-049	Control + nominal 2000 ug Each	200 mL	5 mL	8 mL	25.0 mL, then dilute 0.50 mL to 15.5 mL	Fortify with 1.0 mL of 1980 ug/mL diazinon and 2040 ug/mL malathion mixed fortification solution (Fort-5)

Remarks:

Methylene Chloride Burdick & Jackson, Lot # BN794 CYG 6-27-97

Acetone: Burdick & Jackson, Lot # B0920 CYG 6-27-97

Hexane: NA CYG 6-27-97

Methanol: Burdick & Jackson, Lot # B0820 CYG 6-27-97

Aerosol OT Solution (75% w/w Aqueous), Fisher, Lot Number 963392

Water: Labconco DI

Checked by: BB 03 Jul 1997 Approved by: 28 Jul 97

[43767] 29 767FDS2 Page 1
Reported on 28-JUN-1997 at 09:12
Modified on 27-JUN-1997 at 14:48

List Run Sequence File

ANALYST NAME..... CY Guo
43767 Dislodging Solution Set 1

ANALYSIS INFORMATION

Analysis name..... 767FDS2
Method name..... 767FDS2
Calibration name..... 767FDS2
Calibration sequence..... Average Standard
User parameter 1 name..... Final Volume
User parameter 2 name..... Factor 1
User parameter 3 name..... Factor 2

SAMPLE SUMMARY

SAMPLE NUMBER	LIMS ID	SAMPLE NAME
1	----------	Solvent Blank
2	----------	GCMIX-1 NOMINAL 100 ng/mL
3	----------	GCMIX-2 NOMINAL 60 ng/mL
4	----------	43767-043
5	----------	43767-044
6	----------	43767-045
7	----------	GCMIX-3 NOMINAL 40 ng/mL
8	----------	43767-046
9	----------	43767-047
10	----------	GCMIX-4 NOMINAL 20 ng/mL
11	----------	43767-048
12	----------	43767-049
13	----------	GCMIX-5 NOMINAL 10 ng/mL
14	----------	GCMIX-6 NOMINAL 4 ng/mL

[43767] 29 767FDS2 Page 2
Reported on 28-JUN-1997 at 09:12
Modified on 27-JUN-1997 at 14:48

SAMPLE INFORMATION

SAMPLE NUMBER	TYPE	CALIB LEVEL	UPDATE RT	UPDATE RF	AMOUNT	NUM INJ	BOT NUM
1	Sa	--	-	-	1.00000	1	1
2	St	01	N	I	1.00000	1	2
3	St	02	N	I	1.00000	1	3
4	Sa	--	-	-	1.00000	1	4
5	Sa	--	-	-	1.00000	1	5
6	Sa	--	-	-	1.00000	1	6
7	St	03	N	I	1.00000	1	7
8	Sa	--	-	-	1.00000	1	8
9	Sa	--	-	-	1.00000	1	9
10	St	04	N	I	1.00000	1	10
11	Sa	--	-	-	1.00000	1	11
12	Sa	--	-	-	1.00000	1	12
13	St	05	N	I	1.00000	1	13
14	St	06	N	I	1.00000	1	14

USER PARAMETER VALUES

SAMPLE	FINAL VOLUME	FACTOR 1	FACTOR 2
1	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000
4	1.00000	1.00000	1.00000
5	6.00000	200.00000	5000.00000
6	6.00000	200.00000	5000.00000
7	1.00000	1.00000	1.00000
8	10.00000	200.00000	5000.00000
9	10.00000	200.00000	5000.00000
10	1.00000	1.00000	1.00000
11	25.00000	3100.00000	2500.00000
12	25.00000	3100.00000	2500.00000
13	1.00000	1.00000	1.00000
14	1.00000	1.00000	1.00000

[43767] 29 767FDS2 Page 3
Reported on 28-JUN-1997 at 09:12
Modified on 27-JUN-1997 at 14:48

INTERNAL/DILUTION STANDARDS

SAMPLE NUMBER	ISTD1 AMOUNT	ISTD2 AMOUNT	ISTD3 AMOUNT	DIL1 AMOUNT	DIL2 AMOUNT
1	1.00000	1.00000	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000	1.00000	1.00000
4	1.00000	1.00000	1.00000	1.00000	1.00000
5	1.00000	1.00000	1.00000	1.00000	1.00000
6	1.00000	1.00000	1.00000	1.00000	1.00000
7	1.00000	1.00000	1.00000	1.00000	1.00000
8	1.00000	1.00000	1.00000	1.00000	1.00000
9	1.00000	1.00000	1.00000	1.00000	1.00000
10	1.00000	1.00000	1.00000	1.00000	1.00000
11	1.00000	1.00000	1.00000	1.00000	1.00000
12	1.00000	1.00000	1.00000	1.00000	1.00000
13	1.00000	1.00000	1.00000	1.00000	1.00000
14	1.00000	1.00000	1.00000	1.00000	1.00000

PROCESSING ORDER

SAMPLE NUMBER	TYPE
2	Standard
3	Standard
7	Standard
10	Standard
13	Standard
14	Standard
1	Sample
4	Sample
5	Sample
6	Sample
8	Sample
9	Sample
11	Sample
12	Sample

Gas Chromatographic Instrument Parameters Form

ABC Laboratory Study Number: 43767
Customer Identification: ARTF

Instrument: HP 5890 Series II Material ID# 1652-0120
Autoinjector: HP 7673B Material ID# 1652-802A

Column: HP-5MS; 30 M X 0.25 mm, 0.25 μm film thickness
Serial#: 56253614

Detector Type: FPD/P

Electrometer: Range 4

Temperatures: Injector (°C): 230
Detector(°C): 230
Column:
Initial Temp. (°C): 95
Initial Time: 1.0 min.
Program Rate 1: 30 °C/min to 230 °C, hold 4 min
Program Rate 2: 40 °C/min to 290 °C, hold 4 min

Carrier Gas Flow Rate: He 1.6 mL/min
Septum Purge: He 2.0 mL/min
Make Up Gas: N_2 21 mL/min
Air Flow Rate: 98 mL/min
Hydrogen Flow Rate: 69 mL/min
Purge Valve: Off at 0 min, on at 0.75 min

Injection Volume: 2 μL

Quantitation Standard ID(s) # GCMIX-1, -2, -3, -4, -5, -6

Run Sequence File 767FDS2

Prepared by CY Guo Date: 6-27-97

Checked by Barbara J Bryant Date: 02 Jul 1997

MCDO [43767] 29 767FDS2

ABC Laboratories, Inc.
Sample Information Report ver 3.3

Report Date: 28 JUN 97 at 09:21:17
Page 1

Sample Name	No.	Type	Level	User Parameter 1 Final Volume	User Parameter 2 Factor 1	User Parameter 3 Factor 2
Solvent Blank	1	SA		1.00000	1.00000	1.00000
GCMIX-1 NOMINAL 100 ng/mL	2	ST	01	1.00000	1.00000	1.00000
GCMIX-2 NOMINAL 60 ng/mL	3	ST	02	1.00000	1.00000	1.00000
43767-043	4	SA		1.00000	1.00000	1.00000
43767-044	5	SA		6.00000	200.00000	5000.00000
43767-045	6	SA		6.00000	200.00000	5000.00000
GCMIX-3 NOMINAL 40 ng/mL	7	ST	03	1.00000	1.00000	1.00000
43767-046	8	SA		10.00000	200.00000	5000.00000
43767-047	9	SA		10.00000	200.00000	5000.00000
GCMIX-4 NOMINAL 20 ng/mL	10	ST	04	1.00000	1.00000	1.00000
43767-048	11	SA		25.00000	3100.00000	2500.00000
43767-049	12	SA		25.00000	3100.00000	2500.00000
GCMIX-5 NOMINAL 10 ng/mL	13	ST	05	1.00000	1.00000	1.00000
GCMIX-6 NOMINAL 4 ng/mL	14	ST	06	1.00000	1.00000	1.00000

MCDO [43767] 29 767FDS2

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: DIAZINON

Report Date: 28 JUN 97
Time: 09:21:17
Page: 1

Sample Name	SMP #	INJ #	RT(mins)	Height	ng/mL or ug	CAL. RANG	Peak Type	Bad INJ
Solvent Blank	1	1	0.00	0	0.000	UNDR	OB	---
GCMIX-1 NOMINAL 100 ng/mL	2	1	5.93	109040	102.248		OB	---
GCMIX-2 NOMINAL 60 ng/mL	3	1	5.93	61466	57.749		OB	---
43767-043	4	1	0.00	0	0.000	UNDR	O	---
43767-044	5	1	5.92	5840	1.372		OBF	---
43767-045	6	1	5.93	6942	1.620		OF	---
GCMIX-3 NOMINAL 40 ng/mL	7	1	5.93	41893	39.441		OB	---
43767-046	8	1	5.92	46740	17.590		OB	---
43767-047	9	1	5.93	48708	18.326		OB	---
GCMIX-4 NOMINAL 20 ng/mL	10	1	5.92	19824	18.799		OB	---
43767-048	11	1	5.93	64057	1865.337		OB	---
43767-049	12	1	5.93	61851	1801.388		OB	---
GCMIX-5 NOMINAL 10 ng/mL	13	1	5.93	10224	9.819		OB	---
GCMIX-6 NOMINAL 4 ng/mL	14	1	5.93	4277	4.257		OBF	---

MCDO [43767] 29 767FDS2

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: MALATHION

Report Date: 28 JUN 97
Time: 09:21:17
Page: 1

Sample Name	SMP #	INJ #	RT(mins)	Height	ng/mL or ug	CAL. RANG	Peak Type	Bad INJ
Solvent Blank	1	1	0.00	0	0.000	UNDR	OB	---
GCMIX-1 NOMINAL 100 ng/mL	2	1	6.78	68102	106.210		OB	---
GCMIX-2 NOMINAL 60 ng/mL	3	1	6.78	37429	58.508		OB	---
43767-043	4	1	0.00	0	0.000	UNDR	OF	---
43767-044	5	1	6.78	3519	1.385		O	---
43767-045	6	1	6.78	5541	2.140		OB	---
GCMIX-3 NOMINAL 40 ng/mL	7	1	6.78	25686	40.246		OB	---
43767-046	8	1	6.78	31188	19.521		OB	---
43767-047	9	1	6.78	31629	19.795		OB	---
GCMIX-4 NOMINAL 20 ng/mL	10	1	6.77	12421	19.615		OB	---
43767-048	11	1	6.78	41599	2014.798		OB	---
43767-049	12	1	6.78	39737	1925.021		OB	---
GCMIX-5 NOMINAL 10 ng/mL	13	1	6.78	6286	10.075		OB	---
GCMIX-6 NOMINAL 4 ng/mL	14	1	6.78	2625	4.381		OB	---

Acquisition and Peak Processing Parameters Report Print Date and Time : 28 JUN 97 09:27:18
Page : 1
MCDO [43767] 29 767FDS2 Based on Sample Number : 1 Injection Number : 1

ACQUISITION PARAMETERS
Data Collection :
Length of Run..... 14.95 mins
Post Injection Delay..... 0.00 mins
Sampling Rate..... 15.00 Hz

PEAK PROCESSING PARAMETERS
Auto Process Parameters :
Peak Threshold..... 0.50
Baseline Test..... 4
Peak Trend..... 4
Separation Parameters :
Shoulder Sensitivity..... 0.10
Rider Sensitivity..... 0.05
Rejection Parameters :
Minimum Peak Width..... 0.00 secs
Minimum Peak Height..... 0.00 uV
Minimum Peak Area..... 2000.00 uVs
Ignore Flat Top Peak..... No
User Imposed Action Control :
Forced Baseline..... No
Suppress Integration..... Yes
Tangent Skimming..... No
Shoulder Detection..... No
Data Bunching..... No
Negative Detection..... No
Integration Modes :
Retention Time Integration..... No
Square Root Area and Height..... Yes

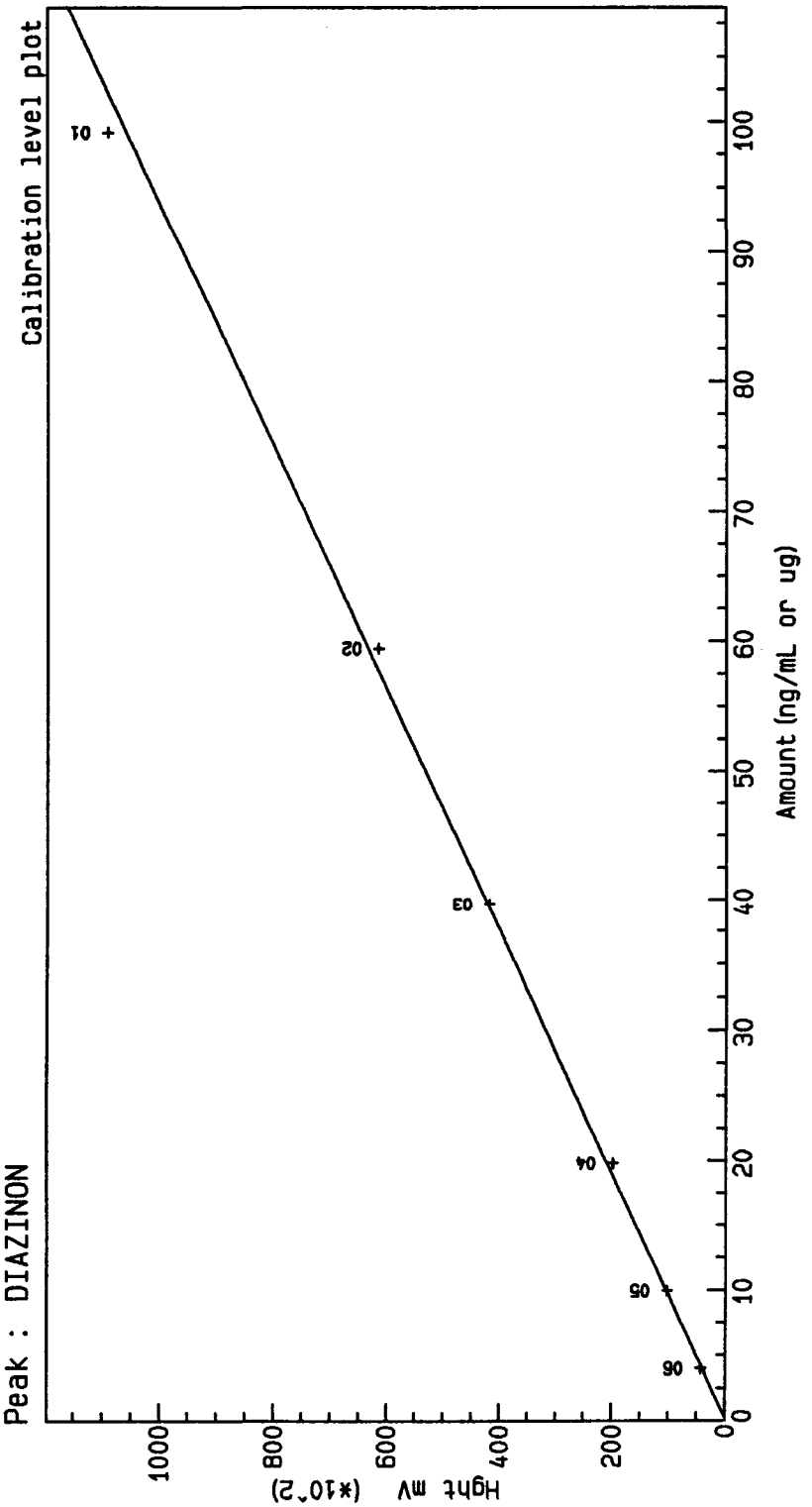
PROCESSING ACTIONS

Time (mins)	Force Baseline	Integrate Suppress	Tangent Skim	Bunch Size	Shoulder Detect	Negative Detect
0.00	--	SS	_	0	--	--
5.30	--	ES	_	0	--	--
7.50	--	SI	_	0	--	--

These parameters apply to all injections of set 767FDS2 with no exceptions

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767FDS2.
43767 Dislodging Solution Set 1
Peak : DIAZINON



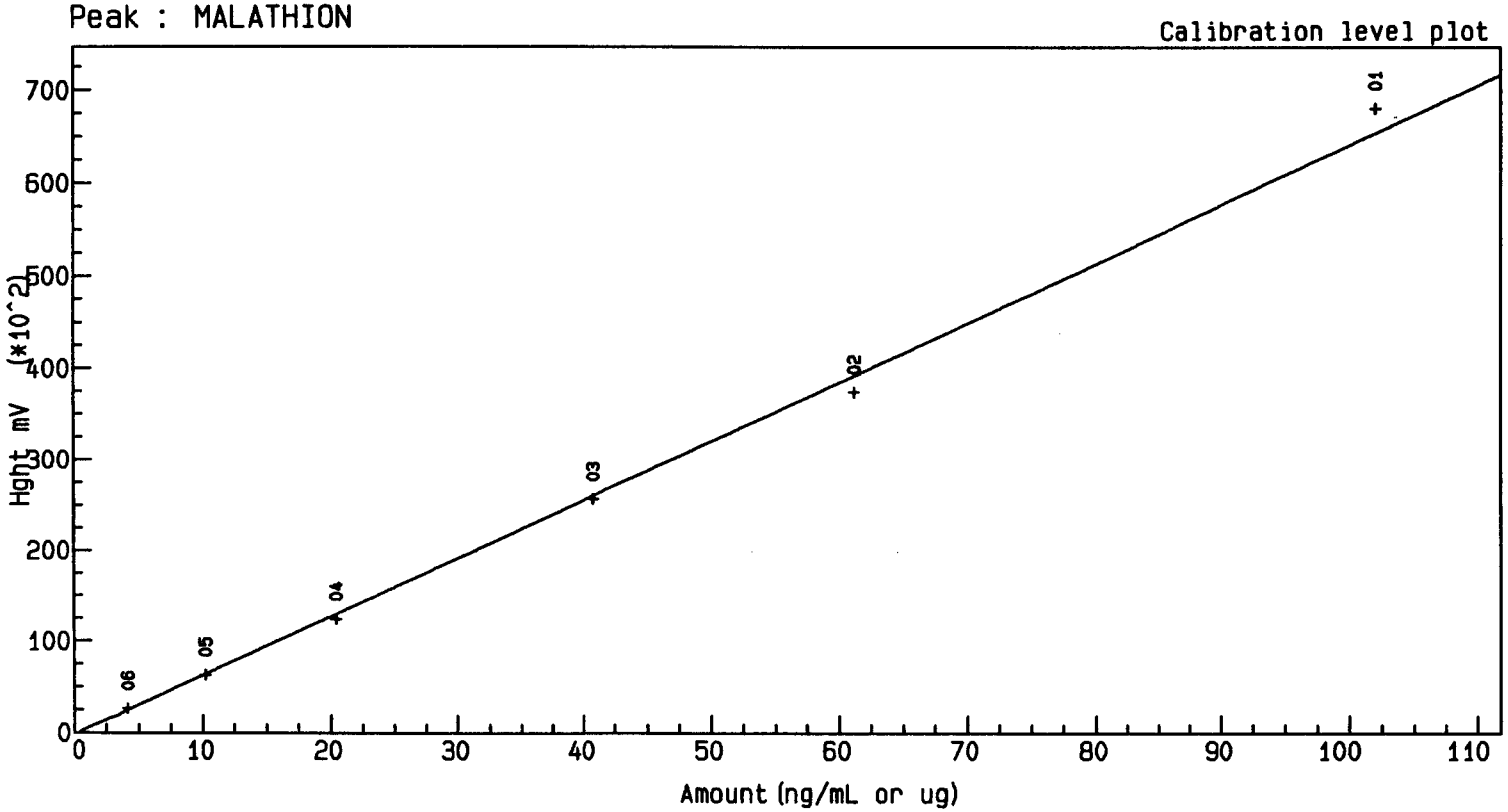
Constant : -2.738614E+2
1st degree : 1.06911E+3

Curve fit : Linear
Correlation coefficient : 0.99901
Standard error : 1.96528E+3

Reported on 28-JUN-1997 at 09:27

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767FDS2.
43767 Dislodging Solution Set 1
Peak : MALATHION



Constant : -1.918287E+2
1st degree : 6.43003E+2

Curve fit : Linear
Correlation coefficient : 0.99822
Standard error : 1.63944E+3

Reported on 28-JUN-1997 at 09:27

ABC Laboratories, Inc.

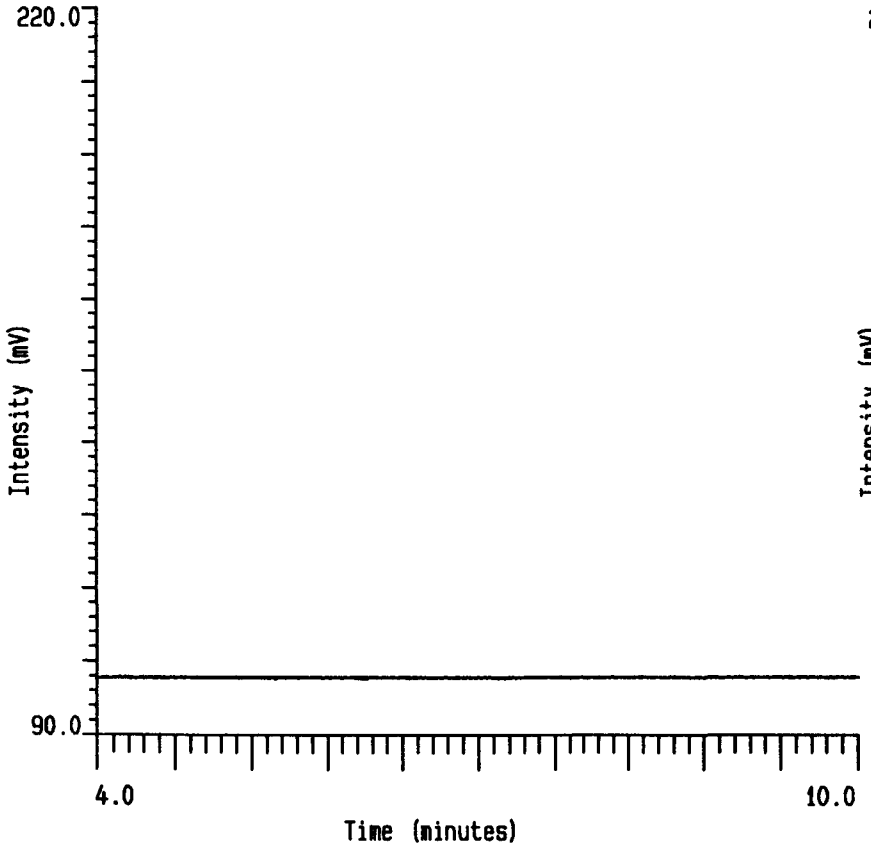
MCPP ver 2.3

43767 Dislodging Solution Set 1

Date of Report: 28 JUN 97 at 09:28:32

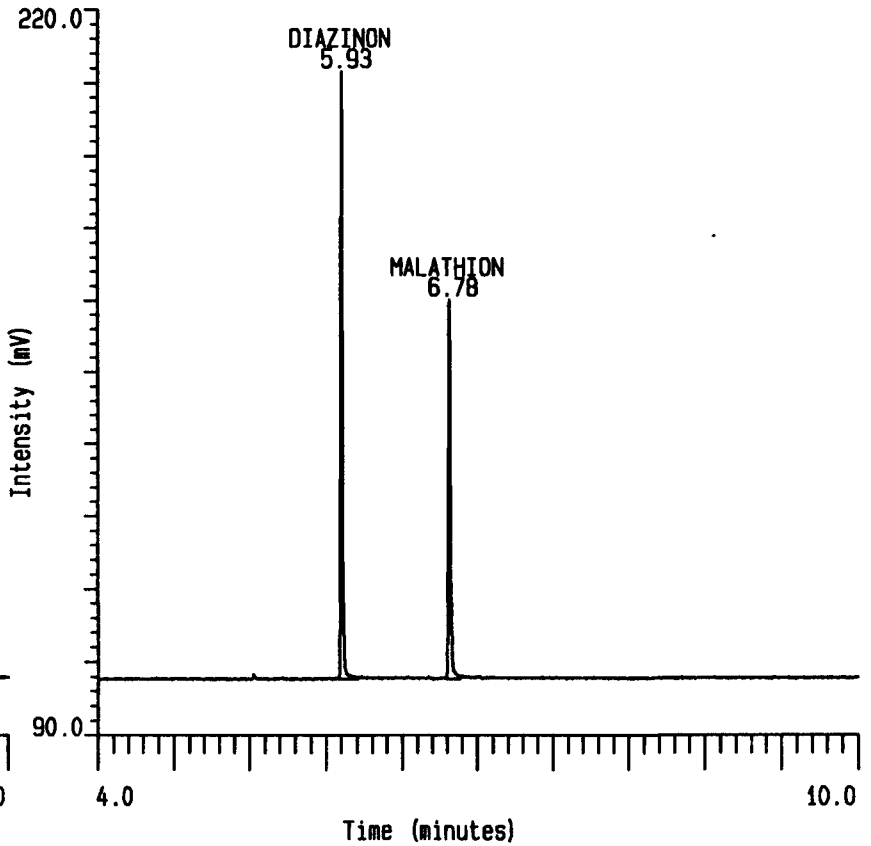
MCDO [43767] 29 767FDS2, 1, 1
Solvent Blank
Acquired on 27-Jun-1997 at 15:54

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	0.00	0	0
MALATHION	0.00	0	0



MCDO [43767] 29 767FDS2, 2, 1
GCMIX-1 NOMINAL 100 ng/mL
Acquired on 27-Jun-1997 at 16:15

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	109040	102.248
MALATHION	6.78	68102	106.210



ABC Laboratories, Inc.

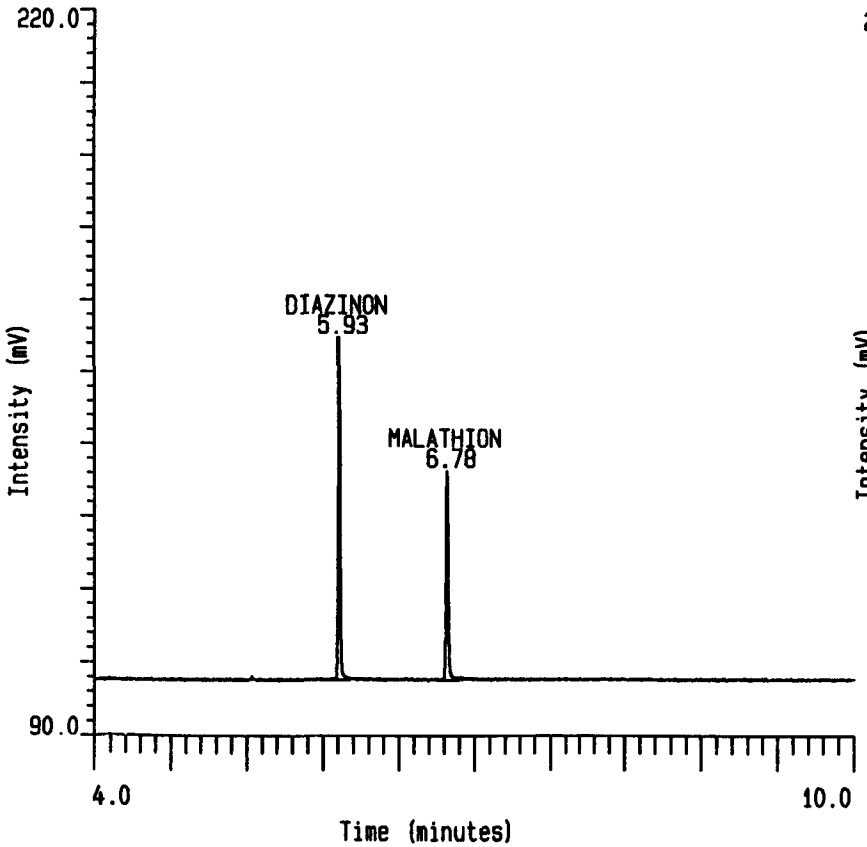
MCPP ver 2.3

43767 Dislodging Solution Set 1

Date of Report: 28 JUN 97 at 09:28:32

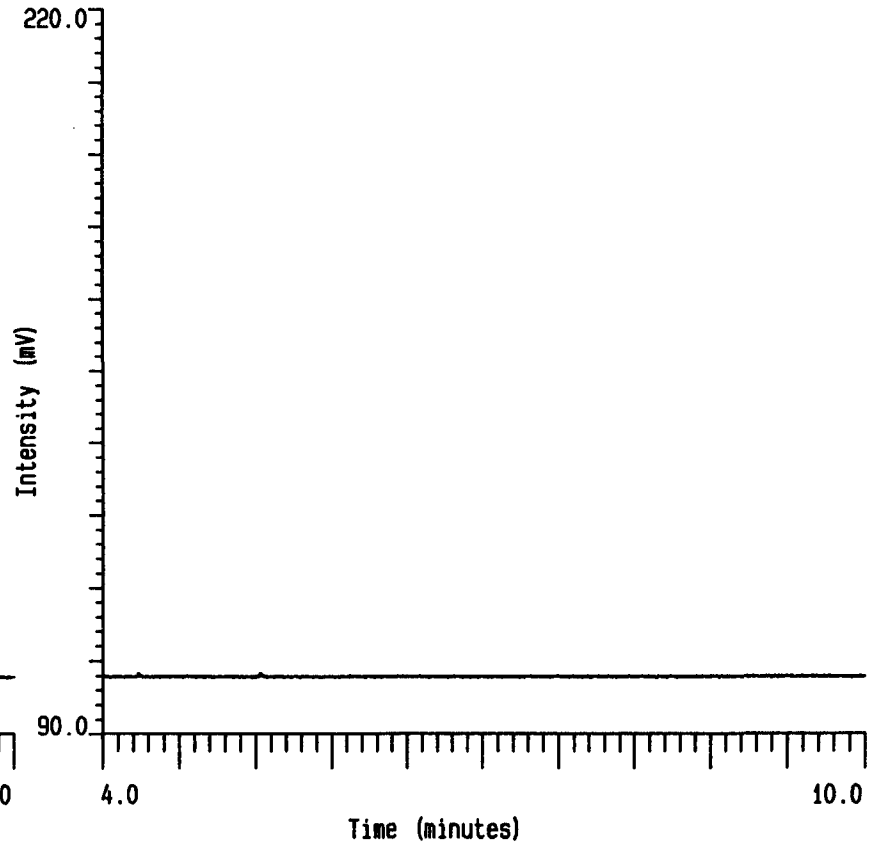
MCDO [43767] 29 767FDS2, 3, 1
GCMIX-2 NOMINAL 60 ng/mL
Acquired on 27-Jun-1997 at 16:35

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	61466	57.749
MALATHION	6.78	37429	58.508



MCDO [43767] 29 767FDS2, 4, 1
43767-043
Acquired on 27-Jun-1997 at 16:55

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	0.00	0	0
MALATHION	0.00	0	0



ABC Laboratories, Inc.

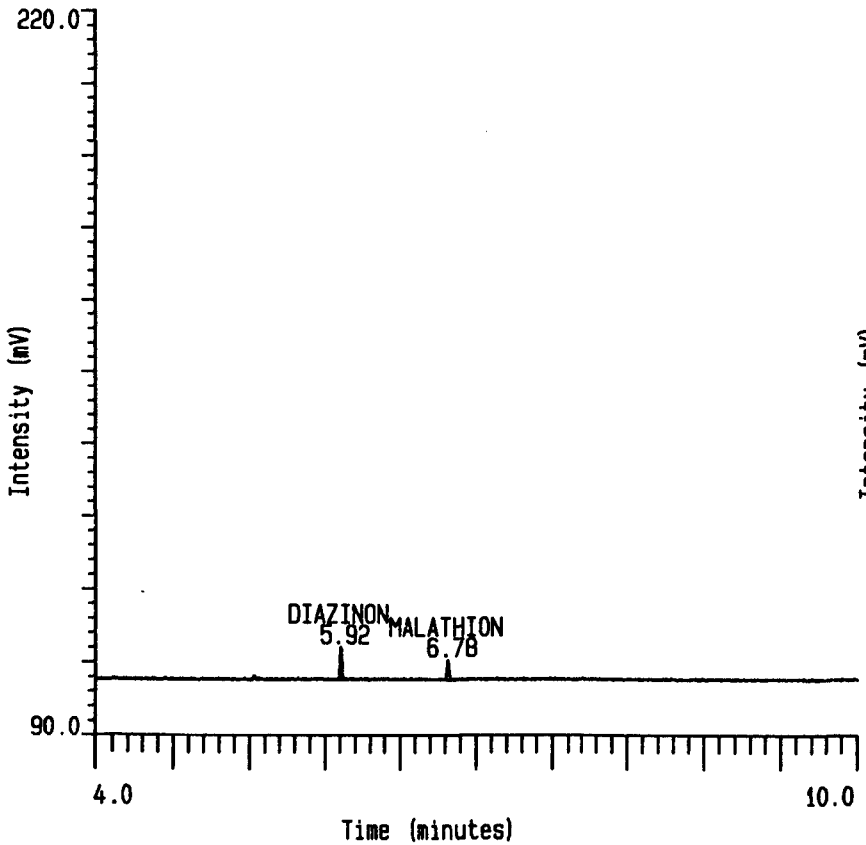
MCPP ver 2.3

43767 Dislodging Solution Set 1

Date of Report: 28 JUN 97 at 09:28:32

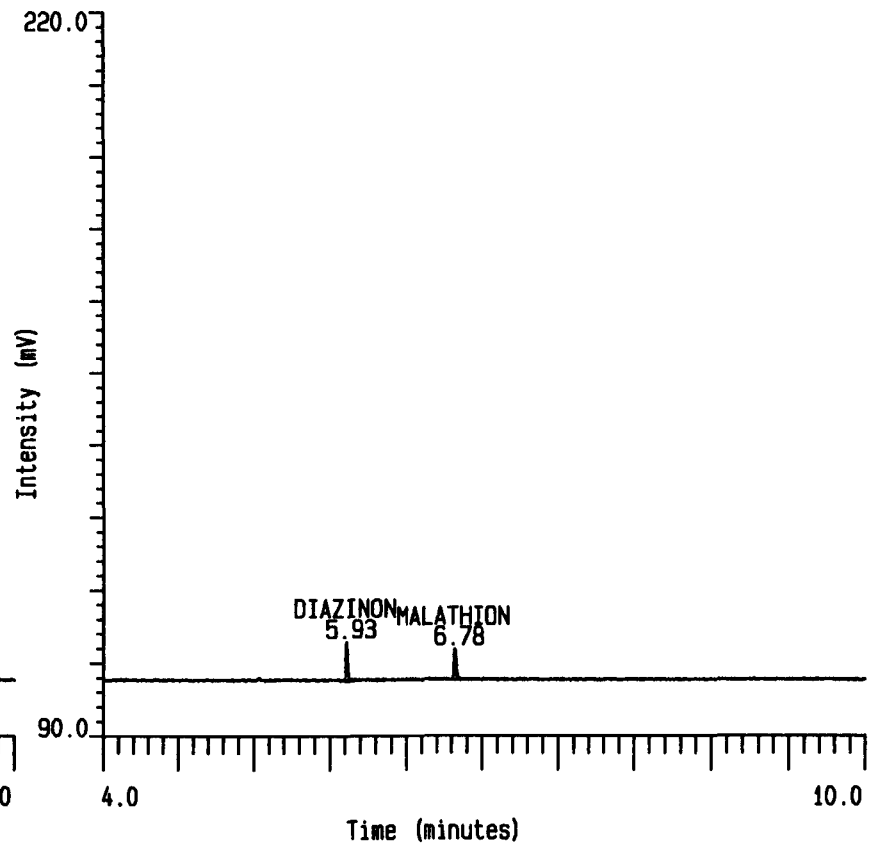
MCDO [43767] 29 767FDS2,5,1
43767-044
Acquired on 27-Jun-1997 at 17:16

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.92	5840	1.372
MALATHION	6.78	3519	1.385



MCDO [43767] 29 767FDS2,6,1
43767-045
Acquired on 27-Jun-1997 at 17:36

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	6942	1.620
MALATHION	6.78	5541	2.140



ABC Laboratories, Inc.

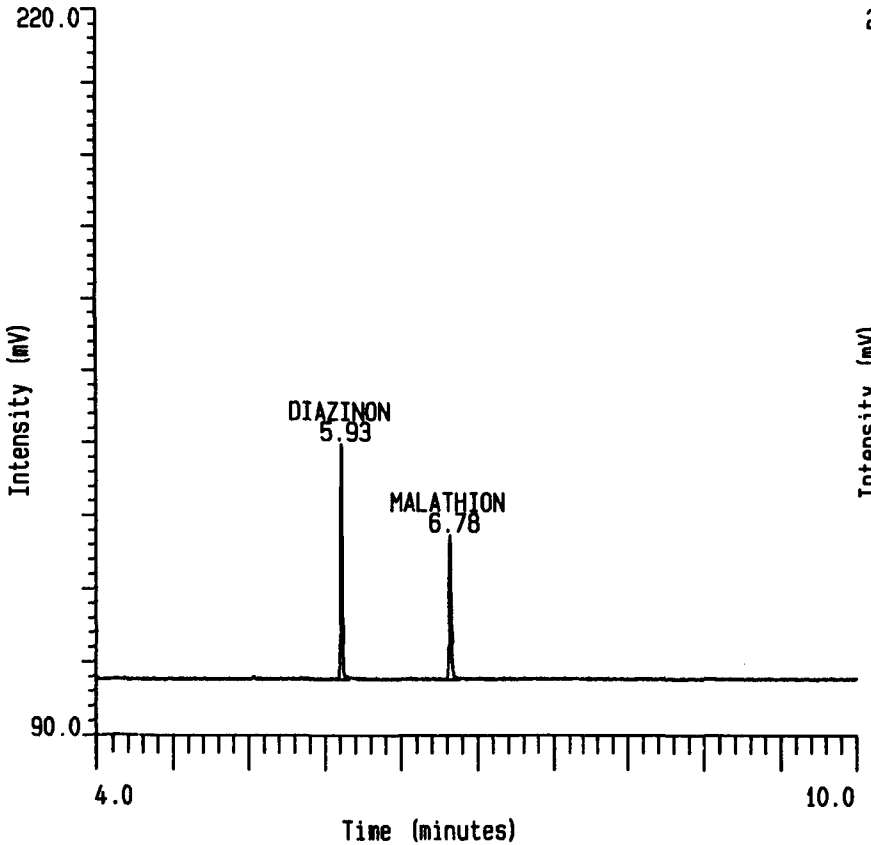
MCPP ver 2.3

43767 Dislodging Solution Set 1

Date of Report: 28 JUN 97 at 09:28:32

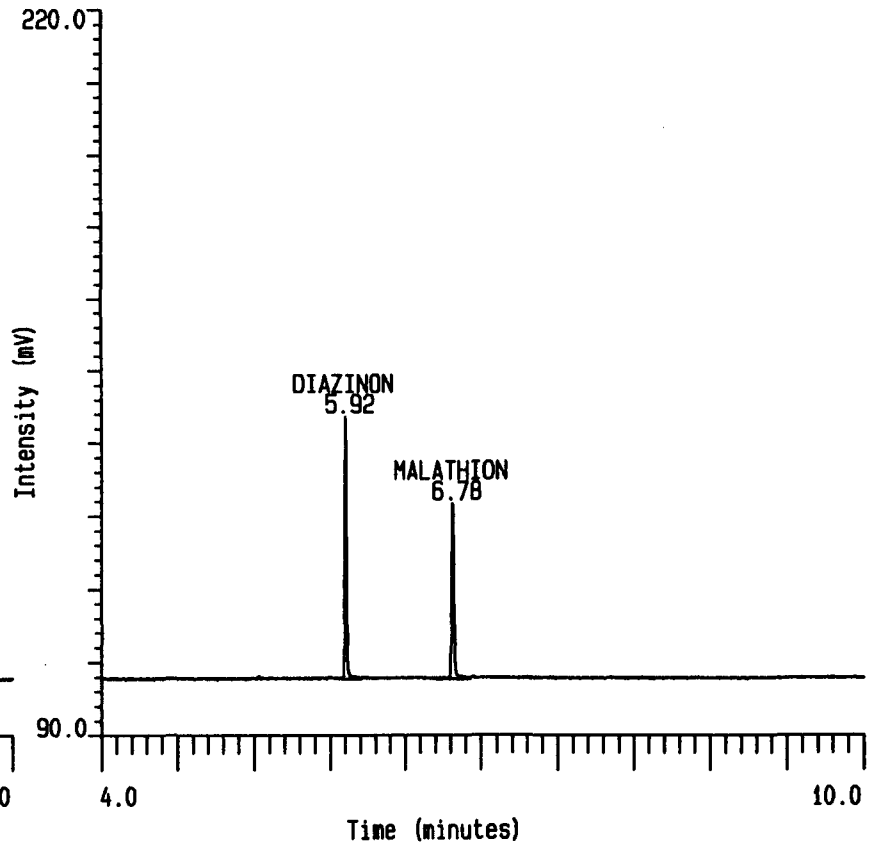
MCDO [43767] 29 767FDS2,7,1
GCMIX-3 NOMINAL 40 ng/mL
Acquired on 27-Jun-1997 at 17:56

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	41893	39.441
MALATHION	6.78	25686	40.246



MCDO [43767] 29 767FDS2,8,1
43767-046
Acquired on 27-Jun-1997 at 18:17

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.92	46740	17.590
MALATHION	6.78	31188	19.521



ABC Laboratories, Inc.

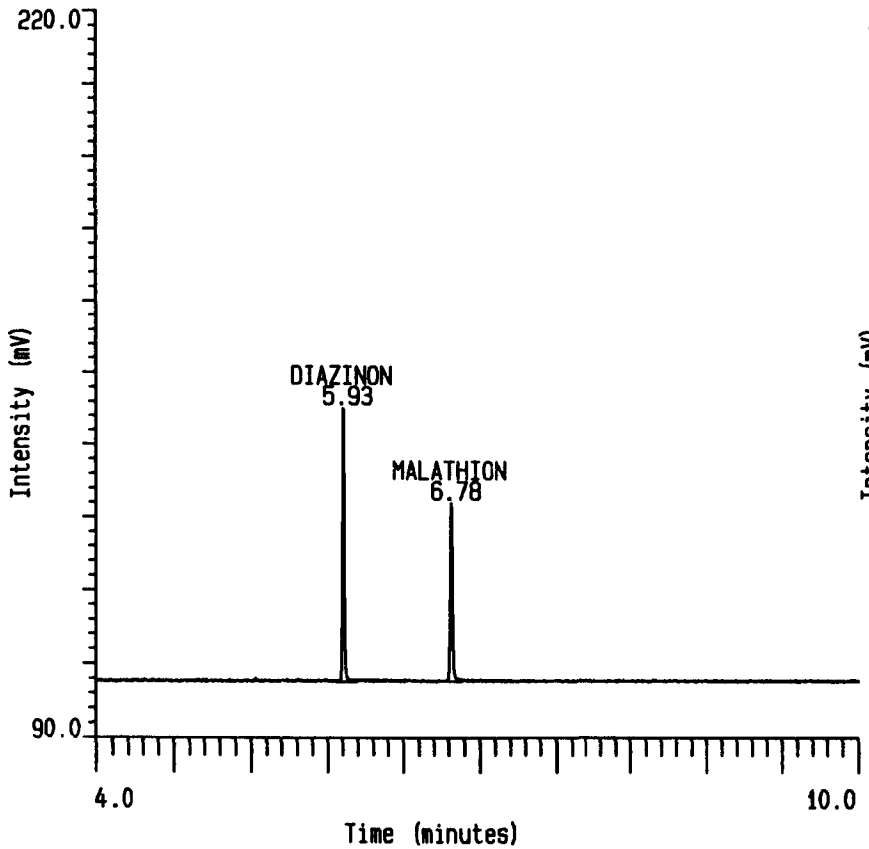
MCPP ver 2.3

43767 Dislodging Solution Set 1

Date of Report: 28 JUN 97 at 09:28:32

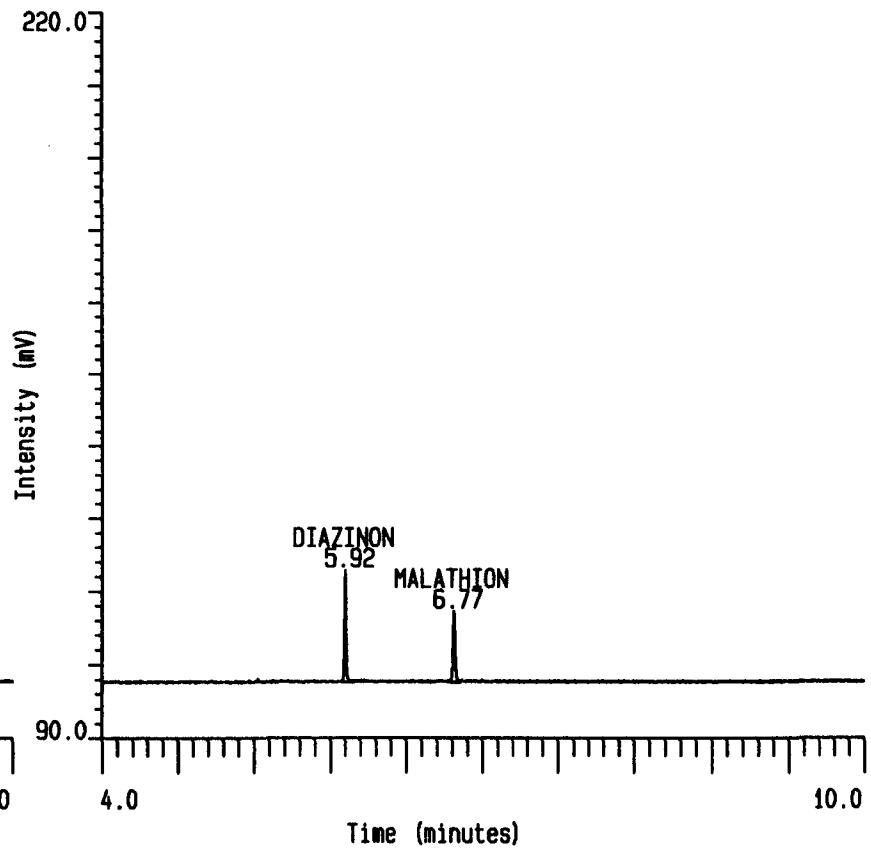
MCDO [43767] 29 767FDS2, 9, 1
43767-047
Acquired on 27-Jun-1997 at 18:37

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	48708	18.326
MALATHION	6.78	31629	19.795



MCDO [43767] 29 767FDS2, 10, 1
GCMIX-4 NOMINAL 20 ng/mL
Acquired on 27-Jun-1997 at 18:57

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.92	19824	18.799
MALATHION	6.77	12421	19.615



ABC Laboratories, Inc.

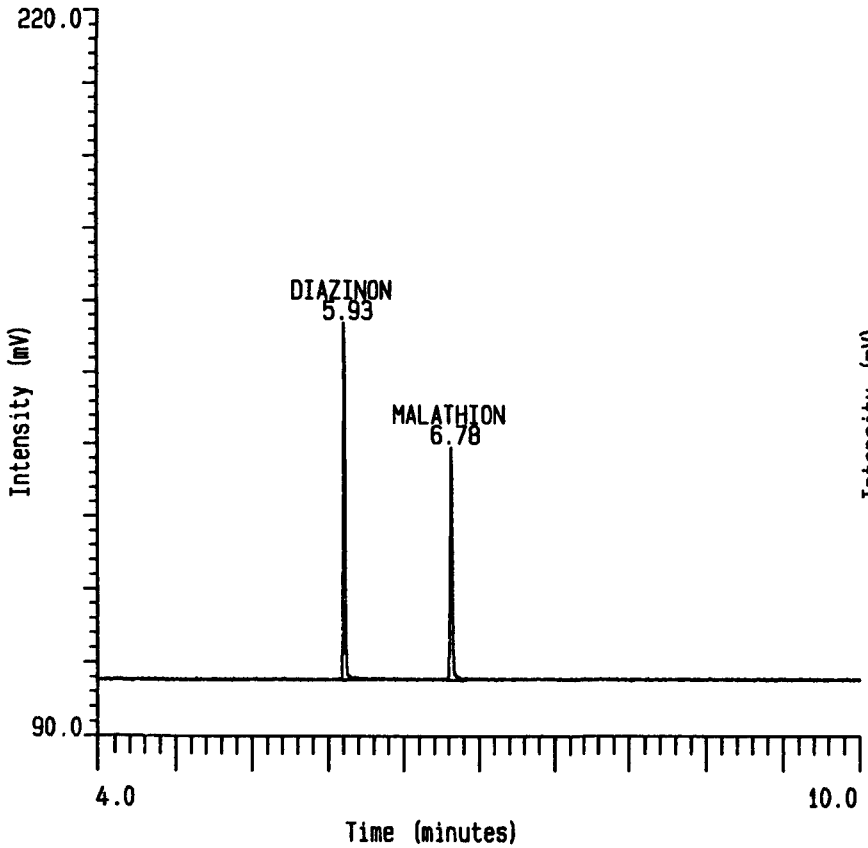
MCPP ver 2.3

43767 Dislodging Solution Set 1

Date of Report: 28 JUN 97 at 09:28:32

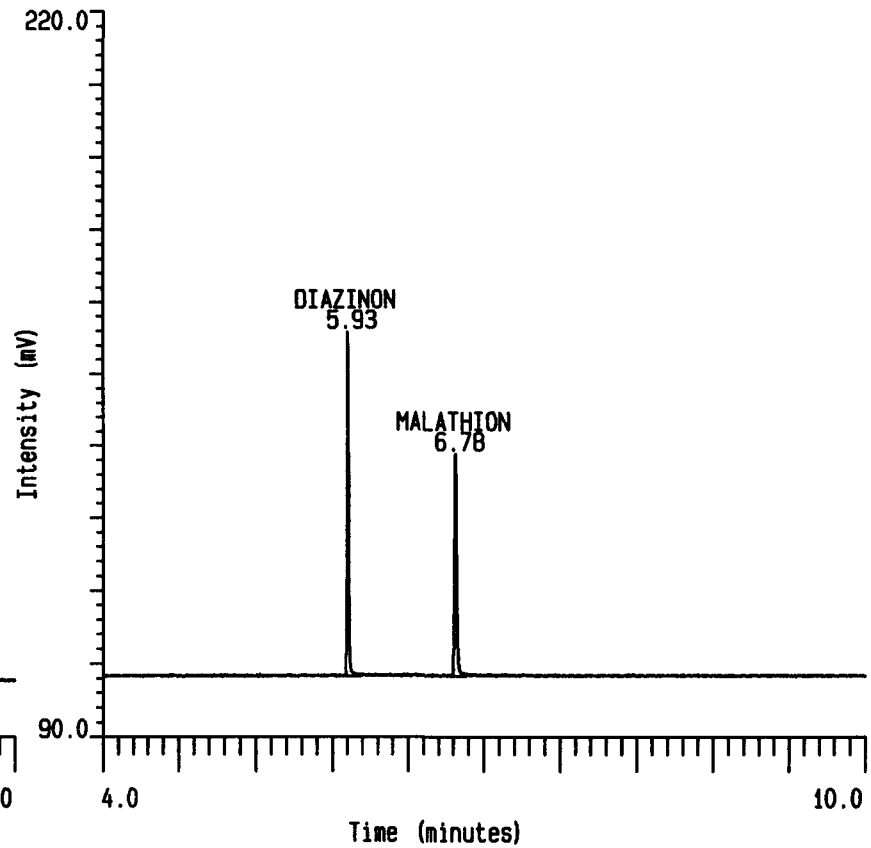
MCDO [43767] 29 767FDS2, 11, 1
43767-048
Acquired on 27-Jun-1997 at 19:18

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	64057	1865.337
MALATHION	6.78	41599	2014.798



MCDO [43767] 29 767FDS2, 12, 1
43767-049
Acquired on 27-Jun-1997 at 19:38

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	61851	1801.388
MALATHION	6.78	39737	1925.021



ABC Laboratories, Inc.

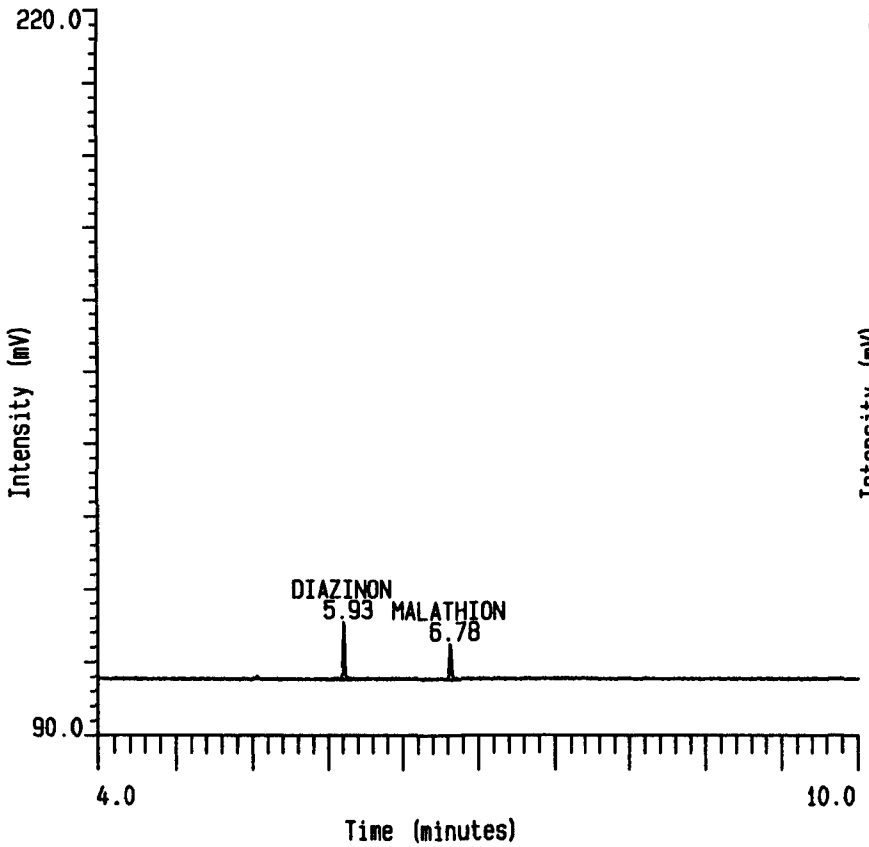
MCPP ver 2.3

43767 Dislodging Solution Set 1

Date of Report: 28 JUN 97 at 09:28:32

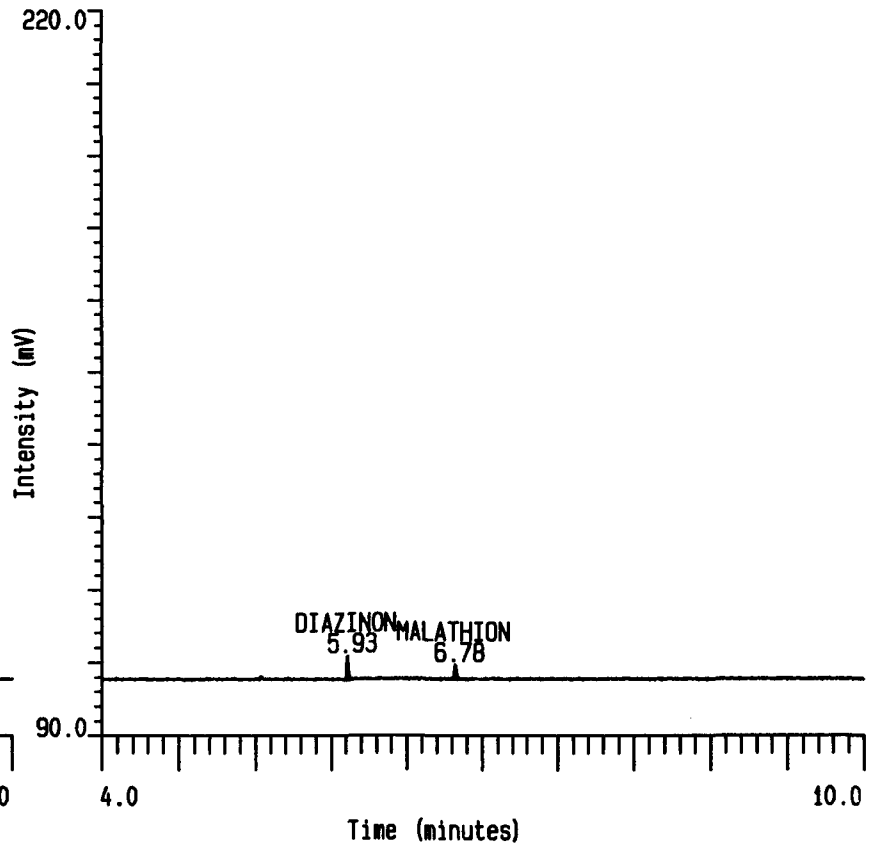
MCDO [43767] 29 767FDS2, 13, 1
GCMIX-5 NOMINAL 10 ng/mL
Acquired on 27-Jun-1997 at 19:58

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	10224	9.819
MALATHION	6.78	6286	10.075



MCDO [43767] 29 767FDS2, 14, 1
GCMIX-6 NOMINAL 4 ng/mL
Acquired on 27-Jun-1997 at 20:19

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	4277	4.257
MALATHION	6.78	2625	4.381



[43767] 29 767FDS2 Page 1
Reported on 30-JUN-1997 at 10:23
Modified on 28-JUN-1997 at 09:17

List Calibration File

CALIBRATION HEADER INFORMATION

Calibration Title : 43767 Dislodging Solution Set 1
General :
Calibration type..... External standard
Units..... ng/mL or ug
Calibration base..... Height
Reference Peak Identification :
Reference window..... 5.0 %
Minimum window..... 0.50 mins
Peak threshold..... 0.0 %
Uncalibrated Peaks Response Factor :
Response factor source..... User set response factor
Response factor..... 0.0000
Additional Information :
Source library..... None
Initialise on 1st standard..... No
Variation tolerance..... 100.00 %
Calibrant Peak Identification :
Calibrant window..... 0.10 mins
Calibrant threshold..... 0.0 %
Response Factor Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... 1 / Y
Retention Value Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... None
Timed Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... None
No group information entered.

[43767] 29 767FDS2 Page 2
Reported on 30-JUN-1997 at 10:23
Modified on 28-JUN-1997 at 09:17

Peak name : DIAZINON
Expected retention time : 5.93 mins (RT range : 5.88 - 5.98 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	3.9700	1077.4197	1
05	9.9200	1030.6323	1
04	19.8000	1001.2290	1
03	39.7000	1055.2269	1
02	59.5000	1033.0400	1
01	99.2000	1099.1949	1

Peak name : MALATHION
Expected retention time : 6.80 mins (RT range : 6.75 - 6.85 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	4.0800	643.4891	1
05	10.2000	616.3026	1
04	20.4000	608.8502	1
03	40.8000	629.5651	1
02	61.2000	611.5870	1
01	102.0000	667.6640	1

[43767] 29 767FDS2R Page 1
Reported on 30-JUN-1997 at 10:19
Modified on 28-JUN-1997 at 09:43

List Run Sequence File

ANALYST NAME..... LOREN C. SCHRIER
43767 Dislodging Solution Set 1 RESHOOT SAMPLE 44

ANALYSIS INFORMATION

Analysis name..... 767FDS2R
Method name..... 767FDS2R
Calibration name..... 767FDS2R
Calibration sequence..... Average Standard
User parameter 1 name..... Final Volume
User parameter 2 name..... Factor 1
User parameter 3 name..... Factor 2

This data not reported - it simply confirms previous result. 2 July 97

SAMPLE SUMMARY

SAMPLE NUMBER	LIMS ID	SAMPLE NAME
1	----------	GCMIX-1 NOMINAL 100 ng/mL
2	----------	GCMIX-2 NOMINAL 60 ng/mL
3	----------	GCMIX-3 NOMINAL 40 ng/mL
4	----------	43767-044 RESHOOT
5	----------	GCMIX-4 NOMINAL 20 ng/mL
6	----------	GCMIX-5 NOMINAL 10 ng/mL
7	----------	GCMIX-6 NOMINAL 4 ng/mL

SAMPLE INFORMATION

SAMPLE NUMBER	TYPE	CALIB LEVEL	UPDATE RT	UPDATE RF	AMOUNT	NUM INJ	BOT NUM
1	St	01	N	I	1.00000	1	2
2	St	02	N	I	1.00000	1	3
3	St	03	N	I	1.00000	1	7
4	Sa	--	-	-	1.00000	1	5
5	St	04	N	I	1.00000	1	10
6	St	05	N	I	1.00000	1	13
7	St	06	N	I	1.00000	1	14

[43767] 29 767FDS2R Page 2
Reported on 30-JUN-1997 at 10:19
Modified on 28-JUN-1997 at 09:43

USER PARAMETER VALUES

SAMPLE	FINAL VOLUME	FACTOR 1	FACTOR 2
1	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000
4	6.00000	200.00000	5000.00000
5	1.00000	1.00000	1.00000
6	1.00000	1.00000	1.00000
7	1.00000	1.00000	1.00000

INTERNAL/DILUTION STANDARDS

SAMPLE NUMBER	ISTD1 AMOUNT	ISTD2 AMOUNT	ISTD3 AMOUNT	DIL1 AMOUNT	DIL2 AMOUNT
1	1.00000	1.00000	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000	1.00000	1.00000
4	1.00000	1.00000	1.00000	1.00000	1.00000
5	1.00000	1.00000	1.00000	1.00000	1.00000
6	1.00000	1.00000	1.00000	1.00000	1.00000
7	1.00000	1.00000	1.00000	1.00000	1.00000

PROCESSING ORDER

SAMPLE NUMBER	TYPE
1	Standard
2	Standard
3	Standard
5	Standard
6	Standard
7	Standard
4	Sample

Gas Chromatographic Instrument Parameters Form

ABC Laboratory Study Number: 43767
Customer Identification: ARTF

Instrument: HP 5890 Series II Material ID# 1652-0120
Autoinjector: HP 7673B Material ID# 1625-802A

Column: HP-5MS, 30 M X 0.25 mm, 0.25 μm film thickness
Serial#: 56253614

Detector Type: FPD/P

Electrometer: Range 4

Temperatures:
- Injector (°C): 230
- Detector (°C): 230
- Column:
  - Initial Temp.(°C): 95
  - Initial Time: 1.0 min.
  - Program Rate 1: 30 °C/min to 230 °C, hold 4 min
  - Program Rate 2: 40 °C/min to 290 °C, hold 4 min

Carrier Gas Flow Rate:	He	1.6 mL/min
Septum Purge:	He	2.0 mL/min
Make Up Gas:	He	21 mL/min
Air Flow Rate:		98 mL/min.
Hydrogen Flow Rate:		69 mL/min.
Purge Valve:	Off at 0 min, on at 0.75 min	

Injection Volume: 2 μL

Run Sequence File: 767FDS2R

Quantitation Standards: GCmix-1 → 6 inclusive

Prepared By: [signature] Date: 28 Jun 97

Checked By: Barbara J Bryant Date: 02 Jul 1997

MCDO [43767] 29 767FDS2R

ABC Laboratories, Inc.
Sample Information Report ver 3.3

Report Date: 30 JUN 97 at 10:26:46
Page 1

Sample Name	No.	Type	Level	User Parameter 1 Final Volume	User Parameter 2 Factor 1	User Parameter 3 Factor 2
GCMIX-1 NOMINAL 100 ng/mL	1	ST	01	1.00000	1.00000	1.00000
GCMIX-2 NOMINAL 60 ng/mL	2	ST	02	1.00000	1.00000	1.00000
GCMIX-3 NOMINAL 40 ng/mL	3	ST	03	1.00000	1.00000	1.00000
43767-044 RESHOOT	4	SA		6.00000	200.00000	5000.00000
GCMIX-4 NOMINAL 20 ng/mL	5	ST	04	1.00000	1.00000	1.00000
GCMIX-5 NOMINAL 10 ng/mL	6	ST	05	1.00000	1.00000	1.00000
GCMIX-6 NOMINAL 4 ng/mL	7	ST	06	1.00000	1.00000	1.00000

MCDO [43767] 29 767FDS2R

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: DIAZINON

Report Date: 30 JUN 97
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Sample Name	SMP #	INJ #	RT(mins)	Height	ng/mL or ug	CAL. RANG	Peak Type	Bad INJ
GCMIX-1 NOMINAL 100 ng/mL	1	1	5.93	103786	100.273		O	---
GCMIX-2 NOMINAL 60 ng/mL	2	1	5.92	60698	58.703		OB	---
GCMIX-3 NOMINAL 40 ng/mL	3	1	5.94	41659	40.334		OB	---
43767-044 RESHOOT	4	1	5.93	5736	1.362		OB	---
GCMIX-4 NOMINAL 20 ng/mL	5	1	5.92	19699	19.148		OB	---
GCMIX-5 NOMINAL 10 ng/mL	6	1	5.93	9671	9.473		OB	---
GCMIX-6 NOMINAL 4 ng/mL	7	1	5.93	4262	4.255		O	---

MCDO [43767] 29 767FDS2R

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: MALATHION

Report Date: 30 JUN 97
Time: 10:26:46
Page: 1

Sample Name	SMP #	INJ #	RT(mins)	Height	ng/mL or ug	CAL. RANG	Peak Type	Bad INJ
GCMIX-1 NOMINAL 100 ng/mL	1	1	6.79	64349	104.298		OB	---
GCMIX-2 NOMINAL 60 ng/mL	2	1	6.77	36529	59.223		OB	---
GCMIX-3 NOMINAL 40 ng/mL	3	1	6.80	25548	41.429		OB	---
43767-044 RESHOOT	4	1	6.79	3540	1.385		O	---
GCMIX-4 NOMINAL 20 ng/mL	5	1	6.78	12171	19.756		OB	---
GCMIX-5 NOMINAL 10 ng/mL	6	1	6.79	6003	9.761		OB	---
GCMIX-6 NOMINAL 4 ng/mL	7	1	6.78	2696	4.403		OBF	---

Acquisition and Peak Processing Parameters Report Print Date and Time : 30 JUN 97 10:31:08
Version 2 Page : 1
MCDO [43767] 29 767FDS2R Based on Sample Number : 1 Injection Number : 1

ACQUISITION PARAMETERS
Data Collection :
Length of Run..... 14.99 mins
Post Injection Delay..... 0.00 mins
Sampling Rate..... 15.00 Hz
Baseline Offset :
Adjust Baseline..... Yes
Baseline Offset..... 10.00 %

PEAK PROCESSING PARAMETERS
Auto Process Parameters :
Peak Threshold..... 0.50
Baseline Test..... 4
Peak Trend..... 4
Separation Parameters :
Shoulder Sensitivity..... 0.10
Rider Sensitivity..... 0.05
Rejection Parameters :
Minimum Peak Width..... 0.00 secs
Minimum Peak Height..... 0.00 uV
Minimum Peak Area..... 2000.00 uVs
Ignore Flat Top Peak..... No
User Imposed Action Control :
Forced Baseline..... No
Suppress Integration..... Yes
Tangent Skimming..... No
Shoulder Detection..... No
Data Bunching..... No
Negative Detection..... No
Integration Modes :
Retention Time Integration..... No
Square Root Area and Height..... Yes

PROCESSING ACTIONS

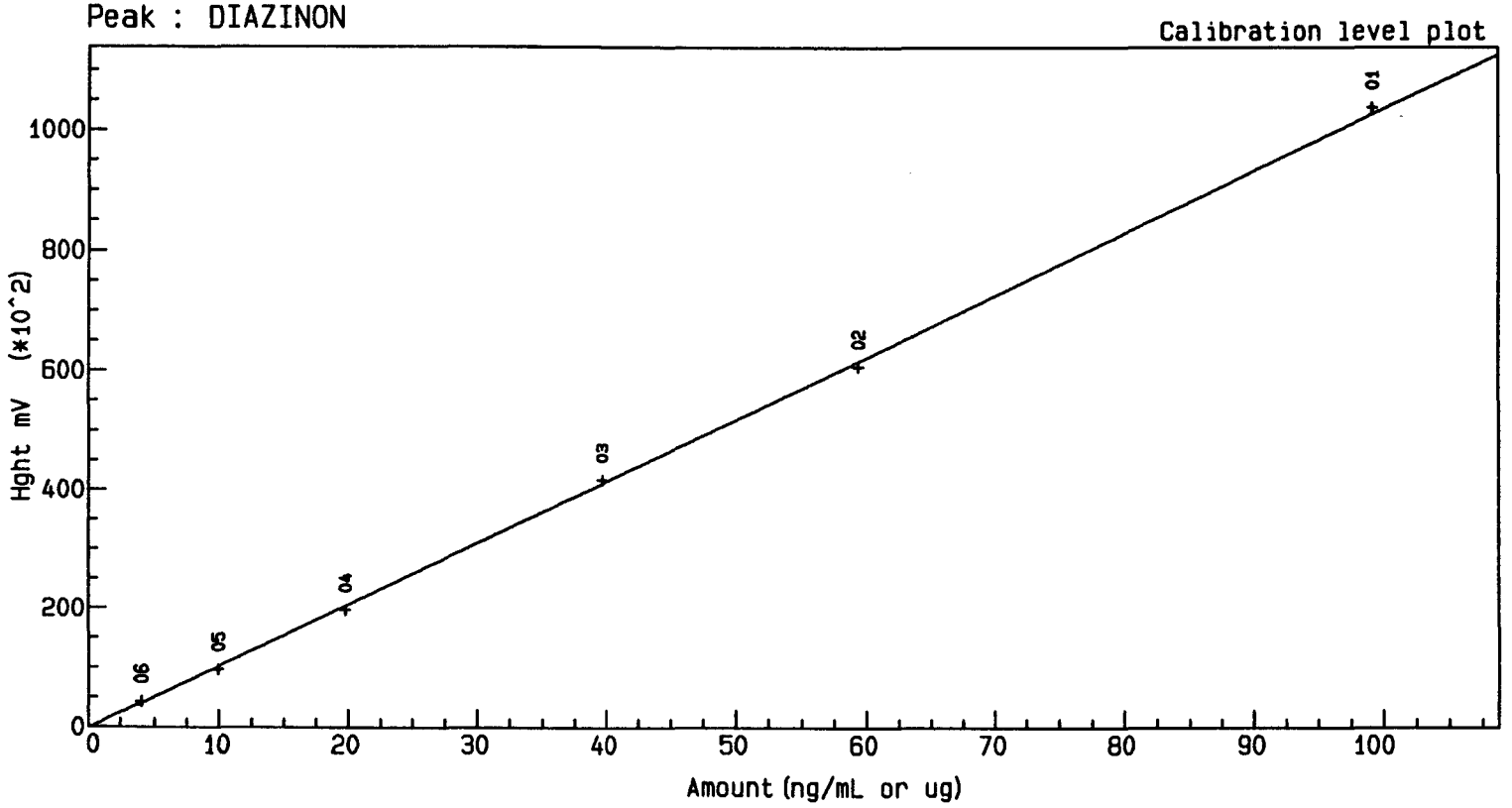
Time (mins)	Force Baseline	Integrate Suppress	Tangent Skim	Bunch Size	Shoulder Detect	Negative Detect
0.00	--	SS	_	0	--	--
5.30	--	ES	_	0	--	--
7.50	--	SI	_	0	--	--

Calibration last modified on 30-Jun-1997 at 10:25
Calibration Sequence..... AVERAGE

These parameters apply to all injections of set 767FDS2R with no exceptions

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767FDS2R.
43767 Dislodging Solution Set 1 RESHOOT SAMPLE 44
Peak : DIAZINON



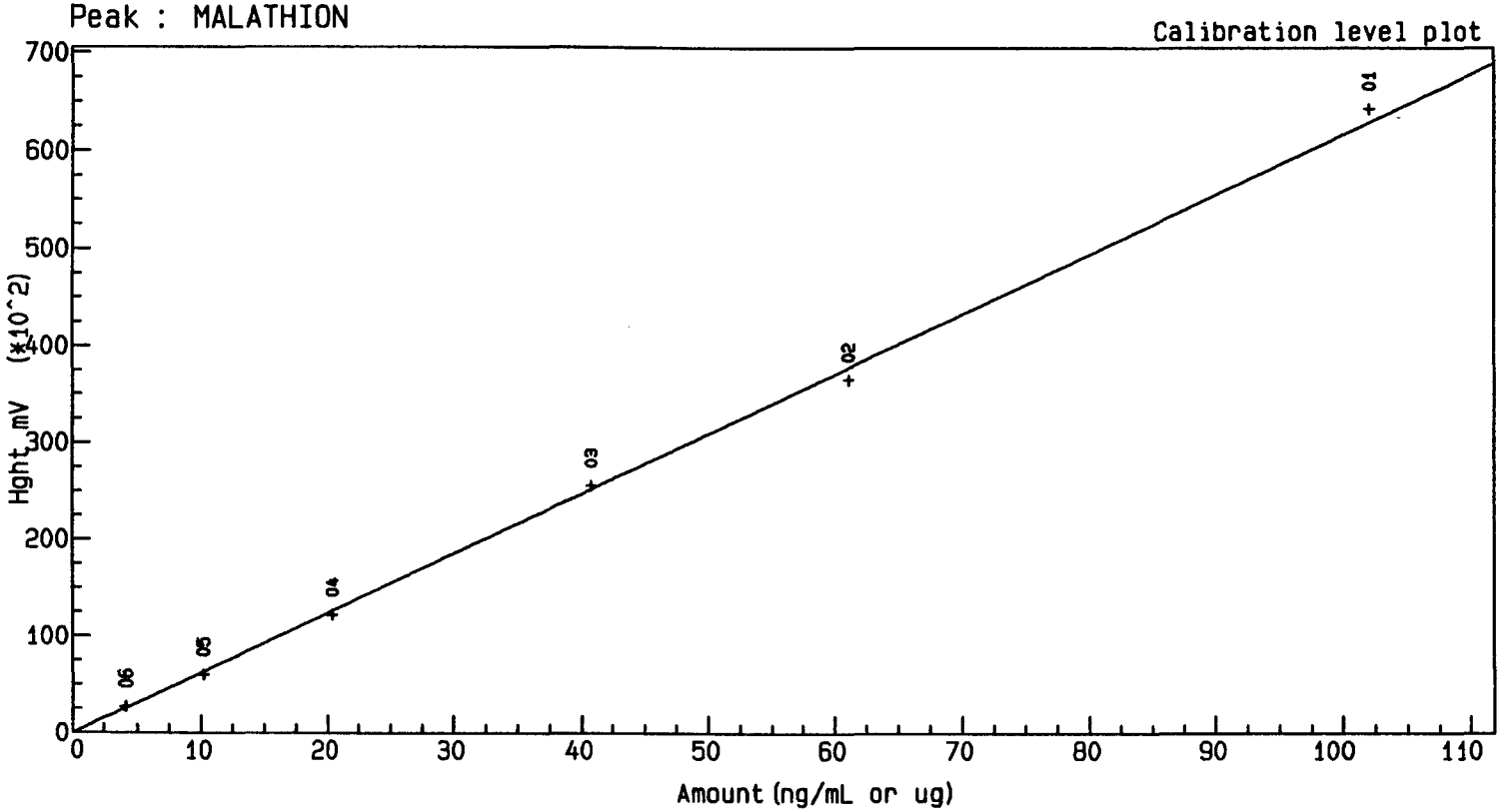
Constant : -1.479857E+2
1st degree : 1.03652E+3

Curve fit : Linear
Correlation coefficient : 0.99978
Standard error : 8.81684E+2

Reported on 30-JUN-1997 at 10:32

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767FDS2R.
43767 Dislodging Solution Set 1 RESHOOT SAMPLE 44
Peak : MALATHION



Constant : -2.165093E+1
1st degree : 6.17176E+2

Curve fit : Linear
Correlation coefficient : 0.99927
Standard error : 9.90280E+2

Reported on 30-JUN-1997 at 10:32

ABC Laboratories, Inc.

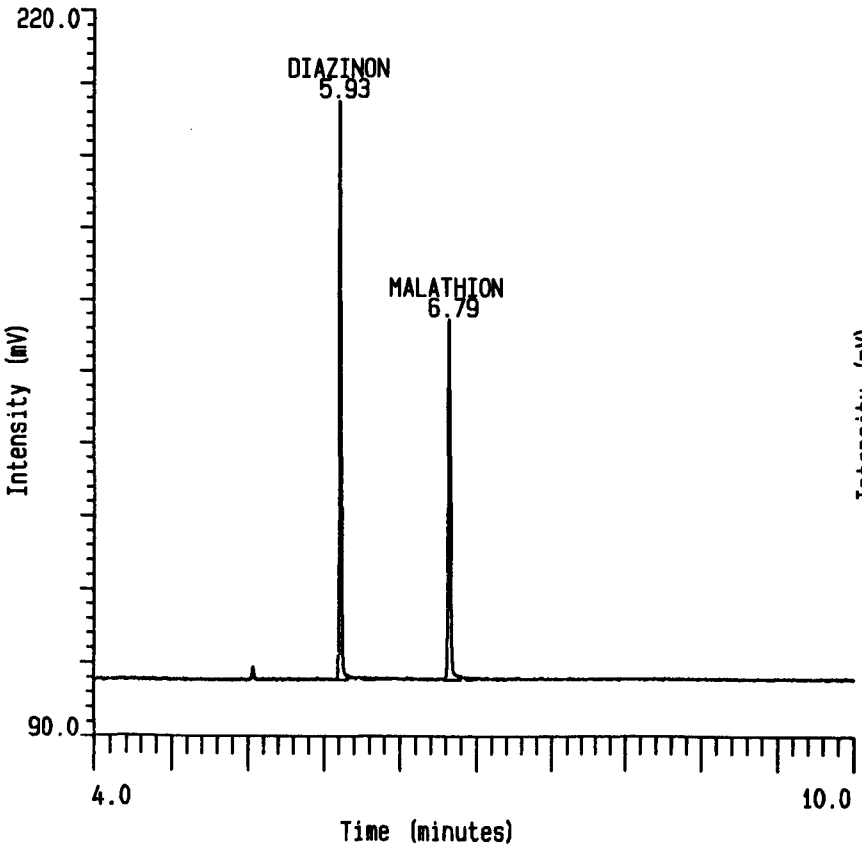
MCPP ver 2.3

43767 Dislodging Solution Set 1 RESHOOT SAMPLE 44

Date of Report: 30 JUN 97 at 10:33:44

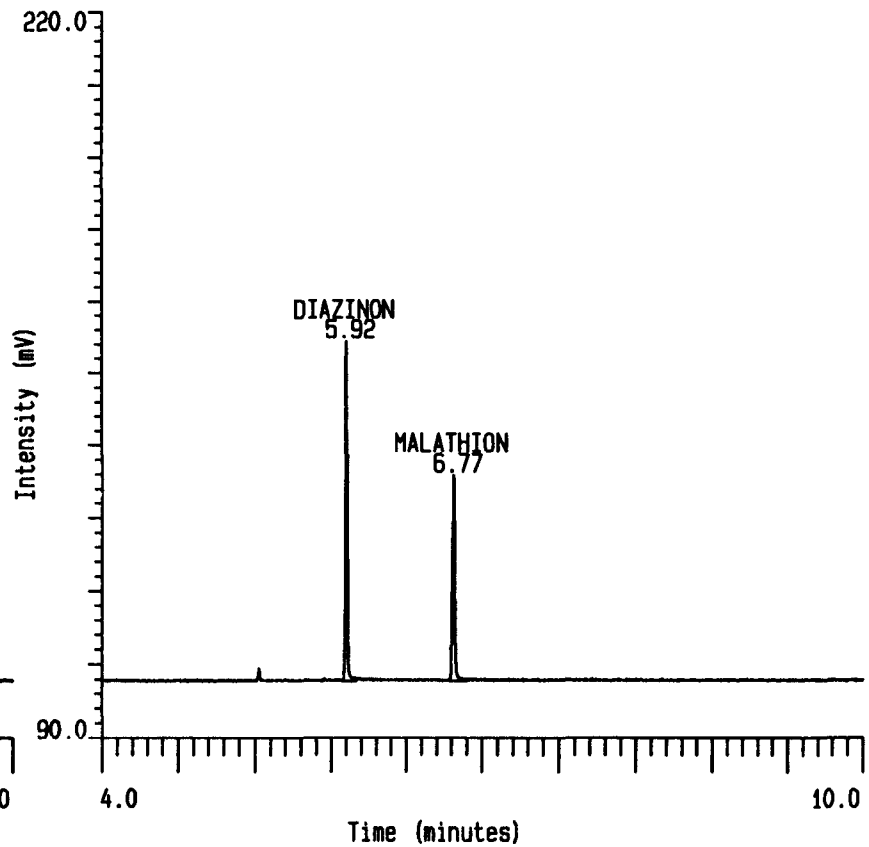
MCDO [43767] 29 767FDS2R, 1, 1
GCMIX-1 NOMINAL 100 ng/mL
Acquired on 28-Jun-1997 at 10:28

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	103786	100.273
MALATHION	6.79	64349	104.298



MCDO [43767] 29 767FDS2R, 2, 1
GCMIX-2 NOMINAL 60 ng/mL
Acquired on 28-Jun-1997 at 10:48

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.92	60698	58.703
MALATHION	6.77	36529	59.223



ABC Laboratories, Inc.

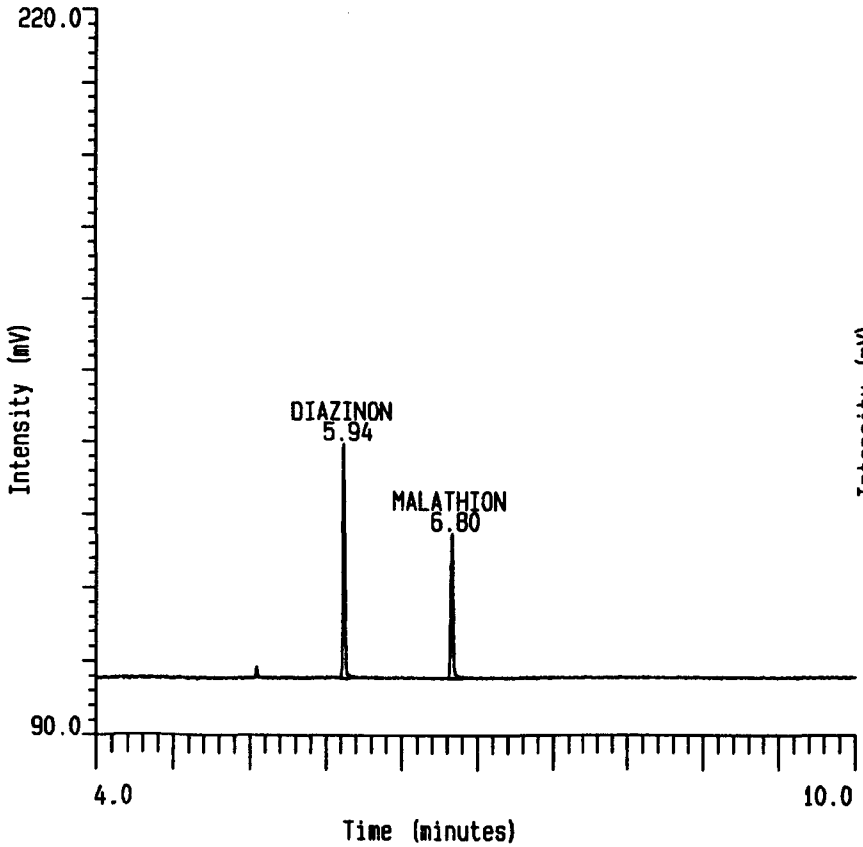
MCPP ver 2.3

43767 Dislodging Solution Set 1 RESHOOT SAMPLE 44

Date of Report: 30 JUN 97 at 10:33:44

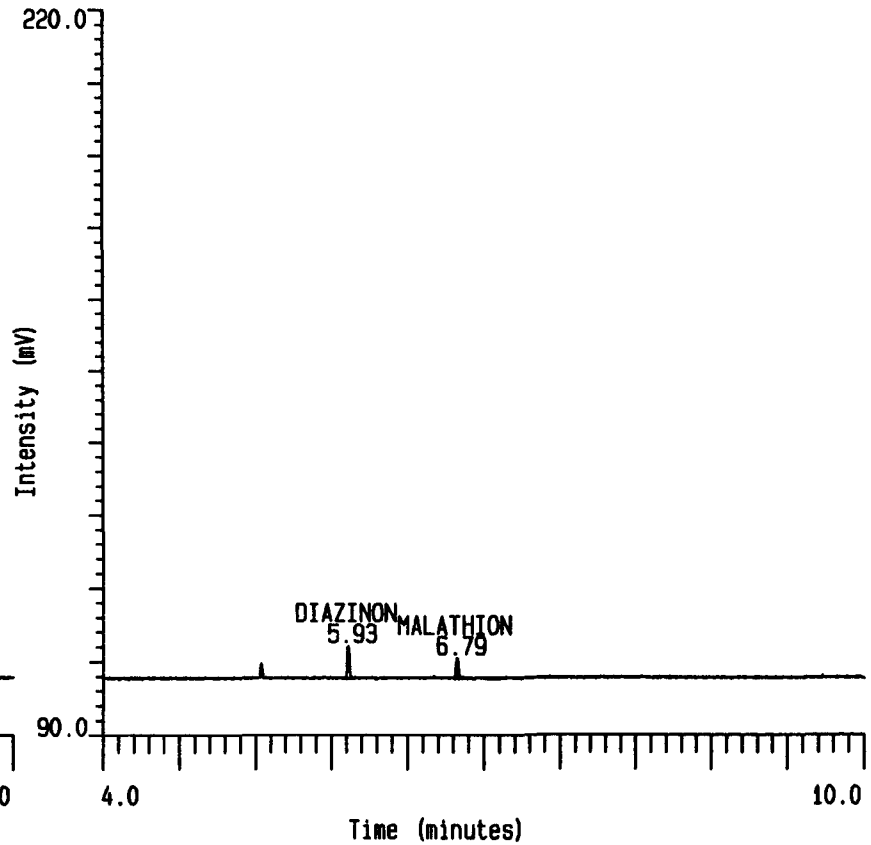
MCDO [43767] 29 767FDS2R,3,1
GCMIX-3 NOMINAL 40 ng/mL
Acquired on 28-Jun-1997 at 11:09

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.94	41659	40.334
MALATHION	6.80	25548	41.429



MCDO [43767] 29 767FDS2R,4,1
43767-044 RESHOOT
Acquired on 28-Jun-1997 at 11:29

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	5736	1.362
MALATHION	6.79	3540	1.385



ABC Laboratories, Inc.

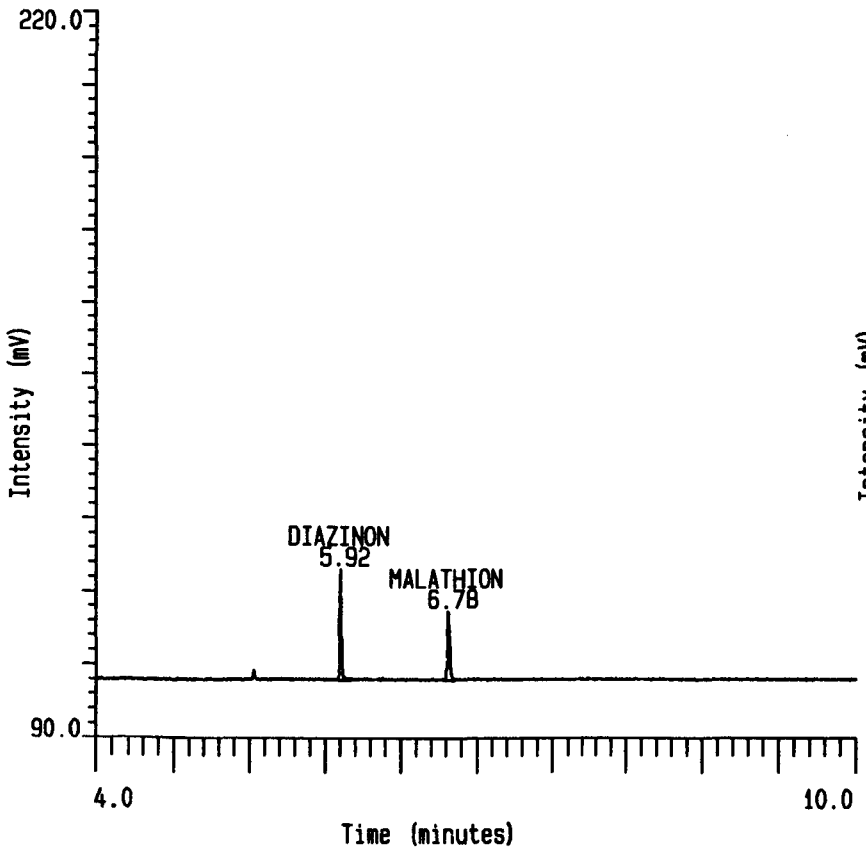
MCPP ver 2.3

43767 Dislodging Solution Set 1 RESHOOT SAMPLE 44

Date of Report: 30 JUN 97 at 10:33:44

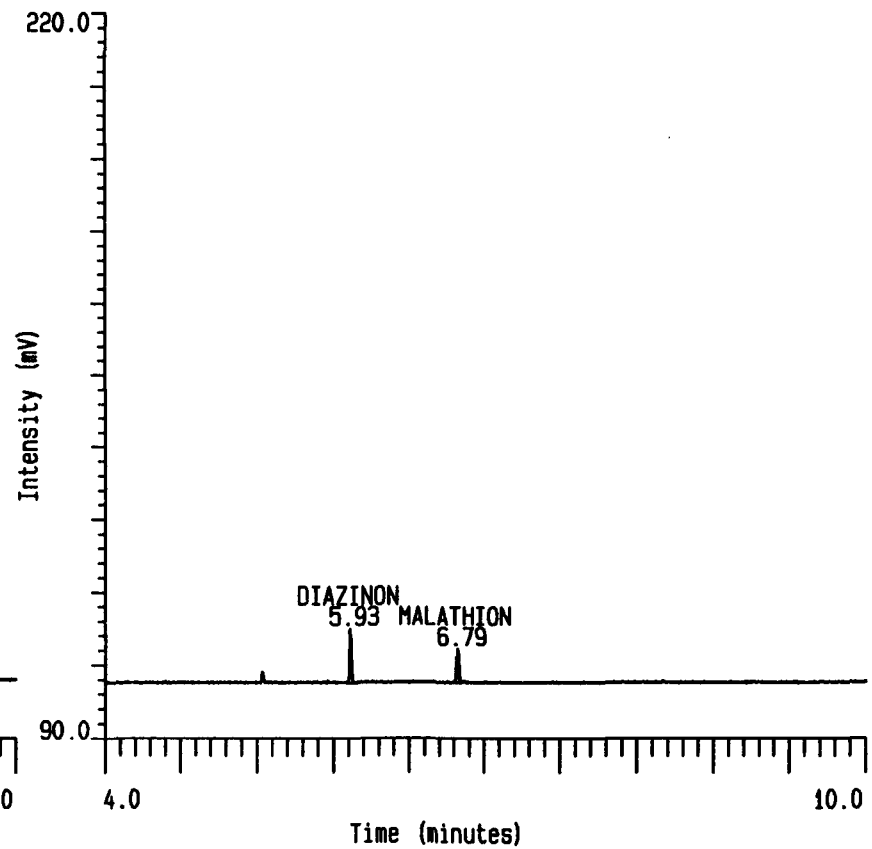
MCDO [43767] 29 767FDS2R,5,1
GCMIX-4 NOMINAL 20 ng/mL
Acquired on 28-Jun-1997 at 11:49

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.92	19699	19.148
MALATHION	6.78	12171	19.756



MCDO [43767] 29 767FDS2R,6,1
GCMIX-5 NOMINAL 10 ng/mL
Acquired on 28-Jun-1997 at 12:10

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	9671	9.473
MALATHION	6.79	6003	9.761



ABC Laboratories, Inc.

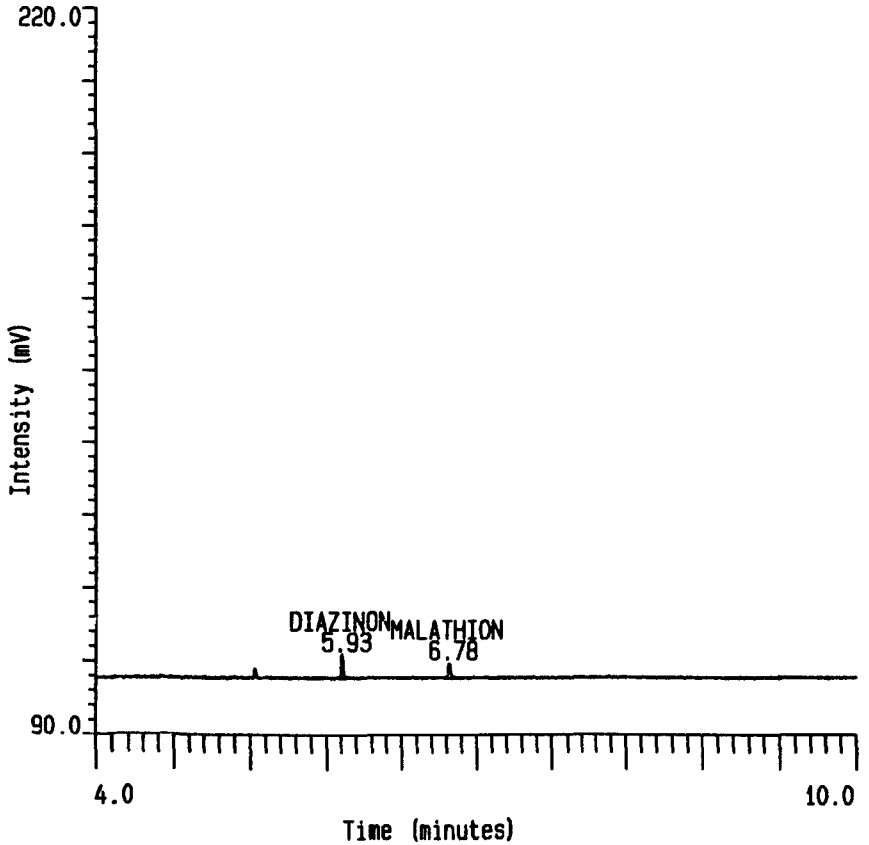
MCPP ver 2.3

43767 Dislodging Solution Set 1 RESHOOT SAMPLE 44

Date of Report: 30 JUN 97 at 10:33:44

MCDO [43767] 29 767FDS2R,7,1
GCMIX-6 NOMINAL 4 ng/mL
Acquired on 28-Jun-1997 at 12:30

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.93	4262	4.255
MALATHION	6.78	2696	4.403



[43767] 29 767FDS2R
Reported on 28-JUL-1997 at 12:49
Modified on 30-JUN-1997 at 10:25

Page 1

List Calibration File

CALIBRATION HEADER INFORMATION

Calibration Title : 43767 Dislodging Solution Set 1 RESHOOT SAMPLE 44
General :
Calibration type..... External standard
Units..... ng/mL or ug
Calibration base..... Height
Reference Peak Identification :
Reference window..... 5.0 %
Minimum window..... 0.50 mins
Peak threshold..... 0.0 %
Uncalibrated Peaks Response Factor :
Response factor source..... User set response factor
Response factor..... 0.0000
Additional Information :
Source library..... None
Initialise on 1st standard..... No
Variation tolerance..... 100.00 %
Calibrant Peak Identification :
Calibrant window..... 0.10 mins
Calibrant threshold..... 0.0 %
Response Factor Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... 1 / Y
Retention Value Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... None
Timed Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... None
No group information entered.

[43767] 29 767FDS2R Page 2
Reported on 28-JUL-1997 at 12:49
Modified on 30-JUN-1997 at 10:25

Peak name : DIAZINON
Expected retention time : 5.93 mins (RT range : 5.88 - 5.98 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	3.9700	1073.6399	1
05	9.9200	974.9287	1
04	19.8000	994.9202	1
03	39.7000	1049.3385	1
02	59.5000	1020.1381	1
01	99.2000	1046.2345	1

Peak name : MALATHION
Expected retention time : 6.80 mins (RT range : 6.75 - 6.85 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	4.0800	660.6876	1
05	10.2000	588.5170	1
04	20.4000	596.6389	1
03	40.8000	626.1645	1
02	61.2000	596.8835	1
01	102.0000	630.8699	1

SAMPLE TRACKING FORM

Customer Name: ARTF	Study Director: Loren C. Schrier	Test Material: Diazinon and Malathion	Matrix: 0.01%AOT (Spinach)
ARTF Protocol: ARF003	ABC Study Number: 43767	0.01% AOT Dislodging Solution Method Validation Set 2	

C-18RP Column Cleanup (Section II. C.2)	GC/FPD Analysis (Section II. D.)	Sequence File	Chromatography review:
CYG 6-30-97	15 July 97	767FD53	2 July 97
			Spreadsheet entry by: 2 Jul 97

ABC Lab Number	Sample Identification	Sample Volume	Sample Volume for Cleanup	Eluent Volume (Methylene Chloride)	Final Volume and Dilutions	Fortified by: CYG 6-30-97 Witnessed by: Barbara Bryant 30 Jun 97
43767-050	Control	200 mL	5 mL	8 mL	6.00 mL	
43767-051	Control + nominal 2 ug Each	200 mL	5 mL	8 mL	6.00 mL	Fortify with 1.0 mL of 1.98 ug/mL diazinon and 2.04 ug/mL malathion mixed fortification solution (Fort-7)
43767-052	Control + nominal 2 ug Each	200 mL	5 mL	8 mL	6.00 mL	Fortify with 1.0 mL of 1.98 ug/mL diazinon and 2.04 ug/mL malathion mixed fortification solution (Fort-7)
43767-053	Control + nominal 20 ug Each	200 mL	5 mL	8 mL	10.0 mL	Fortify with 1.0 mL of 19.8 ug/mL diazinon and 20.4 ug/mL malathion mixed fortification solution (Fort-6)
43767-054	Control + nominal 20 ug Each	200 mL	5 mL	8 mL	10.0 mL	Fortify with 1.0 mL of 19.8 ug/mL diazinon and 20.4 ug/mL malathion mixed fortification solution (Fort-6)
43767-055	Control + nominal 2000 ug Each	200 mL	5 mL	8 mL	25.0 mL, then dilute 0.50 mL to 15.5 mL	Fortify with 1.0 mL of 1980 ug/mL diazinon and 2040 ug/mL malathion mixed fortification solution (Fort-5)
43767-056	Control + nominal 2000 ug Each	200 mL	5 mL	8 mL	25.0 mL, then dilute 0.50 mL to 15.5 mL	Fortify with 1.0 mL of 1980 ug/mL diazinon and 2040 ug/mL malathion mixed fortification solution (Fort-5)

Remarks:

Methylene Chloride Burdick & Jackson, Lot # BN794 CYG 6-30-97

Acetone: Burdick & Jackson, Lot # BO920 CYG 6-30-97

Hexane: NA CYG 6-30-97

Methanol: Burdick & Jackson, Lot # BO820 CYG 6-30-97

Aerosol OT Solution (75% w/w Aqueous), Fisher, Lot Number 963392

Water: Labconco DI

Checked by: B/B 02 Jul 1997 Approved by: 28 July 97

[43767] 29 767FDS3 Page 1
Reported on 1-JUL-1997 at 16:52
Modified on 1-JUL-1997 at 09:58

List Run Sequence File

ANALYST NAME..... LOREN C. SCHRIER
43767 Dislodging Solution Set 2

ANALYSIS INFORMATION

Analysis name..... 767FDS3
Method name..... 767FDS3
Calibration name..... 767FDS3
Calibration sequence..... Average Standard
User parameter 1 name..... Final Volume
User parameter 2 name..... Factor 1
User parameter 3 name..... Factor 2

SAMPLE SUMMARY

SAMPLE NUMBER	LIMS ID	SAMPLE NAME
1	----------	Solvent Blank
2	----------	GCMIX-1 NOMINAL 100 ng/mL
3	----------	GCMIX-2 NOMINAL 60 ng/mL
4	----------	43767-050
5	----------	43767-051
6	----------	43767-052
7	----------	GCMIX-3 NOMINAL 40 ng/mL
8	----------	43767-053
9	----------	43767-054
10	----------	GCMIX-4 NOMINAL 20 ng/mL
11	----------	43767-055
12	----------	43767-056
13	----------	GCMIX-5 NOMINAL 10 ng/mL
14	----------	GCMIX-6 NOMINAL 4 ng/mL

[43767] 29 767FDS3 Page 2
Reported on 1-JUL-1997 at 16:52
Modified on 1-JUL-1997 at 09:58

SAMPLE INFORMATION

SAMPLE NUMBER	TYPE	CALIB LEVEL	UPDATE RT	UPDATE RF	AMOUNT	NUM INJ	BOT NUM
1	Sa	--	-	-	1.00000	1	1
2	St	01	N	I	1.00000	1	2
3	St	02	N	I	1.00000	1	3
4	Sa	--	-	-	1.00000	1	4
5	Sa	--	-	-	1.00000	1	5
6	Sa	--	-	-	1.00000	1	6
7	St	03	N	I	1.00000	1	7
8	Sa	--	-	-	1.00000	1	8
9	Sa	--	-	-	1.00000	1	9
10	St	04	N	I	1.00000	1	10
11	Sa	--	-	-	1.00000	1	11
12	Sa	--	-	-	1.00000	1	12
13	St	05	N	I	1.00000	1	13
14	St	06	N	I	1.00000	1	14

USER PARAMETER VALUES

SAMPLE	FINAL VOLUME	FACTOR 1	FACTOR 2
1	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000
4	1.00000	1.00000	1.00000
5	6.00000	200.00000	5000.00000
6	6.00000	200.00000	5000.00000
7	1.00000	1.00000	1.00000
8	10.00000	200.00000	5000.00000
9	10.00000	200.00000	5000.00000
10	1.00000	1.00000	1.00000
11	25.00000	3100.00000	2500.00000
12	25.00000	3100.00000	2500.00000
13	1.00000	1.00000	1.00000
14	1.00000	1.00000	1.00000

[43767] 29 767FDS3 Page 3
Reported on 1-JUL-1997 at 16:52
Modified on 1-JUL-1997 at 09:58

INTERNAL/DILUTION STANDARDS

SAMPLE NUMBER	ISTD1 AMOUNT	ISTD2 AMOUNT	ISTD3 AMOUNT	DIL1 AMOUNT	DIL2 AMOUNT
1	1.00000	1.00000	1.00000	1.00000	1.00000
2	1.00000	1.00000	1.00000	1.00000	1.00000
3	1.00000	1.00000	1.00000	1.00000	1.00000
4	1.00000	1.00000	1.00000	1.00000	1.00000
5	1.00000	1.00000	1.00000	1.00000	1.00000
6	1.00000	1.00000	1.00000	1.00000	1.00000
7	1.00000	1.00000	1.00000	1.00000	1.00000
8	1.00000	1.00000	1.00000	1.00000	1.00000
9	1.00000	1.00000	1.00000	1.00000	1.00000
10	1.00000	1.00000	1.00000	1.00000	1.00000
11	1.00000	1.00000	1.00000	1.00000	1.00000
12	1.00000	1.00000	1.00000	1.00000	1.00000
13	1.00000	1.00000	1.00000	1.00000	1.00000
14	1.00000	1.00000	1.00000	1.00000	1.00000

PROCESSING ORDER

SAMPLE NUMBER	TYPE
2	Standard
3	Standard
7	Standard
10	Standard
13	Standard
14	Standard
1	Sample
4	Sample
5	Sample
6	Sample
8	Sample
9	Sample
11	Sample
12	Sample

Gas Chromatographic Instrument Parameters Form

ABC Laboratory Study Number: 43767
Customer Identification: ARTF

Instrument: HP 5890 Series II Material ID# 1652-0120
Autoinjector: HP 7673B Material ID# 1625-802A

Column: HP-5MS, 30 M X 0.25 mm, 0.25 μm film thickness
Serial#: 56253614

Detector Type: FPD/P

Electrometer: Range 4

Temperatures:
- Injector (°C): 230
- Detector (°C): 230
- Column:
  - Initial Temp.(°C): 95
  - Initial Time: 1.0 min.
  - Program Rate 1: 30 °C/min to 230 °C, hold 4 min
  - Program Rate 2: 40 °C/min to 290 °C, hold 4 min

Carrier Gas Flow Rate:	He	1.6 mL/min
Septum Purge:	He	2.0 mL/min
Make Up Gas:	He	21 mL/min
Air Flow Rate:		98 mL/min.
Hydrogen Flow Rate:		69 mL/min.
Purge Valve:	Off at 0 min, on at 0.75 min	

Injection Volume: 2 μL

Run Sequence File: 767FDS3

Quantitation Standards: GC mix-1→6 inclusive

Prepared By: [signature] Date: 1 Jul 97

Checked By: Barbara J Bryant Date: 02 Jul 1997

MCDO [43767] 29 767FDS3

ABC Laboratories, Inc.
Sample Information Report ver 3.3

Report Date: 01 JUL 97 at 17:00:56
Page 1

Sample Name	No.	Type	Level	User Parameter 1 Final Volume	User Parameter 2 Factor 1	User Parameter 3 Factor 2
Solvent Blank	1	SA		1.00000	1.00000	1.00000
GCMIX-1 NOMINAL 100 ng/mL	2	ST	01	1.00000	1.00000	1.00000
GCMIX-2 NOMINAL 60 ng/mL	3	ST	02	1.00000	1.00000	1.00000
43767-050	4	SA		1.00000	1.00000	1.00000
43767-051	5	SA		6.00000	200.00000	5000.00000
43767-052	6	SA		6.00000	200.00000	5000.00000
GCMIX-3 NOMINAL 40 ng/mL	7	ST	03	1.00000	1.00000	1.00000
43767-053	8	SA		10.00000	200.00000	5000.00000
43767-054	9	SA		10.00000	200.00000	5000.00000
GCMIX-4 NOMINAL 20 ng/mL	10	ST	04	1.00000	1.00000	1.00000
43767-055	11	SA		25.00000	3100.00000	2500.00000
43767-056	12	SA		25.00000	3100.00000	2500.00000
GCMIX-5 NOMINAL 10 ng/mL	13	ST	05	1.00000	1.00000	1.00000
GCMIX-6 NOMINAL 4 ng/mL	14	ST	06	1.00000	1.00000	1.00000

MCDO [43767] 29 767FDS3

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: DIAZINON

Report Date: 01 JUL 97
Time: 17:00:56
Page: 1

Sample Name	SMP #	INJ #	RT(mins)	Height	ng/mL or ug	CAL. RANG	Peak Type	Bad INJ
Solvent Blank	1	1	0.00	0	0.000	UNDR	O	---
GCMIX-1 NOMINAL 100 ng/mL	2	1	5.96	98846	103.206		OB	---
GCMIX-2 NOMINAL 60 ng/mL	3	1	5.97	55538	57.803		OB	---
43767-050	4	1	0.00	0	0.000	UNDR	OF	---
43767-051	5	1	5.96	8807	2.115		OB	---
43767-052	6	1	5.96	7163	1.701		OBF	---
GCMIX-3 NOMINAL 40 ng/mL	7	1	5.96	36614	37.964		OB	---
43767-053	8	1	5.96	45966	19.107		OB	---
43767-054	9	1	5.95	46374	19.278		OB	---
GCMIX-4 NOMINAL 20 ng/mL	10	1	5.95	18732	19.217		OB	---
43767-055	11	1	5.97	62317	2012.189		OBF	---
43767-056	12	1	5.96	62841	2029.244		OBF	---
GCMIX-5 NOMINAL 10 ng/mL	13	1	5.95	9904	9.961		OB	---
GCMIX-6 NOMINAL 4 ng/mL	14	1	5.96	4464	4.258		OB	---

MCDO [43767] 29 767FDS3

ABC Laboratories, Inc.
Results Information Report ver 3.3
Component Name: MALATHION

Report Date: 01 JUL 97
Time: 17:00:56
Page: 1

Sample Name	SMP #	INJ #	RT(mins)	Height	ng/mL or ug	CAL. RANG	Peak Type	Bad INJ
Solvent Blank	1	1	0.00	0	0.000	UNDR	OBF	---
GCMIX-1 NOMINAL 100 ng/mL	2	1	6.82	61665	104.272		OBF	---
GCMIX-2 NOMINAL 60 ng/mL	3	1	6.83	36448	61.439		OB	---
43767-050	4	1	0.00	0	0.000	UNDR	O	---
43767-051	5	1	6.82	5652	2.191		O	---
43767-052	6	1	6.82	4912	1.890		OB	---
GCMIX-3 NOMINAL 40 ng/mL	7	1	6.82	23071	38.717		OB	---
43767-053	8	1	6.82	30233	20.353		OB	---
43767-054	9	1	6.81	31198	21.009		OBF	---
GCMIX-4 NOMINAL 20 ng/mL	10	1	6.81	11960	19.846		OB	---
43767-055	11	1	6.83	39324	2056.044		OB	---
43767-056	12	1	6.82	42086	2201.492		OBF	---
GCMIX-5 NOMINAL 10 ng/mL	13	1	6.81	6335	10.292		OB	---
GCMIX-6 NOMINAL 4 ng/mL	14	1	6.82	2808	4.301		OBF	---

Acquisition and Peak Processing Parameters Report Print Date and Time : 01 JUL 97 17:05:58
Page : 1

MCDO [43767] 29 767FDS3 Based on Sample Number : 1 Injection Number : 1

ACQUISITION PARAMETERS

Data Collection :

Length of Run..... 14.95 mins
Post Injection Delay..... 0.00 mins
Sampling Rate..... 15.00 Hz

PEAK PROCESSING PARAMETERS

Auto Process Parameters :

Peak Threshold..... 0.50
Baseline Test..... 4
Peak Trend..... 4

Separation Parameters :

Shoulder Sensitivity..... 0.10
Rider Sensitivity..... 0.05

Rejection Parameters :

Minimum Peak Width..... 0.00 secs
Minimum Peak Height..... 0.00 uV
Minimum Peak Area..... 2000.00 uVs
Ignore Flat Top Peak..... No

User Imposed Action Control :

Forced Baseline..... No
Suppress Integration..... Yes
Tangent Skimming..... No
Shoulder Detection..... No
Data Bunching..... No
Negative Detection..... No

Integration Modes :

Retention Time Integration..... No
Square Root Area and Height..... Yes

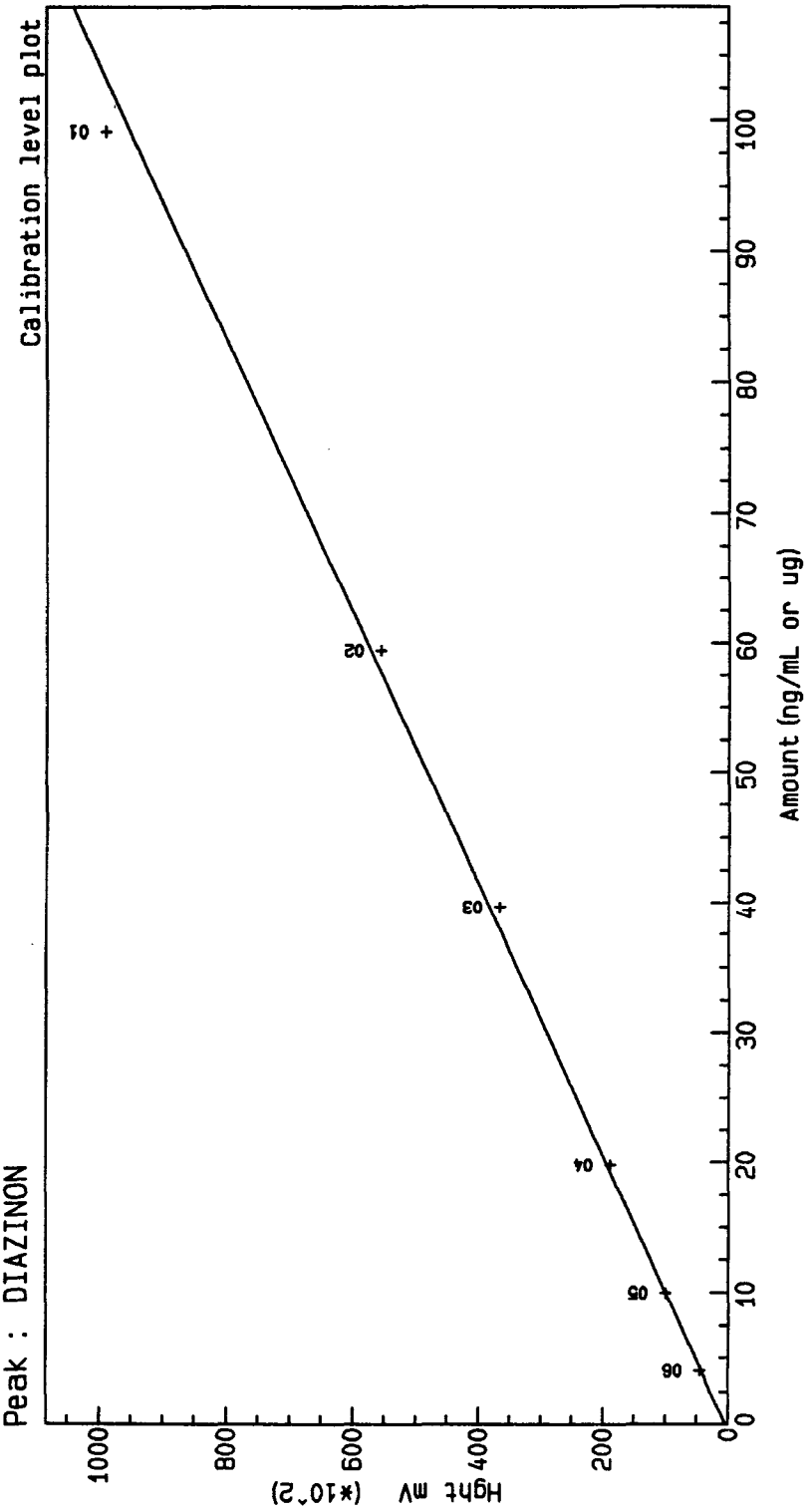
PROCESSING ACTIONS

Time (mins)	Force Baseline	Integrate Suppress	Tangent Skim	Bunch Size	Shoulder Detect	Negative Detect
0.00	--	SS	_	0	--	--
5.30	--	ES	_	0	--	--
7.50	--	SI	_	0	--	--

These parameters apply to all injections of set 767FDS3 with no exceptions

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767FDS3.
43767 Dislodging Solution Set 2
Peak : DIAZINON



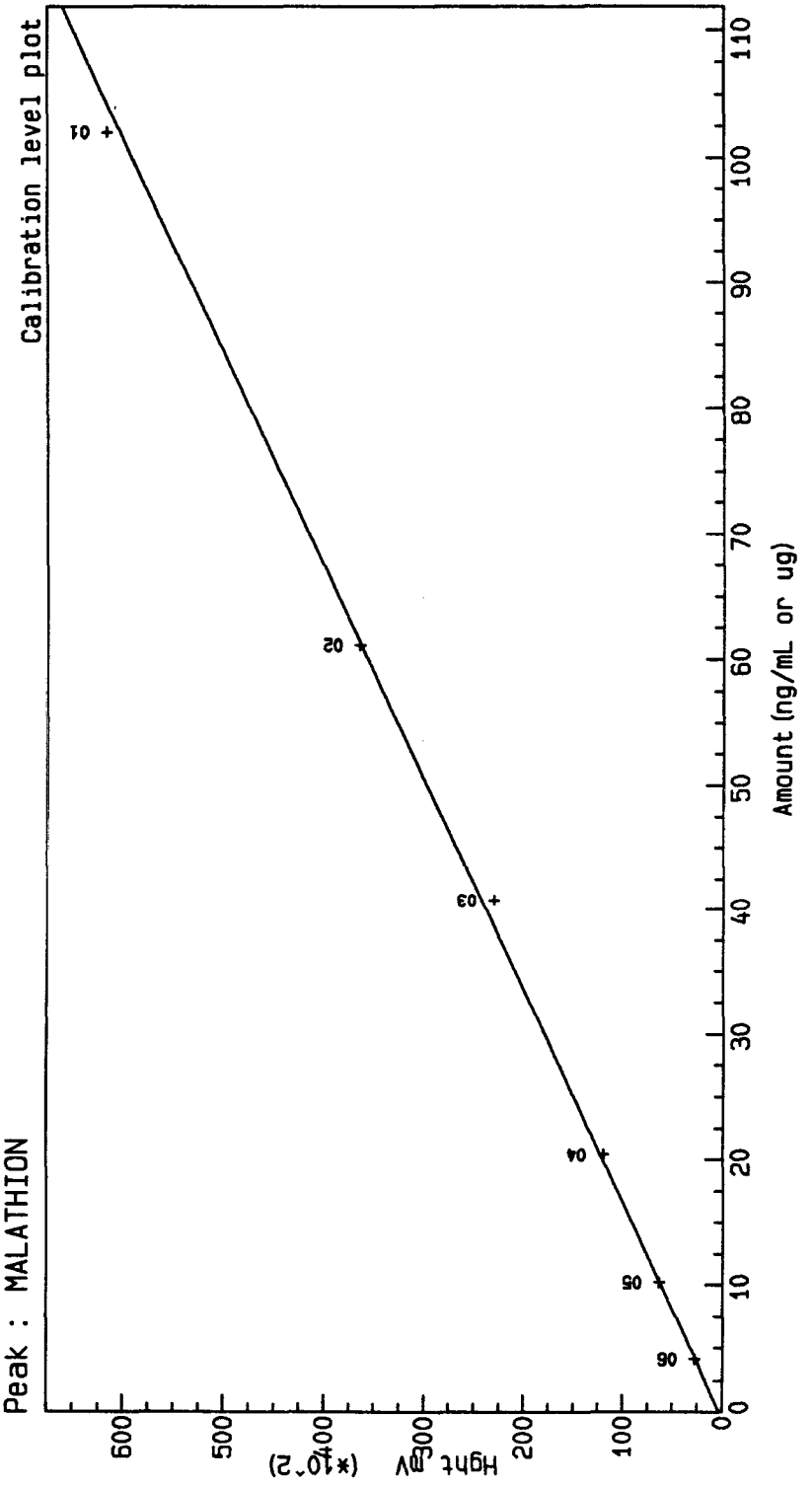
Constant : 4.02368E+2
1st degree : 9.53858E+2

Curve fit : Linear
Correlation coefficient : 0.99838
Standard error : 2.25560E+3

Reported on 1-JUL-1997 at 17:06

ABC Laboratories, Inc. Multichrom ver 1.8-2

Calibration Name : 29 767FDS3.
43767 Dislodging Solution Set 2
Peak : MALATHION



Constant : 2.76225E+2
1st degree : 5.88740E+2

Curve fit : Linear
Correlation coefficient : 0.99931
Standard error : 9.27138E+2

Reported on 1-JUL-1997 at 17:06

ABC Laboratories, Inc.

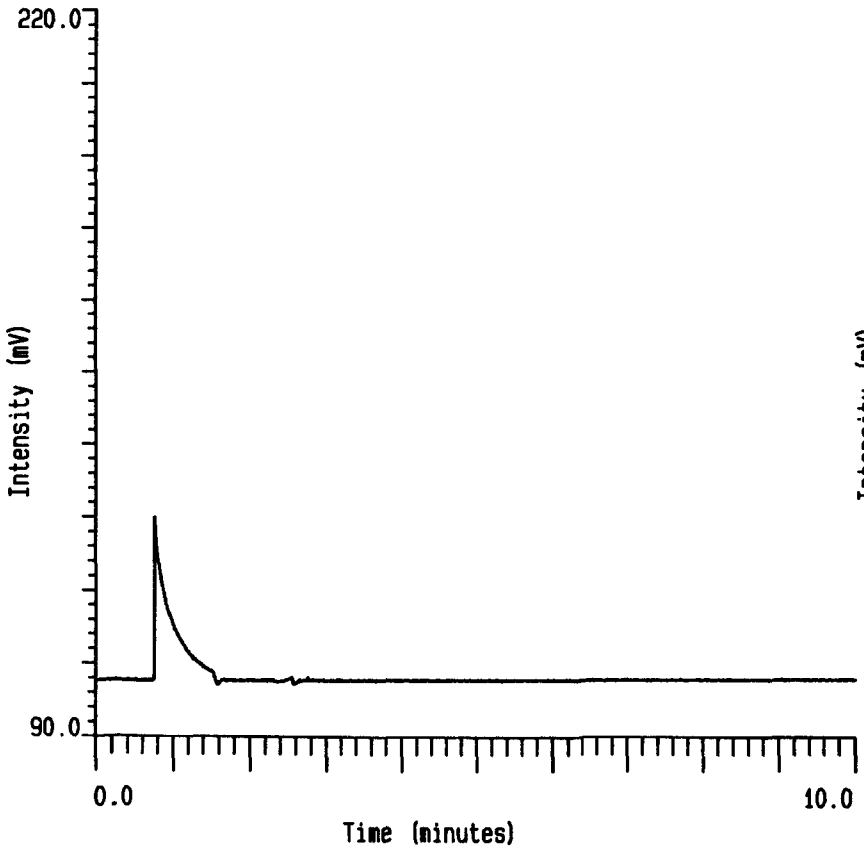
MCPP ver 2.3

43767 Dislodging Solution Set 2

Date of Report: 01 JUL 97 at 17:07:51

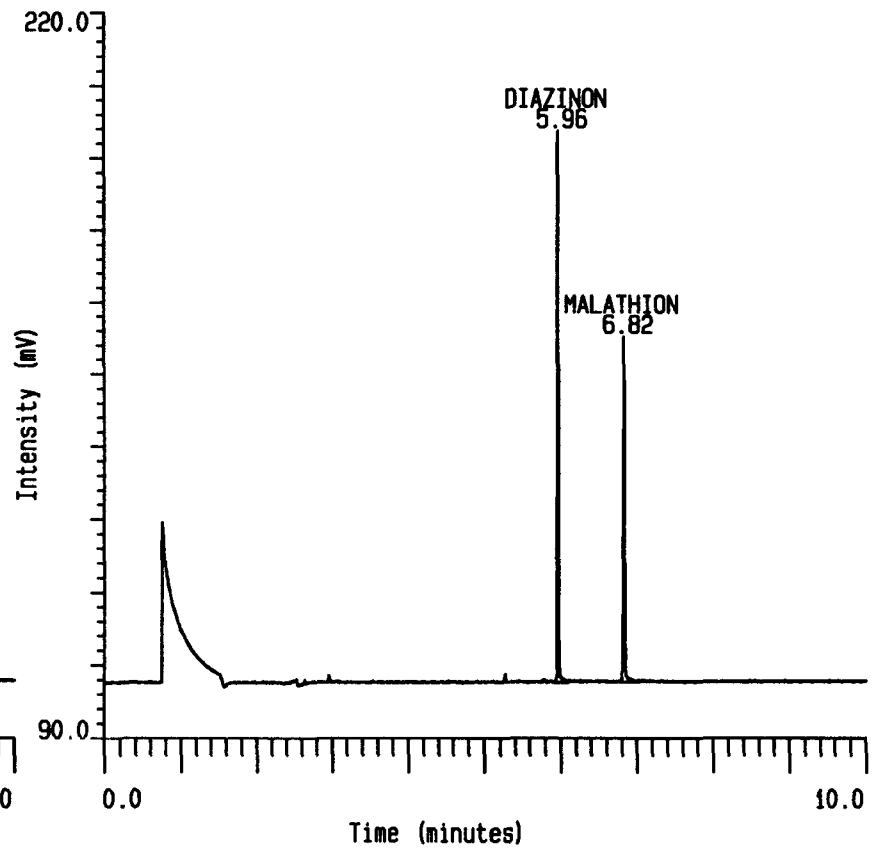
MCDO [43767] 29 767FDS3, 1, 1
Solvent Blank
Acquired on 1-Jul-1997 at 10:53

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	0.00	0	0
MALATHION	0.00	0	0



MCDO [43767] 29 767FDS3, 2, 1
GCMIX-1 NOMINAL 100 ng/mL
Acquired on 1-Jul-1997 at 11:13

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.96	98846	103.206
MALATHION	6.82	61665	104.272



ABC Laboratories, Inc.

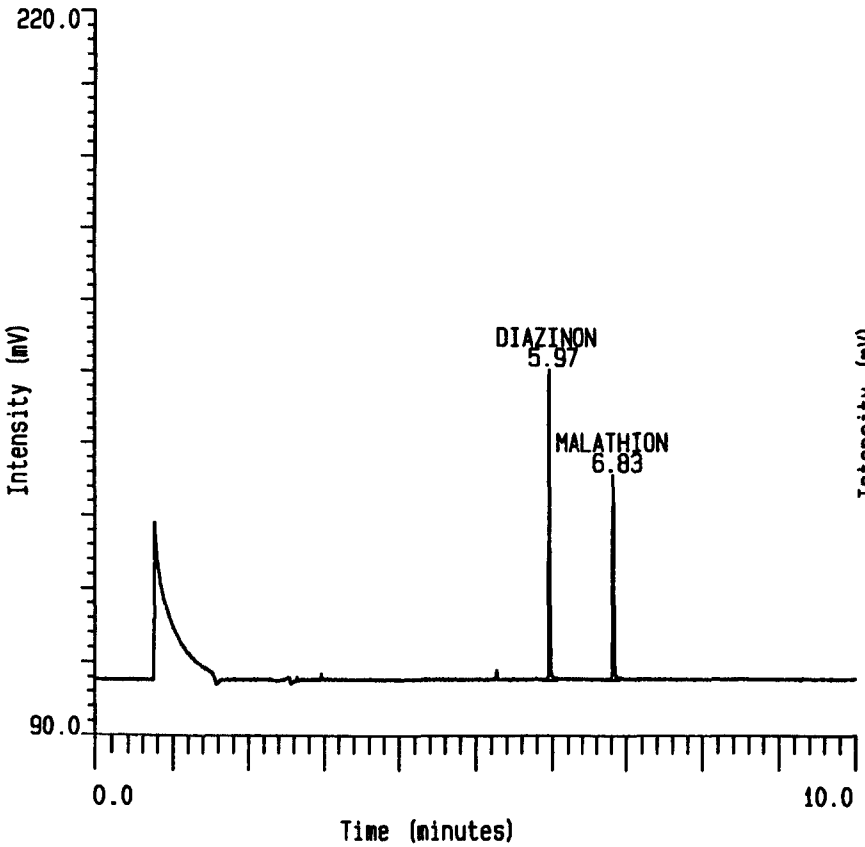
MCPP ver 2.3

43767 Dislodging Solution Set 2

Date of Report: 01 JUL 97 at 17:07:51

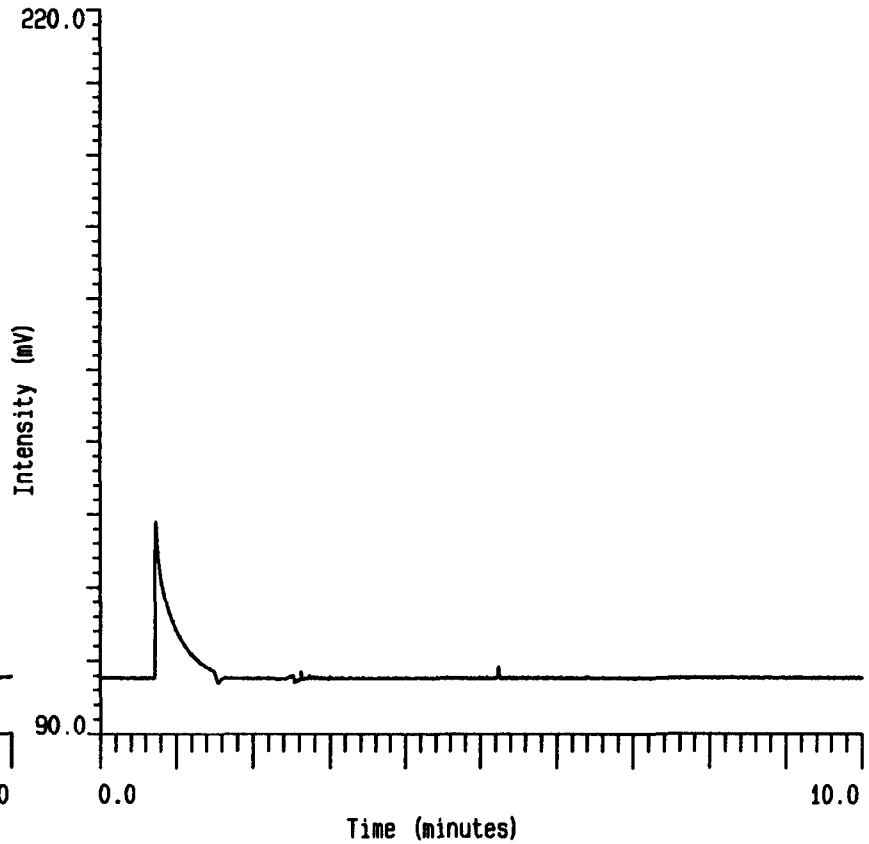
MCDO [43767] 29 767FDS3, 3, 1
GCMIX-2 NOMINAL 60 ng/mL
Acquired on 1-Jul-1997 at 11:34

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.97	55538	57.803
MALATHION	6.83	36448	61.439



MCDO [43767] 29 767FDS3, 4, 1
43767-050
Acquired on 1-Jul-1997 at 11:54

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	0.00	0	0
MALATHION	0.00	0	0



ABC Laboratories, Inc.

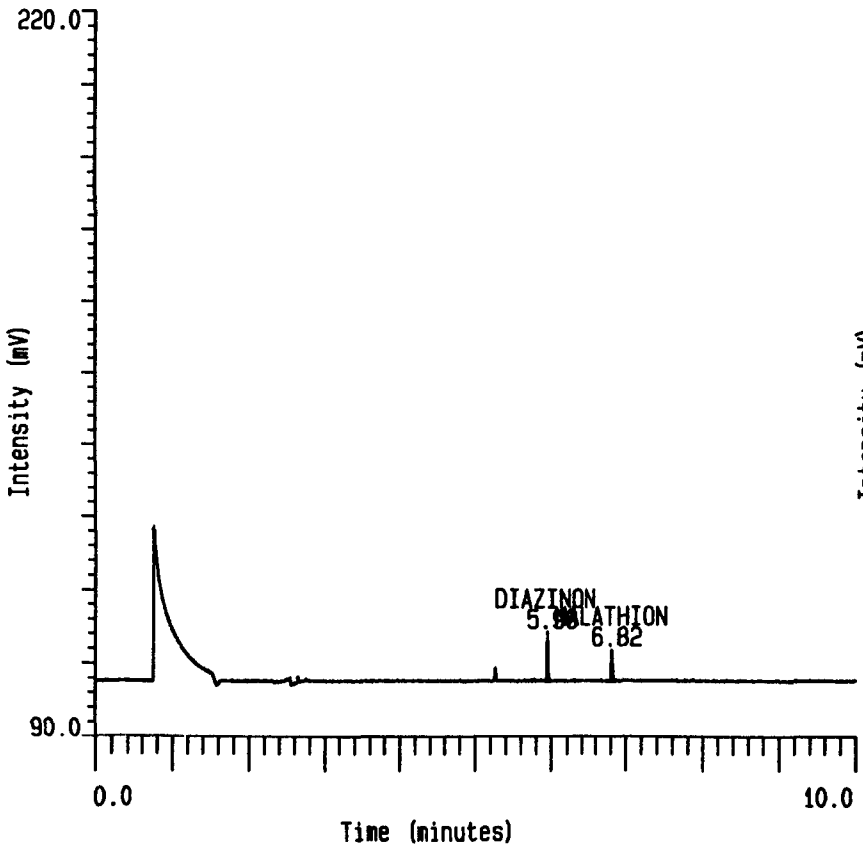
MCPP ver 2.3

43767 Dislodging Solution Set 2

Date of Report: 01 JUL 97 at 17:07:51

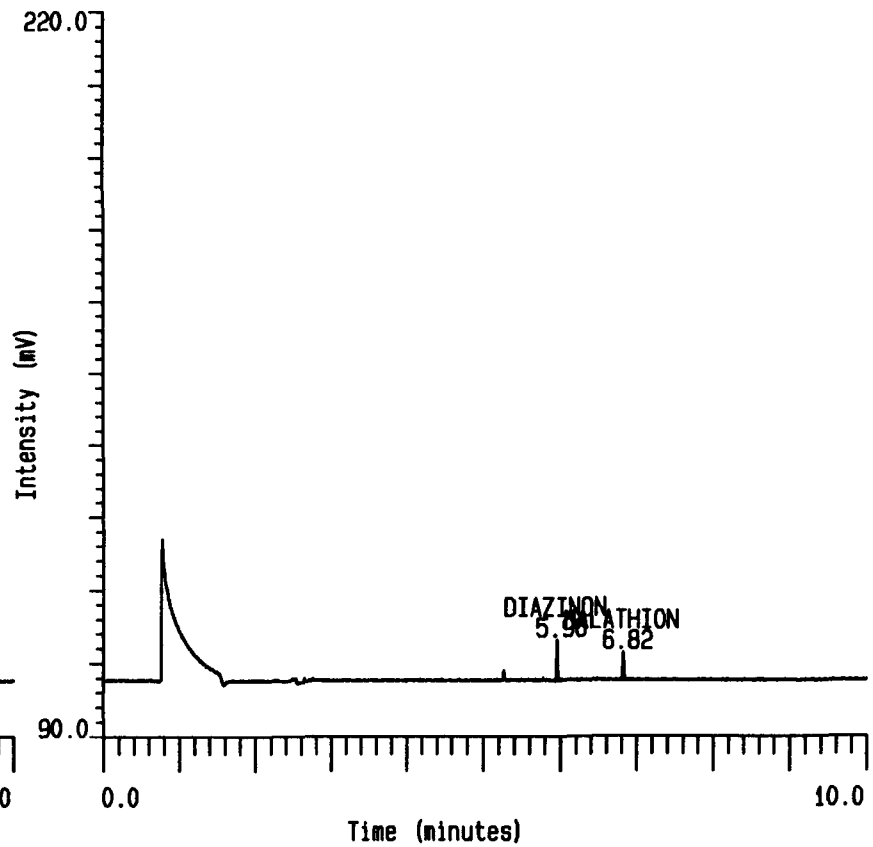
MCDO [43767] 29 767FDS3,5,1
43767-051
Acquired on 1-Jul-1997 at 12:15

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.96	8807	2.115
MALATHION	6.82	5652	2.191



MCDO [43767] 29 767FDS3,6,1
43767-052
Acquired on 1-Jul-1997 at 12:35

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.96	7163	1.701
MALATHION	6.82	4912	1.890



ABC Laboratories, Inc.

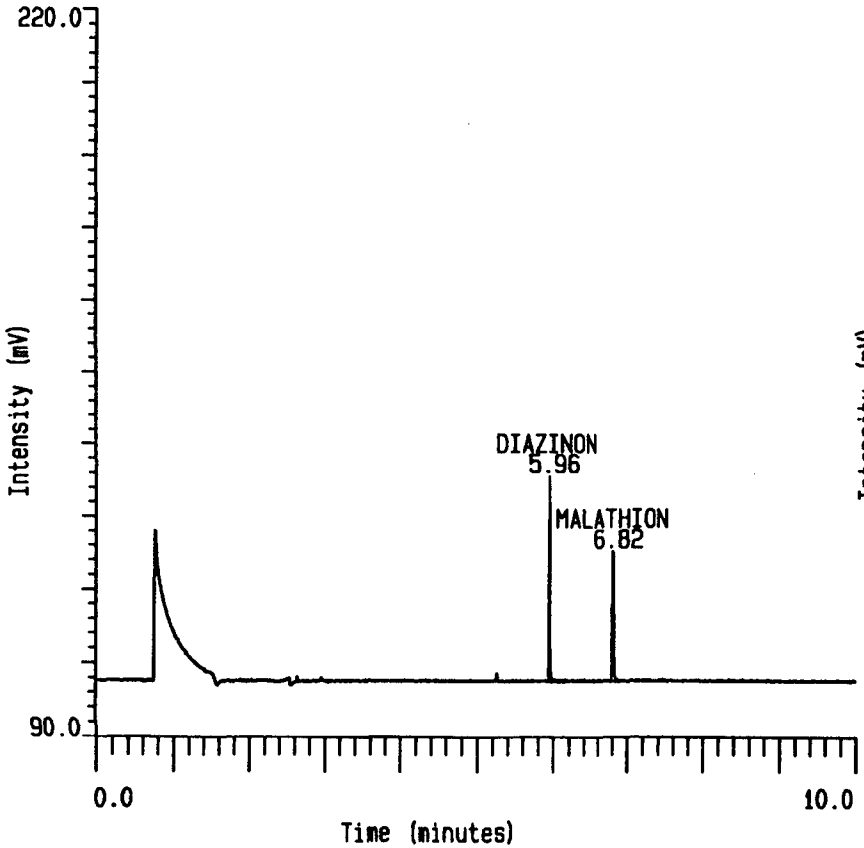
MCPP ver 2.3

43767 Dislodging Solution Set 2

Date of Report: 01 JUL 97 at 17:07:51

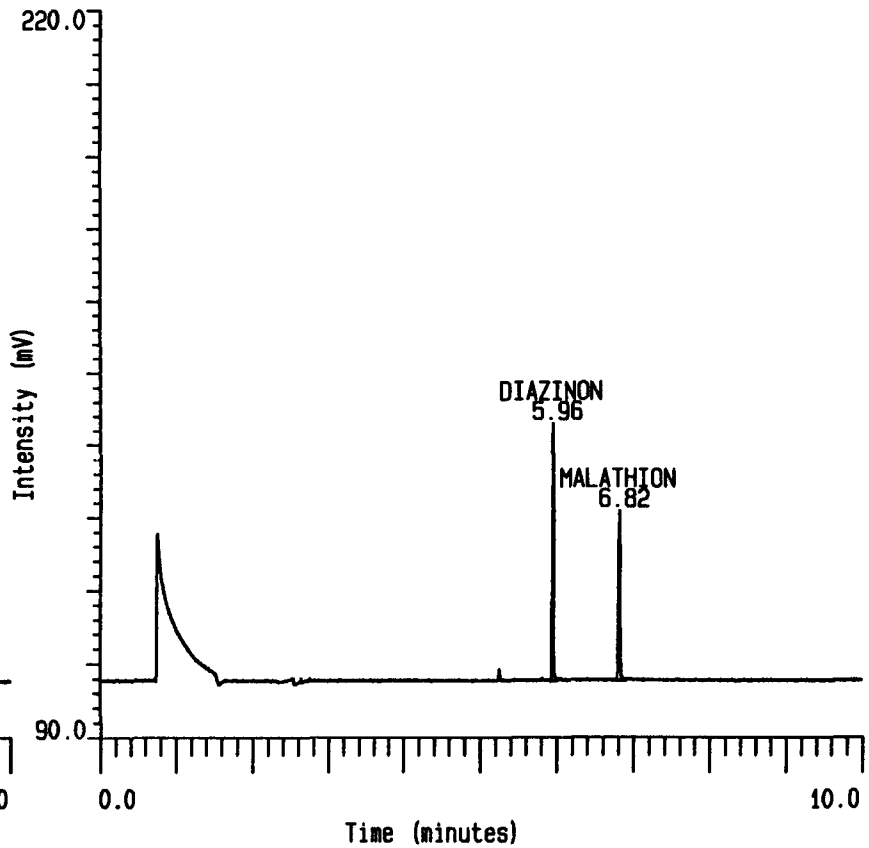
MCDO [43767] 29 767FDS3, 7, 1
GCMIX-3 NOMINAL 40 ng/mL
Acquired on 1-Jul-1997 at 12:55

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.96	36614	37.964
MALATHION	6.82	23071	38.717



MCDO [43767] 29 767FDS3, 8, 1
43767-053
Acquired on 1-Jul-1997 at 13:16

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.96	45966	19.107
MALATHION	6.82	30233	20.353



ABC Laboratories, Inc.

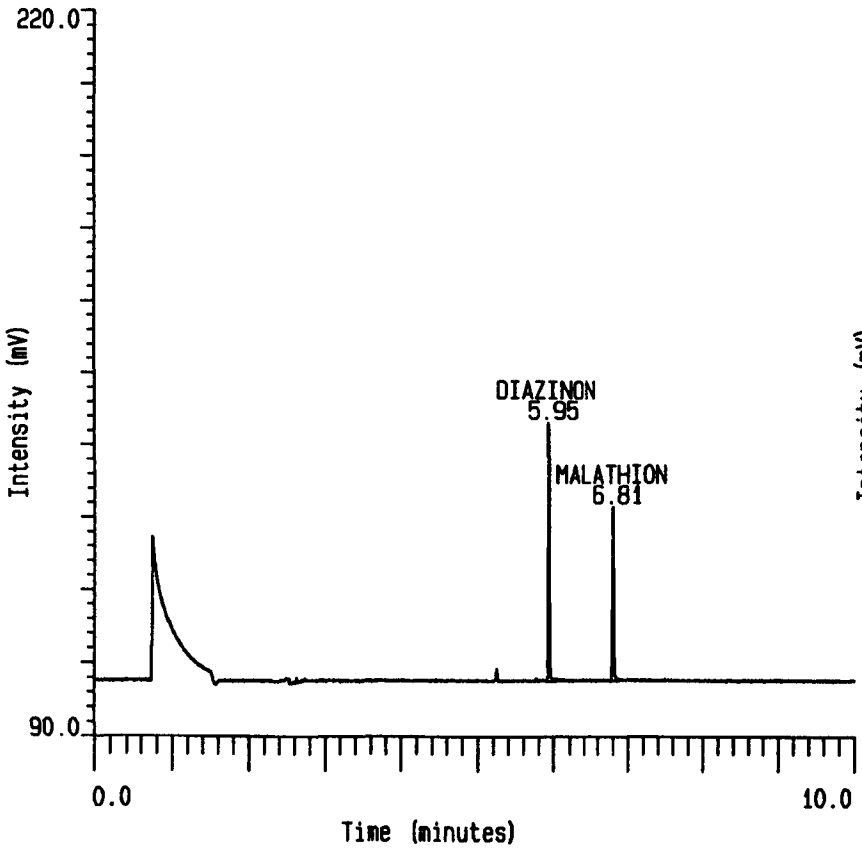
MCPP ver 2.3

43767 Dislodging Solution Set 2

Date of Report: 01 JUL 97 at 17:07:51

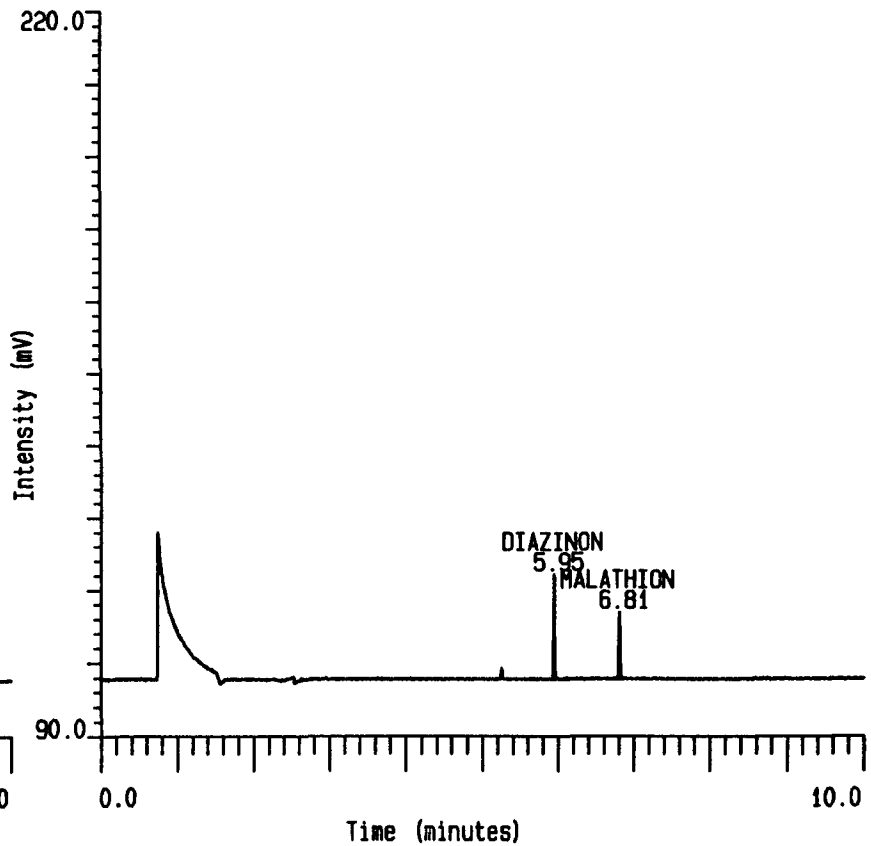
MCDO [43767] 29 767FDS3, 9, 1
43767-054
Acquired on 1-Jul-1997 at 13:36

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	46374	19.278
MALATHION	6.81	31198	21.009



MCDO [43767] 29 767FDS3, 10, 1
GCMIX-4 NOMINAL 20 ng/mL
Acquired on 1-Jul-1997 at 13:56

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	18732	19.217
MALATHION	6.81	11960	19.846



ABC Laboratories, Inc.

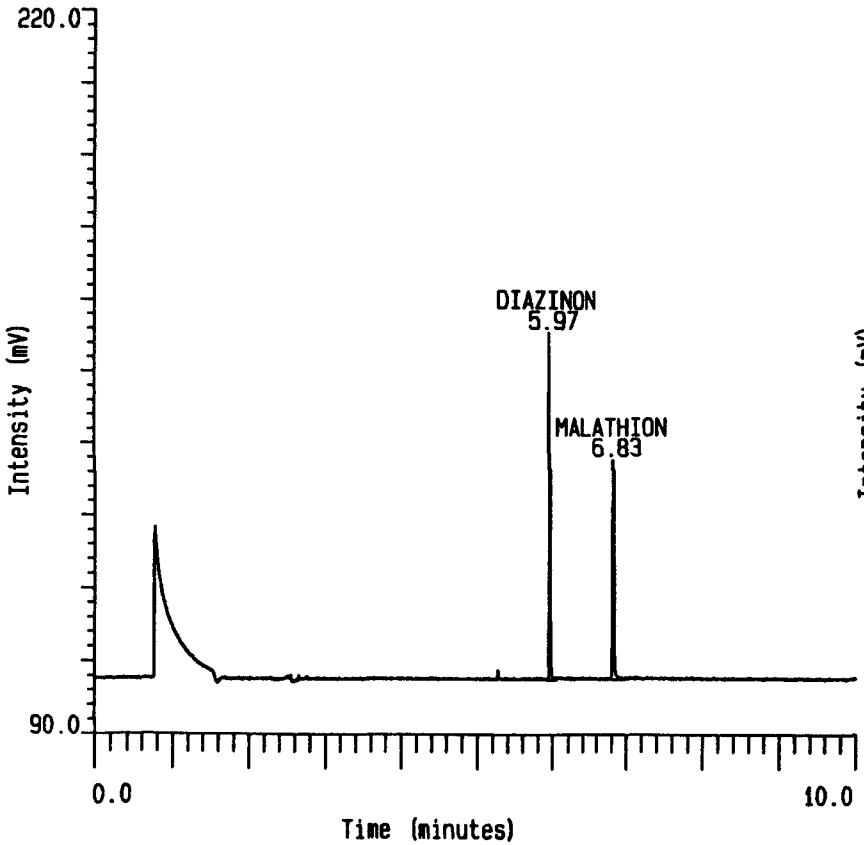
MCPP ver 2.3

43767 Dislodging Solution Set 2

Date of Report: 01 JUL 97 at 17:07:51

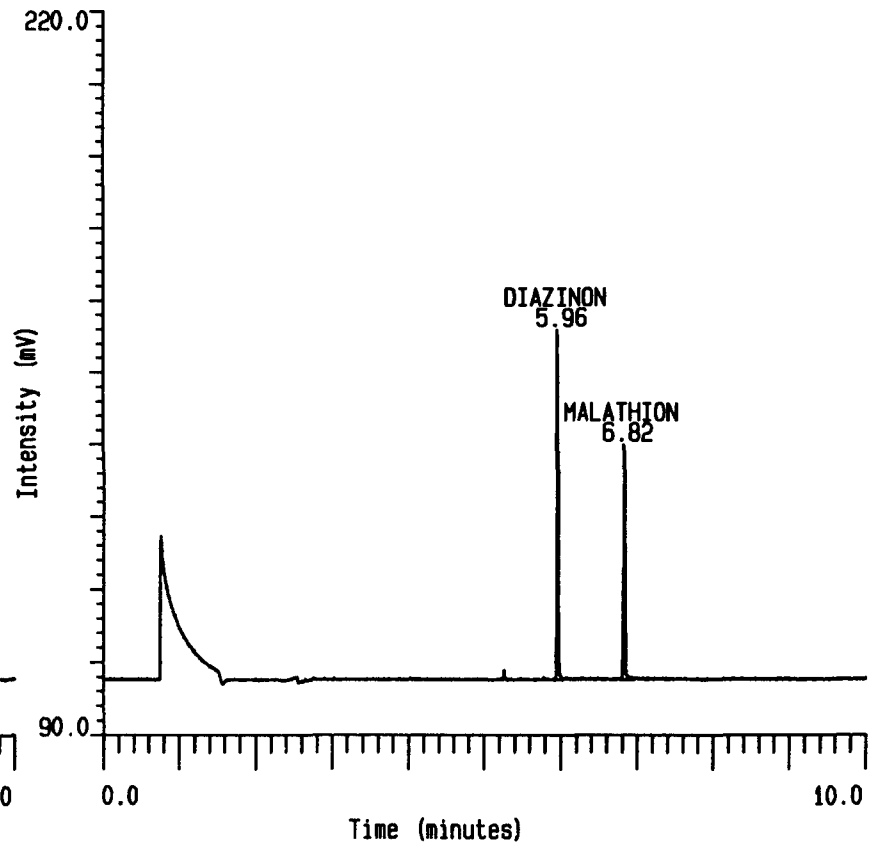
MCDO [43767] 29 767FDS3, 11, 1
43767-055
Acquired on 1-Jul-1997 at 14:17

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.97	62317	2012.189
MALATHION	6.83	39324	2056.044



MCDO [43767] 29 767FDS3, 12, 1
43767-056
Acquired on 1-Jul-1997 at 14:37

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.96	62841	2029.244
MALATHION	6.82	42086	2201.492



ABC Laboratories, Inc.

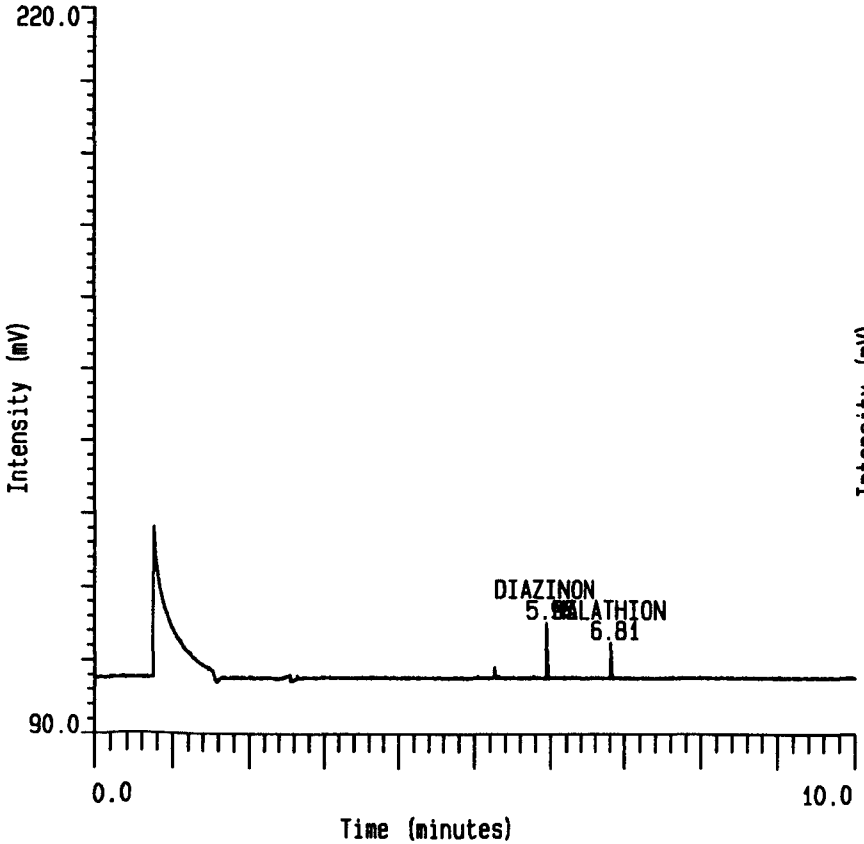
MCPP ver 2.3

43767 Dislodging Solution Set 2

Date of Report: 01 JUL 97 at 17:07:51

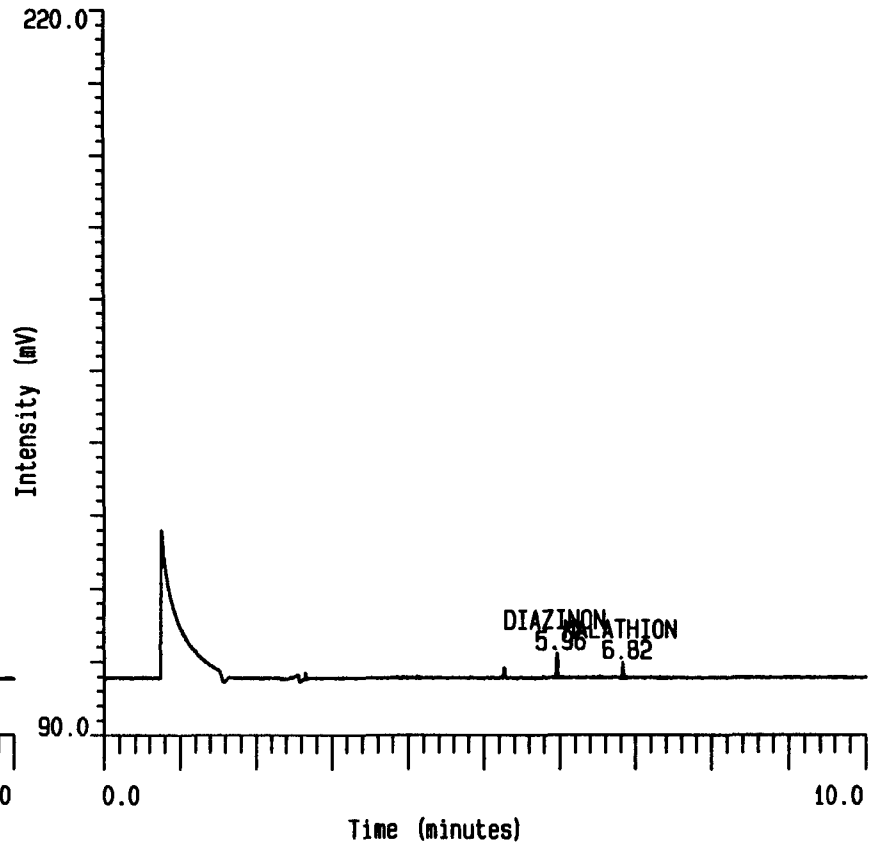
MCDO [43767] 29 767FDS3, 13, 1
GCMIX-5 NOMINAL 10 ng/mL
Acquired on 1-Jul-1997 at 14:57

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.95	9904	9.961
MALATHION	6.81	6335	10.292



MCDO [43767] 29 767FDS3, 14, 1
GCMIX-6 NOMINAL 4 ng/mL
Acquired on 1-Jul-1997 at 15:18

Peak Name	RT (mins)	Height	ng/mL or ug
DIAZINON	5.96	4464	4.258
MALATHION	6.82	2808	4.301



[43767] 29 767FDS3 Page 1
Reported on 2-JUL-1997 at 08:08
Modified on 1-JUL-1997 at 16:55

List Calibration File

CALIBRATION HEADER INFORMATION

Calibration Title : 43767 Dislodging Solution Set 2
General :
Calibration type..... External standard
Units..... ng/mL or ug
Calibration base..... Height
Reference Peak Identification :
Reference window..... 5.0 %
Minimum window..... 0.50 mins
Peak threshold..... 0.0 %
Uncalibrated Peaks Response Factor :
Response factor source..... User set response factor
Response factor..... 0.0000
Additional Information :
Source library..... None
Initialise on 1st standard..... No
Variation tolerance..... 100.00 %
Calibrant Peak Identification :
Calibrant window..... 0.10 mins
Calibrant threshold..... 0.0 %
Response Factor Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... 1 / Y
Retention Value Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... None
Timed Calibration Curve :
Curve fit..... Linear
Force through zero..... No
X transformation..... None
Y transformation..... None
Weighting..... None
No group information entered.

[43767] 29 767FDS3 Page 2
Reported on 2-JUL-1997 at 08:08
Modified on 1-JUL-1997 at 16:55

Peak name : DIAZINON
Expected retention time : 5.93 mins (RT range : 5.88 - 5.98 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	3.9700	1124.3282	1
05	9.9200	998.3657	1
04	19.8000	946.0740	1
03	39.7000	922.2750	1
02	59.5000	933.4155	1
01	99.2000	996.4337	1

Peak name : MALATHION
Expected retention time : 6.78 mins (RT range : 6.73 - 6.83 mins)
Peak window mode..... Global
Group name identifier..... ----
Peak identification mode..... Largest
Must peak..... No
Reference peak..... No
Dilution peak..... No
Retention standard..... No
Response factor mode..... Internal Levels
Purity..... 100.0000

Calibration level	Standard amount	Response factor	Calibration count
06	4.0800	688.3497	1
05	10.2000	621.1038	1
04	20.4000	586.2946	1
03	40.8000	565.4591	1
02	61.2000	595.5510	1
01	102.0000	604.5613	1