Study Title

Validation of Method for the Analysis of Worker Exposure and Reentry Matrices for Chlorothalonil
Study Number ARF004

Study Number

ARF004

Data Requirement

EPA Residue Chemistry Test Guidelines
OPPTS 860.1340

Study Director and Author

Sharon Webster

Report Date

May 6, 1999

Testing Facility

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STATEMENT OF NO DATA CONFIDENTIALITY CLAIMS

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

Paula Paul

Paula Paul
Administrative Committee Chair
Agricultural Reentry Task Force

12-16-99

Date

GLP COMPLIANCE STATEMENT

Centre Analytical Laboratories (CAL) Study Number 017-01, entitled "Validation of Method for the Analysis of Worker Exposure and Reentry Matrices for Chlorothalonil", conducted and reported for the Agricultural Reentry Task Force Study Number ARF004, was performed in compliance with US EPA Good Laboratory Practice Standards (40 CFR, Part 160, FR 08/17/89) by Centre Analytical Laboratories, Inc. with the following exceptions:

1. There was no expiration date or storage condition on the label of the reference substance that was received at Centre Analytical Laboratories on January 21, 1997. This was added upon discovery. [§160.105 (c)]

Sharon Webster — 5-6-99

Sharon Webster
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ARTF Quality Assurance Unit Statement

Study ARF004 was audited by the Agricultural Reentry Task Force Quality Assurance Unit (QAU) for compliance with the EPA's Good Laboratory Practice Standards (40 CFR Part 160). All findings were reported to the Study Director, Study Director's Management, and ARTF Management. The Quality Assurance Statement from the Testing Facility Quality Assurance Unit is located on the following page.

Phase Inspected	Dates of Inspection	Date Findings Reported to the Study Director/Management
Protocol	02/28/97	03/31/97
Final Report	03/25 & 04/07/99	03/16/99

Daniel O. Carey
ARTF Quality Assurance Officer

05 May 99
Date

CENTRE ANALYTICAL LABORATORIES (CAL) QUALITY ASSURANCE STATEMENT

CAL Study Number 017-01 was reviewed by Centre Analytical Laboratories' Quality Assurance Unit. All reviewed phases were reviewed for conduct according to Centre Analytical Laboratories' Standard Operating Procedures, Study Protocol, and all applicable Good Laboratory Practice Standards. All findings were reported to the study director and to management.

Phase	Date Inspected	Date Reported to Study Director	Date Reported to CAL Management	Date Reported to Sponsor's Representative and Sponsor Management
1. Protocol Review	02/14/97	02/14/97	02/18/97	03/07/97
2. Extraction	02/14/97	03/03/97	03/25/97	04/09/97
3. Raw Data Review	02/24-25/97	03/04/97	03/25/97	04/09/97
4. Raw Data Review	03/25-26/97	04/07/97	04/09/97	05/15/97
5. Raw Data Review	08/06/97	08/20/97	09/04/97	10/06/97
6. Raw Data Review	10/07/97	10/13/97	10/29/97	11/07/97
7. Draft Analytical Phase Report Review	10/21-22/98, 11/18,19,23/98	03/09/99	03/18/99	04/02/99
8. Second Draft Analytical Phase Report Review	02/03-04,09-10/99	03/09/99	03/18/99	04/02/99
8. Final Analytical Phase Report Review	04/28-29/99	05/06/99	05/06/99	05/06/99

Stacy Toretti

Stacy Toretti
Quality Assurance Auditor

Date 5/6/99

STUDY IDENTIFICATION AND APPROVAL

Title: Validation of Method for the Analysis of Worker Exposure and Reentry Matrices for Chlorothalonil

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Testing Facility: Centre Analytical Laboratories, Inc.
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Sharon Webster 07/31/98 – present

Study Initiation Date: February 14, 1997

Study Completion Date: May 3, 1999

Study Personnel:

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Sharareh Zolghadr	Technician	Ben Grazzini	Technician
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This report is approved and issued by:

Sharon Webster — 5-6-99
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Centre Analytical Laboratories, Inc.

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President
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James R. Clark — 5/17/99
James Clark, Ph.D. — **Date**
Sponsor Representative
Technical Committee Chair
Agricultural Reentry Task Force

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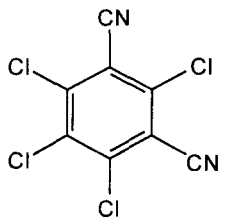
1.0 INTRODUCTION

This study, "Validation of Method for the Analysis of Worker Exposure and Reentry Matrices for Chlorothalonil", was performed by Centre Analytical Laboratories, Inc. (CAL) to validate, under GLP, methods that are proposed for use in ARTF worker exposure studies utilizing chlorothalonil as a surrogate test compound. The original method to be validated was Ricerca Method # 6445-95-0086-CR-001 and subsequently there were three additional methods written at CAL (ARTF-001, ARTF-003 and ARTF-004). These methods were validated on the following matrices:

1. Full Sized Worn Outer Dermal Dosimeters (Shirts, Pants), LOQ = 1.0 µg/sample
2. Inner Whole Body Dermal Dosimeters, LOQ = 1.0 µg/sample
3. Cotton Facial/Neck Wipes (J&J Gauze Sponges), LOQ = 1.0 µg/sample
4. OVS Air Sampling Tubes, LOQ = 0.01 µg/sample
5. Handwash Solution (Aerosol® OT-75), LOQ = 1.0 µg/sample
6. Foliar Dislodgeable Solution (Aerosol® OT-75 Cauliflower Leaf Wash), LOQ = 1.0 µg/sample

2.0 MATERIALS

2.1 Test/Reference Substance



Common Name: chlorothalonil

CAS Chemical Name: tetrachloroisophthalonitrile

CAS Registry Number: 1897-45-6

Lot Number: SDS-2787-2601

Purity: 99.7%

Expiration Date: 12/31/00

Storage Conditions: Frozen

Source: Ricerca, Inc.

2.2 Test Matrices

All matrices, except for the handwash solution (Aerosol® OT-75) (prepared in-house) and the cauliflower leaves (purchased at local supermarket) which were used with the handwash solution (Aerosol® OT-75), were supplied by ARTF and consisted of the following:

1. Full Sized Worn Outer Dosimeters (Shirts, Pants): Consisted of a 100% cotton, white, long-sleeved shirt cut into segments of front, back, top sleeve, and bottom sleeve segments. Also consisted of 100% cotton white pants cut into top and bottom segments. Each segment represented one analytical sample, (Universal Overall).
2. Inner Whole Body Dermal Dosimeters: Consisted of a 100% cotton, white long underwear garment cut into 20cm x 20cm samples, each representing one analytical sample, (The Original Arizona Jean Company).
3. Facial/Neck Wipes (J&J Gauze Sponges): Consisted of two 4" x 4" 8-ply cotton gauze pads, (Johnson & Johnson Medical Inc.).
4. Air Sampling Tubes (with Chromosorb 102): Glass fiber filter + 500 mg/150 mg Chromosorb 102, (#S2-0277, SKC Inc.).
5. Handwash Solution (Aerosol® OT-75): Consisted of 250 mL of 0.01% (v/v) Aerosol® OT-75 solution made from laboratory deionized water and 75% (w/w) aqueous Aerosol® OT-75 solution, (Fisher Scientific, Lot # 963392).
6. Dislodging Solution (Aerosol® OT-75 Cauliflower Leaf Wash): Consisted of cauliflower leaves washed with 250 mL of 0.01% (v/v) Aerosol® OT-75 solution made from laboratory deionized water and 75% (w/w) aqueous Aerosol® OT-75 solution, (Fisher Scientific, Lot # 963392).

2.3 Reagents

Ethyl Acetate, Pesticide grade, Burdick & Jackson

Toluene, Pesticide grade, Burdick & Jackson

Petroleum Ether, J.T. Baker

Diethyl Ether, Pesticide grade, Burdick & Jackson

Sodium Chloride, J.T. Baker

Mineral Oil, White, Light, Mallinckrodt NF

Sulfuric Acid, J.T. Baker

Aerosol® OT-75

Hexane, J.T. Baker

3.0 METHODS

3.1 Preparation of Spiking Solutions

A 1,000 µg/mL stock standard was prepared by transferring 0.1000 g (corrected for purity) chlorothalonil analytical standard into a 100-mL volumetric flask and diluted to volume with ethyl acetate. This stock standard was serially diluted with ethyl acetate to produce fortification standard solutions at concentrations of 100 and 10 µg/mL. These fortification standard solutions were used for full sized worn outer dosimeters (shirts, pants), whole body dermal dosimeters (inner), facial/neck wipes, handwash solution, dislodging solution .

Fortification standard solutions used for the air sampling tubes were prepared in toluene. The 10 µg/mL fortification standard solution was prepared using the 1000 µg/mL stock standard solution and the 1 µg/mL fortification solution was prepared from the 10 µg/mL fortification standard solution.

3.2 Analytical Procedure for Full Sized Worn Outer Dosimeters (Shirts, Pants)

Each sample consisted of a shirt or pants cut into segments. The shirt was cut into four segments: front torso (cut at side seams), back torso (cut at side seams), right and left upper arms (shoulder to elbow), and right and left lower arms (elbow to cuff). The pants were cut into two segments: top and bottom, top being from waist to knee and bottom being from knee to cuff. All samples were cut according to ARTF SOP ARTF-8.D./0. One set, consisting of one control and the six full sized worn outer dosimeter samples (as described above), was extracted for this matrix. The samples were fortified, by syringe, with 1.0 µg of chlorothalonil by adding 100 µL of a 10 µg/mL fortification solution. The fortification solution was distributed evenly over the dosimeter allowed to dry for approximately 10 minutes. Then each sample was placed into separate 2 liter jars. Two liters of hexane were added and the jars were placed on a mechanical shaker for ~ 30 minutes. After shaking, the jars were shaken by hand for 30 seconds. From the jars, about 150 mL hexane extract was removed and filtered. The first 70 mL was discarded and the remaining 80 ml was collected. From the 80 ml, a 20 mL aliquot was collected in a flat bottom flask and the sample was rotary evaporated to approximately 5 mL. The sample was added to a Florisil column which was pre-rinsed with 15 mL of 10% ethyl acetate:hexane followed by 15 mL 10% ether:hexane followed by 15 mL hexane. These rinses are discarded. The sample was applied to the column and eluted with 60 mL of 10% ether:hexane. It was rotary evaporated to near dryness, and then the remaining sample was dried with nitrogen. The final volume was 2 ml of ethyl acetate, which was collected for analysis.

3.3 Analytical Procedure for Inner Whole Body Dermal Dosimeters

The dermal dosimeters were cut into 20 x 20 cm samples. Two sets, consisting of one control and two fortification samples at each of three spiking levels, were extracted and analyzed on separate days. Fortifications, by syringe using a 100 µg/mL fortification solution, were made at 5 µg (by adding 50 µL), 25 µg (by adding 250 µL), and 125 µg (by adding 1250 µL). The fortification solution was distributed evenly over the dosimeter allowed to dry for approximately 10 minutes. The samples were then transferred to Teflon bottles. The ethyl acetate extraction volume for the dosimeters was 100 mL. After the samples were extracted on a reciprocating shaker for 30 minutes, ~2 mL were collected for analysis.
Note: The method validated in this study for inner whole body dermal dosimeters used 20 cm x 20 cm sample sizes. The method later used in the field studies followed the extraction procedure for full sized outer dosimeter samples (ARTF-001).

3.4 Analytical Procedure for Facial/Neck Wipes

Two sets, consisting of one control and two fortification samples at each of three spiking levels, were extracted and analyzed on separate days. A third set consisting of one control and three fortification samples at 1 µg was additionally extracted and analyzed. Two cotton wipes were placed in glass jars with teflon lined caps and wetted with 8 mL of 0.01% Aerosol® OT-75 solution. Fortifications, by syringe using a 100 µg/mL fortification solution, were made at 5 µg (by adding 50 µL), 25 µg (by adding 250 µL), and 125 µg (by adding 1250 µL). Fortifications at 1 µg were made, by syringe, using 100 µL of a 10 µg/mL fortification solution. The samples were extracted with 100 mL of ethyl acetate on a reciprocating shaker for 30 minutes. After extraction, ~2 mL were collected for analysis.

3.5 Analytical Procedure for Air Sampling Tubes

Two sets, consisting of one control and two fortification samples at each of three spiking levels, were extracted and analyzed on separate days. Separate validations were performed on the front and rear sections of the sorbent tube. Using forceps, the Teflon ring, the glass fiber filter consisting of the front Chromosorb 102, and the middle glass wool plug were all emptied into a 20-mL scintillation vial. The rear section of the tube, consisting of the rear Chromosorb 102 and glass wool plug, was emptied into a second 20-mL scintillation vial using forceps. The front and rear sections were then fortified, by syringe, using 50 µL of a 1 µg/mL fortification solution for the 0.05 µg samples. Fortifications at 25 µg and 125 µg were made, by syringe, using 25 µL and 125 µL, respectively, of a 10 µg/mL fortification solution. Following fortification, 3.5 mL of toluene were added to each scintillation vial and shaken by hand for ~2 minutes. After extraction, ~2 mL were collected for analysis.

3.6 Analytical Procedure for Hand Washes

Each hand wash sample consisted of 250 mL of 0.01% Aerosol® OT-75 solution. Two sets, consisting of one control and two fortification samples at each of three spiking levels, were extracted and analyzed on separate days. The samples were placed in 500-mL separatory funnels and fortified. Fortifications, by syringe using a 100 µg/mL fortification solution, were made at 5 µg (by adding 50 µL), 25 µg (by adding 250 µL), and 125 µg (by adding 1250 µL). Fifty milliliters of 1:1 petroleum ether:diethyl ether (v:v), 10 mL of 20% NaCl (w:w), and 2 mL of 10*N* H_2SO_4 were added to each funnel. After shaking the funnels for two minutes and allowing for phase separation, the petroleum ether extracts were collected in a 500-mL round bottom flask. A second extraction was performed with another 50 mL of petroleum ether mix. The ether extracts were combined and 0.4 mL of the "keeper" solution (consisting of 2 mL mineral oil in 100 mL petroleum ether) was added. The samples were evaporated to ~2 mL in a waterbath, then evaporated with nitrogen to just dryness. The samples were redissolved in 10 mL ethyl acetate and ~2 mL were collected for analysis.

3.7 Analytical Procedure for Dislodging Solutions

Each sample consisted of 400 cm^2 of cauliflower leaves (hole-punched, the front and back of leaf were included in the area count) and 250 mL of 0.01% Aerosol® OT-75 solution. The 400 cm^2 of cauliflower leaves were added to 500-mL separatory funnels containing 250 mL of 0.01% Aerosol® OT-75 solution and shaken. After shaking, the 250 mL of solution was decanted, and the leaves were discarded. One set, consisting of one control and two fortification samples at each of three spiking levels, were extracted and analyzed. Fortifications, by syringe using a 100 µg/mL fortification solution, were made at 5 µg (by adding 50 µL), 25 µg (by adding 250 µL), and 125 µg (by adding 1250 µL). After the fortification of the samples the extraction procedure was conducted in the same manner as the extraction for the handwash solution (Aerosol® OT-75).

3.8 Chromatographic Conditions

The following chromatographic conditions were used for the analysis of chlorothalonil in full sized worn outer dosimeters (shirts, pants), whole body inner dermal dosimeters, facial/neck wipes, air sampling tubes, hand wash solutions, and dislodging solutions.

GC System: HP 5890 GC, electron capture detector, HP Chemstation software

Column: Fused silica capillary, 30 m x 0.53-mm I.D., 0.50-micron film thickness, RTX-5 (Restek, Inc.)

Carrier Gas: Helium at 8mL/min

Detector Make-up Gas: Nitrogen at 30mL/min

Injector Temperature: 270°C

Detector Temperature: 300°C

Column Temperatures:
a. 160° for 1 min. then 20°C/min. to 240°C for 1 min.
b. 160° for 1 min. then 20°C/min. to 240°C for 2min., then 25°C/min. to 270°C and hold for 6 min.(for full-sized worn outer dosimeters and the third set of cotton facial/neck wipes)

Injector Volume: 1 µL

Retention Time: ~ 5 min

Total Run Time:
a. ~ 6 min
b. ~ 8 min. (for full-sized worn outer dosimeters and the third set of facial/neck wipes)

3.9 Calibration Standards

The 10 µg/mL fortification standard solutions were used to prepare calibration standard solutions in ethyl acetate and toluene at concentrations of 0.001, 0.005, 0.01, 0.05, and 0.1 µg/mL. The dilutions are indicated in the table below:

Standard Solution Concentration (µg/mL)	Aliquot (mL)	Final Volume (mL)	Final Concentration (µg/mL)
10	1	100	0.1
0.1	50	100	0.05
0.1	10	100	0.01
0.01	50	100	0.005
0.005	5	10	0.0025
0.01	10	100	0.001

Each GC run began with an injection of solvent (ethyl acetate or toluene), followed by four calibration standards at concentrations of 0.05, 0.01, 0.005, and 0.0025 µg/mL for full sized worn outer dosimeters (shirts, pants), 0.1, 0.05, 0.01, and 0.005 µg/mL whole body inner dermal dosimeters, facial/neck wipes (J&J gauze sponges), handwash solution (Aerosol® OT-75), and dislodging solution (Aerosol® OT-75 cauliflower leaf wash). For air sampling tubes, the calibration standard concentrations were 0.05, 0.01, 0.005, and 0.001 µg/mL. Calibration standards were thereafter injected to bracket each set of sample injections.

A linear regression standard curve was created using standard concentrations (µg/mL), chlorothalonil peak heights, and the equation $y = mx + b$, where:

y = peak height response
x = µg/mL found for the chlorothalonil peak
m = slope
b = y-intercept

The minimum accepted correlation coefficient calculated from the curve was 0.9931. The minimum correlation coefficient that is considered acceptable is ≥ 0.9900.

3.10 Statistics and Quantitations

Data were acquired and subsequently processed with a Hewlett Packard GC2D ChemStation. Statistical methods employed for analyzing the data included linear regression analysis and calculations of the mean and standard deviation.

Calculations for instrumental analysis were conducted on a Gateway 486\50 computer using Microsoft Excel® software to create a standard curve based on linear regression. These regression functions were used to calculate a best fit line from a set of standard concentrations in µg/mL versus peak response. From this line the concentration of the analyte found during sample analysis was determined.

3.11 Example Calculations

The chlorothalonil concentration (µg/mL) for all samples was determined using a linear regression equation. The sample concentration was then multiplied by the dilution factor to determine the final result in units of µg chlorothalonil. The percent recovery was also calculated for each fortified sample.

Calculations to determine the concentration of chlorothalonil and the percent recovery obtained are provided for the CAL sample 972168 (full-sized worn outer dosimeter), fortified with 1 µg chlorothalonil.

µg/mL found= *(peak height - intercept)/slope*

µg/mL found= (8738.1 – (-3737))/2594387) = 0.0048 µg/mL

The amount of chlorothalonil (µg/dosimeter) found in the full sized worn outer dosimeter sample was calculated according to the following equation:

$$\mu g/dosimeter\ found = \frac{(\mu g/mL) \times (mL\ extr.\ solvent) \times (mL\ final\ volume) \times (df)}{(one\ dosimeter\ section) \times (mL\ aliquot)}$$

$$\mu g/dosmeter = \frac{0.0048\ \mu g/mL \times 2000\ mL \times 2\ mL \times 1}{1 \times 20\ mL} = 0.9617$$

Where,

µg/dosimeter = total µg of analyte present per section of sample analyzed

µg/mL = concentration of analyte derived from the standard curve based on peak response of the sample injected utilizing the linear regression equation of y = mx + b

mL extr. solv. = extraction solvent volume (2000 mL)

mL aliquot = volume of sample extract taken from initial extraction (20 mL)

one dosimeter section = amount of sample taken through the extraction process

mL final vol. = volume of final extract submitted to instrumentation (2 mL)

df = dilution of sample extract required to produce an analyte response within the standard curve range

The percent recovery was calculated as follows:

$$\%\ Recovery = \frac{\mu g/dosimeter\ found\ in\ fortified\ control}{\mu g/dosimeter\ added\ to\ fortified\ control} \times 100$$

$$\%\ Recovery = \frac{0.9617\ \mu g/dosimeter\ found}{1\ \mu g/dosimeter\ added} \times 100$$

$$\%\ Recovery = 96\%$$

All other matrices used the following equation to calculate the µg/sample:

$$\mu g/sample = \frac{(\mu g/mL) \times (mL\ final\ volume) \times (dilution\ factor)}{(sample)}$$

Where,

µg/sample	=	total µg of analyte present per sample analyzed
µg/mL	=	concentration of analyte derived from the standard curve based on peak response of the sample injected utilizing the linear regression equation of y = mx + b
sample	=	One sample taken through the extraction process
mL final volume	=	volume of final extract submitted to instrumentation (10 mL for hand washes and dislodging solutions, 3.5 mL for air sampling tube samples, and 100 mL for inner whole body dermal dosimeters and facial/neck wipes)
dilution factor	=	dilution of sample extract required to produce an analyte response bracketed by standards (hand washes and dislodging solutions were always a dilution factor of at least 10)

3.12 Changes to Protocol

1. Section 3.0: The matrix Aerosol® OT-75 Cauliflower Leaf Wash was added to the validation.

2. Section 3.0: The matrix Full-Sized Worn Outer Dosimeter (Shirts, Pants) was added to the validation.

3. Section 4.0: The length of the study period was extended.

4. Section 6.0: The lot number and the CAS number for chlorothalonil were listed incorrectly. They should be SDS-2787-2601and 1897-45-6, respectively.

5. Section 7.0: Initially the method to be validated was the Ricerca method # 6445-95-0086-CR-001. This method was later modified to include larger sample sizes for

outer dosimeters. The methods written and validated at CAL in this study were ARTF-001, ARTF-003, and ARTF-004.

6. Section 8.0: The new methods ARTF-001 (revised for larger sample sizes), ARTF-003, and ARTF-004 were not provided by the ARTF. Instead, they were written at Centre Analytical, based on the Ricerca method, at the request of the ARTF.

7. Addition to Section 8.0: Fortification solutions will be applied directly to samples via syringe before extraction.

8. Section 9.0: The sample identification was to be an ARTF sample number, however, there were no numbers associated with the samples, therefore, only CAL identification numbers were assigned.

9. Section 9.0: The Handwash Solution (Aerosol® OT-75) was not provided by the ARTF, it was prepared in-house at Centre Analytical Laboratories, Inc. and assigned a CAL identification number.

10. Section 13.0: The protocol amendment and deviation forms had not yet been finalized by the sponsor and therefore are not attached to the protocol.

11. Section 15.0: The Study Director was changed from Julie Burton to Sharon Webster.

All Protocol Amendments and Deviations are documented in Appendix A.

3.13 Archive Statement

The original signed report and all original raw data will be maintained at the ARTF archives, located at Quality Associates, Inc., 9017 Red Branch Road, Suite 102, Columbia, MD 21042. A copy of the report as well as the originals of all facility-specific raw data will also be maintained at Centre Analytical Laboratories, Inc.

4.0 RESULTS

Each matrix type was analyzed in multiple sets. Each set contained calibration standards, a solvent blank, an unspiked control matrix, and laboratory validation spikes. A back calculation of the standards to the corresponding calibration curve was performed for each analysis set. There were four analysis sets included in the accepted raw data which showed standards outside the range suggested in the ARTF guidelines (20% for the LOQ standard and 15% for other standards). These sets include the following: Inner dosimeters analyzed 2/20/97 which showed a 21% and 25% difference for the 0.005 µg/mL (LOQ) standards. The 3/5/97 analysis of OVS air tubes showed a 75% and 53% difference for the 0.001 µg/mL (LOQ) standards and a 16% difference in one of the 0.01 µg/mL standards. The 3/3/97 analysis of OVS air tubes showed a 106% and 91% difference for the 0.001 µg/mL (LOQ) standards and a 20% difference in one of the

0.01 µg/mL standards. The 6/13-14/97 analysis of full sized worn outer dosimeters showed a 32% difference for the 0.0025 µg/mL (LOQ) standard, a 15% difference in one of the 0.005 µg/mL standards, and a 15% difference in one of the 0.01 µg/mL standards. All of these sets showed acceptable R-square values (<0.990) and were therefore considered acceptable.

4.1 Solvent Blanks and Lab Controls

All solvent blanks as well as Laboratory controls analyzed in this study were free of quantifiable chlorothalonil residue.

4.2 Laboratory Validation Spikes

The results of for the laboratory validation spikes for each matrix and each fortification level were as follows:

	Mean Percent Recovery ± Standard Deviation			
Matrix	**LOQ**	**5x LOQ**	**25x LOQ**	**125x LOQ**
Full Sized Worn Outer Dosimeters (Shirts)	90.6 ± 5.34 (n=4)	-	-	-
Full Sized Worn Outer Dosimeters (Pants)	102 ± 1.30 (n=2)	-	-	-
Inner Whole Body Dermal Dosimeters	-	91.0 ± 3.73 (n=4)	105 ± 10.26 (n=4)	108 ± 8.25 (n=4)
Facial/Neck Wipes	81.8 ± 1.79 (n=3)	100 ± 7.18 (n=4)	109 ± 6.33 (n=4)	110 ± 5.89 (n=4)
Air Sampling Tubes	-	103 ± 2.61 (n=8)	97.9 ± 2.45 (n=8)	93.2 ± 7.48 (n=8)
Handwash Solution	-	97.0 ± 1.56 (n=4)	102 ± 6.02 (n=4)	93.0 ± 13.15 (n=4)
Foliar Dislodging Solution	-	107 ± 3.03 (n=2)	105 (n=1)	105 ± 0.07 (n=2)

For each matrix, the mean recovery (± standard deviation) fell within the EPA's requirement of 70-120% (standard deviation ± 20%), thus validating the results obtained for the samples.

4.3 Chromatograms, Spreadsheets, and Standard Curves

Representative chromatograms, spreadsheets, and standard curves are included in Attachments 1-6. Chromatograms are provided for calibration standards, a solvent blank, a laboratory control, and laboratory fortification samples, for each matrix. In addition, a standard curve of the calibration standards and a spreadsheet for each matrix is included.

Tables

TABLE 1. Determination of Chlorothalonil in Full Sized Worn Outer Dosimeters

CAL ID#	µg/Dosimeter Found	µg Compound Added	Percent Recovery	Mean	Standard Deviation	Relative Standard Deviation
Solvent Blank	0	na	na	na	na	na
Solvent Blank	0	na	na	na	na	na
970217 Blk	0	na	na	na	na	na
972168 S-F	0.96	1.0	96.2%	90.6%	5.34%	5.90%
972168 S-B	0.86	1.0	85.7%			
972168 S-U-S	0.86	1.0	86.3%			
972168 S-L-S	0.94	1.0	94.1%			
972169 P-T	1.03	1.0	103%	102%	1.30%	1.27%
972169 P-B	1.01	1.0	101%			

NOTE: The Mean and Standard Deviation was calculated using NON-rounded percent recoveries.

TABLE 2. Determination of Chlorothalonil in Inner Whole Body Dermal Dosimeters

CAL ID#	µg/Dosimeter Found	µg Compound Added	Percent Recovery	Mean	Standard Deviation	Relative Standard Deviation
Solvent Blank	0	na	na	na	na	na
Solvent Blank	0	na	na	na	na	na
970205 Blk	0	na	na	na	na	na
Solvent Blank	0	na	na	na	na	na
Solvent Blank	0	na	na	na	na	na
970205 Blk	0	na	na	na	na	na
970205 Spk A	4.41	5	88.1%			
970205 Spk B	4.40	5	88.0%	91.0%	3.73%	4.10%
970205 Spk A	4.60	5	92.0%			
970205 Spk B	4.79	5	95.8%			
970205 Spk C	23.4	25	93.6%			
970205 Spk D	24.9	25	99.4%	105%	10.3%	9.77%
970205 Spk C	27.9	25	112%			
970205 Spk D	28.9	25	116%			
970205 Spk E	126	125	101%			
970205 Spk F	127	125	102%	108%	8.25%	7.65%
970205 Spk E	139	125	111%			
970205 Spk F	148	125	118%			

NOTE: The Mean and Standard Deviation were calculated using NON-rounded percent recoveries.

TABLE 3. Determination of Chlorothalonil in Facial/Neck Wipes

CAL ID#	µg/Dosimeter Found	µg Compound Added	Percent Recovery	Mean	Standard Deviation	Relative Standard Deviation
Solvent Blank	0.00	na	na	na	na	na
Solvent Blank	0.00	na	na	na	na	na
970170 Blk	0.00	na	na	na	na	na
Solvent Blank	0.00	na	na	na	na	na
Solvent Blank	0.00	na	na	na	na	na
970170 Blk	0.00	na	na	na	na	na
Solvent Blank	0.00	na	na	na	na	na
Solvent Blank	0.00	na	na	na	na	na
970185 Blk	0.00	na	na	na	na	na
970193 Spk A	0.802	1	80.2%			
970194 Spk B	0.837	1	83.7%	82%	1.79%	2.19%
970195 Spk C	0.815	1	81.5%			
970178 Spk A	4.60	5	92.0%			
970179 Spk B	4.81	5	96.2%	100%	7.18%	7.17%
970171 Spk A	5.29	5	106%			
970172 Spk B	5.32	5	106%			
970180 Spk C	25.6	25	102%			
970181 Spk D	26.3	25	105%	109%	6.33%	5.80%
970173 Spk C	28.4	25	114%			
970174 Spk D	28.8	25	115%			
970182 Spk E	129	125	103%			
970183 Spk F	133	125	106%	110%	5.89%	5.37%
970175 Spk E	144	125	115%			
970176 Spk F	143	125	114%			

NOTE: The Mean and Standard Deviation were calculated using NON-rounded percent recoveries.

TABLE 4. Determination of Chlorothalonil in Air Sampling Tubes

CAL ID#	µg/Dosimeter Found	µg Compound Added	Percent Recovery	Mean	Standard Deviation	Relative Standard Deviation
Solvent Blank	0	na	na	na	na	na
Solvent Blank	0	na	na	na	na	na
Solvent Blank	0	na	na	na	na	na
970986 Blank, Front	0	na	na	na	na	na
970986 Blank, Rear	0	na	na	na	na	na
970994 Spk A Front	0.0519	0.05	104%			
970995 Spk B Front	0.0512	0.05	102%			
970994 Spk A Rear	0.0520	0.05	104%			
970995 Spk B Rear	0.0541	0.05	108%	103%	2.61%	2.52%
970987 Spk A Front	0.0506	0.05	101%			
970988 Spk B Front	0.0507	0.05	101%			
970987 Spk A Rear	0.0504	0.05	101%			
970988 Spk B Rear	0.0530	0.05	106%			
970996 Spk C Front	0.246	0.25	98.5%			
970997 Spk D Front	0.236	0.25	94.5%			
970996 Spk C Rear	0.244	0.25	97.7%			
970997 Spk D Rear	0.244	0.25	97.5%	97.9%	2.45%	2.50%
970989 Spk C Front	0.248	0.25	99.4%			
970990 Spk D Front	0.242	0.25	96.6%			
970989 Spk C Rear	0.257	0.25	103%			
970990 Spk D Rear	0.240	0.25	96.1%			
970998 Spk E Front	1.03	1.25	82.2%			
970999 Spk F Front	1.06	1.25	84.7%			
970998 Spk E Rear	1.15	1.25	91.8%			
970999 Spk F Rear	1.18	1.25	94.0%	93.2%	7.48%	8.02%
970991 Spk E Front	1.30	1.25	104%			
970992 Spk F Front	1.16	1.25	93.1%			
970991 Spk E Rear	1.17	1.25	93.5%			
970992 Spk F Rear	1.28	1.25	102%			

NOTE: The Mean and Standard Deviation were calculated using NON-rounded percent recoveries.

TABLE 5. Determination of Chlorothalonil in Handwash Solutions

CAL ID#	µg/Dosimeter Found	µg Compound Added	Percent Recovery	Mean	Standard Deviation	Relative Standard Deviation
Solvent Blank	0.00	na	na	na	na	na
Solvent Blank	0.00	na	na	na	na	na
971362 Blk	0.00	na	na	na	na	na
Solvent Blank	0.00	na	na	na	na	na
Solvent Blank	0.00	na	na	na	na	na
971362 Blk	0.00	na	na	na	na	na
971362 Spk A	4.89	5	97.8%			
971362 Spk B	4.88	5	97.7%	97.0%	1.56%	1.61%
971362 Spk A	4.74	5	94.7%			
971362 Spk B	4.90	5	98.0%			
971362 Spk C	24.3	25	97.2%			
971362 Spk D	27.2	25	109%	102%	6.02%	5.92%
971362 Spk C	26.1	25	105%			
971362 Spk D	24.0	25	96.1%			
971362 Spk E	123	125	98.4%			
971362 Spk F	136	125	109%	93.0%	13.1%	14.1%
971362 Spk E	100	125	79.6%			
971362 Spk F	106	125	85.1%			

NOTE: The Mean and Standard Deviation were calculated using NON-rounded percent recoveries.

TABLE 6. Determination of Chlorothalonil in Dislodging Solution

CAL ID#	µg/Sample Found	µg Compound Added	Percent Recovery	Mean	Standard Deviation	Relative Standard Deviation
Solvent Blank	0	na	na	na	na	na
Solvent Blank	0	na	na	na	na	na
971362 OT-75 Blk*	0	na	na	na	na	na
971362 Blk (w/leaves)	0	na	na	na	na	na
971362 Spk A	5.45	5.0	109%	107%	3.03%	2.83%
971362 Spk B	5.24	5.0	105%			
971362 Spk C	26.3	25.0	105%	na	na	na
971362 Spk D	131	125.0	104%	105%	0.0734%	0.0702%
971362 Spk E	131	125.0	105%			

* (w/o leaves)

NOTE: The Mean and Standard Deviation was calculated using NON-rounded percent recoveries.

Attachments

Attachment 1

Representative Chromatograms, Standard Curve, and Spreadsheet
Full Sized Worn Outer Dosimeters (Shirts, Pants)

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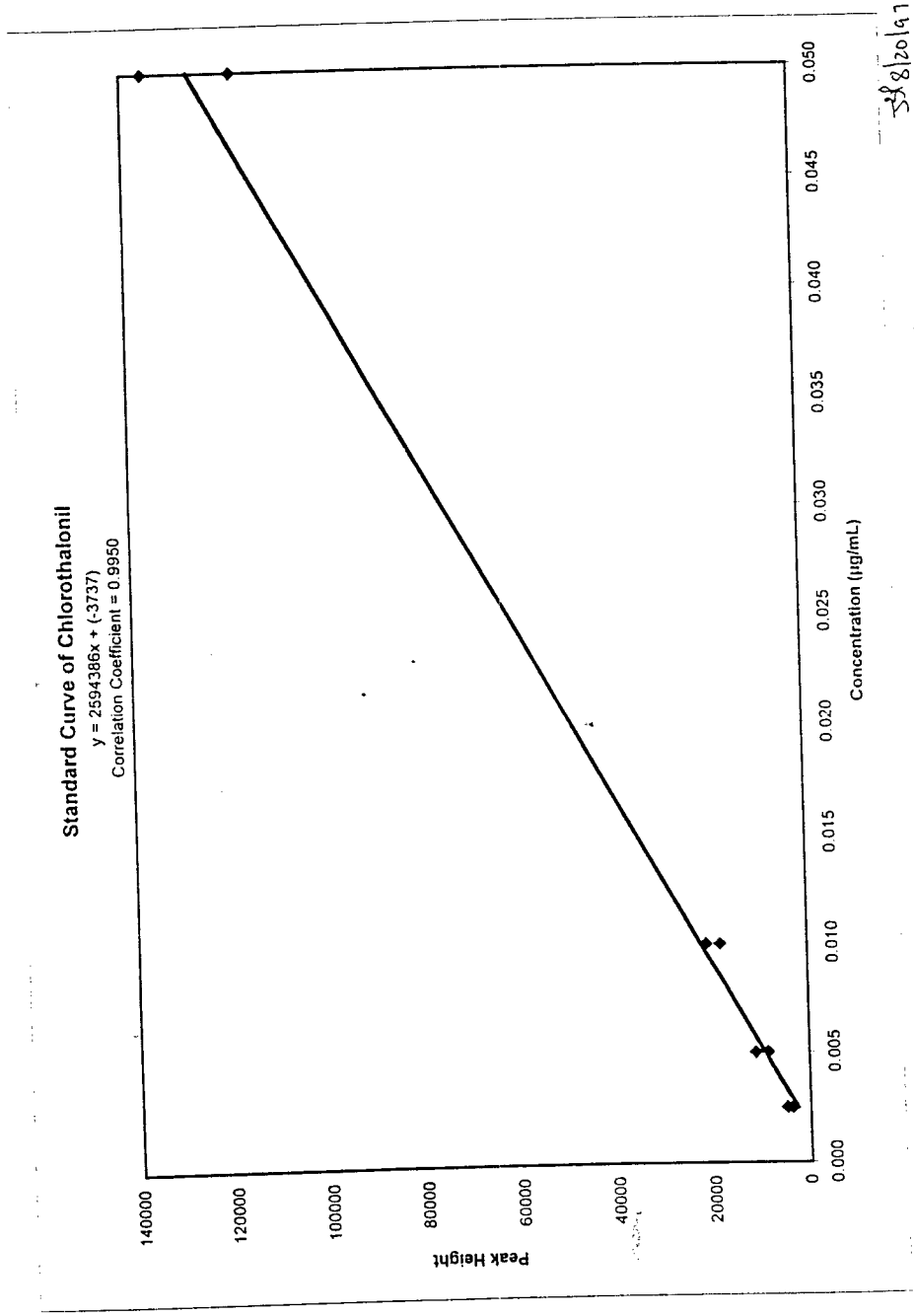
Figure 1. Linear Regression Analysis

Analysis Date: 6/13-14/97



3/8/20/97
CAL Study No. 017-01

Extraction Date: 6/05/97

ARTF Study No. ARF004

Figure 2: Ethyl Acetate Blank

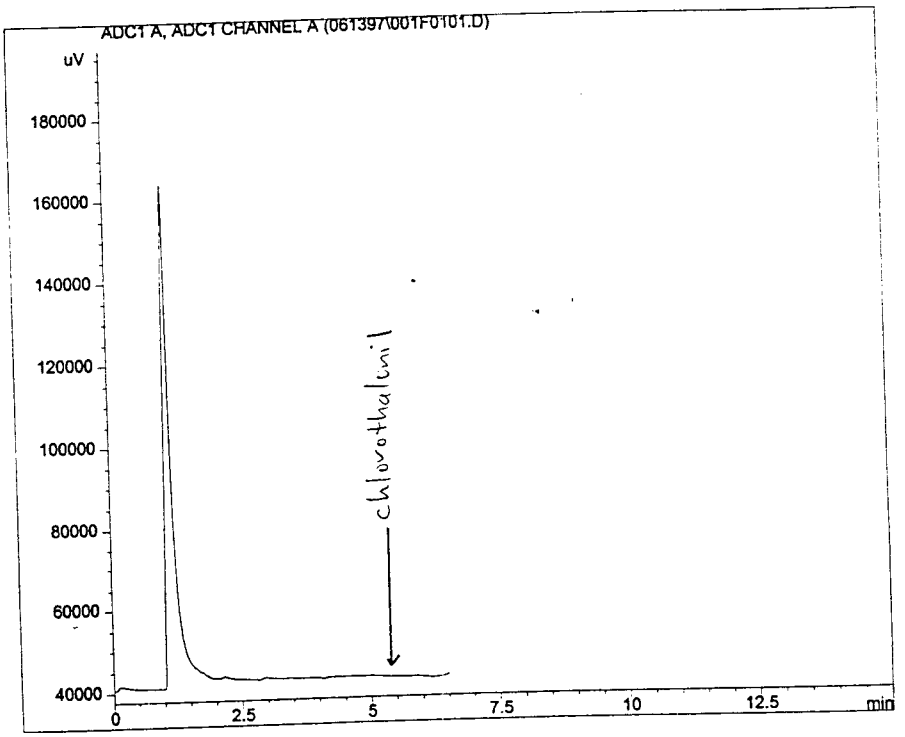
Analysis of Chlorothalonil

Run No.: 1

Sample No: NA
Sample Info: Solvent Blank

Injected on: 6/13/97 7:35:34 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01
ARTF Study Number: ARF004

Operator: Julie B. Petit

Figure 3: Calibration Standard 0.0025 µg/mL

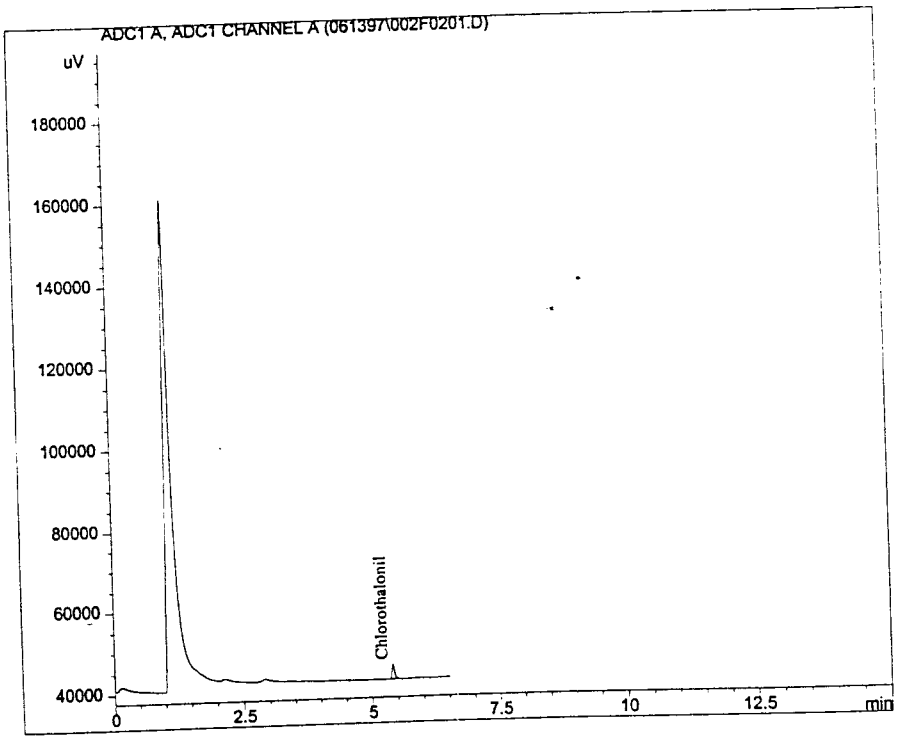
Analysis of Chlorothalonil

Run No.: 2

Sample No: NA
Sample Info: 0.0025 µg/mL Standard, ~~C060297-1~~ C043097-1 RE 8-21-97

Injected on: 6/13/97 7:53:09 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.401	Chlorothalonil	3737.1	12910.548

CAL Study Number: 017-01
ARTF Study Number: ARF004

Operator: Julie B. Petit

Figure 4: Calibration Standard 0.005 µg/mL

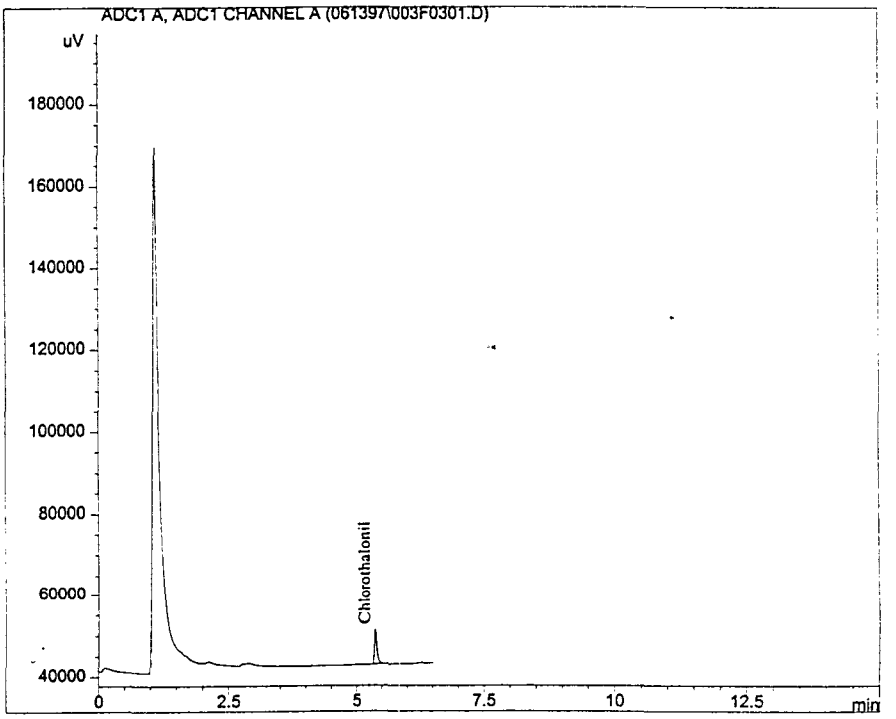
Analysis of Chlorothalonil

Run No.: 3

Sample No: NA
Sample Info: 0.005 µg/mL Standard, ~~C060297-6~~ C021097-4 8-21-97

Injected on: 6/13/97 8:10:47 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.367	Chlorothalonil	8603.0	31119.275

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 5: Calibration Standard 0.01 µg/mL

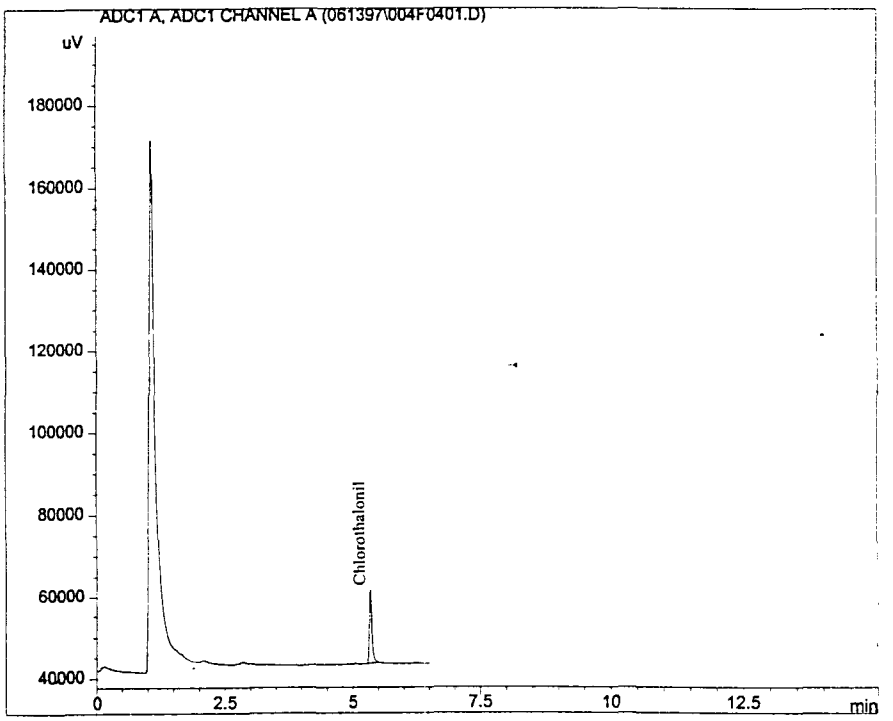
Analysis of Chlorothalonil

Run No.: 4

Sample No: NA
Sample Info: 0.01 µg/mL Standard, ~~C060297-5~~ C021097-3 8-21-97

Injected on: 6/13/97 8:28:22 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.339	Chlorothalonil	18187.8	67116.758

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 6: Calibration Standard 0.05 µg/mL

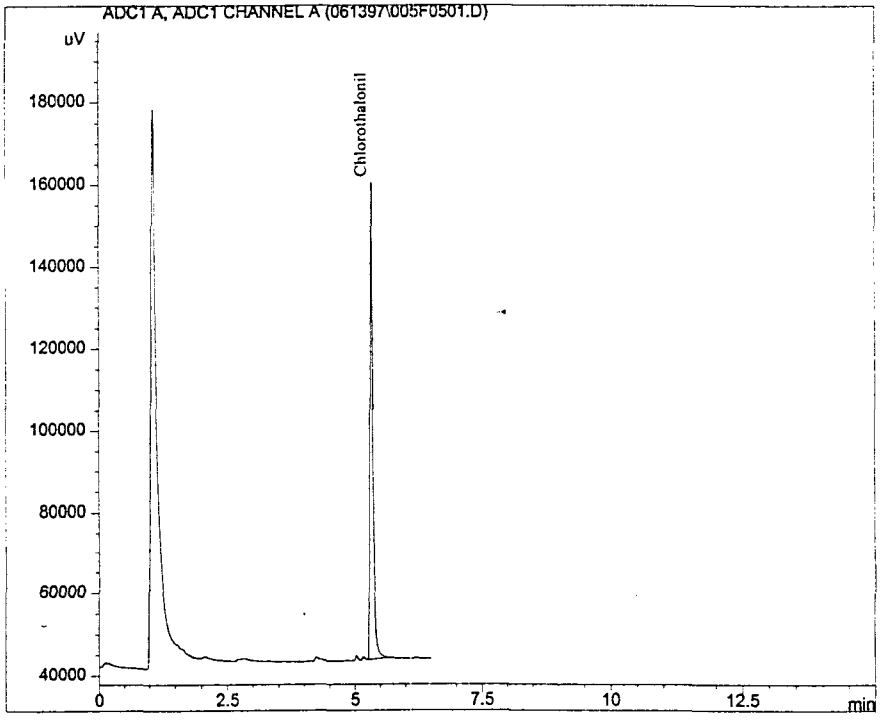
Analysis of Chlorothalonil

Run No.: 5

Sample No: NA
Sample Info: 0.05 µg/mL Standard, ~~C060297-4~~ C021097-2 ~~C047097-1~~ 8-21-97

Injected on: 6/13/97 8:46:00 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.323	Chlorothalonil	116985.9	471808.844

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 7. Full Sized Worn Outer Dosimeters Control

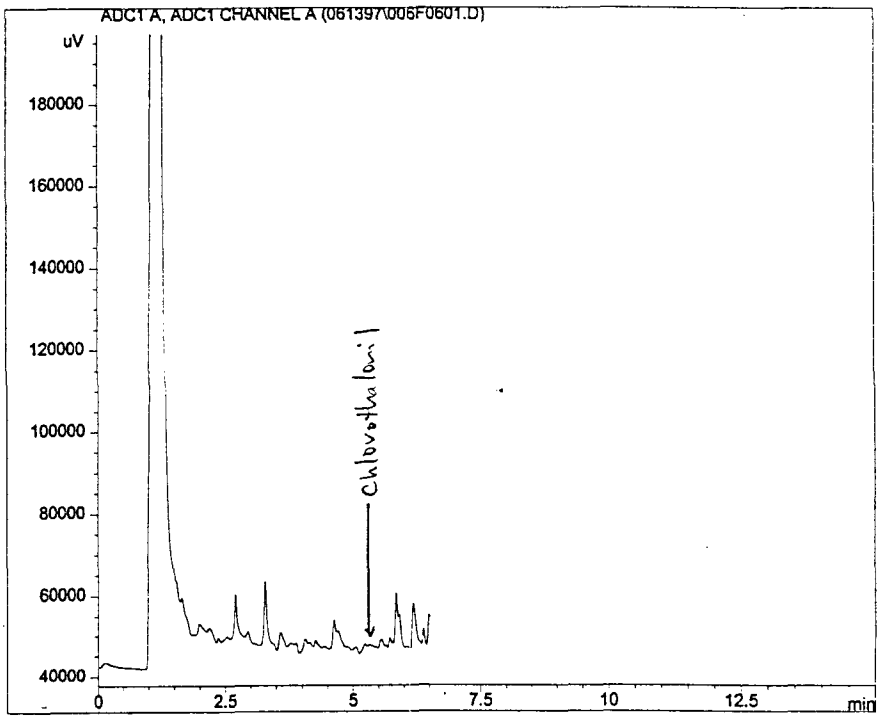
Analysis of Chlorothalonil

Run No.: 6

Sample No: CAL 970217 Blk
Sample Info: Control, Final Volume = 2 mL

Injected on: 6/13/97 9:03:38 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 8. Full Sized Worn Outer Dosimeters (Shirt, Front) Fortified with 1 µg Chlorothalonil

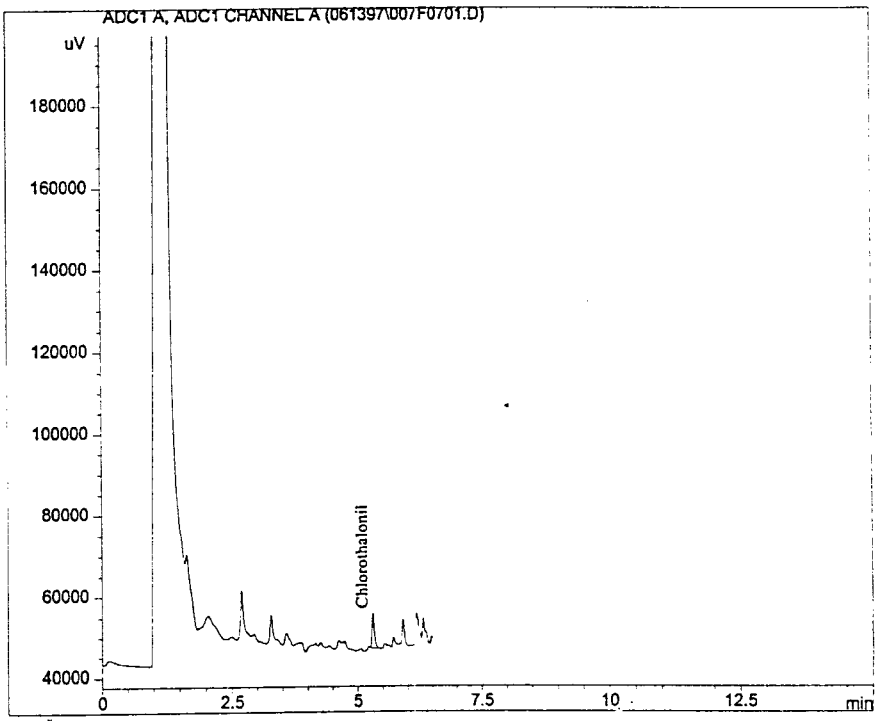
Analysis of Chlorothalonil

Run No.: 7

Sample No: CAL 972168 S-F
Sample Info: Fortified at 1 µg, Final Volume = 2 mL

Injected on: 6/13/97 9:21:16 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.307	Chlorothalonil	8738.1	30089.127

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Analytical Data and Recoveries for CAL Study # 017-01: Determination of Chlorothalonil in Full Sized Worn Outer Dosimeters

Extraction Date: 6/5/97 **Analysis Date:** 6/13-14/97 **Matrix: Sectioned Shirts and Pants**

SW 3-17-99

STANDARD CURVE:

Conc. (µg/mL)	Peak Height
0.0025	3737.1
0.005	8603.0
0.01	18187.8
0.05	116985.9
0.0025	4832.1
0.005	11163.8
0.01	21116.9
0.05	135716.2

Linear Calibration Equation: y = mx+b
m= 2594387
b= -3737
Correlation Coefficient = 0.9950

DATA:

CAL ID#	Client ID	Compound Found	Peak Height	µg/mL Compound Found	Extraction Volume (mL)	Aliquot Volume (mL)	Final Volume (mL)	Dilution Factor	µg/Dosimeter Found	µg Compound Added	Percent Recovery
Solvent Blank	NA	Chlorothalonil	0	0.0000	2000	20	na	1	0.0	na	na
Solvent Blank	NA	Chlorothalonil	0	0.0000	2000	20	na	1	0.0	na	na
970217 Blk	NA	Chlorothalonil	0	0.0000	2000	20	2	1	0.0	na	na
972168 S-F	NA	Chlorothalonil	8738.1	0.0048	2000	20	2	1	0.9617	1	96.2%
972168 S-B	NA	Chlorothalonil	7376.7	0.0043	2000	20	2	1	0.8568	1	85.7%
972168 S-U-S	NA	Chlorothalonil	7458.3	0.0043	2000	20	2	1	0.8631	1	86.3%
972168 S-L-S	NA	Chlorothalonil	8462.9	0.0047	2000	20	2	1	0.9405	1	94.1%
972169 P-T	NA	Chlorothalonil	9600.7	0.0051	2000	20	2	1	1.0282	1	103%
972169 P-B	NA	Chlorothalonil	9362.6	0.0050	2000	20	2	1	1.0099	1	101%

Figure 9: Spreadsheet, Full Sized Worn Outer Dosimeters

Attachment 2

Representative Chromatograms, Standard Curve, and Spreadsheet
Inner Whole Body Dermal Dosimeters

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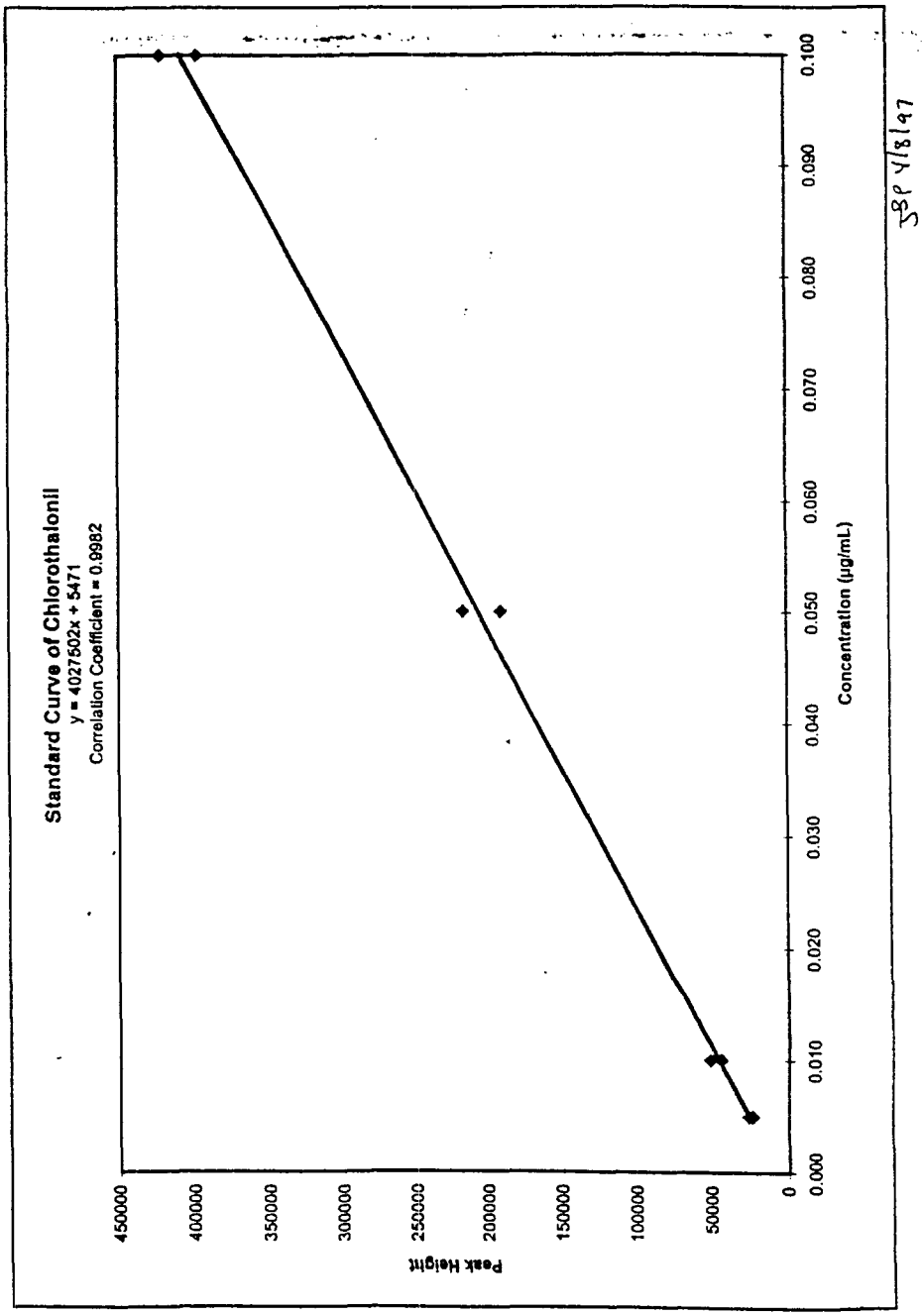
Figure 11: Spreadsheet, Inner Whole Body Dermal Dosimeter 54

Analysis Date: 2/21/97

CAL Study No. 017-01

Figure 1: Linear Regression Analysis



JBP 4/8/97

Extraction Date: 2/21/97

ARTF Study No. ARF004

Figure 2: Ethyl Acetate Blank

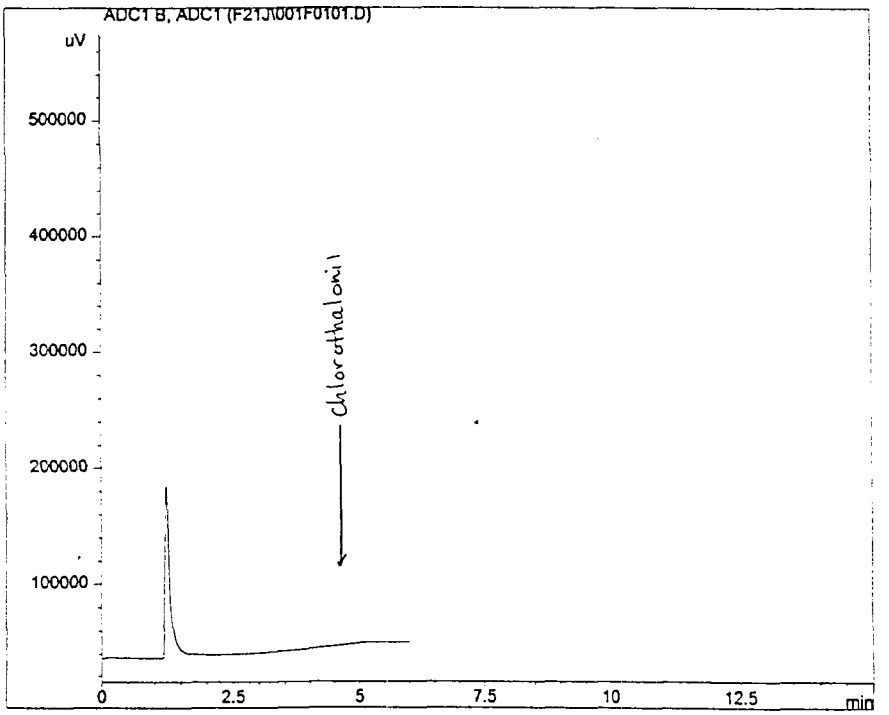
Analysis of Chlorothalonil

Run No.: 1

Sample No: NA
Sample Info: Solvent Blank

Injected on: 2/21/97 10:04:05 AM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 3: Calibration Standard 0.1 µg/mL

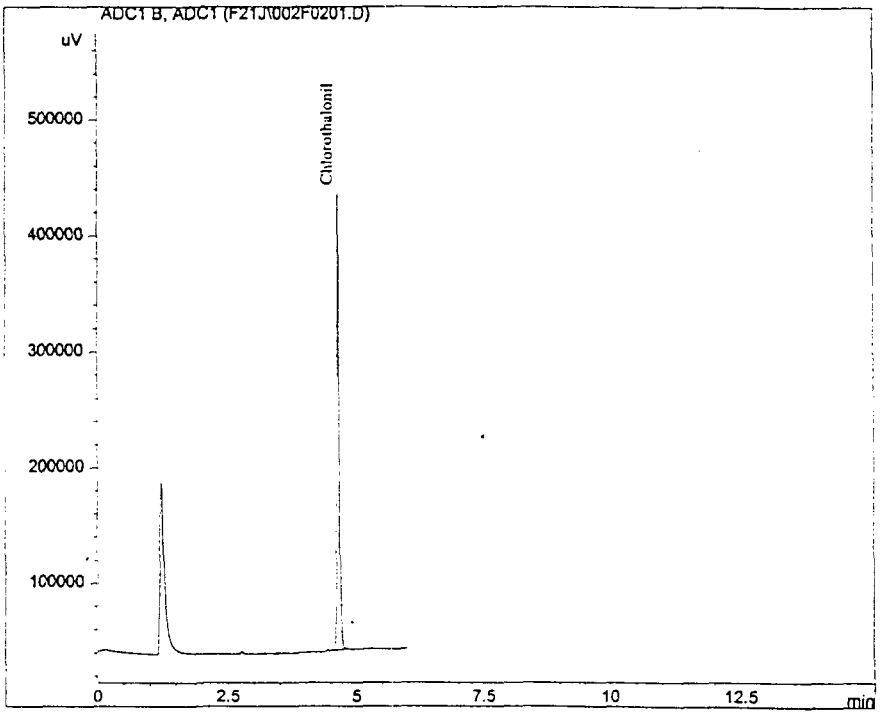
Analysis of Chlorothalonil

Run No.: 2

Sample No: NA
Sample Info: 0.1 µg/mL Standard, C021097-1

Injected on: 2/21/97 10:16:21 AM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.634	Chlorothalonil	397178.5	1.255e+006

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 4: Calibration Standard 0.05 µg/mL

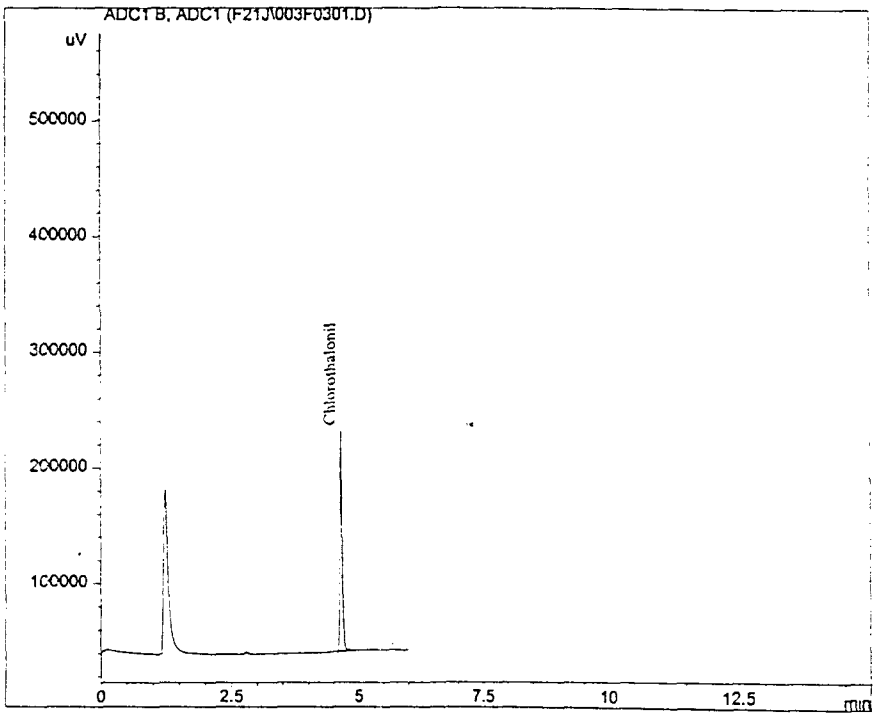
Analysis of Chlorothalonil

Run No.: 3

Sample No: NA
Sample Info: 0.05 µg/mL Standard, C021097-2

Injected on: 2/21/97 10:28:33 AM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.636	Chlorothalonil	191105.3	606241.500

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 5: Calibration Standard 0.01 µg/mL

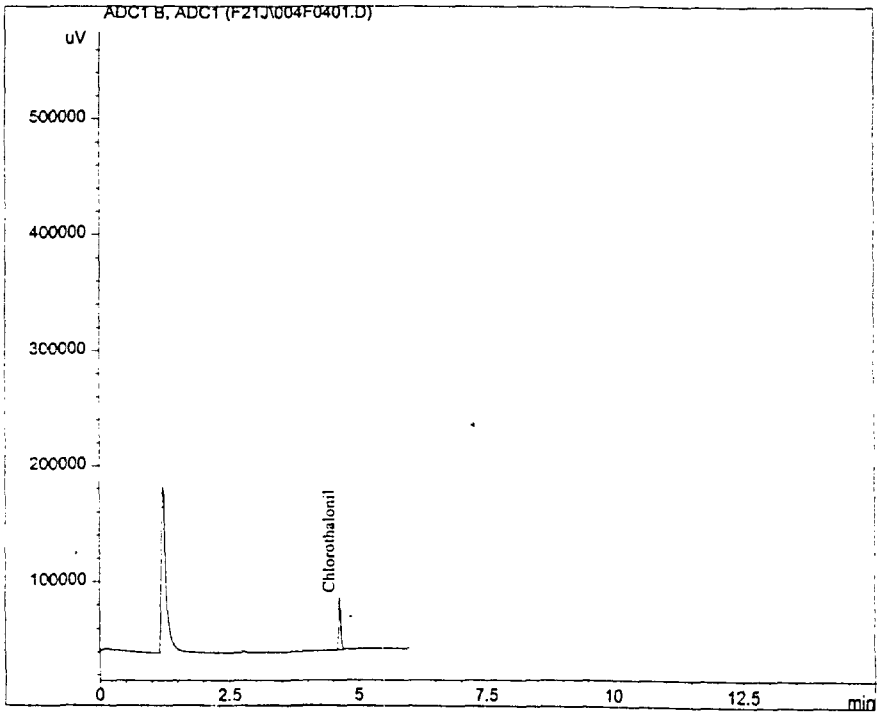
Analysis of Chlorothalonil

Run No.: 4

Sample No: NA
Sample Info: 0.01 µg/mL Standard, C021097-3

Injected on: 2/21/97 10:40:46 AM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.630	Chlorothalonil	44375.6	131103.172

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 6: Calibration Standard 0.005 µg/mL

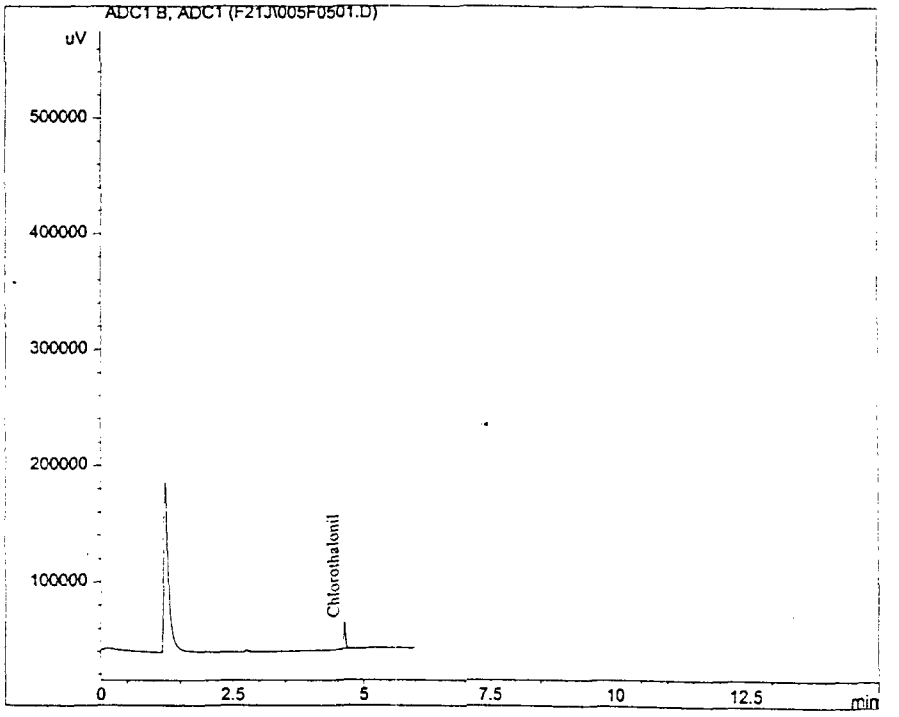
Analysis of Chlorothalonil

Run No.: 5

Sample No: NA
Sample Info: 0.005 µg/mL Standard, C021097-4

Injected on: 2/21/97 10:53:02 AM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.631	Chlorothalonil	23707.6	65867.109

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 7: Inner Whole Body Dermal Dosimeter Control

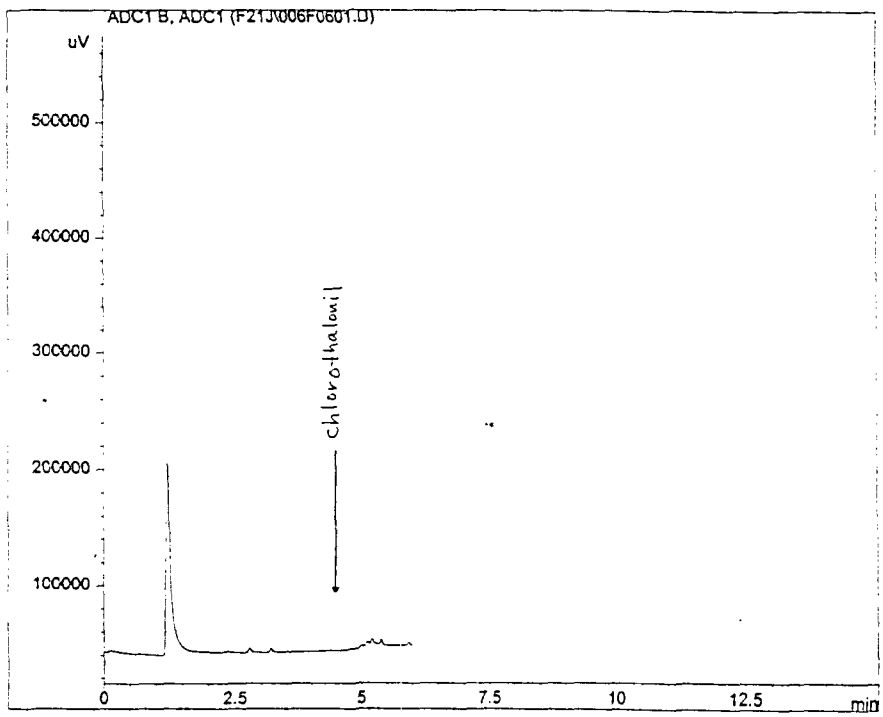
Analysis of Chlorothalonil

Run No.: 6

Sample No: CAL 970205 Blk
Sample Info: Control, Final Volume = 100 mL

Injected on: 2/21/97 11:05:17 AM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 8: Inner Whole Body Dermal Dosimeter Fortified with 5 µg Chlorothalonil

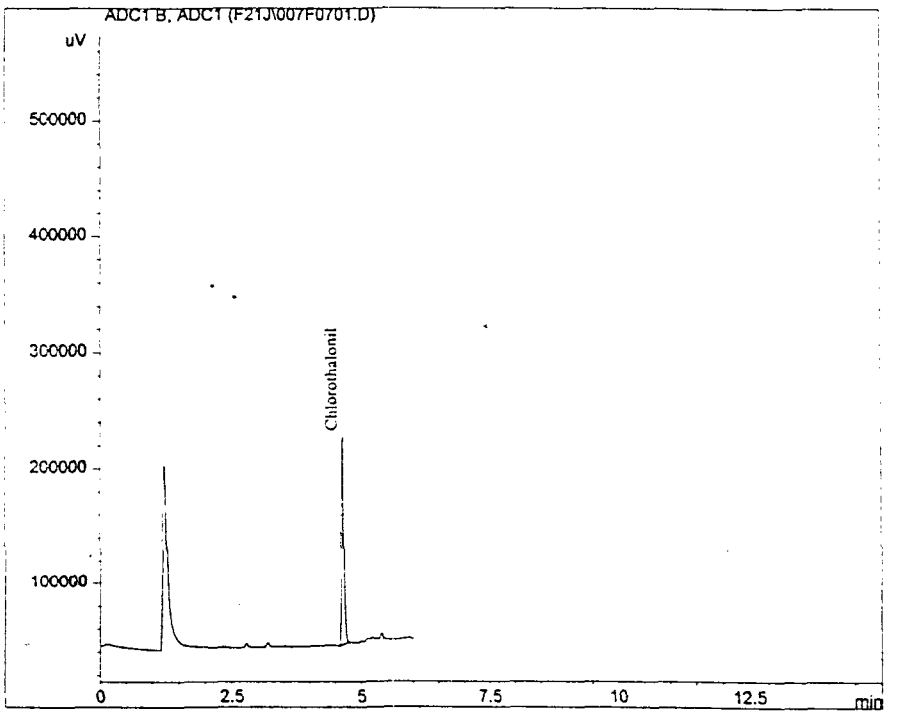
Analysis of Chlorothalonil

Run No.: 7

Sample No: CAL 970205 Spk A
Sample Info: Control Fortified at 5 µg, Final Volume = 100 mL

Injected on: 2/21/97 11:17:28 AM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.632	Chlorothalonil	182953.8	576437.375

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 9: Inner Whole Body Dermal Dosimeter Fortified with 25 µg Chlorothalonil

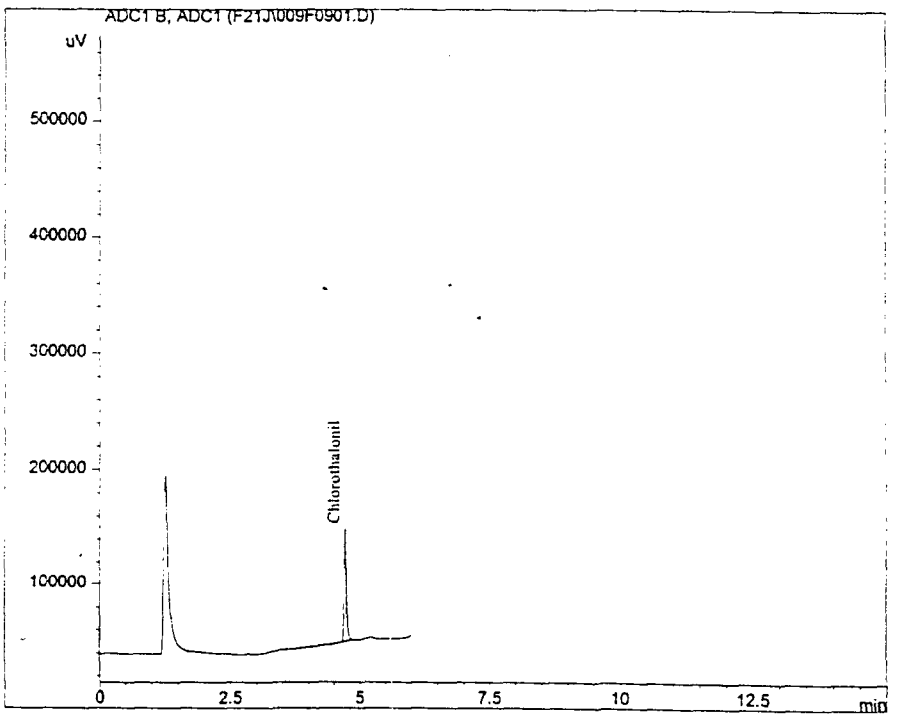
Analysis of Chlorothalonil

Run No.: 9

Sample No: CAL 970205 Spk C
Sample Info: Control Fortified at 25 µg, Final Volume = 100 mL
Dilution Factor = 10

Injected on: 2/21/97 12:18:14 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.717	Chlorothalonil	99754.1	324630.375

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 10: Inner Whole Body Dermal Dosimeter Fortified with 125 µg Chlorothalonil

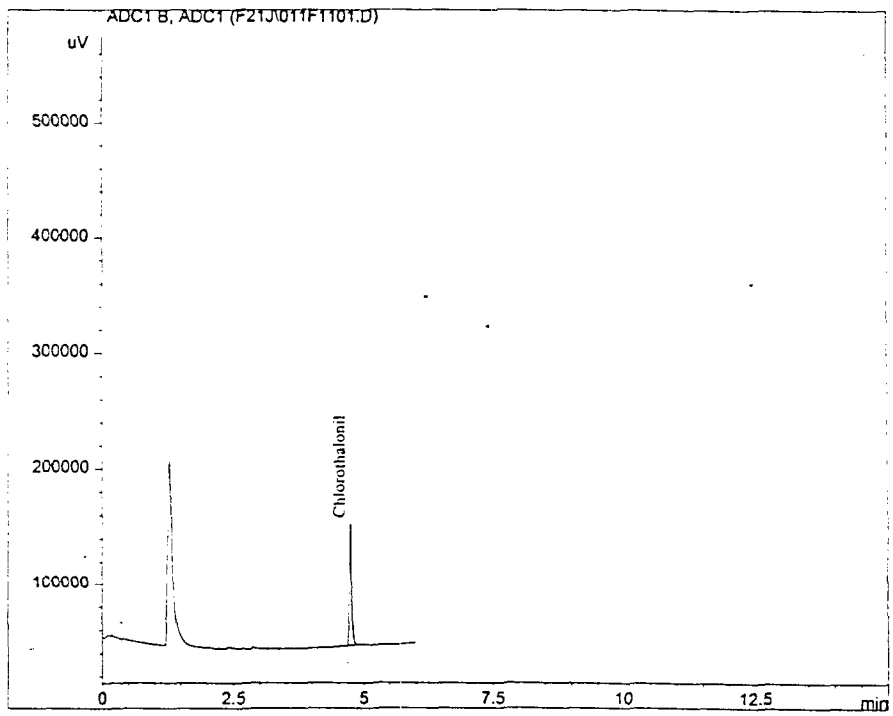
Analysis of Chlorothalonil

Run No.: 11

Sample No: CAL 970205 Spk E
Sample Info: Control Fortified at 125 µg, Final Volume = 100 mL
Dilution Factor = 50

Injected on: 2/21/97 12:42:37 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.739	Chlorothalonil	106870.0	330734.062

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 11: Spreadsheet, Inner Whole Body Dermal Dosimeter

Analytical Data and Recoveries for CAL Study # 017-01: Determination of Chlorothalonil in Inner Whole Body Dermal Dosimeters

Extraction Date: 2/21/97 **Analysis Date:** 2/21/97 **Matrix:** Inner Dosimeter

STANDARD CURVE:

Conc. (µg/mL)	Peak Height
0.10	397179
0.05	191105
0.01	44376
0.005	23708
0.10	421535
0.05	217301
0.01	51533
0.005	26107

Linear Calibration Equation: y = mx+b
m= 4027502
b= 5471
Correlation Coefficient = 0.9982

DATA:

CAL ID#	Client ID	Compound Found	Peak Height	Peak Height Corrected	µg/mL Compound Found	Final Volume (mL)	Dilution Factor	µg/Dosimeter Found	µg Compound Added	Percent Recovery
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
970205 Blk	NA	Chlorothalonil	0	0	0.0000	100	1	0.0	na	na
970205 Spk A	NA	Chlorothalonil	182954	182954	0.0441	100	1	4.41	5	88.1%
970205 Spk B	NA	Chlorothalonil	182582	182582	0.0440	100	1	4.40	5	88.0%
970205 Spk C	NA	Chlorothalonil	99754	99754	0.0234	100	10	23.4	25	93.6%
970205 Spk D	NA	Chlorothalonil	105593	105593	0.0249	100	10	24.9	25	99.4%
970205 Spk E	NA	Chlorothalonil	106870	106870	0.0252	100	50	126	125	101%
970205 Spk F	NA	Chlorothalonil	107945	107945	0.0254	100	50	127	125	102%

DCD 5-16-97

Attachment 3

Representative Chromatograms, Standard Curve, and Spreadsheet
Facial/Neck Wipes

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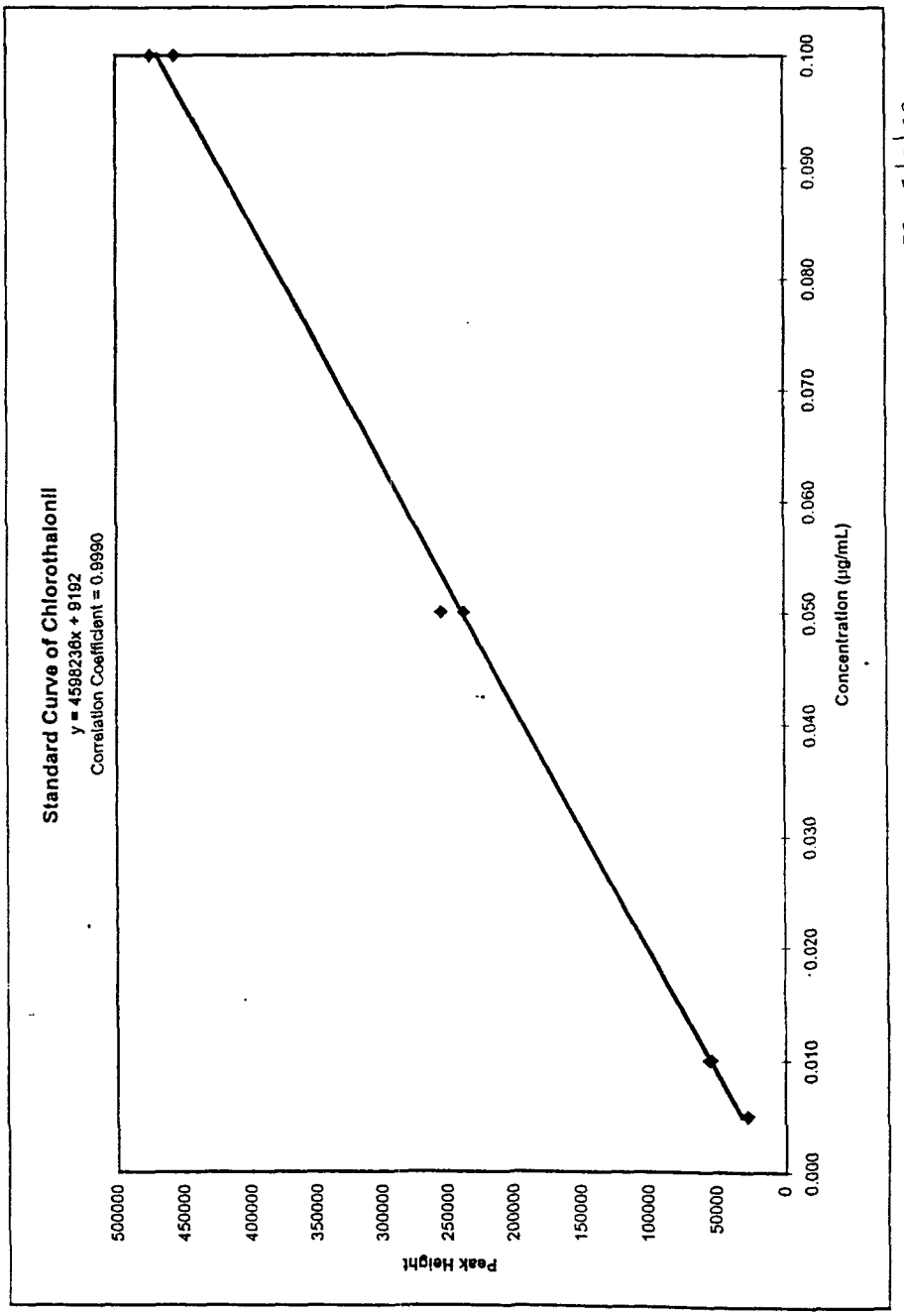
Figure 1: Linear Regression Analysis

Analysis Date: 2/24/97



BP 3/7/97

CAL Study No. 017-01

Extraction Date: 2/24/97

ARTF Study No. ARF004

Figure 2: Ethyl Acetate Blank

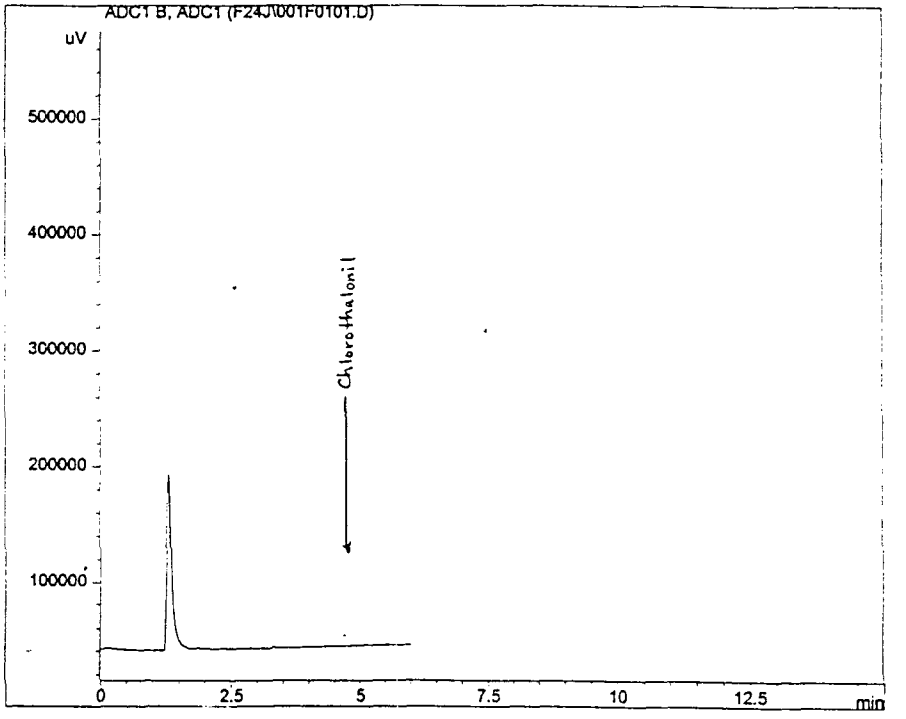
Analysis of Chlorothalonil

Run No.: 1

Sample No: NA
Sample Info: Solvent Blank

Injected on: 2/24/97 6:05:49 PM

Is chromatogram used? Yes/No: (✓), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 3: Calibration Standard 0.1 µg/mL

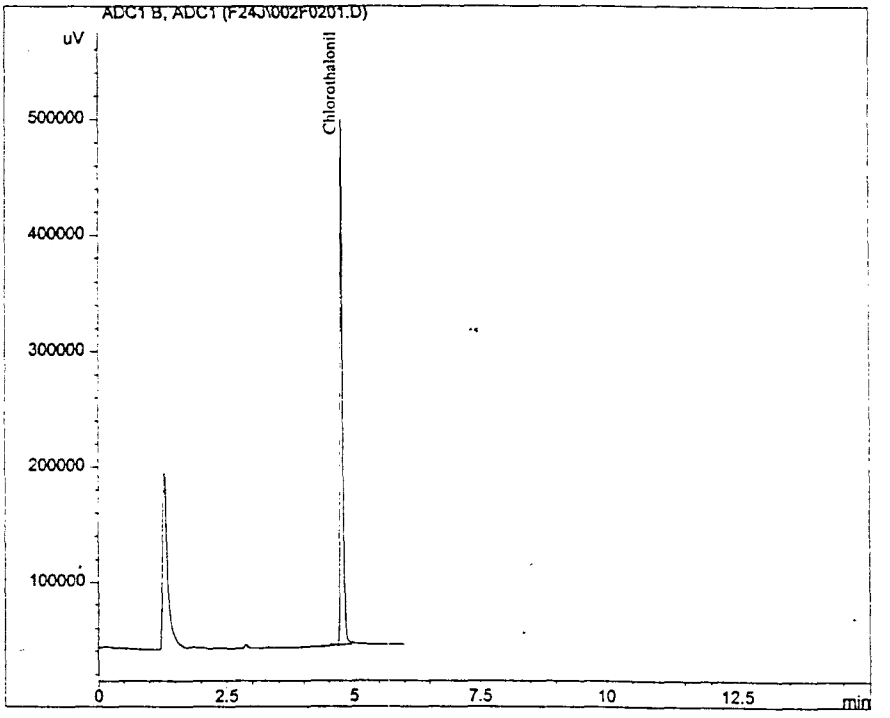
Analysis of Chlorothalonil

Run No.: 2

Sample No: NA
Sample Info: 0.1 µg/mL Standard, C021097-1

Injected on: 2/24/97 6:18:04 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.745	Chlorothalonil	456659.4	1.597e+006

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 4: Calibration Standard 0.05 µg/mL

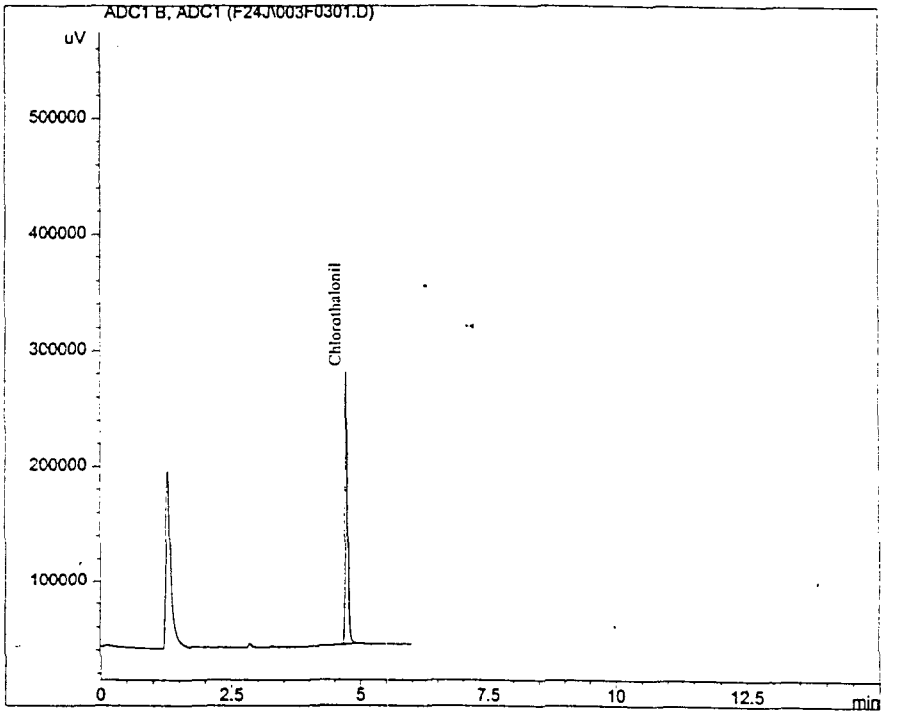
Analysis of Chlorothalonil

Run No.: 3

Sample No: NA
Sample Info: 0.05 µg/mL Standard, C021097-2

Injected on: 2/24/97 6:30:17 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.732	Chlorothalonil	237684.6	810411.750

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 5: Calibration Standard 0.01 µg/mL

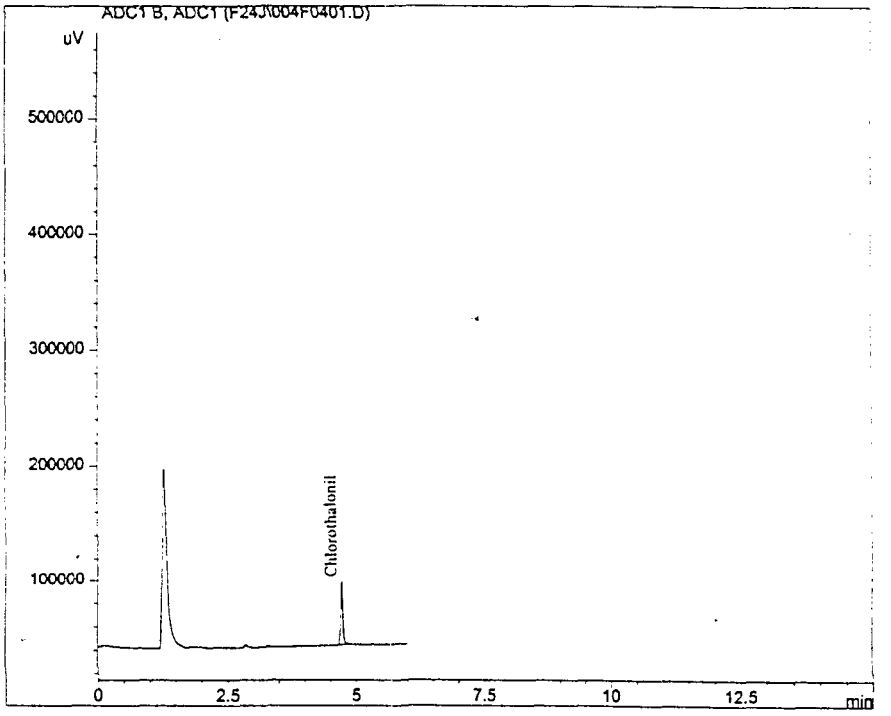
Analysis of Chlorothalonil

Run No.: 4

Sample No: NA
Sample Info: 0.01 µg/mL Standard, C021097-3

Injected on: 2/24/97 6:42:30 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.725	Chlorothalonil	54841.6	166773.406

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 6: Calibration Standard 0.005 µg/mL

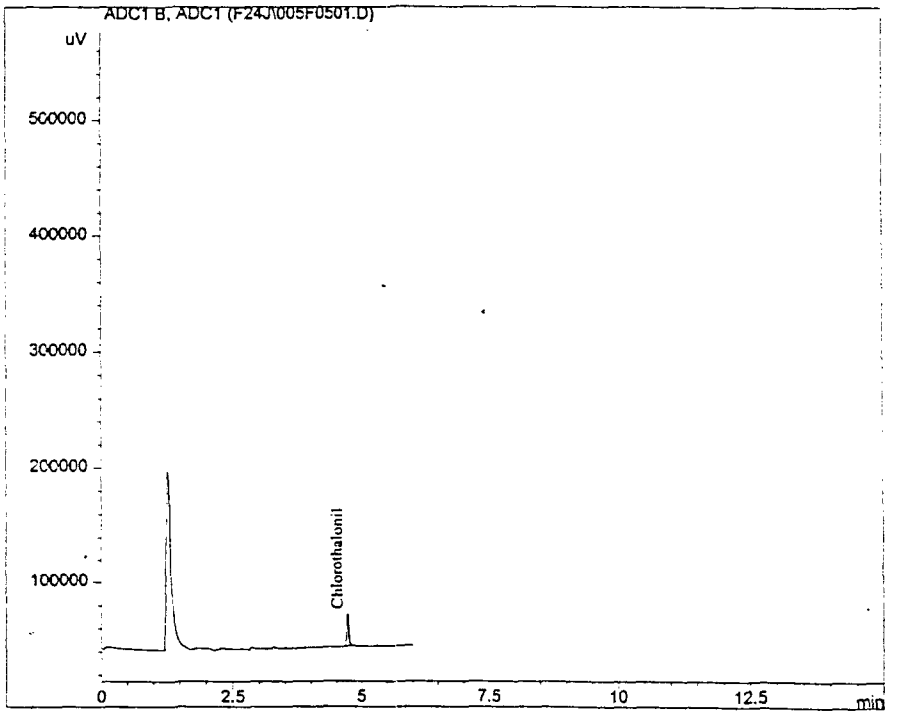
Analysis of Chlorothalonil

Run No.: 5

Sample No: NA
Sample Info: 0.005 µg/mL Standard, C021097-4

Injected on: 2/24/97 6:54:44 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.722	Chlorothalonil	27924.1	81804.227

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 7: Facial/Neck Wipes Control

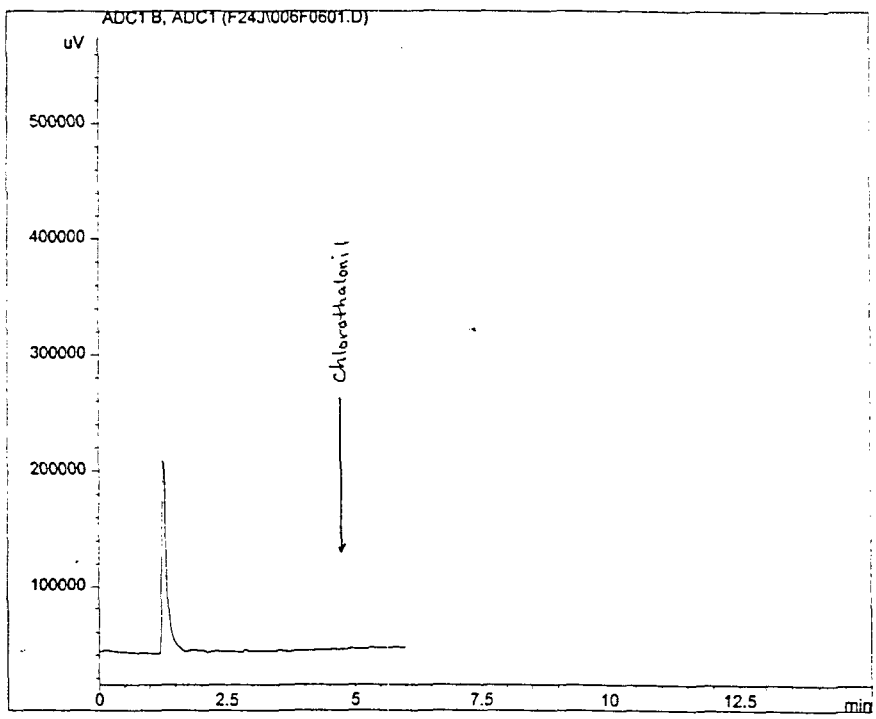
Analysis of Chlorothalonil

Run No.: 6

Sample No: CAL 970170 Blk
Sample Info: Control, Final Volume = 100 mL

Injected on: 2/24/97 7:06:59 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 8: Facial/Neck Wipes Fortified with 5 µg Chlorothalonil

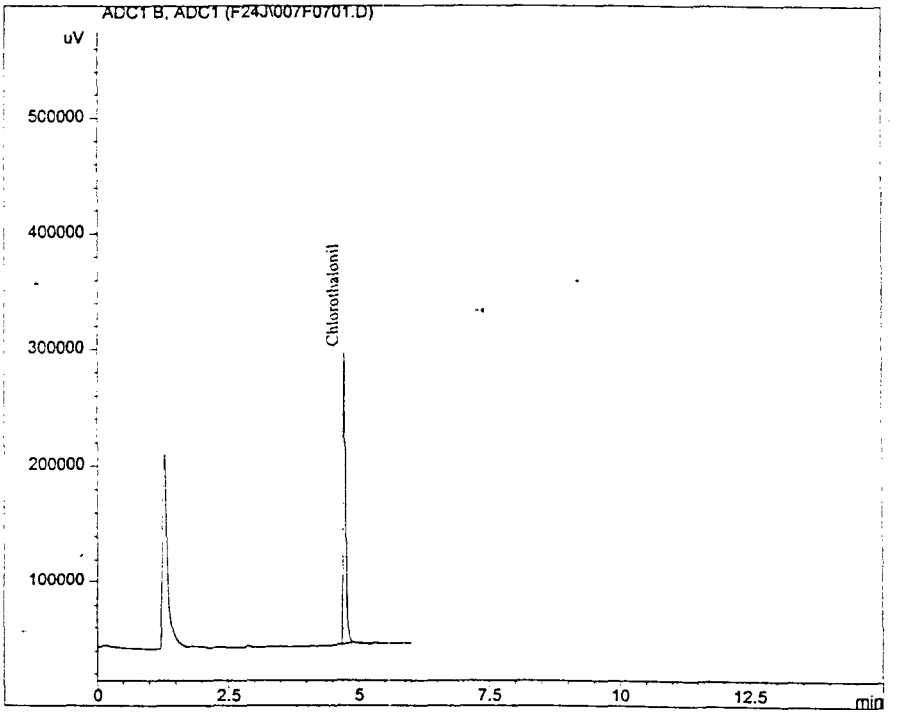
Analysis of Chlorothalonil

Run No.: 7

Sample No: CAL 970171 Spk A
Sample Info: Control Fortified at 5 µg, Final Volume = 100 mL

Injected on: 2/24/97 7:19:09 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.721	Chlorothalonil	252602.2	855381.437

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 9: Facial/Neck Wipes Fortified with 25 µg Chlorothalonil

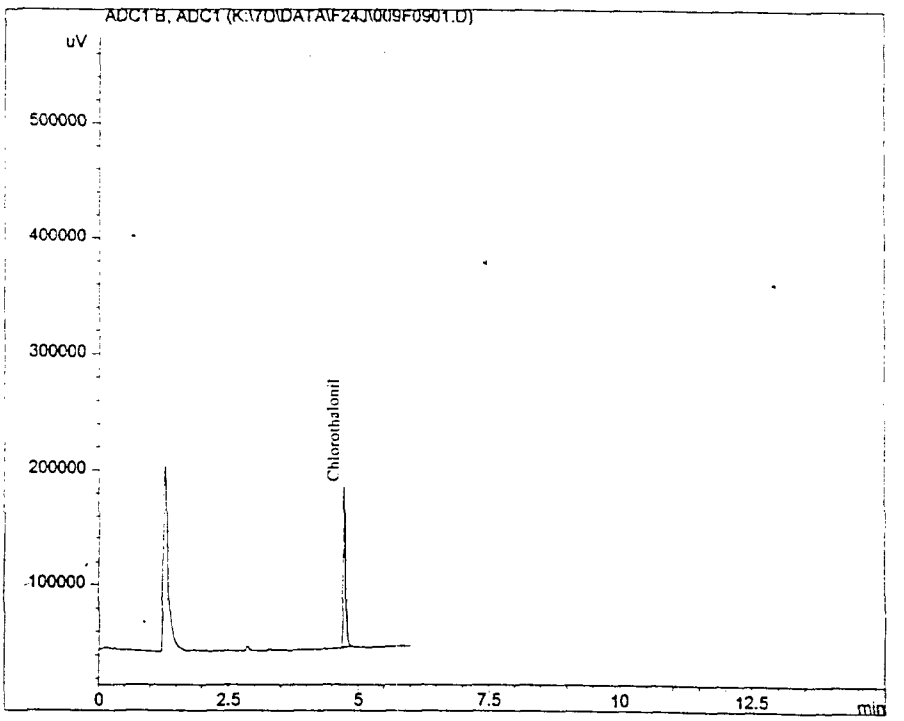
Analysis of Chlorothalonil

Run No.: 9

Sample No: CAL 970173 Spk C
Sample Info: Control Fortified at 25 µg, Final Volume = 100 mL
Dilution Factor = 10

Injected on: 2/24/97 7:43:28 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.725	Chlorothalonil	139743.9	453667.844

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 10: Facial/Neck Wipes Fortified with 125 µg Chlorothalonil

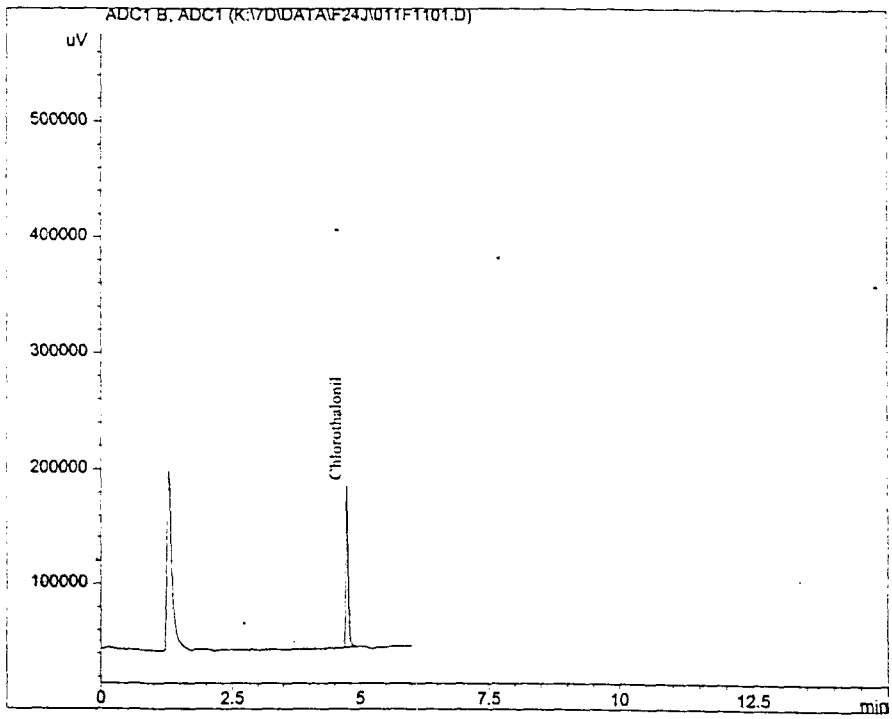
Analysis of Chlorothalonil

Run No.: 11

Sample No: CAL 970175 Spk E
Sample Info: Control Fortified at 125 µg, Final Volume = 100 mL
Dilution Factor = 50

Injected on: 2/24/97 8:07:54 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.736	Chlorothalonil	141653.1	458441.438

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 11: Spreadsheet, Facial/Neck Wipes

Analytical Data and Recoveries for CAL Study # 017-01: Determination of Chlorothalonil in Cotton Facial/Neck Wipes

Extraction Date: 2/24/97 **Analysis Date:** 2/24/97 **Matrix:** Cotton Facial/Neck Wipes J&J Gauze Sponges

STANDARD CURVE:

Conc. (µg/mL)	Peak Height
0.10	456659
0.05	237685
0.01	54842
0.005	27924
0.10	474526
0.05	254891
0.01	56267
0.005	28161

Linear Calibration Equation: y = mx+b
m= 4598236
b= 9192
Correlation Coefficient = 0.9990

DATA:

CAL ID#	Client ID	Compound Found	Peak Height	Peak Height Corrected	µg/mL Compound Found	Final Volume (mL)	Dilution Factor	µg/Sample Found	µg Compound Added	Percent Recovery
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
970170 Blk	NA	Chlorothalonil	0	0	0.0000	100	1	0.0	na	na
970171 Spk A	NA	Chlorothalonil	252602	252602	0.0529	100	1	5.29	5	106%
970172 Spk B	NA	Chlorothalonil	254043	254043	0.0532	100	1	5.32	5	106%
970173 Spk C	NA	Chlorothalonil	139744	139744	0.0284	100	10	28.4	25	114%
970174 Spk D	NA	Chlorothalonil	141763	141763	0.0288	100	10	28.8	25	115%
970175 Spk E	NA	Chlorothalonil	141653	141653	0.0288	100	50	144	125	115%
970176 Spk F	NA	Chlorothalonil	140679	140679	0.0286	100	50	143	125	114%

KF 1/28/99

Attachment 4

Representative Chromatograms, Standard Curve, and Spreadsheet Hand Washes

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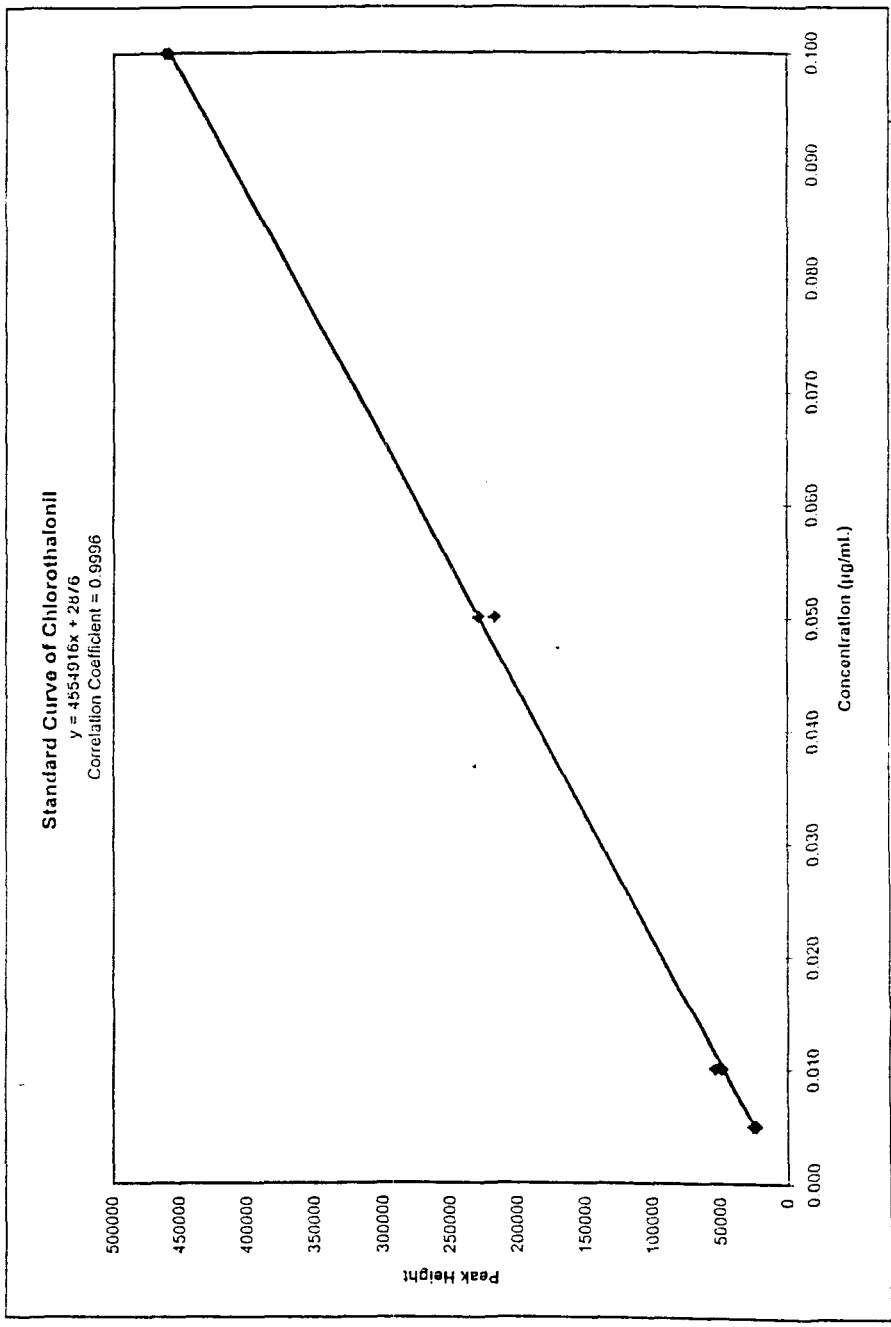
Figure 11: Spreadsheet, Handwash Solution 80

Figure 1: Linear Regression Analysis



Analysis Date: 3/04/97

Extraction Date: 3/04/97

CAL Study No. 017-01

ARTF Study No. ARF004

Figure 2: Ethyl Acetate Blank

Analysis of Chlorothalonil

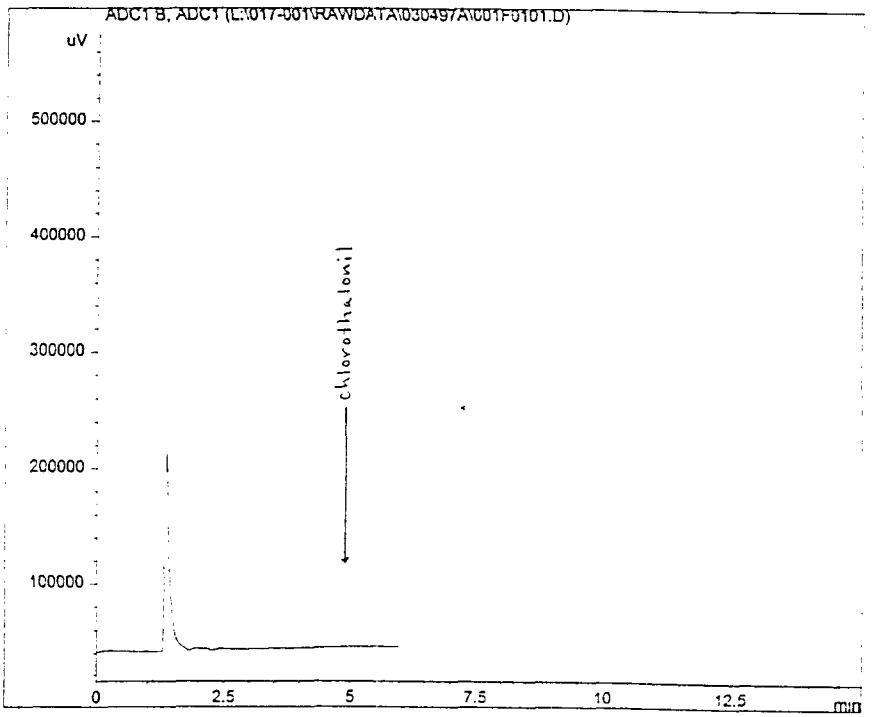
Run No.: 1

Sample No: NA
Sample Info: Solvent Blank

Initials DCD
Date 3-5-97
Page 1 To 17

Injected on: 3/4/97 4:55:33 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01
ARTF Study Number: ARF004

Operator: Julie B. Petit

Figure 3: Calibration Standard 0.1 µg/mL

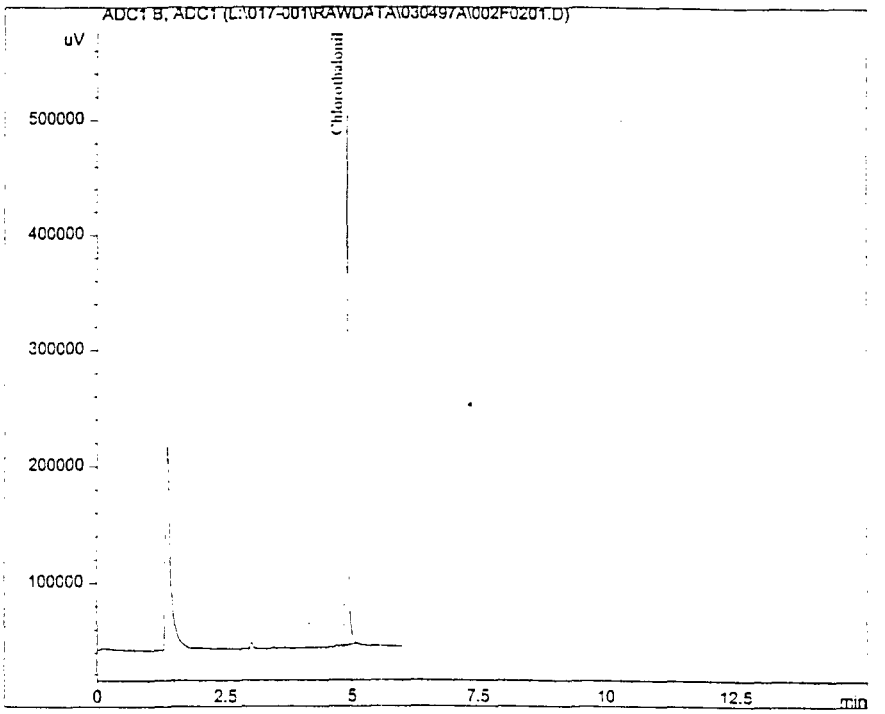
Analysis of Chlorothalonil

Run No.: 2

Sample No: NA
Sample Info: 0.1 µg/mL Standard, C021097-1

Injected on: 3/4/97 5:12:15 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.883	Chlorothalonil	462415.3	1.589e+006

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 4: Calibration Standard 0.05 µg/mL

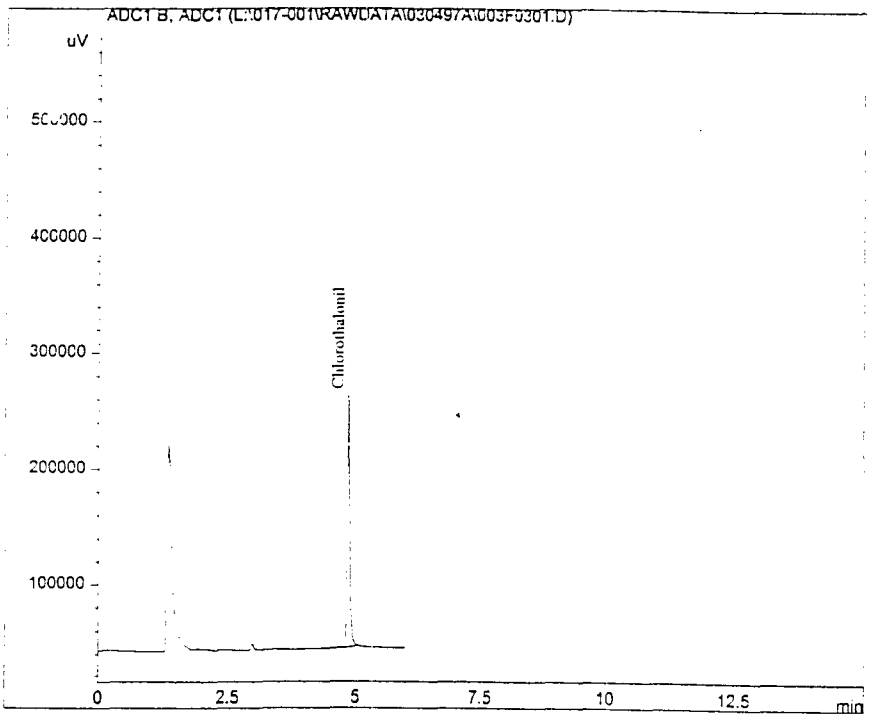
Analysis of Chlorothalonil

Run No.: 3

Sample No: NA
Sample Info: 0.05 µg/mL Standard, C021097-2

Injected on: 3/4/97 5:29:01 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.850	Chlorothalonil	218813.1	761048.625

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 5: Calibration Standard 0.01 µg/mL

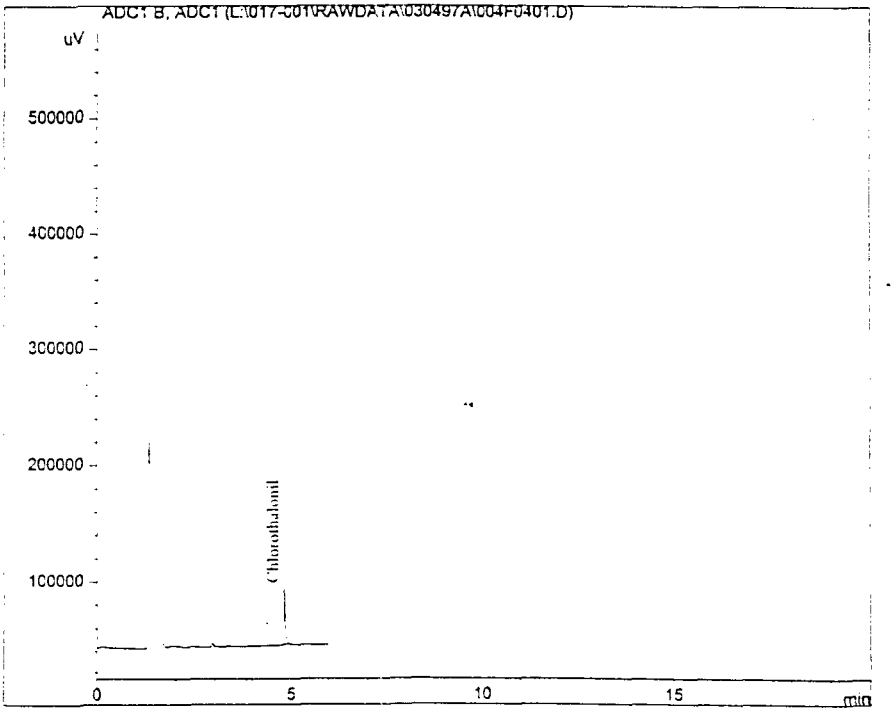
Analysis of Chlorothalonil

Run No.: 4

Sample No: NA
Sample Info: 0.01 µg/mL Standard, C021097-3

Injected on: 3/4/97 5:45:44 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.811	Chlorothalonil	49578.0	153965.969

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 6: Calibration Standard 0.005 µg/mL

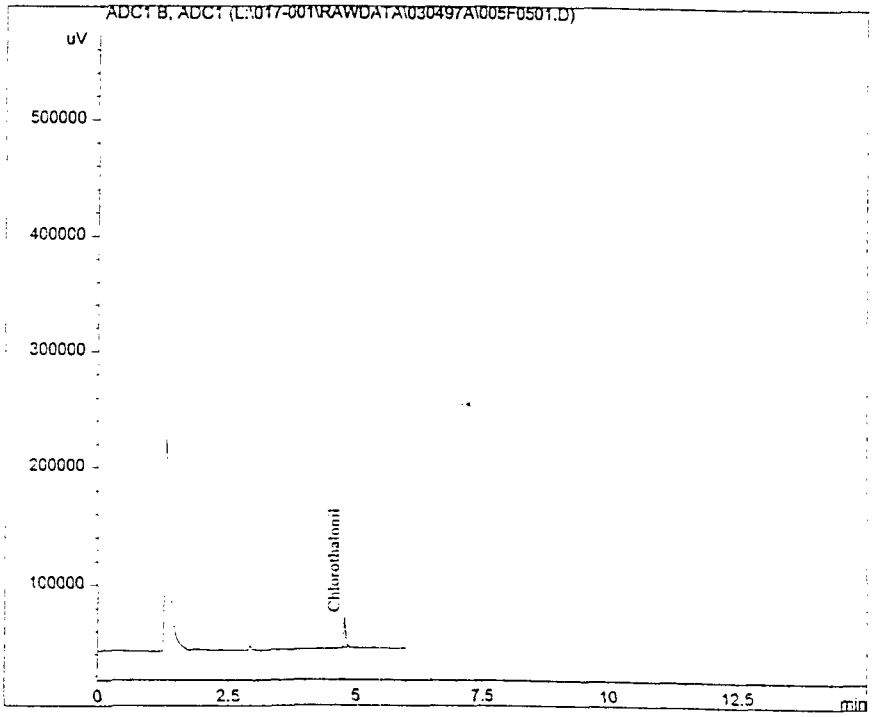
Analysis of Chlorothalonil

Run No.: 5

Sample No: NA
Sample Info: 0.005 µg/mL Standard, C021097-4

Injected on: 3/4/97 6:02:31 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.776	Chlorothalonil	26542.2	77438.211

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 7: Handwash Solution Control

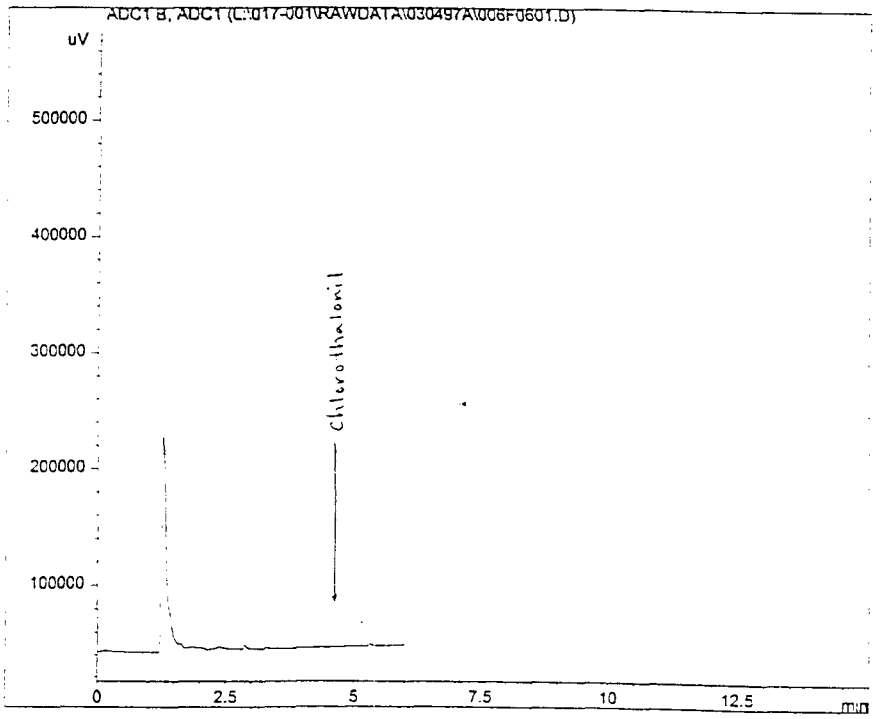
Analysis of Chlorothalonil

Run No.: 6

Sample No: Blk 971362 (16) DCD 4-3-97
Sample Info: Control, Final Volume = 10 mL
Dilution Factor = 10

Injected on: 3/4/97 6:19:16 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01
ARTF Study Number: ARF004

Operator: Julie B. Petit

Figure 8: Handwash Solution Fortified with 5 µg Chlorothalonil

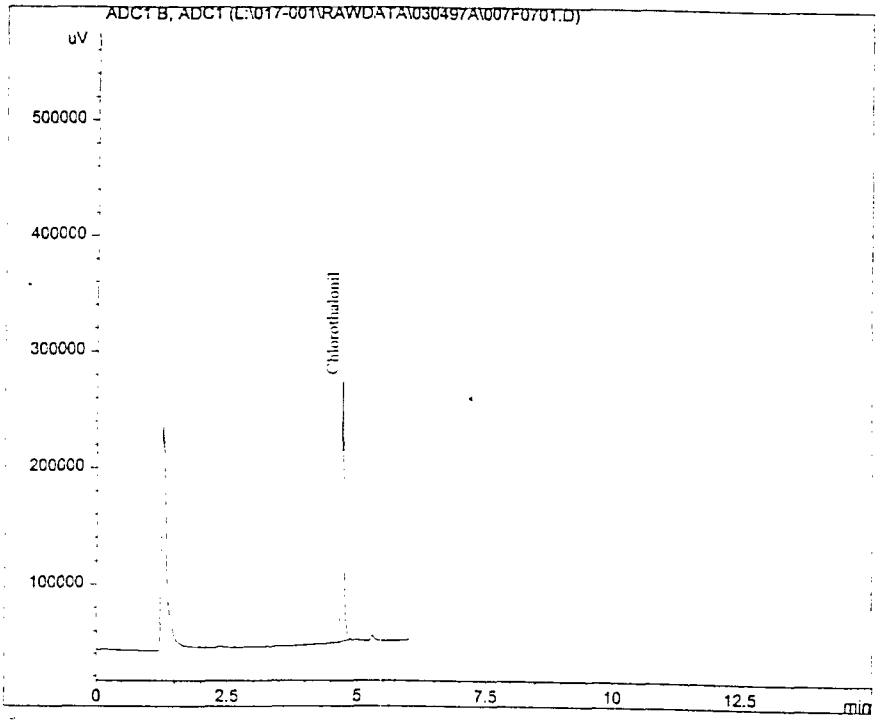
Analysis of Chlorothalonil

Run No.: 7

Sample No: Spk A 971362 DLD 4-3-97
Sample Info: Control Fortified at 5 µg, Final Volume = 10 mL
Dilution Factor = 10

Injected on: 3/4/97 6:35:58 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.701	Chlorothalonil	225565.8	769377.563

CAL Study Number: 017-01
ARTF Study Number: ARF004

Operator: Julie B. Petit

Figure 9: Handwash Solution Fortified with 25 µg Chlorothalonil

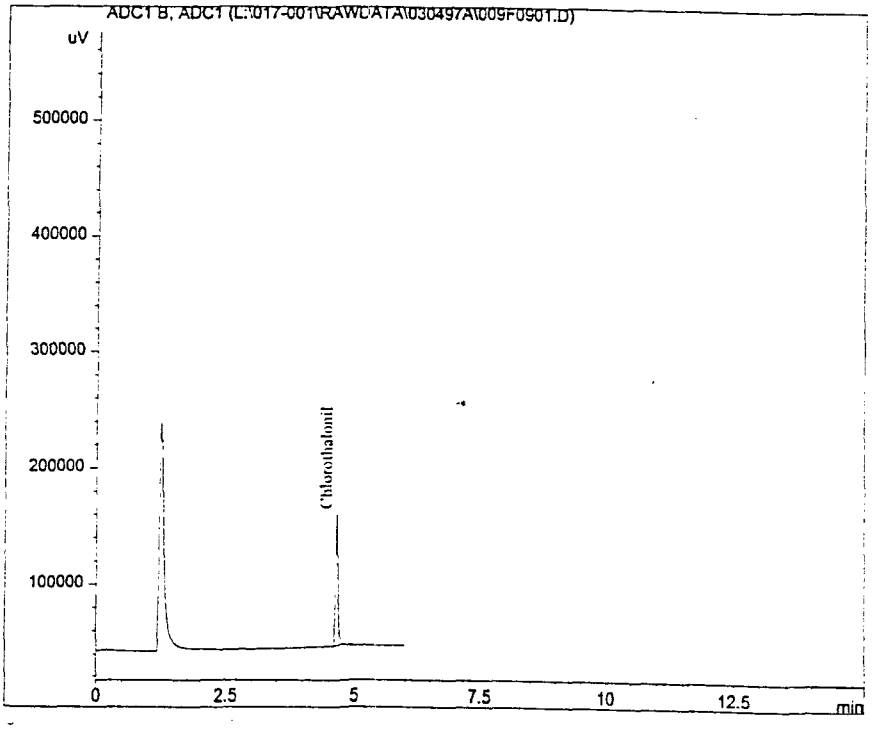
Analysis of Chlorothalonil

Run No.: 9

Sample No: Spk C 971362 @ OCD 4347
Sample Info: Control Fortified at 25 µg, Final Volume = 10 mL
Dilution Factor = 100

Injected on: 3/4/97 7:09:23 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.649	Chlorothalonil	113577.7	369577.656

CAL Study Number: 017-01
ARTF Study Number: ARF004

Operator: Julie B. Petit

Figure 10: Handwash Solution Fortified with 125 µg Chlorothalonil

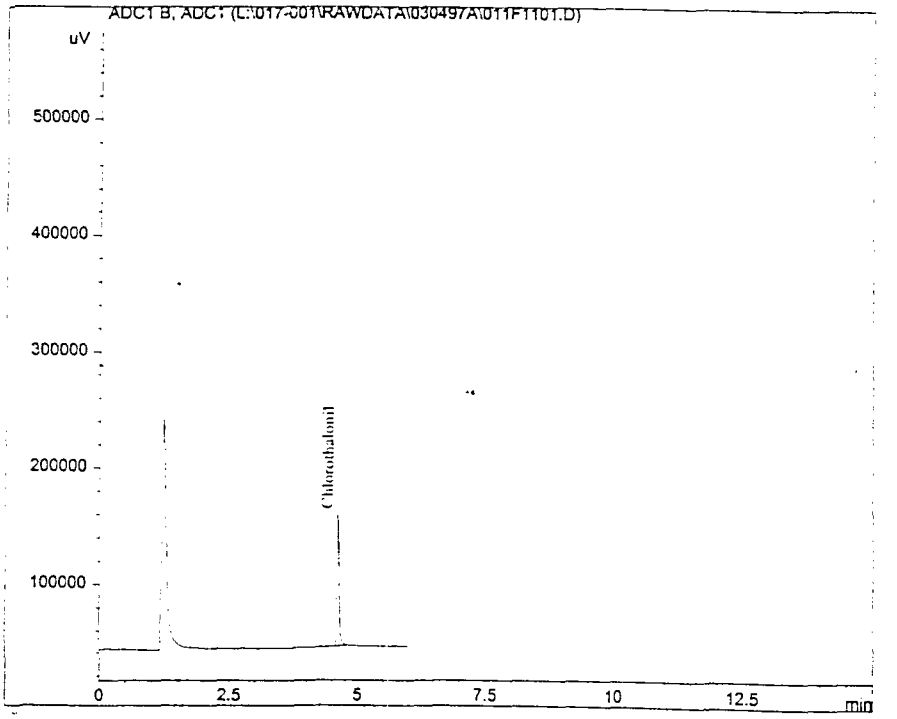
Analysis of Chlorothalonil

Run No.: 11

Sample No: Spk E 971362 DCD 4-3-97
Sample Info: Control Fortified at 125 µg, Final Volume = 10 mL
Dilution Factor = 500

Injected on: 3/4/97 7:42:53 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.615	Chlorothalonil	114898.5	379336.719

CAL Study Number: 017-01
ARTF Study Number: ARF004

Operator: Julie B. Petit

Figure 11: Spreadsheet, Handwash Solution

Analytical Data and Recoveries for CAL Study # 017-01: Determination of Chlorothalonil in Handwash Solutions

Extraction Date: 3/04/97 **Analysis Date:** 3/04/97 **Matrix:** Aerosol OT-75

STANDARD CURVE:

Conc. (µg/mL)	Peak Height
0.10	462415
0.05	218813
0.01	49578
0.005	26542
0.10	459439
0.05	230822
0.01	54473
0.005	24047

Linear Calibration Equation: y = mx+b
m= 4554916
b= 2876
Correlation Coefficient = 0.9996

DATA:

CAL ID#	Client ID	Compound Found	Peak Height	Peak Height Corrected	µg/mL Compound Found	Final Volume (mL)	Dilution Factor	µg/Sample Found	µg Compound Added	Percent Recovery
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
971362 Blk	NA	Chlorothalonil	0	0	0.0000	10	10	0.0	na	na
971362 Spk A	NA	Chlorothalonil	225566	225566	0.0489	10	10	4.89	5	97.8%
971362 Spk B	NA	Chlorothalonil	225284	225284	0.0488	10	10	4.88	5	97.7%
971362 Spk C	NA	Chlorothalonil	113578	113578	0.0243	10	100	24.3	25	97.2%
971362 Spk D	NA	Chlorothalonil	126695	126695	0.0272	10	100	27.2	25	109%
971362 Spk E	NA	Chlorothalonil	114899	114899	0.0246	10	500	123	125	98.4%
971362 Spk F	NA	Chlorothalonil	126744	126744	0.0272	10	500	136	125	109%

KF 1/28/99

Attachment 5

Representative Chromatograms, Standard Curve, and Spreadsheet
Air Sampling Tubes

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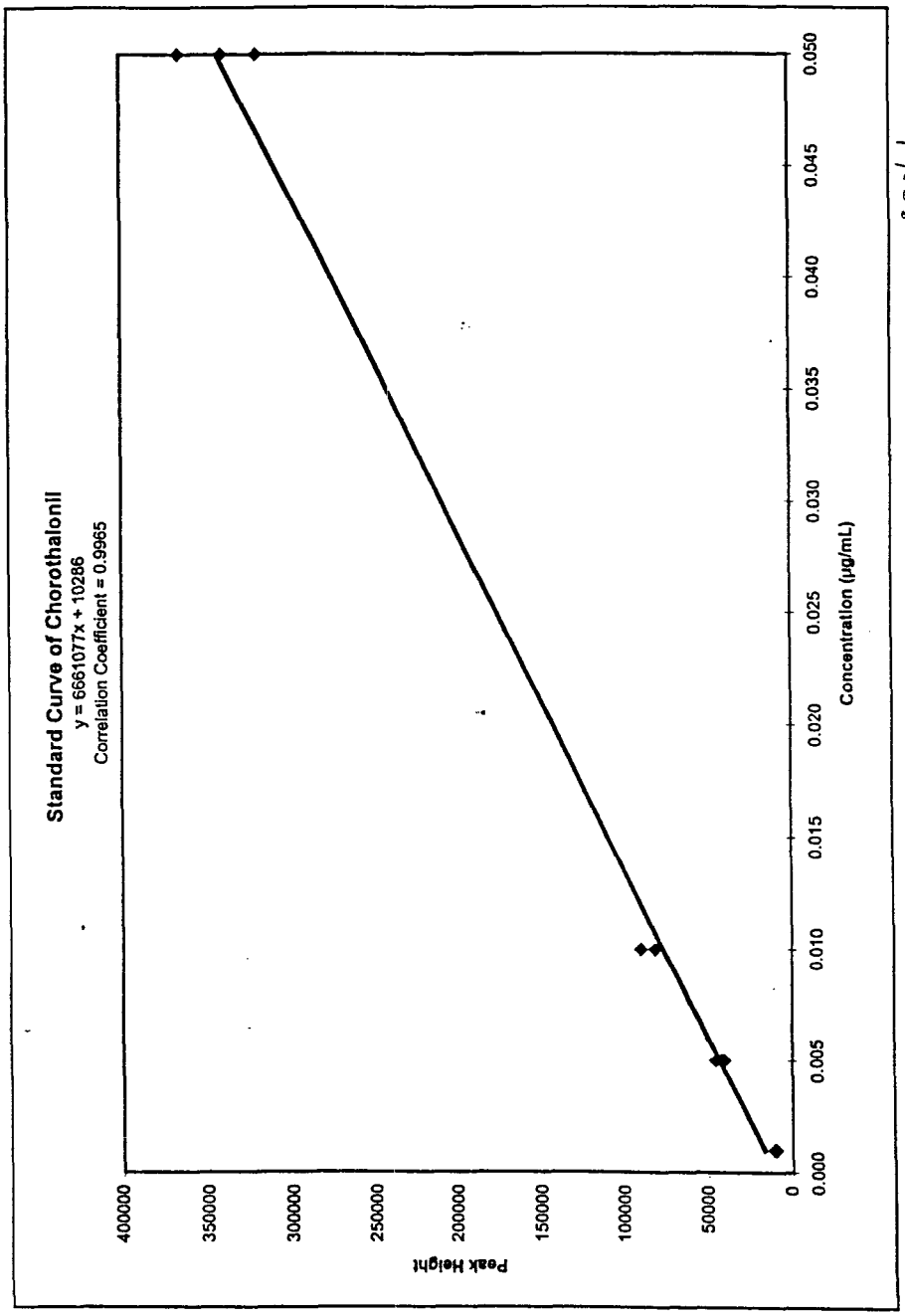
Figure 1: Linear Regression Analysis

Analysis Date: 3/3/97



JBP 3/7/97

CAL Study No. 017-01

Extraction Date: 2/27/97

ARTF Study No. ARF004

Figure 2: Toluene Blank

Initials KF
Date 3/4/97
Run# 1 To 27

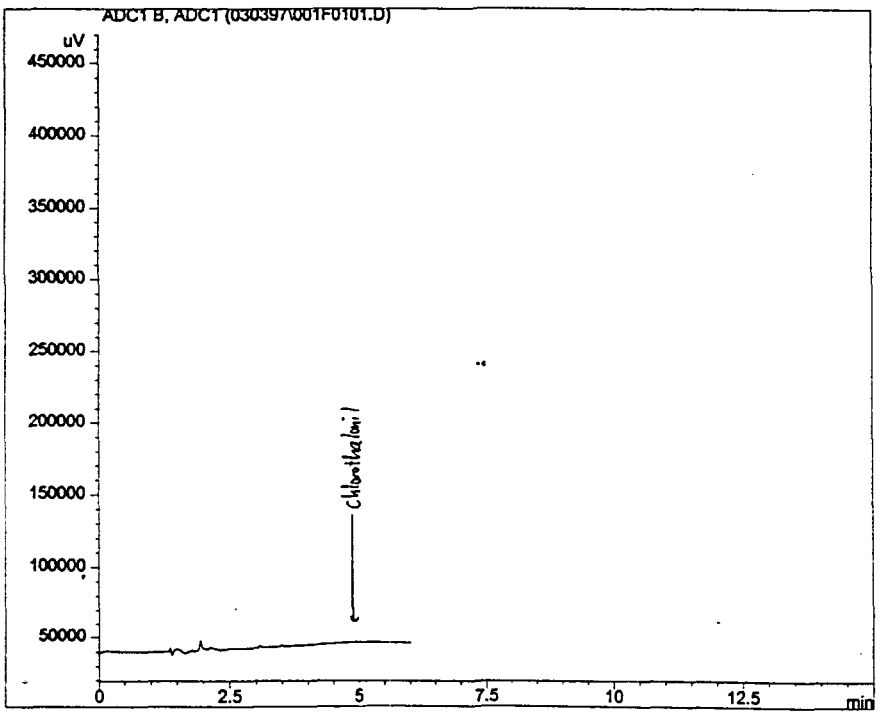
Analysis of Chlorothalonil

Run No.: 1

Sample No: NA
Sample Info: Solvent Blank

Injected on: 3/3/97 1:58:20 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 3: Calibration Standard 0.05 µg/mL

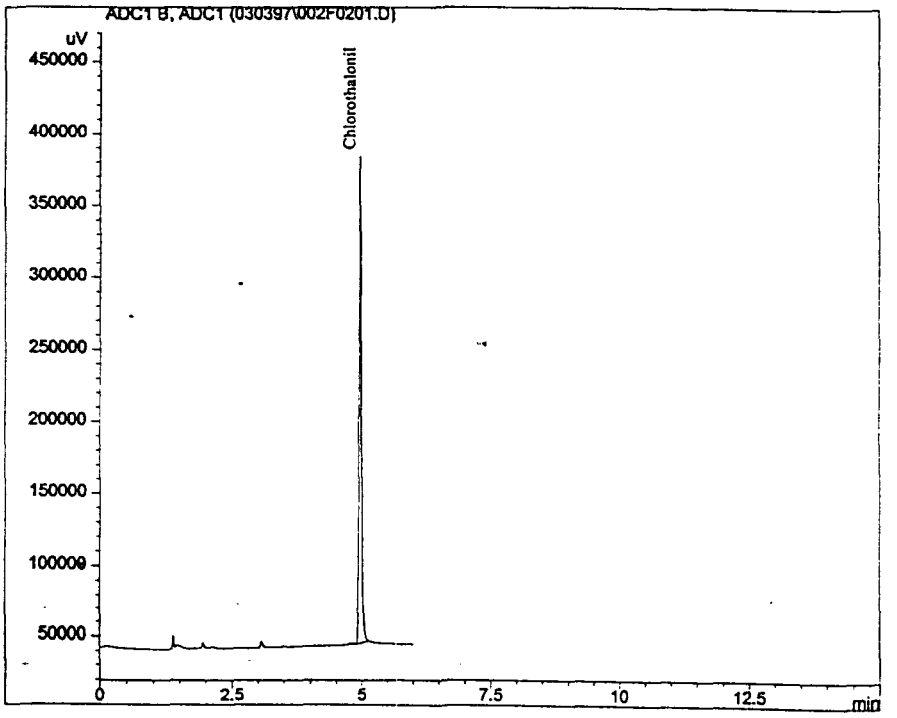
Analysis of Chlorothalonil

Run No.: 2

Sample No: NA
Sample Info: 0.05 µg/mL Standard, C021097-7

Injected on: 3/3/97 2:10:31 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.956	Chlorothalonil	340627.8	1.087e+006

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 4: Calibration Standard 0.01 µg/mL

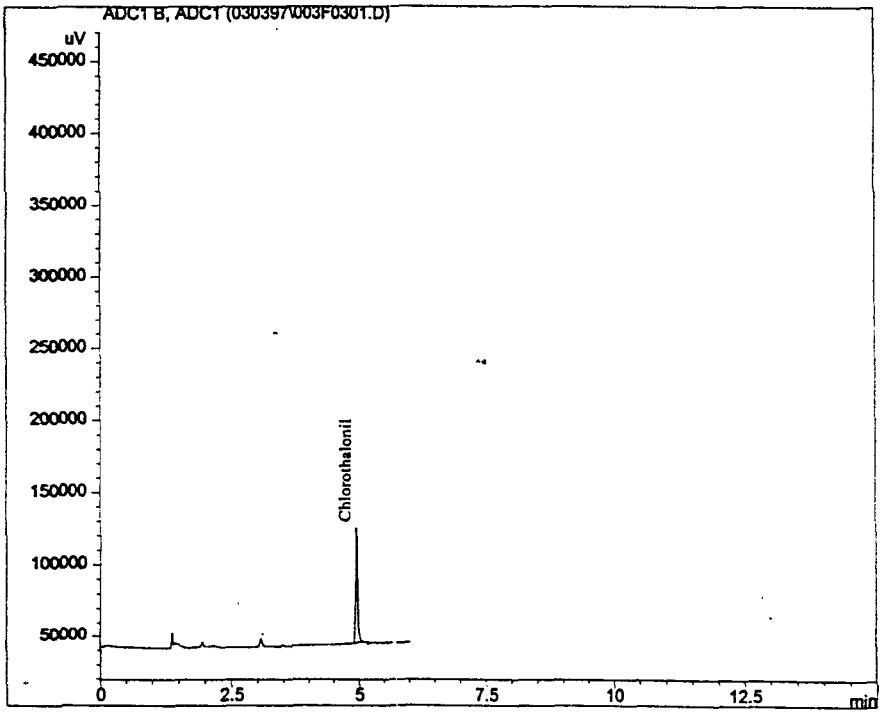
Analysis of Chlorothalonil

Run No.: 3

Sample No: NA
Sample Info: 0.01 µg/mL Standard, C021097-8

Injected on: 3/3/97 2:22:44 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.945	Chlorothalonil	81746.5	241230.094

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 5: Calibration Standard 0.005 µg/mL

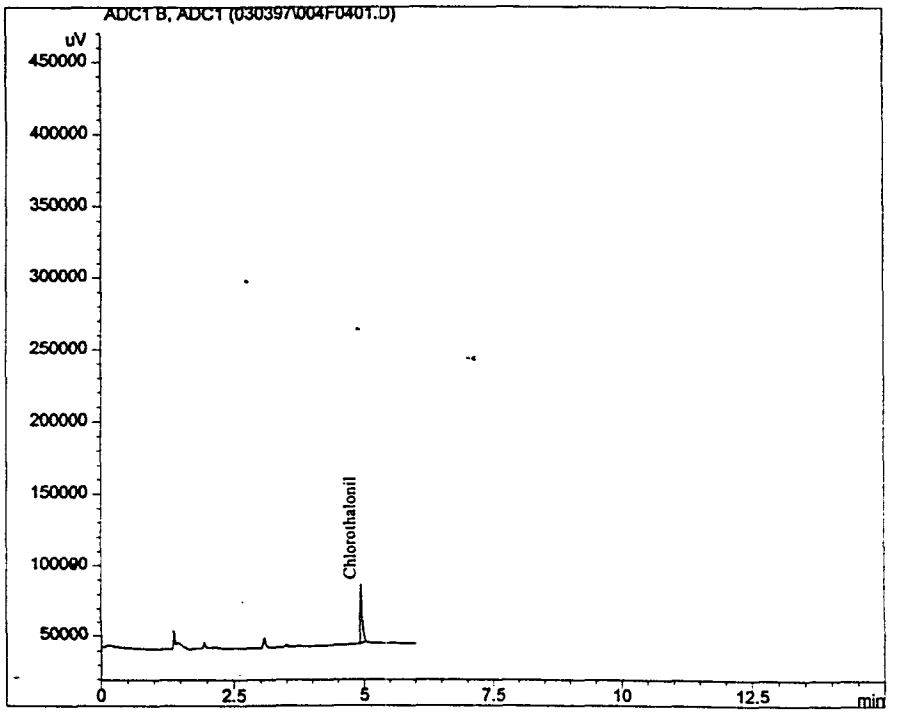
Analysis of Chlorothalonil

Run No.: 4

Sample No: NA
Sample Info: 0.005 µg/mL Standard, C021097-9

Injected on: 3/3/97 2:34:56 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.941	Chlorothalonil	42285.9	118662.594

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 6: Calibration Standard 0.001 µg/mL

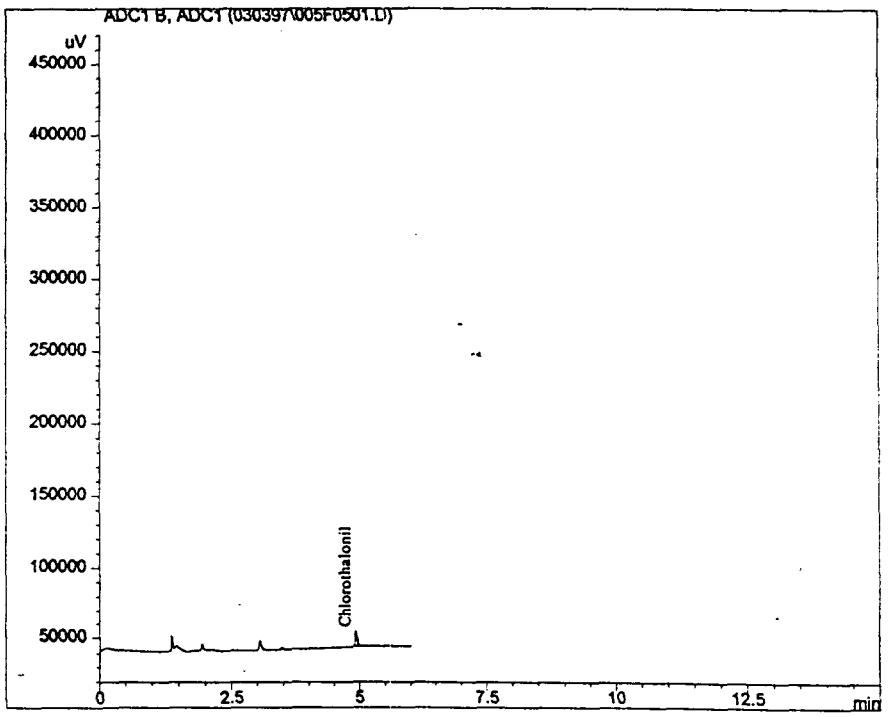
Analysis of Chlorothalonil

Run No.: 5

Sample No: NA
Sample Info: 0.001 µg/mL Standard, C021097-10

Injected on: 3/3/97 2:47:12 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.924	Chlorothalonil	9858.4	25545.248

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 7: Air Sampling Tubes Front Control

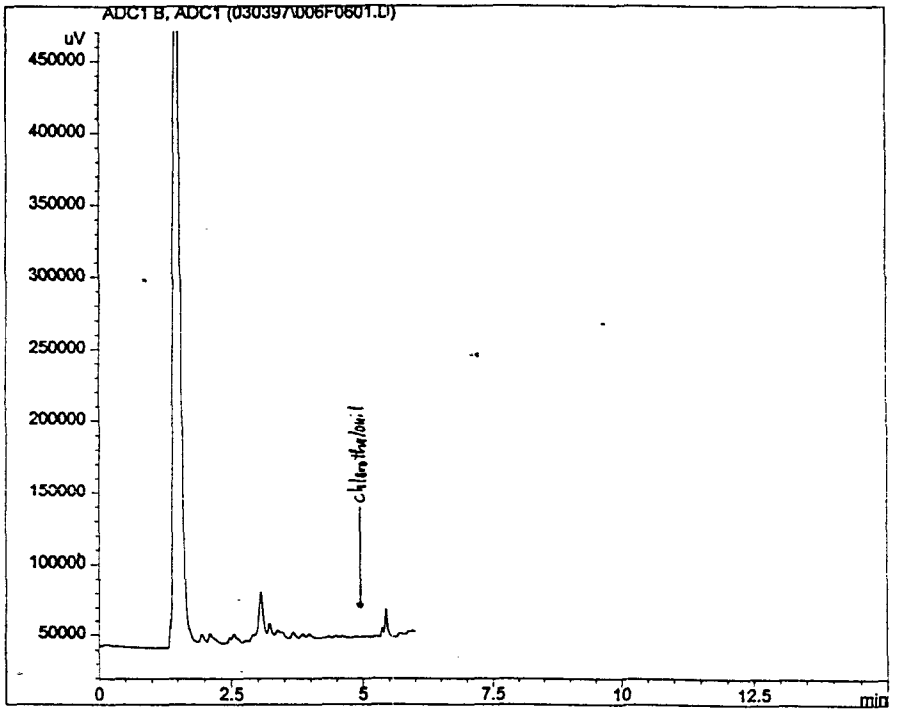
Analysis of Chlorothalonil

Run No.: 6

Sample No: CAL 970993 Blk
Sample Info: Control, Front, Final Volume = 3.5 mL

Injected on: 3/3/97 2:59:26 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 8: Air Sampling Tubes Front fortified with 0.05 µg Chlorothalonil

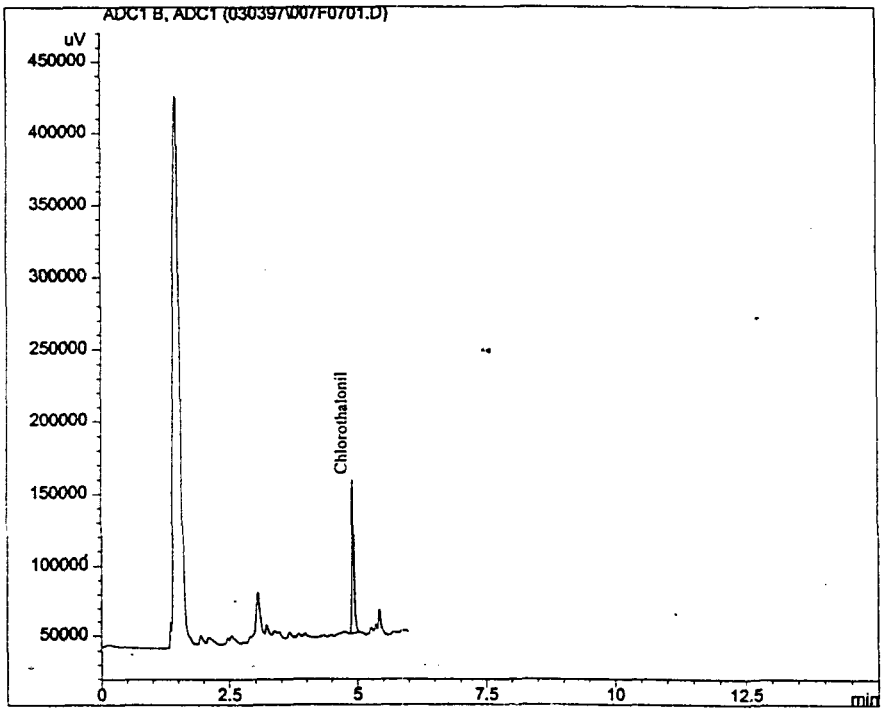
Analysis of Chlorothalonil

Run No.: 7

Sample No: CAL 970994 Spk A
Sample Info: Control Fortified at 0.05 µg, Front
Final Volume = 3.5 mL

Injected on: 3/3/97 3:11:40 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.912	Chlorothalonil	109064.3	330669.406

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 9: Air Sampling Tubes Front fortified with 0.25 µg Chlorothalonil

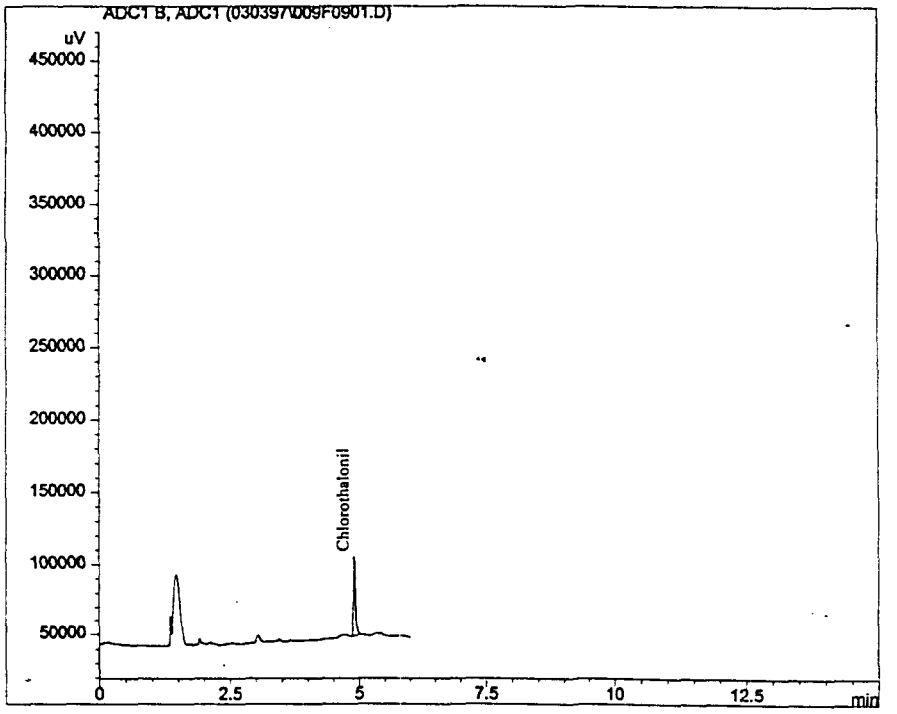
Analysis of Chlorothalonil

Run No.: 9

Sample No: CAL 970996 Spk C
Sample Info: Control Fortified at 0.25 µg, Front
Final Volume = 3.5 mL, Dilution Factor = 10

Injected on: 3/3/97 3:36:02 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.904	Chlorothalonil	57164.2	167301.875

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 10: Air Sampling Tubes Front fortified with 1.25 µg Chlorothalonil

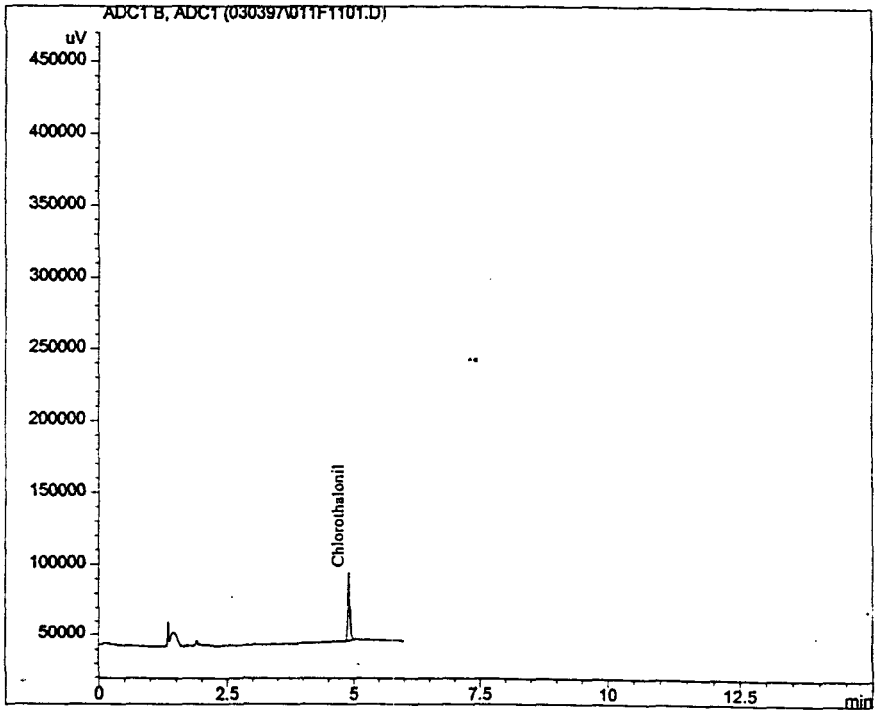
Analysis of Chlorothalonil

Run No.: 11

Sample No: CAL 970998 Spk E
Sample Info: Control Fortified at 1.25 µg, Front
Final Volume = 3.5 mL, Dilution Factor = 50

Injected on: 3/3/97 4:00:30 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.903	Chlorothalonil	49410.9	144948.125

CAL Study Number: 017-01
ARTF Study Number: ARF004

Operator: Julie B. Petit

Figure 11: Spreadsheet, Air Sampling Tubes

Analytical Data and Recoveries for CAL Study # 017-01: Determination of Chlorothalonil in OVS Air Sampling Tubes with Chromosorb 102

Extraction Date: 2/27/97 **Analysis Date:** 3/3/97 **Matrix:** OVS Tubes w/Chromosorb 102

STANDARD CURVE:

Conc. (µg/mL)	Peak Height
0.05	340628
0.01	81747
0.005	42286
0.001	9858
0.050	320324
0.005	40820
0.05	365869
0.01	90313
0.005	45762
0.001	10877

Linear Calibration Equation: y = mx+b
m= 10286
b= 6661077
Correlation Coefficient = 0.9965

DATA:

CAL ID#	Client ID	Compound Found	Peak Height	Peak Height Corrected	µg/mL Compound Found	Final Volume (mL)	Dilution Factor	µg/Sample Found	µg Compound Added	Percent Recovery
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
970993 Blk, Front	NA	Chlorothalonil	0	0	0.0000	3.5	1	0.0	na	na
970993 Blk, Rear	NA	Chlorothalonil	0	0	0.0000	3.5	1	0.0	na	na

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11/28/99

Analytical Data and Recoveries for CAL Study # 017-01:
Determination of Chlorothalonil in OVS Air Sampling Tubes with Chromosorb 102

Extraction Date: 2/27/97 **Analysis Date:** 3/3/97 **Matrix:** OVS Tubes w/Chromosorb 102

DATA:

CAL ID#	Client ID	Compound Found	Peak Height	Peak Height Corrected	µg/mL Compound Found	Final Volume (mL)	Dilution Factor	µg/Sample Found	µg Compound Added	Percent Recovery
970994 Spk A Front	NA	Chlorothalonil	109064	109064	0.0148	3.5	1	0.052	0.05	104%
970995 Spk B Front	NA	Chlorothalonil	107738	107738	0.0146	3.5	1	0.051	0.05	102%
970996 Spk C Front	NA	Chlorothalonil	57164	57164	0.0070	3.5	10	0.246	0.25	98.5%
970997 Spk D Front	NA	Chlorothalonil	55239	55239	0.0067	3.5	10	0.236	0.25	94.5%
970998 Spk E Front	NA	Chlorothalonil	49411	49411	0.0059	3.5	50	1.03	1.25	82.2%
970999 Spk F Front	NA	Chlorothalonil	50609	50609	0.0061	3.5	50	1.06	1.25	84.7%
970994 Spk A Rear	NA	Chlorothalonil	109269	109269	0.0149	3.5	1	0.052	0.05	104%
970995 Spk B Rear	NA	Chlorothalonil	113317	113317	0.0155	3.5	1	0.054	0.05	108%
970996 Spk C Rear	NA	Chlorothalonil	56757	56757	0.0070	3.5	10	0.244	0.25	97.7%
970997 Spk D Rear	NA	Chlorothalonil	56685	56685	0.0070	3.5	10	0.244	0.25	97.5%
970998 Spk E Rear	NA	Chlorothalonil	53940	53940	0.0066	3.5	50	1.15	1.25	91.8%
970999 Spk F Rear	NA	Chlorothalonil	55026	55026	0.0067	3.5	50	1.18	1.25	94.0%

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Attachment 6

Representative Chromatograms, Standard Curve, and Spreadsheet Dislodging Solutions

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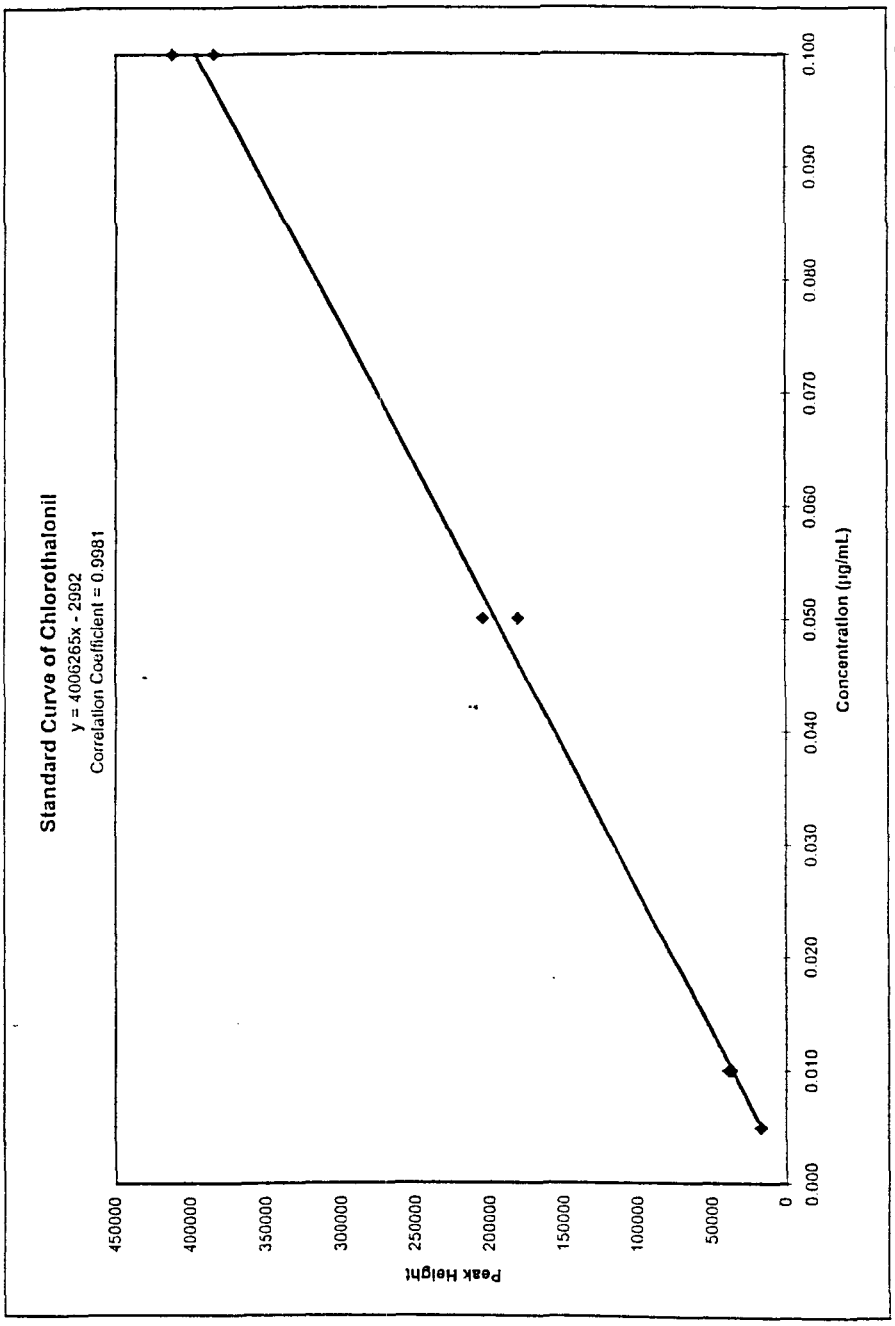
Figure 12: Spreadsheet, Dislodging Solution 108

Figure 1: Linear Regression Analysis

Analysis Date: 4/10/97



DCD 5-16-97

CAL Study No. 017-01

Extraction Date: 4/09/97

ARTF Study No. ARF004

Figure 2: Ethyl Acetate Blank

Analysis of Chlorothalonil

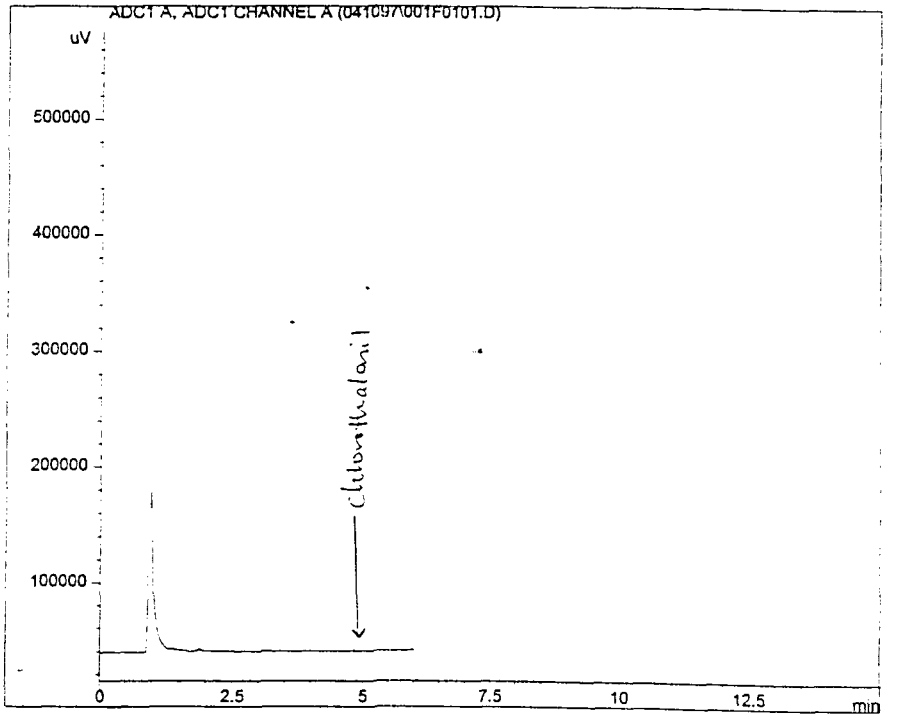
Run No.: 1

Sample No: NA
Sample Info: Solvent Blank

Initials DCD
Date 4-18-97
Run# 1 to 17

Injected on: 4/10/97 6:04:16 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 3: Calibration Standard 0.1 µg/mL

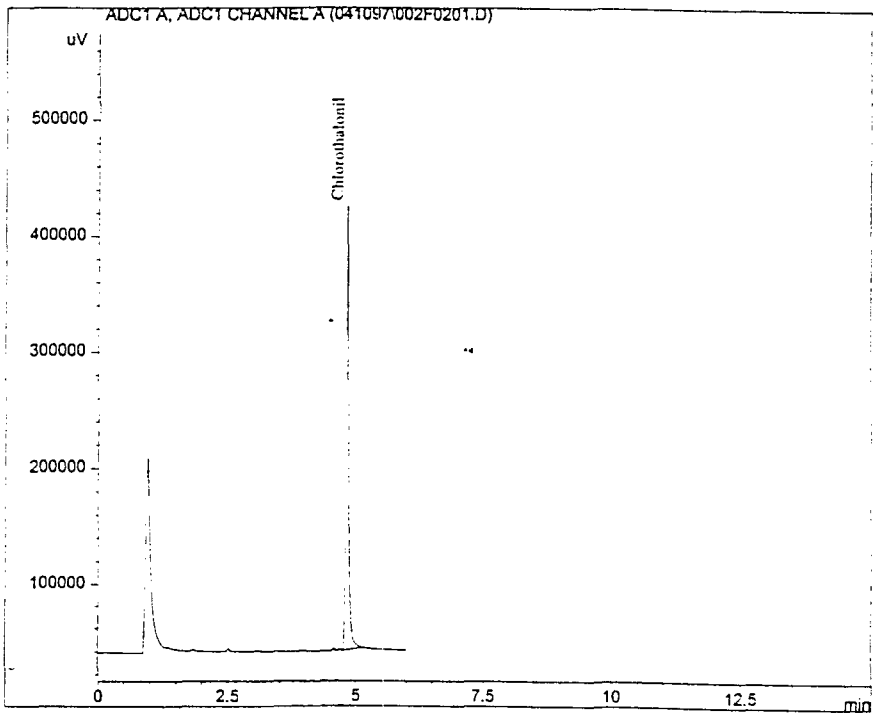
Analysis of Chlorothalonil

Run No.: 2

Sample No: NA
Sample Info: 0.1 µg/mL Standard, C021097-1

Injected on: 4/10/97 6:22:02 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.814	Chlorothalonil	385603.9	1.438e+006

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 4: Calibration Standard 0.05 µg/mL

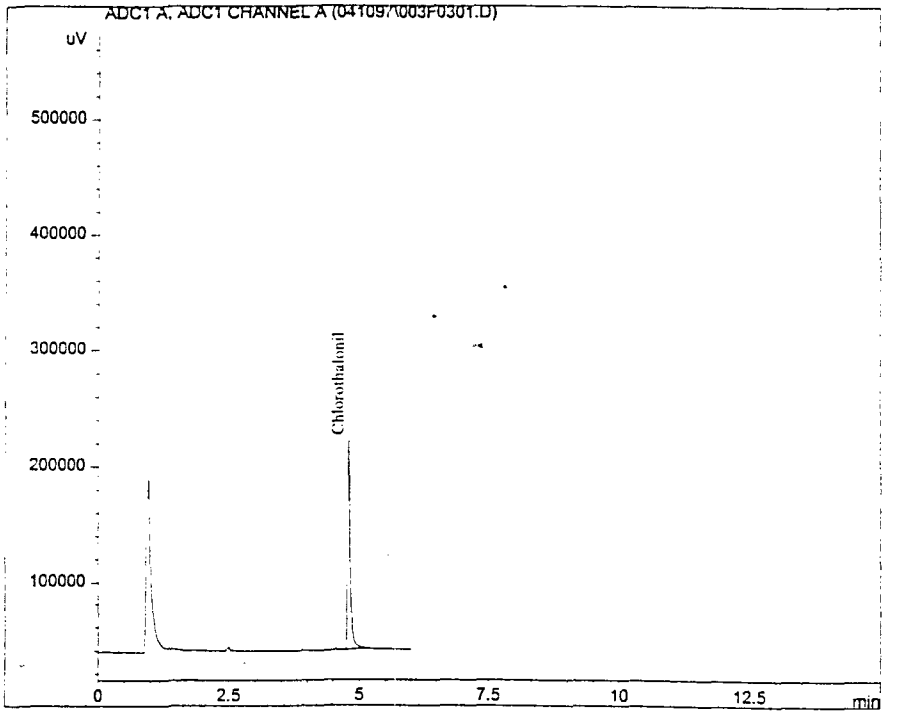
Analysis of Chlorothalonil

Run No.: 3

Sample No: NA
Sample Info: 0.05 µg/mL Standard, C021097-2

Injected on: 4/10/97 6:39:45 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.784	Chlorothalonil	181845.9	682533.625

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 5: Calibration Standard 0.01 µg/mL

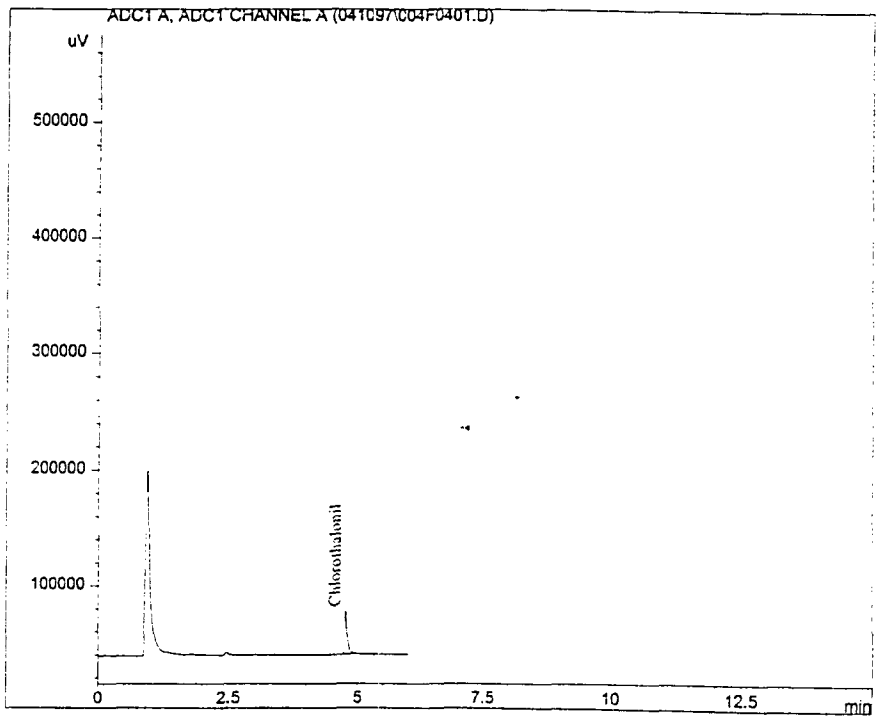
Analysis of Chlorothalonil

Run No.: 4

Sample No: NA
Sample Info: 0.01 µg/mL Standard, C021097-3

Injected on: 4/10/97 6:57:30 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.764	Chlorothalonil	37633.7	139182.844

CAL Study Number: 017-01
ARTF Study Number: ARF004

Operator: Julie B. Petit

Figure 6: Calibration Standard 0.005 µg/mL

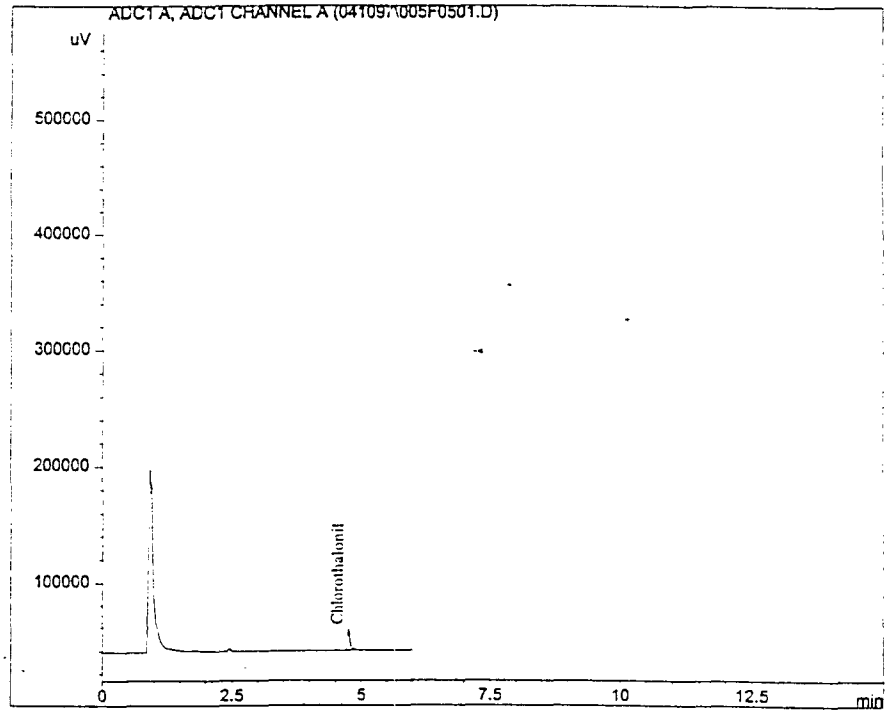
Analysis of Chlorothalonil

Run No.: 5

Sample No: NA
Sample Info: 0.005 µg/mL Standard, C021097-4

Injected on: 4/10/97 7:15:16 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.744	Chlorothalonil	17626.8	62015.887

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 7: Dislodging Solution (Cauliflower Leaf Wash without leaves) Control

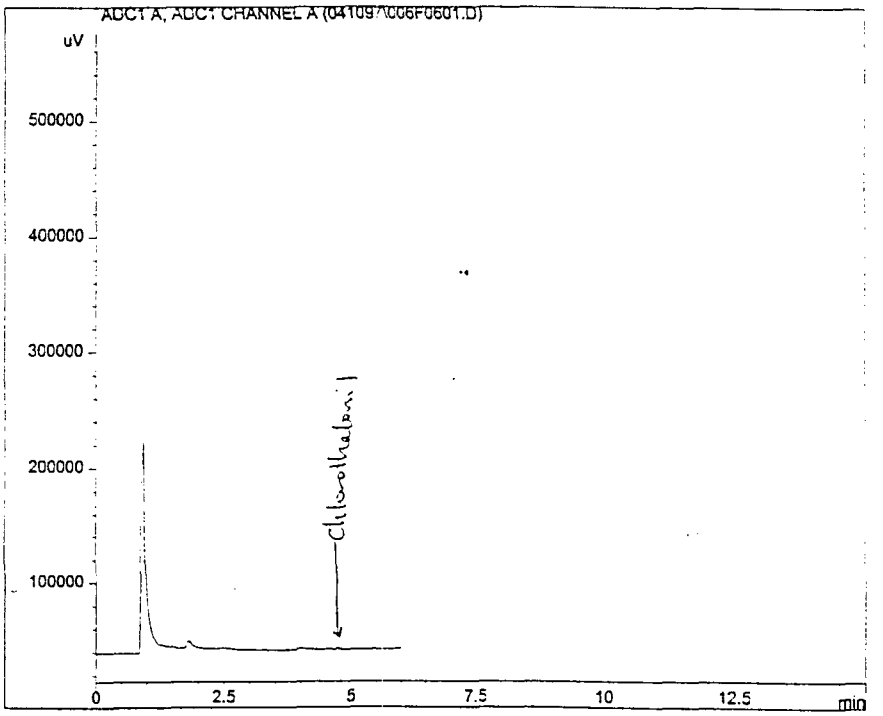
Analysis of Chlorothalonil

Run No.: 6

Sample No: CAL 971362 Blk (07-75 BLK) (CE) SW 10-10-97
Sample Info: Control (without leaves), Final Volume = 10 mL, Dilution Factor = 10

Injected on: 4/10/97 7:33:04 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 8: Dislodging Solution (Cauliflower Leaf Wash with leaves) Control

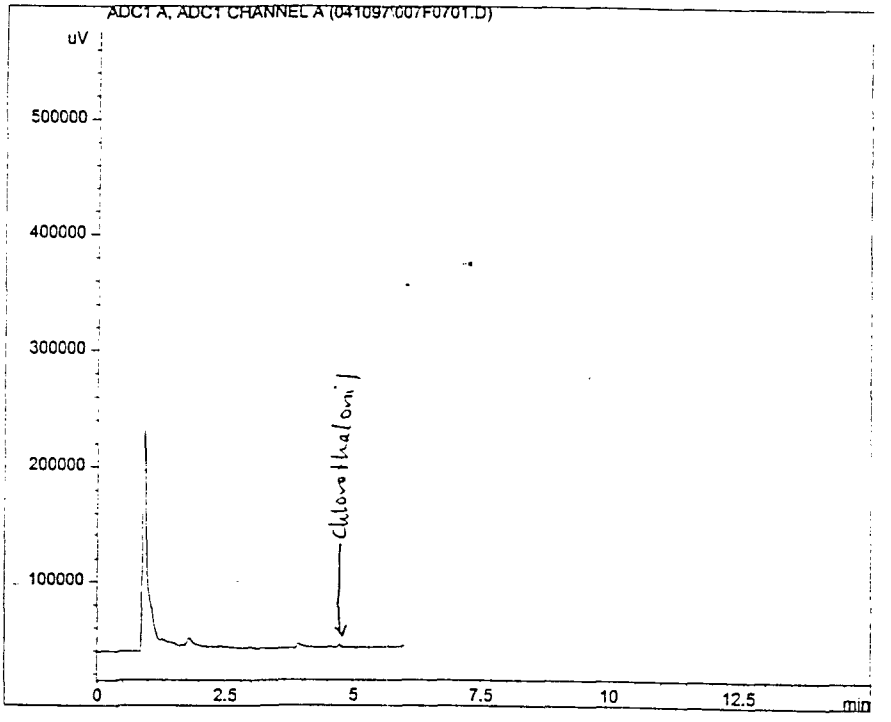
Analysis of Chlorothalonil

Run No.: 7

Sample No: CAL 971362 Blk
Sample Info: Control (with leaves), Final Volume = 10 mL, Dilution Factor = 10

Injected on: 4/10/97 7:50:48 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 9: Dislodging Solution (Cauliflower Leaf Wash) Fortified with 5 µg Chlorothalonil

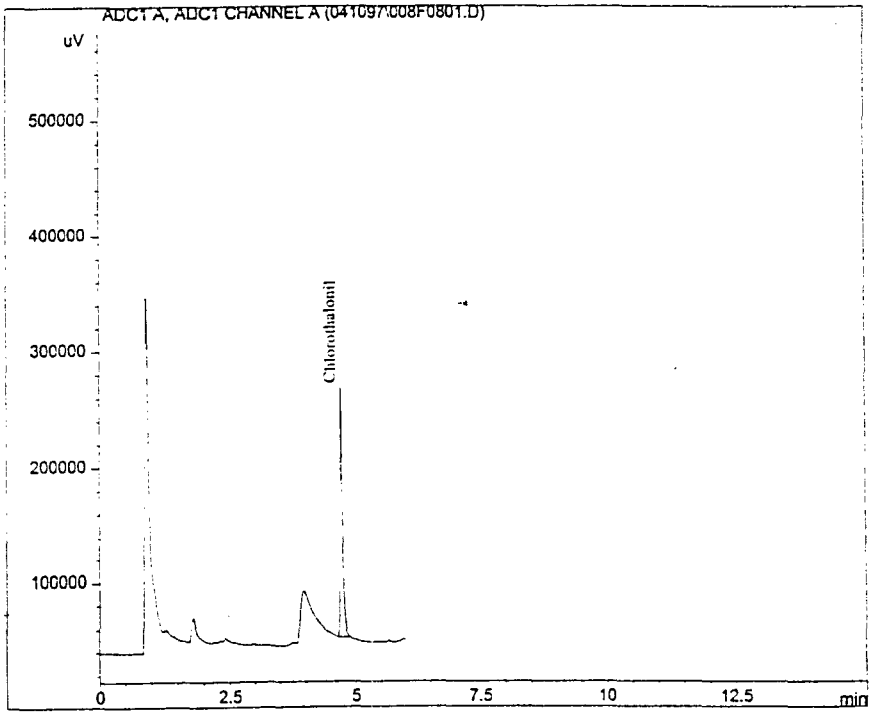
Analysis of Chlorothalonil

Run No.: 8

Sample No: CAL 971362 Spk A
Sample Info: Control Fortified at 5 µg, Final Volume = 10 mL
Dilution Factor = 10

Injected on: 4/10/97 8:08:34 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.713	Chlorothalonil	215366.8	746765.125

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 10: Dislodging Solution (Cauliflower Leaf Wash) Fortified with 25 µg Chlorothalonil

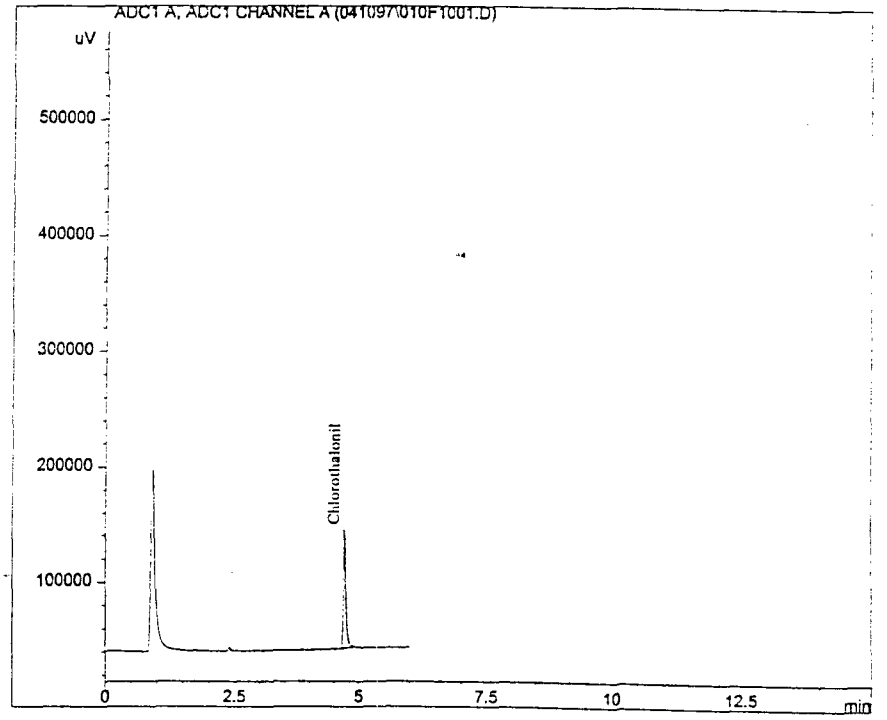
Analysis of Chlorothalonil

Run No.: 10

Sample No: CAL 971362 Spk C
Sample Info: Control Fortified at 25 µg, Final Volume = 10 mL
Dilution Factor = 100

Injected on: 4/10/97 8:44:05 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.704	Chlorothalonil	102343.3	369294.438

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 11: Dislodging Solution (Cauliflower Leaf Wash) Fortified with 125 µg Chlorothalonil

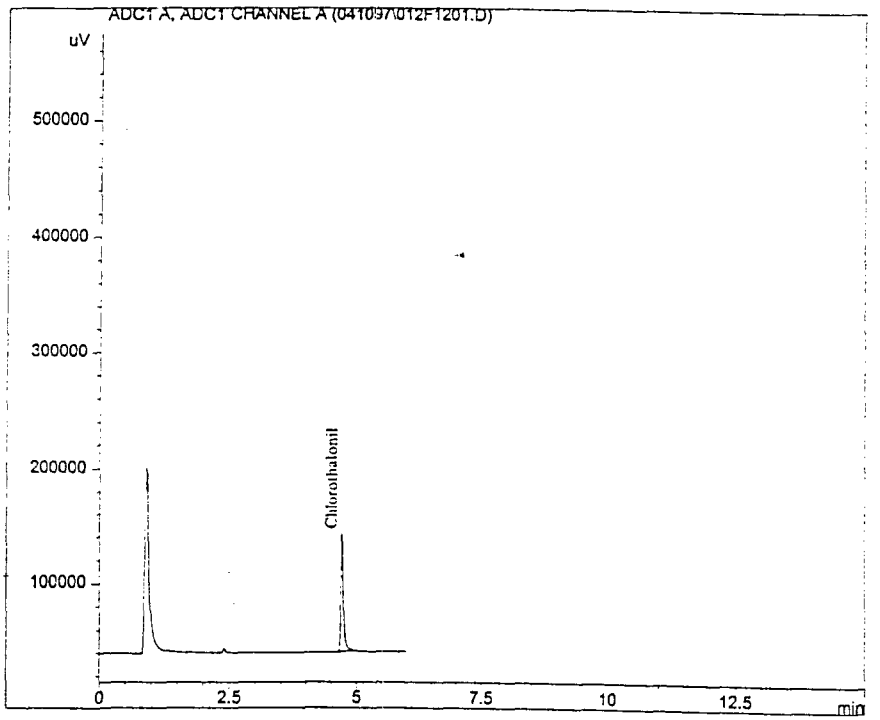
Analysis of Chlorothalonil

Run No.: 12

Sample No: CAL 971362 Spk E
Sample Info: Control Fortified at 125 µg, Final Volume = 10 mL
Dilution Factor = 500

Injected on: 4/10/97 9:19:36 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.706	Chlorothalonil	101771.3	374197.875

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

Figure 12: Spreadsheet, Dislodging Solution

Analytical Data and Recoveries for CAL Study # 017-01: Determination of Chlorothalonil in Foliar Dislodgeable Solution

Extraction Date: 4/09/97 **Analysis Date:** 4/10/97 **Matrix:** Aerosol OT-75 Cauliflower Leaf Wash

STANDARD CURVE:

Conc. (µg/mL)	Peak Height
0.10	385604
0.05	181846
0.01	37634
0.005	17627
0.10	412914
0.05	205575
0.01	39800
0.005	17136

Linear Calibration Equation: y = mx+b
m= 4006265
b= -2992
Correlation Coefficient = 0.9981

DATA:

CAL ID#	Client ID	Compound Found	Peak Height	Peak Height Corrected	µg/mL Compound Found	Final Volume (mL)	Dilution Factor	µg/Sample Found	µg Compound Added	Percent Recovery
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
971362 OT-75 Blk*	NA	Chlorothalonil	0	0	0.0000	10	10	0.0	na	na
971362 Blk (w/leaves)	NA	Chlorothalonil	0	0	0.0000	10	10	0.0	na	na
971362 Spk A	NA	Chlorothalonil	215367	215367	0.0545	10	10	5.45	5	109%
971362 Spk B	NA	Chlorothalonil	206796	206796	0.0524	10	10	5.24	5	105%
971362 Spk C	NA	Chlorothalonil	102343	102343	0.0263	10	100	26.3	25	105%
971362 Spk D	NA	Chlorothalonil	101667	101667	0.0261	10	500	131	125	104%
971362 Spk E	NA	Chlorothalonil	101771	101771	0.0261	10	500	131	125	105%

*(w/o leaves)

KF 1/28/99

Appendix A

Protocol and Protocol Amendments/Deviations

ARTF Protocol Number

ARF004

Sponsor/Testing Facility

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

Study Title

VALIDATION OF METHOD FOR THE ANALYSIS OF WORKER EXPOSURE AND REENTRY MATRICES FOR CHLOROTHALONIL

Testing Laboratory

Centre Analytical Laboratories
3048 Research Drive
State College, PA 16801
TE 814/231-8032

Testing Laboratory Study Number

017-01

Total No. of Pages : 8

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1.0 STUDY PURPOSE

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

2.0 GLP COMPLIANCE STATEMENT

This study will be conducted in compliance with Centre Analytical 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 Chromasorb 102, and facial/neck wipes that will be used in worker exposure monitoring during application of chlorothalonil to turf.

4.0 STUDY PERIOD

Proposed Experimental Start Date: January 1, 1997

Proposed Experimental Termination Date: April 1, 1997

5.0 STUDY SITE

Centre Analytical Laboratories
3048 Research Drive
State College, PA 16801
Phone 814/231-8032
Fax 814/231-1253

6.0 TEST/REFERENCE SUBSTANCE

Common Name: chlorothalonil
Chemical Name: tetrachloroisophthalonitrile
Lot Number: 2797-2601
Purity: 99.7%
CAS No.: 1897-456

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.

7.0 ANALYTICAL METHODS TO BE VALIDATED

1. Determination of Chlorothalonil in Dermal Dosimeters

2. Determination of Chlorothalonil in OVS Air Sampling Tubes with Chromosorb 102

3. Determination of Chlorothalonil in Handwash Solutions

4. Determination of Chlorothalonil 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 chlorothalonil 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

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:

a. A GLP compliance statement (40 CFR 160) signed by the Study Director.

b. A Centre Analytical Laboratories QAU statement giving dates of inspections and dates that findings were reported to the Study Director and Management.

c. A detailed description of each method validation.

d. Example calculations.

e. A summary of each method validation procedure and a summary of the recovery data in the format described in the STATISTICAL METHODS SECTION.

f. Representative chromatograms of control samples, fortified control samples and calibration standards.

g. A typical standard curve.

h. 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.

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

Study Director — Date: 1/29/97

Sponsor — Date: 1/10/97

Testing Laboratory Management — Date: 24-JAN-97

16.0 DISTRIBUTION LIST

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

Study Director / Julie Barton-Petit, Centre Analytical Laboratories

Testing Laboratory Management / Rick Grazzini, Centre Analytical Laboratories

Quality Assurance / Centre Analytical Laboratories

Quality Assurance / Agricultural Reentry Task Force (ARTF)

Agriculture Re-Entry Task Force
Protocol Amendment

Protocol Number: ARF004 Protocol Amendment No.: 1

Effective Date: April 1, 1997 CAL ID No. 017-001

I. Change/Add to Section **3.0**:

Cauliflower leaf disks will be included as a model matrix for dislogeable foliar residue (DFR) studies.

I. Reason for this Change/Addition

A DFR matrix was inadvertently omitted from the original protocol.

Approved by:

Julie B. Petit — 4/1/97
Julie B. Petit
Study Director
Date

David R Johnson — 4/8/97
David R. Johnson, Ph.D.
ARTF Technical Committee Manager
Sponsor Representative
Date

Agriculture Re-Entry Task Force
Protocol Amendment

Protocol Number: ARF004 Protocol Amendment No.: 2

Effective Date: April 10, 1997 CAL ID No. 017-001

I. Change/Add to Section **8.0, Paragraph 3**:

Fortification solution will be applied directly to the samples before extraction.

I. Reason for this Change/Addition

The method of administration of the test substance was inadvertently omitted from the original protocol.

II. Change/Add to Section **7.0**:

The four methods identified are Ricerca method 6445-95-0086-CR-001 for all matrices.

II. Reason for this Change/Addition

To more accurately identify the actual method to be validated.

III. Change/Add to Section **13.0**:

The protocol amendment form and protocol deviation form have not been finalized by the sponsor. The forms will be sent to the ARTF QAU when finalized.

III. Reason for this Change/Addition

The forms have not been finalized and therefore, were not attached to the protocol.

III. Change/Add to Section **Amendment No. 1** :

Aerosol OT-75 cauliflower leaf disk wash will be included as a matrix for validation.

III. Reason for this Change/Addition

To clarify the matrix being validated.

Approved by:

Julie B. Petit — 4/11/97

Julie B. Petit
Study Director
Date

David R. Johnson — 4/14/97

David R. Johnson, Ph.D.
ARTF Technical Committee Manager
Sponsor Representative
Date

Agriculture Re-Entry Task Force
Protocol Amendment

Protocol Number: ARF004 Protocol Amendment No.: 3

Effective Date: April 29, 1997 CAL ID No. 017-001

I. Change/Add to Section **Amendment No. 2, section I**:

Fortification solution will be applied directly to the samples by syringe before extraction.

I. Reason for this Change/Addition

Clarification of amendment no. 2.

II. Change/Add to Section **Amendment No. 2, section II**:

Only one method, Ricerca method 6445-95-0086-CR-001, is being validated. This method describes the procedures for extracting and analyzing all matrices used for this study.

II. Reason for this Change/Addition

Clarification of protocol section 7 and amendment no. 2.

III. Change/Add to Section **Amendment No. 2, section IV**:

Ricerca method 6445-95-0086-CR-001, Section "Handwash", was used to validate the Aerosol OT-75 cauliflower leaf disk wash.

III. Reason for this Change/Addition

Identification of the method of analysis.

IV. Change/Add to Section 3.0:

Full-sized worn outer dosimeters will be included in the test system. The method of analysis will follow Morse Laboratories, Inc. SOP# Meth-103 with some modifications. All modifications will be documented in the raw data for the study.

IV. Reason for this Change/Addition

Additional matrix to be validated.

Approved by:

Julie B. Petit — 5/9/97
Julie B. Petit
Study Director
Date

David R Johnson — 5/22/97
David R. Johnson, Ph.D.
ARTF Technical Committee Manager
Sponsor Representative
Date

Agriculture Re-Entry Task Force
Protocol Amendment

Protocol Number: ARF004 Protocol Amendment No.: 4

Effective Date: April 29, 1997 CAL ID No. 017-001

I. Change/Add to Section **section 16**:

The Study Director is Sharon Webster at Centre Analytical Laboratories.

I. Reason for this Change/Addition

Julie Burton Petit is no longer employed at Centre Analytical Laboratories.

II. Change/Add to Section **Amendment No. 3, section II**:

The Ricerca method 6445-95-0086-CR-001 was modified by CAL at the request of ARTF. As a result the following methods were also validated in this study: ARTF-003, and ARTF-004.

II. Reason for this Change/Addition

Clarification of protocol section 7 and amendment no. 3.

III. Change/Add to Section **Amendment No. 3, section IV**:

The Ricerca method 6445-95-0086-CR-001 was modified by CAL, in order to accommodate larger sized samples, at the request of ARTF. As a result the modifications were incorporated into method ARTF-001, also validated in this study.

III. Reason for this Change/Addition

Clarification of protocol section 7 and amendment no. 3.

To match above
DRJ 12/13/99

IV. Change/Add to Section **section 6.0**:

The lot number for chlorothalonil is SDS-2787-2601. The CAS No. is 1897-45-6.

IV. Reason for this Change/Addition

The lot number and CAS No. for chlorothalonil were listed incorrectly.

V. Change/Add to Section **section 4.0**:

The Proposed Experimental Termination Date is March, 1999.

V. Reason for this Change/Addition

The study was not completed within the specified timeframe.

VI. Change/Add to Section **section 8.0**:

The analytical methods ARTF-001, ARTF003, and ARTF-004 were written and validated at CAL.

VI. Reason for this Change/Addition

CAL was requested, by the ARTF, to write and validate these methods.

Approved by:

Sharon Webster — 3-19-99
Sharon Webster, Study Director — Date

David R Johnson — 4/3/99
David R. Johnson, Ph.D., ARTF Technical Committee Manager, Sponsor Representative — Date

Centre Analytical Laboratories, Inc.
3048 Research Drive State College, PA 16801
Phone: (814) 231-8032 Facsimile: (814) 231-1253

PROTOCOL/SOP/METHOD DEVIATION

Deviation Number: 1
Date of Occurrence: Entire Study

CAL Project Number: 017-001 Sponsor Study Number: ARF004

DESCRIPTION OF DEVIATION

Is this deviation a X PROTOCOL, or ____SOP, or ____METHOD deviation?

Section 9.0 SAMPLE DESCRIPTION:

1. Section 9.0 indicates that an ARTF sample identification number must be included in the documentation of samples, however, no sample numbers were assigned by the ARTF. Therefore, only CAL ID numbers were included in the documentation of samples.
2. The handwash solution (Aerosol OT®) was prepared in-house and was not given a CAL ID number at the time of preparation.

ACTIONS TAKEN
i.e., amendment issued, SOP revision, etc...

1. Protocol deviation issued.
2. The solution was logged in and assigned a CAL ID number which was then added to the data. Protocol deviation issued.

Recorded By/Date: Julie B. Petit / 4/3/97

IMPACT ON THE STUDY

There are no negative effects resulting from this deviation.

Julie B. Petit 4/3/97
Study Director Signature Date

CAL QAU Review ST 4/3/97

May 1993/1

Acknowledged
David Johnson
Sponsor Representative

Centre Analytical Laboratories, Inc.
3048 Research Drive State College, PA 16801
Phone: (814) 231-8032 Fax: (814) 231-1253 or (814) 231-1580

PROTOCOL DEVIATION

Deviation Number: 2
Date of Occurrence: Entire Study

CAL Study Number: 017-01 Sponsor Study Number: ARF004

DESCRIPTION OF DEVIATION

Section 8.0 #4 of the protocol indicates that for the validation to be considered acceptable the mean minus two standard deviations must be greater than or equal to 70%, and the mean plus two standard deviations must be less than or equal to 120%. Five results were outside this range.

ACTIONS TAKEN

i.e., amendment issued, SOP revision, etc...

The method was deemed to be acceptable, as all recoveries obtained were within EPA's acceptability criteria of the mean recovery being between 70-120% with a standard deviation of ≤ 20%. A protocol deviation was issued

Recorded By/Date: Kim Folmar 1/28/99

IMPACT ON THE STUDY

There are no negative effects resulting from this deviation

Sharon Webster 3-19-99
Study Director Signature Date

CAL QAU Review ST 2/4/99

February 12, 1998/2

Centre Analytical Laboratories, Inc.
3048 Research Drive State College, PA 16801
Phone: (814) 231-8032 Fax: (814) 231-1253 or (814) 231-1580

PROTOCOL DEVIATION

Deviation Number: 3
Date of Occurrence: 04/09/97 [1], 06/05/97 [2]

CAL Study Number: 017-01 Sponsor Study Number: ARF004

DESCRIPTION OF DEVIATION

1. Section 8.0 #2 of the protocol indicates that two sets of samples will be run for each method validation and that each set will include three levels of spikes in duplicate. There was only one set Foliar Dislodgeable Solution (Aerosol OT-75 Cauliflower Leaf Wash) which included two 5 µg spikes, one 25 µg spike and two 125 µg spikes.

2. Section 8.0 #2 of the protocol indicates that two sets of samples will be run for each method validation and that each set will include three levels of spikes in duplicate. There was only one set of Full-Sized Worn Outer Dosimeters which included 6 spikes at the LOQ.

ACTIONS TAKEN

i.e., amendment issued, SOP revision, etc...

1. and 2. Protocol Deviation was issued.

Recorded By/Date: Sharon Webster 3-3-99

IMPACT ON THE STUDY

1. and 2. There are less data points for these matrices, however this poses no significant impact on the study.

Sharon Webster 3-19-99
Study Director Signature Date

CAL QAU Review ST 3/10/99

Appendix B

Analytical Methods

INTRODUCTION

Analytical method 6445-95-0086-CR-001, developed by Ricerca, Inc., was modified by Centre Analytical Laboratories, Inc., at the request of the Agricultural Re-entry Task Force (ARTF). The enclosed method, ARTF-001, is the revised method from Centre Analytical Laboratories, Inc.

DETERMINATION OF CHLOROTHALONIL IN DERMAL DOSIMETERS

Analytical Method: ARTF-001

Authors:
Julie B. Petit and M. Michael Arjmand
CENTRE ANALYTICAL LABORATORIES, INC.
State College, Pennsylvania
Telephone: 814/231-8032
Fax: 814/231-1580

Date of Issue: October 17, 1997

1.0 PRINCIPLE

Tetrachloroisophthalonitrile (common name - chlorothalonil) is extracted from dermal cotton dosimeter sections with hexane. An aliquot of the extract is subjected to Florisil column chromatography and analyzed by electron-capture gas chromatography. The method is applicable to samples containing residue levels ranging from 1 µg to 5000 µg. The limit of quantitation (LOQ) is 1 µg.

2.0 EQUIVALENCE STATEMENT

During the conduct of this analysis, equivalent apparatus, solvents, glassware, or techniques (such as sample concentration) may be substituted for those specified in this method, except where otherwise noted. Use of equivalent techniques or equipment will be documented, when appropriate.

3.0 APPARATUS AND EQUIPMENT

Jars: 4-L with Teflon® lined caps, VWR, Catalog # 16196-284.

Filter paper: grade 415, 25 cm-diameter, VWR, Catalog # 28320-201.

Gas Chromatograph: Hewlett-Packard (HP) gas chromatograph Model 5890 Series II equipped with a ^{63}Ni electron capture detector, HP Model 7673 autosampler and HP ChemStation data system.

Laboratory Platform Shaker (reciprocating): Eberbach Model 6000. (Eberbach Corp., Ann Arbor, MI)

Rotary Evaporator: Büchi rotovapor R-114, Büchi water bath B-480, Büchi vacobox B-177, WK 500 Lauda recirculator, Brinkman Instruments, Inc.

Standard laboratory glassware: beakers, flasks, separatory funnels, etc.

Outer Dosimeter (Shirts): 100% cotton, white long-sleeved shirt cut as described in SOP No. ARTF-8.D. (Attachment 1), (Universal Overall).

Outer Dosimeter (Pants): 100% cotton, long pants cut as described in SOP No. ARTF-8.D. (Attachment 1), (Universal Overall).

Inner Dosimeter: 100% cotton, long underwear garment cut as described in SOP No. ARTF-8.E. (Attachment 2), (The Original Arizona Jean Company).

4.0 REAGENTS AND MATERIALS

Chlorothalonil:	Tetrachloroisophthalonitrile.
Ether:	Residue grade or equivalent
Ethyl acetate:	Residue grade or equivalent
Florisil:	Residue grade or equivalent
Hexane:	Residue grade or equivalent
Nitrogen (gas):	High purity
Sodium sulfate (Na_2SO_4):	Residue grade or equivalent, anhydrous

5.0 REAGENTS AND MATERIALS TO BE PREPARED

Solution	Reagent Volumes[1]
10% Ether:Hexane	Ether-100 mL, Hexane-900 mL
10 % Ethyl Acetate:Hexane	Ethyl Acetate-100 mL, Hexane-900 mL

[1]The absolute volumes of the reagents may be varied by the analyst provided the correct proportions are maintained.

6.0 SAMPLE PREPARATION

Inner body dosimeters (consisting of a one-piece, 100% cotton, white, long underwear garment) and outer body dosimeters (consisting of one white, 100% cotton, long-sleeved shirt and one pair of white, 100% cotton pants) are each divided into sections (representing specific body regions) as described in SOP No. ARTF-8.D and ARTF-8.E. Each section represents one analytical sample.

7.0 STANDARD PREPARATION

7.1 Stock Solution:

Correcting for purity, prepare a stock standard solution of chlorothalonil by weighing an appropriate amount into a volumetric flask, dissolving with ethyl acetate, and diluting to the mark. For example, weigh 0.1 g of chlorothalonil into a 100-mL volumetric flask, dissolve in ethyl acetate, and dilute to the mark with ethyl acetate. The concentration of the stock solution is approximately 1000 µg/mL. The stock solution is stored frozen (≤ -10°C) and remade at one year intervals.

If necessary, prepare serial dilutions from the stock solution of chlorothalonil in other solvents (such as toluene) for GC analysis.

7.2 Fortification Solutions:

Dilute the stock solution and/or the appropriate fortification solution(s) with ethyl acetate to generate 500-µg/mL, 50-µg/mL, and 10-µg/mL fortification solutions. Other concentrations may be prepared as needed. Suggested preparation is as follows:

Standard Solution Concentration (µg/mL)	Aliquot (mL)	Final Volume (mL)	Final Concentration (µg/mL)
5000	25	250	500
5000	1	100	50
50	20	100	10

7.3 Instrument Calibration Solutions:

Dilute the appropriate fortification/calibration solution(s) with ethyl acetate to generate instrumentation (calibration) solutions in a range appropriate for the expected residue levels. Suggested preparation is as follows:

Standard Solution Concentration (µg/mL)	Aliquot (mL)	Final Volume (mL)	Final Concentration (µg/mL)
10	1	100	0.1
0.1	50	100	0.05
0.1	10	100	0.01
0.01	50	100	0.005
0.005	50	100	0.0025

All fortification and calibration standards are stored frozen (≤ -10°C) and should be remade at one year intervals.

8.0 FORTIFICATION

8.1 Laboratory Fortifications:

Prepare laboratory fortifications by applying the appropriate amount of fortification solution to the sample via Hamilton syringe or equivalent. Distribute the solution evenly over the dosimeter and allow the solvents to evaporate for approximately 10 minutes prior to extraction.

9.0 SAMPLE EXTRACTION AND CLEANUP PROCEDURES

9.1 Extraction:

1. Prepare dosimeter samples by cutting whole dosimeters into sections as described in SOP No. ARTF-8.D and ARTF-8.E. Place each dosimeter section into a separate 4-L jar. Fortify the appropriate samples and allow to dry for at least 10 minutes before placing into the jar. Add a total extraction volume of 2 L - 2.5 L of hexane to the jar. Cap the jar tightly and shake for ~30 minutes on a platform shaker (placing the jar on its side). After shaking, store samples at room temperature for at least 8 hours. Agitate samples before proceeding to step 2.

   NOTE: Rinse the inner surface of the foil wrapping for field dosimeter samples with at least 50 mL of extraction solvent, which is a part of the total extraction volume.

2. Decant approximately 150 mL of the extract through filter paper. Discard the first ~70 mL and collect the next ~80 mL into a wide mouth jar. Rotary-evaporate a 20 mL - 25 mL aliquot of the filtered extract to approximately 5 mL.

   NOTE: Record both the total extraction volume and the aliquot volume for each sample so that an accurate extraction dilution factor may be used for recovery calculations.

9.2 Florisil Column Cleanup:

1. Pack a glass chromatographic column, 300-mm x 11-mm, with 3 g of Florisil and top with ~1 cm of anhydrous sodium sulfate. Pre-rinse the column with 15 mL of 10% ethyl acetate:hexane, followed by 15 mL of 10% ether:hexane, followed by 15 mL of hexane. Discard these rinses.

2. Add the ~ 5 mL sample extract from Step 9.1.2 to the column. Just as the sample level reaches the top of the sodium sulfate, rinse the column with an additional 10 mL of hexane, followed by 15 mL of 10% ether:hexane. Discard these rinses.

3. Elute the column with 60 mL of 10% ethyl acetate:hexane. Collect the eluate in a round-bottom flask.

9.3 Final Volume:

1. Rotary-evaporate the sample to approximately 0.5 mL. Concentrate the remainder of the sample to dryness under nitrogen and redissolve in 2 mL of ethyl acetate. Dilute samples with ethyl acetate, if necessary.

10.0 QUANTITATION BY ELECTRON CAPTURE GAS CHROMATOGRAPHY

The following columns and conditions are suggested and may be modified, within reason, to attain optimum chromatography.

Analytical conditions:

Instrument:	Hewlett Packard Gas Chromatograph, model 5890 Series II
Column:	RTX-5, fused silica capillary, 30 m x 0.53-mm i.d., 0.5-µm film thickness (available from Restek, Bellefonte, PA 16823)
Detector:	^{63}Ni Electron Capture Detector
Temperature:	160 °C for 1 min then 20 °C/min to 240 °C. Hold at 240 °C for 2 min, then 25 °C/min to 270 °C, hold for 6 min
Injection Port Temperature:	270 °C
Detector Temperature:	300 °C
Carrier Gas:	High purity helium, 8 mL/min
Make-up Gas:	High purity nitrogen, 30 mL/min
Injection Volume:	1 µL
Approximate Retention Time:	4.5 minutes
Total Run Time:	~ 15 minutes

11.0 CALIBRATION

Calibrate the gas chromatograph by injecting a minimum of four standard solutions in the concentration range of 0.0025 µg/mL to 0.1 µg/mL. Prepare a calibration curve by plotting standard concentration versus response. This calibration curve also serves as the standard curve used for calculation purposes.

12.0 CALCULATIONS

12.1 Calculations for instrumental analysis are conducted using Microsoft Excel® software to create a standard curve based on linear regression. These regression functions are used to calculate a best fit line (from a set of standard concentrations

in µg/mL versus peak response) and to determine concentration of the analyte found during sample analysis from the calculated best fit line.

The equation used for the least squares fit is:

$y = mx + b$

Where,

y = peak response (height or area)
x = µg/mL found
m = slope
b = y-intercept

12.2 The amount of chlorothalonil measured in each dosimeter is calculated according to the following equation:

$$\mu g/\text{dosimeter} = \frac{(\mu g/mL) \times (mL\ extr.\ solvent) \times (mL\ final\ volume) \times (dilution\ factor)}{(\text{one dosimeter section}) \times (mL\ aliquot)}$$

Where,

µg/dosimeter	=	total µg of analyte present per section of sample analyzed
µg/mL	=	concentration of analyte derived from the standard curve based on peak response from the sample injected utilizing the linear regression equation of $y = mx + b$
mL extr. solvent	=	extraction solvent volume (2 L-2.5L)
mL aliquot	=	volume of sample extract taken from initial extraction (20 mL-25mL)
one dosimeter section	=	amount of sample taken through the extraction process
mL final volume	=	volume of final extract submitted to instrumentation (2 mL)
dilution factor	=	dilution of sample extract required to produce an analyte response within the standard curve range

12.3 The percent recovery for fortified control samples is calculated as follows:

$$\% \text{ Recovery} = \frac{\mu g/\text{dosimeter found in fortified control}}{\mu g/\text{dosimeter added to fortified control}} \times 100$$

13.0 REFERENCES

Ricerca, Inc. Report / SDS-2787, 6445-95-0086-CR-001

APPENDIX I

Recoveries for Chlorothalonil in Dermal Dosimeters

Analytical Data and Recoveries for CAL Study # 017-01:
Determination of Chlorothalonil in Whole Body Dermal Dosimeters

Extraction Date: 6/5/97 **Analysis Date: 6/13-14/97** **Matrix: Whole Body Dermal Dosimeters (Outers-shirts/pants)**

STANDARD CURVE:

Conc. (µg/mL)	Peak Height
0.0025	3737.1
0.005	8603.0
0.01	18187.8
0.05	116985.9
0.0025	4832.1
0.005	11163.8
0.01	21116.9
0.05	135716.2

Linear Calibration Equation: y = mx+b
m= 2594387
b= -3737
Correlation Coefficient = 0.9950

DATA:

CAL ID#	Client ID	Compound Found	Peak Height	µg/mL Compound Found	Extraction Volume (mL)	Aliquot Volume (mL)	Final Volume (mL)	Dilution Factor	µg/Dosimeter Found	µg Compound Added	Percent Recovery
Solvent Blank	NA	Chlorothalonil	0.0	0.0000	2000	20	2	1	0.0	na	na
Solvent Blank	NA	Chlorothalonil	0.0	0.0000	2000	20	2	1	0.0	na	na
970217 Blk	NA	Chlorothalonil	0.0	0.0000	2000	20	2	1	0.0	na	na
972618 S-F	NA	Chlorothalonil	8738	0.0048	2000	20	2	1	0.962	1	96%
972168 S-B	NA	Chlorothalonil	7377	0.0043	2000	20	2	1	0.857	1	86%
972168 S-U-S	NA	Chlorothalonil	7458	0.0043	2000	20	2	1	0.863	1	86%
972168 S-L-S	NA	Chlorothalonil	8463	0.0047	2000	20	2	1	0.941	1	94%
972169 P-T	NA	Chlorothalonil	9601	0.0051	2000	20	2	1	1.028	1	103%
972169 P-B	NA	Chlorothalonil	9363	0.0050	2000	20	2	1	1.010	1	101%
										Average (n=6):	**94%**
										Standard Deviation:	**7.2%**

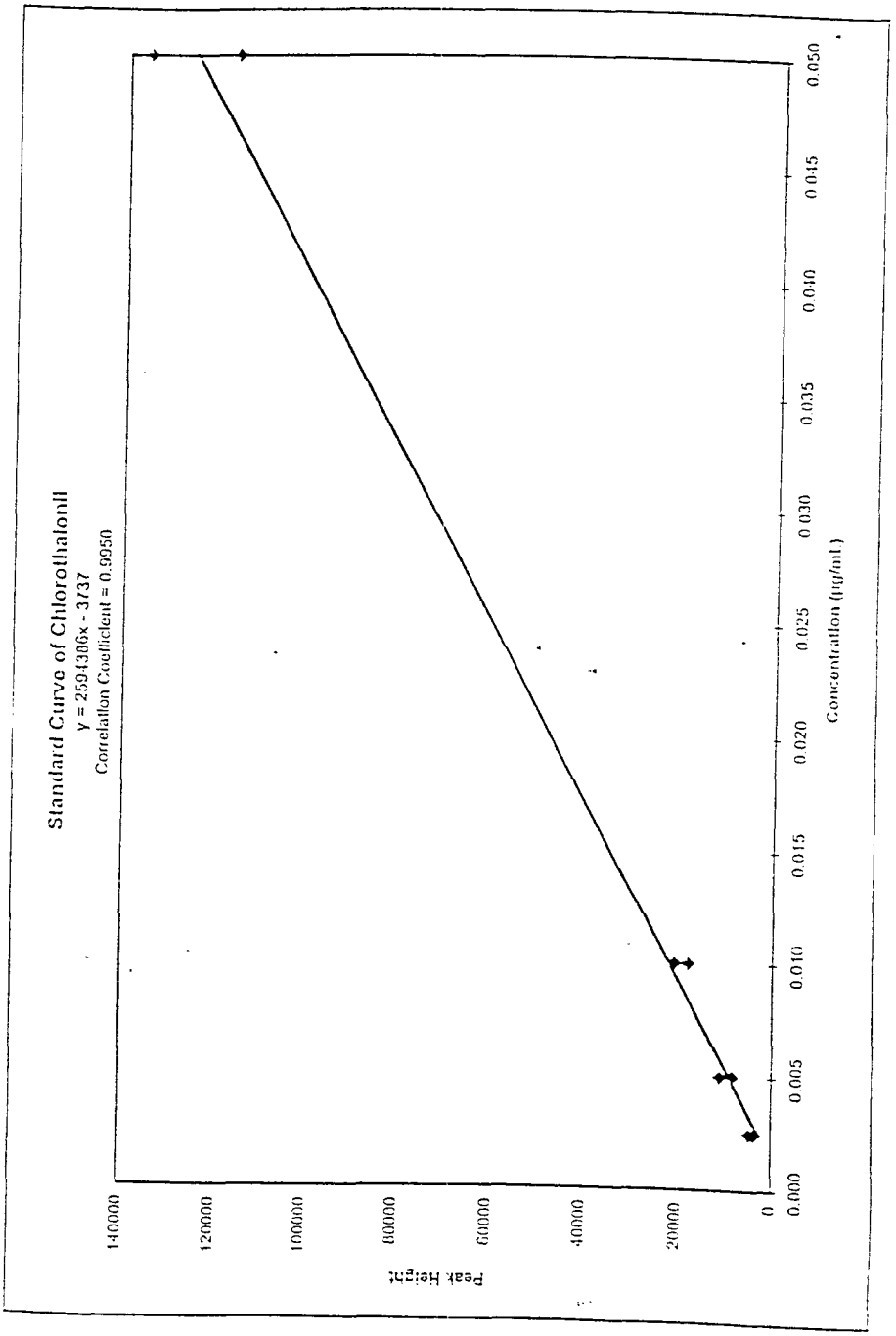
[1] S-F = Shirt-Front Torso Section
[2] S-B = Shirt-Back Torso Section
[3] S-U-S = Shirt-Upper Sleeve
[4] S-L-S = Shirt-Lower Sleeve
[5] P-T = Pant-Top (Upper leg)
[6] P-B = Pant-Bottom (Lower leg)

APPENDIX II

Calibration Curve and Example Chromatograms

Analysis Date: 6/13/97

CAL Study No. 017-01



Extraction Date: 6/05/97

ARTF Study No. ARF004

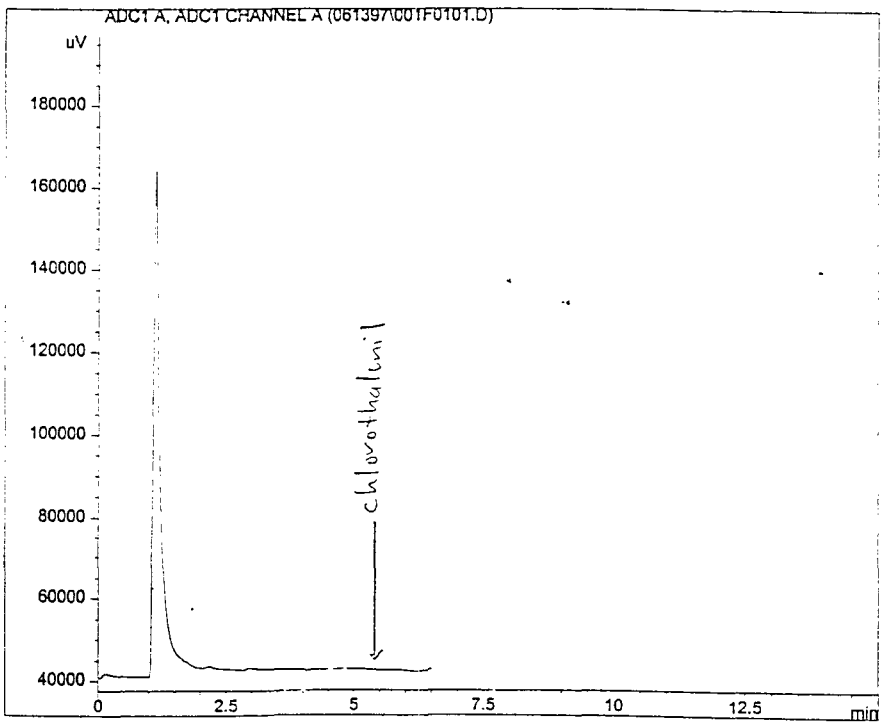
Analysis of Chlorothalonil

Run No.: 1

Sample No: NA
Sample Info: Solvent Blank

Injected on: 6/13/97 7:35:34 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

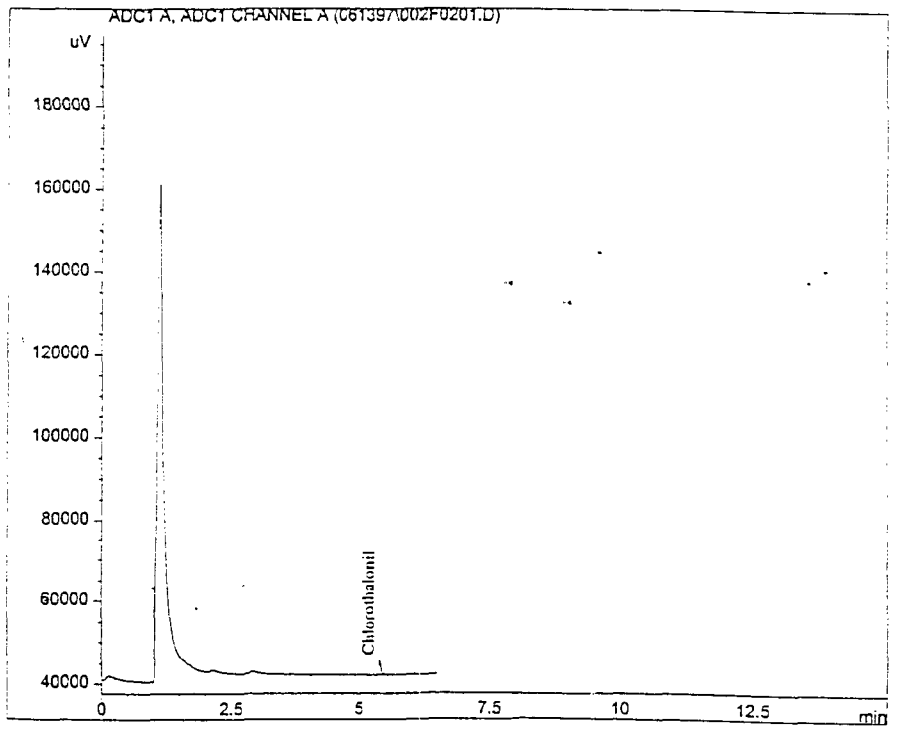
Analysis of Chlorothalonil

Run No.: 2

Sample No: NA
Sample Info: 0.0025 µg/mL Standard, ~~C060297-7~~ C043097-1 8-21-97

Injected on: 6/13/97 7:53:09 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.401	Chlorothalonil	3737.1	12910.548

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

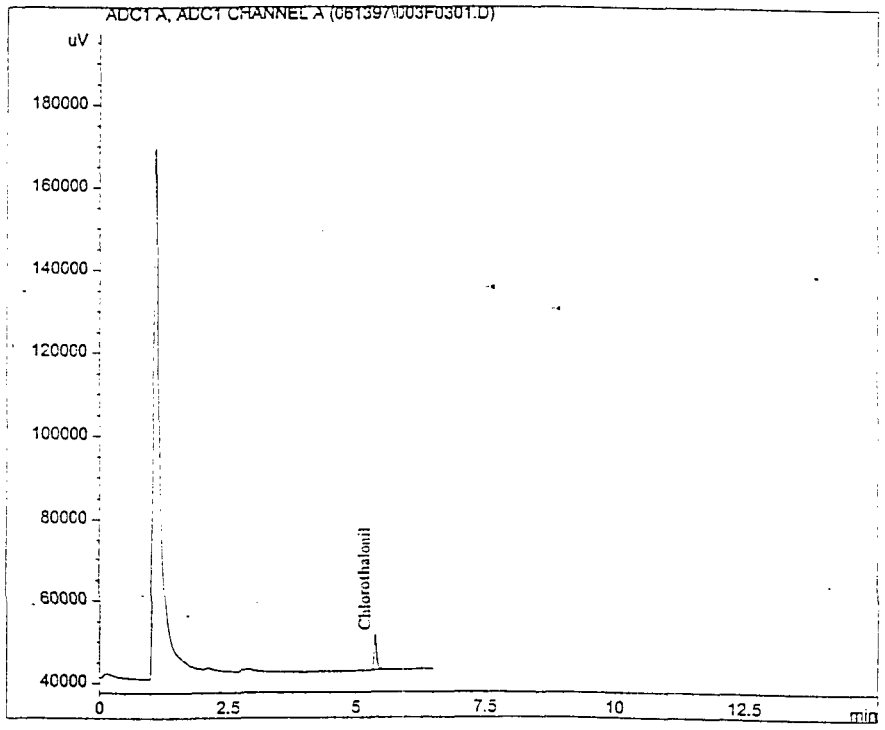
Analysis of Chlorothalonil

Run No.: 3

Sample No: NA
Sample Info: 0.005 µg/mL Standard, ~~C060297-6~~ C021097-4 8-21-97

Injected on: 6/13/97 8:10:47 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.367	Chlorothalonil	8603.0	31119.275

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

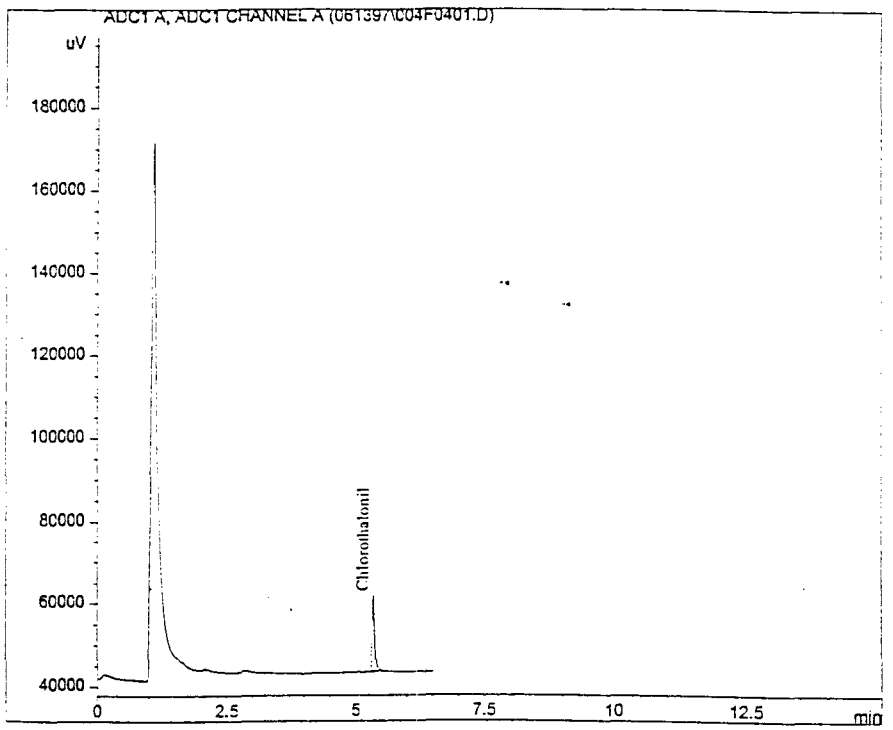
Analysis of Chlorothalonil

Run No.: 4

Sample No: NA
Sample Info: 0.01 µg/mL Standard, ~~C060297-5~~ C021097-3 8-21-97

Injected on: 6/13/97 8:28:22 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.339	Chlorothalonil	18187.8	67116.758

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

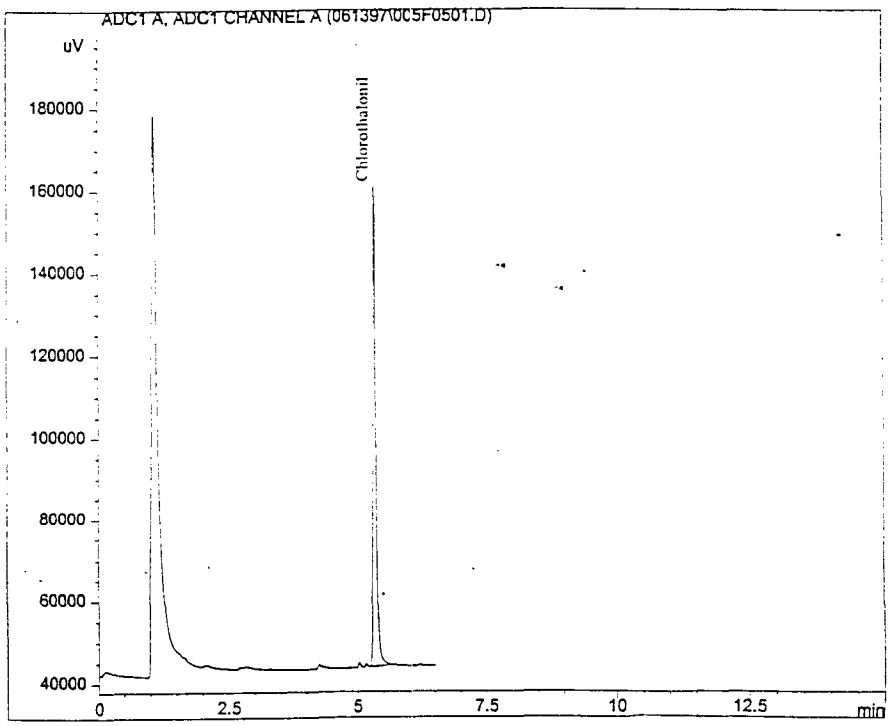
Analysis of Chlorothalonil

Run No.: 5

Sample No: NA
Sample Info: 0.05 µg/mL Standard, ~~C060297-4~~ C021097-2 ~~L043097-1~~ 8-21-97

Injected on: 6/13/97 8:46:00 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.923	Chlorothalonil	116985.9	471808.844

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

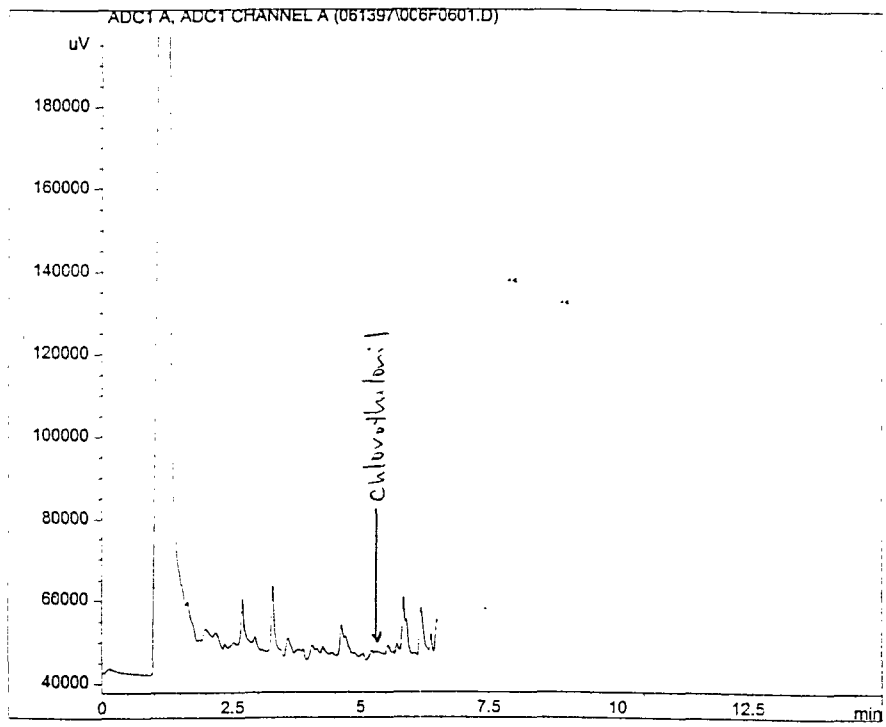
Analysis of Chlorothalonil

Run No.: 6

Sample No: CAL 970217 Blk
Sample Info: Control, Final Volume = 2 mL

Injected on: 6/13/97 9:03:38 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

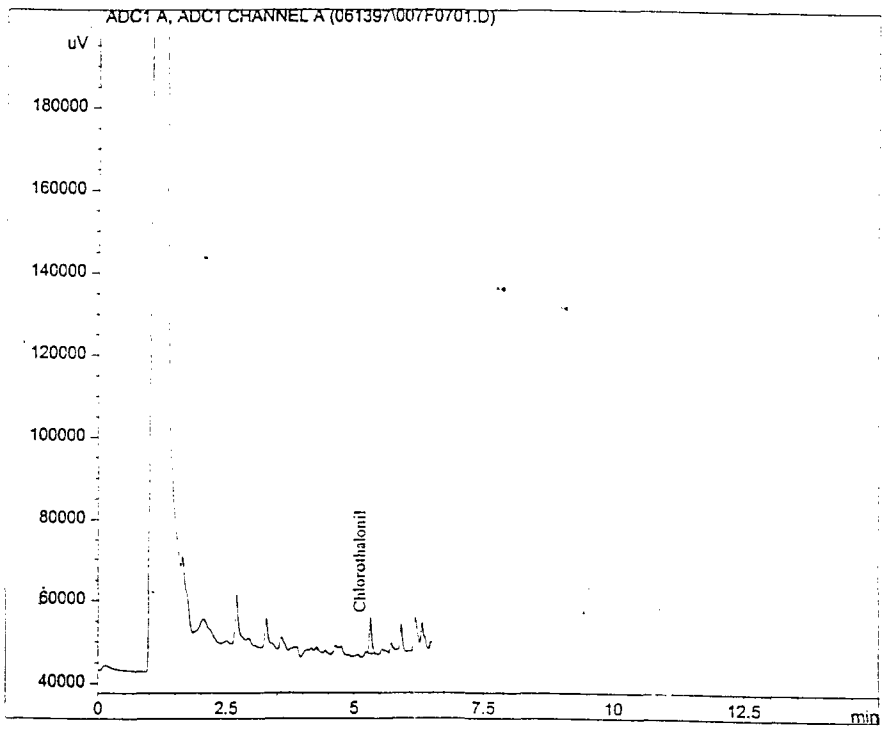
Analysis of Chlorothalonil

Run No.: 7

Sample No: CAL 972168 S-F
Sample Info: Fortified at 1 µg, Final Volume = 2 mL

Injected on: 6/13/97 9:21:16 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.307	Chlorothalonil	8738.1	30089.127

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

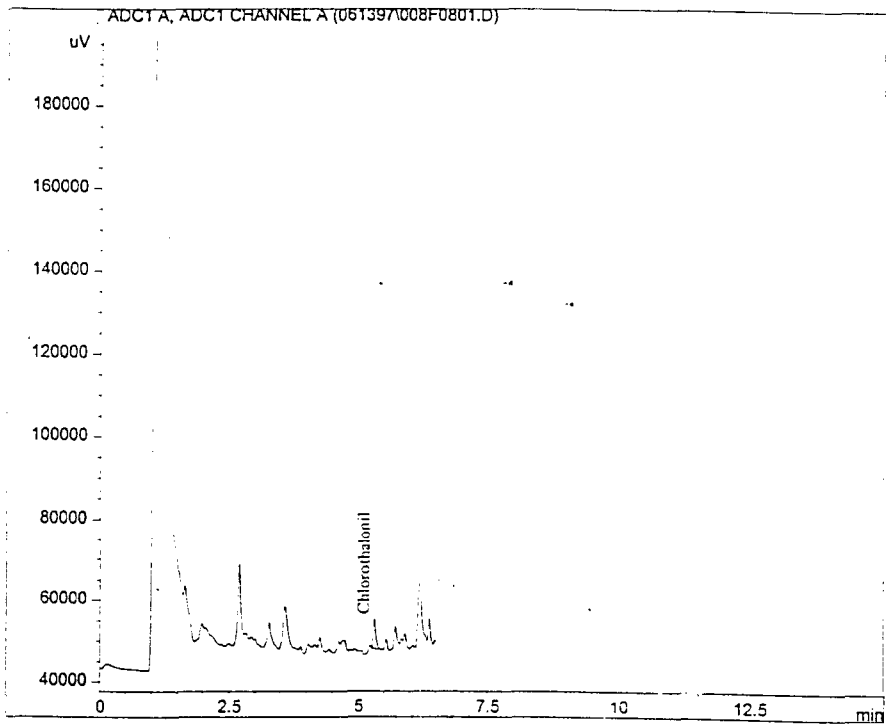
Analysis of Chlorothalonil

Run No.: 8

Sample No: CAL 972168 S-B
Sample Info: Fortified at 1 µg, Final Volume = 2 mL

Injected on: 6/13/97 9:38:52 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.305	Chlorothalonil	7376.7	25799.695

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

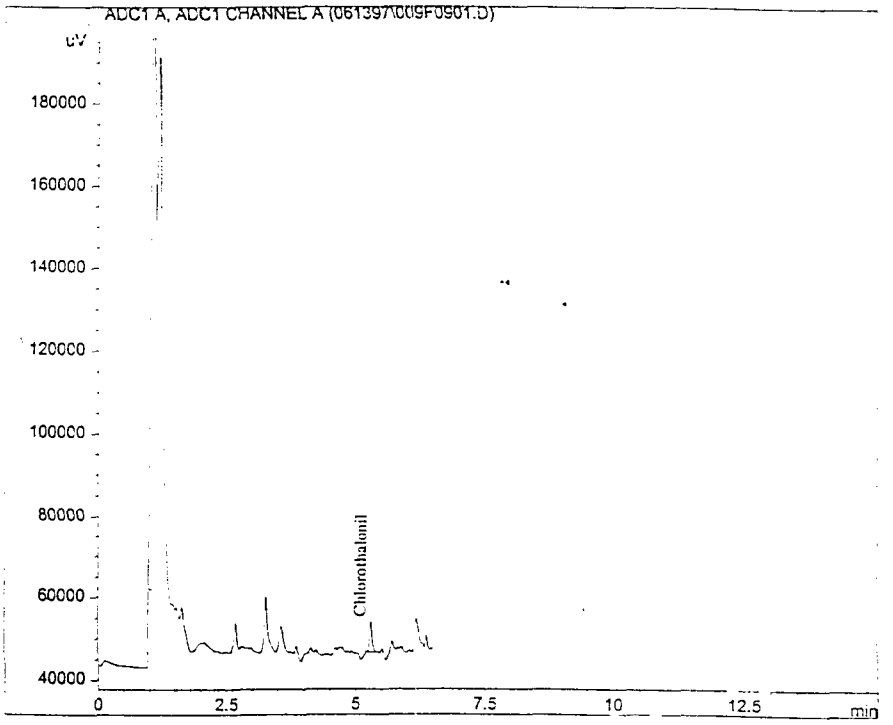
Analysis of Chlorothalonil

Run No.: 9

Sample No: CAL 972168 S-U-S
Sample Info: Fortified at 1 µg, Final Volume = 2 mL

Injected on: 6/13/97 9:56:30 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.304	Chlorothalonil	7458.3	25588.404

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

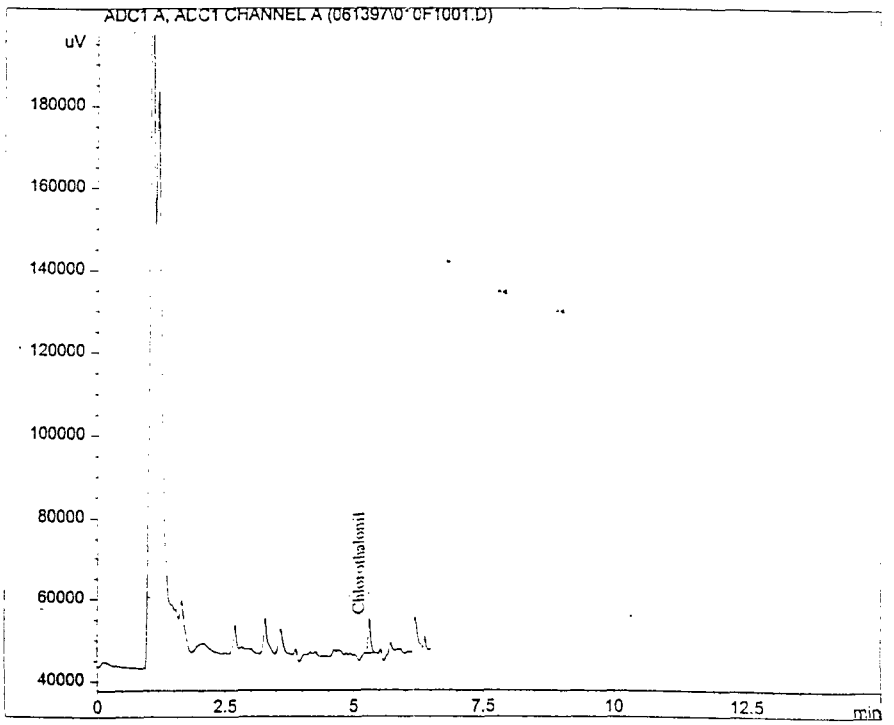
Analysis of Chlorothalonil

Run No.: 10

Sample No: CAL 972168 S-L-S
Sample Info: Fortified at 1 µg, Final Volume = 2 mL

Injected on: 6/13/97 10:14:07 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.306	Chlorothalonil	8462.9	29508.584

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

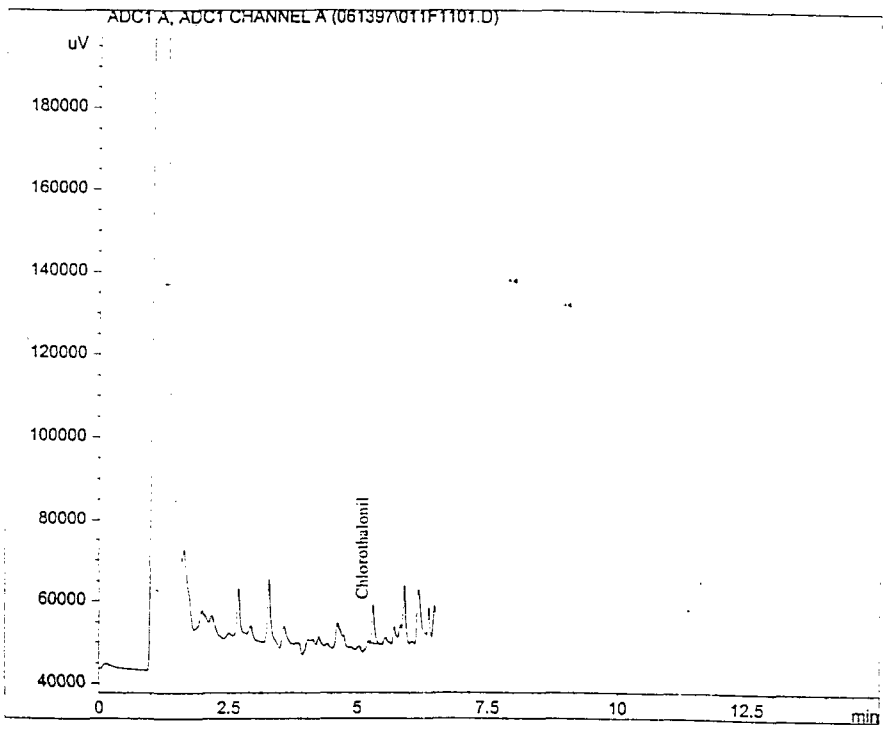
Analysis of Chlorothalonil

Run No.: 11

Sample No: CAL 972169 P-T
Sample Info: Fortified at 1 µg, Final Volume = 2 mL

Injected on: 6/13/97 10:31:46 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.303	Chlorothalonil	9600.7	34862.426

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

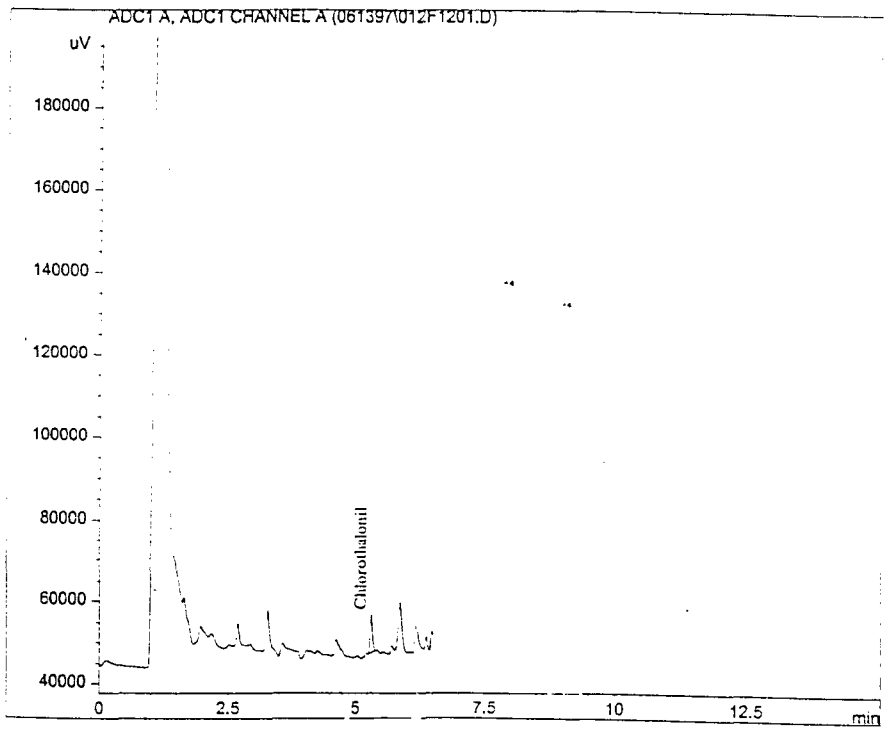
Analysis of Chlorothalonil

Run No.: 12

Sample No: CAL 972169 P-B
Sample Info: Fortified at 1 µg, Final Volume = 2 mL

Injected on: 6/13/97 10:49:22 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.301	Chlorothalonil	9362.6	30926.752

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

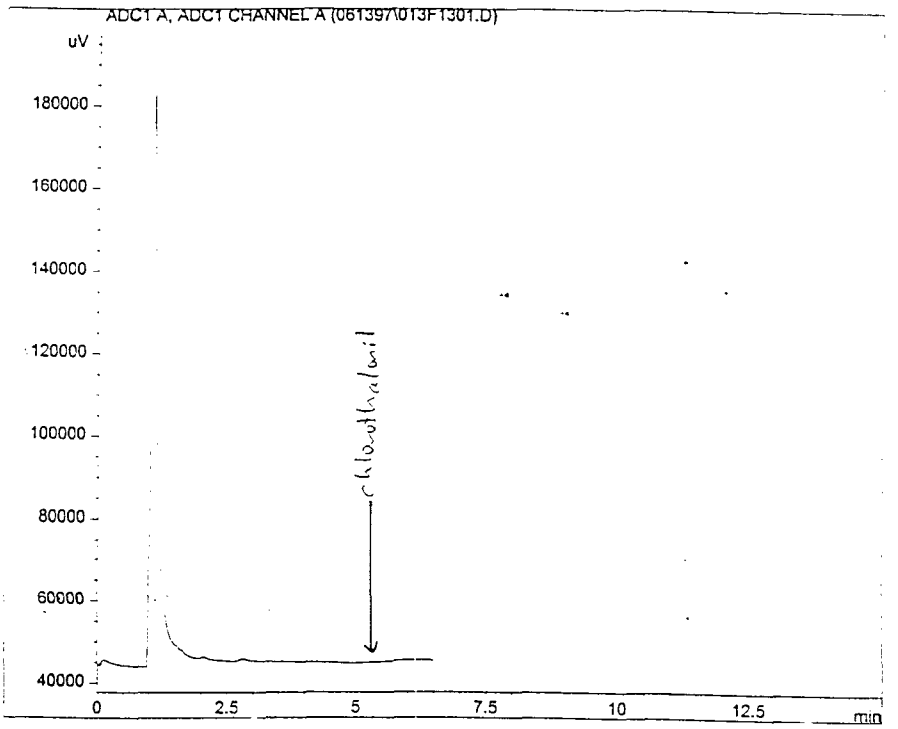
Analysis of Chlorothalonil

Run No.: 13

Sample No: NA
Sample Info: Solvent Blank

Injected on: 6/13/97 11:06:59 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

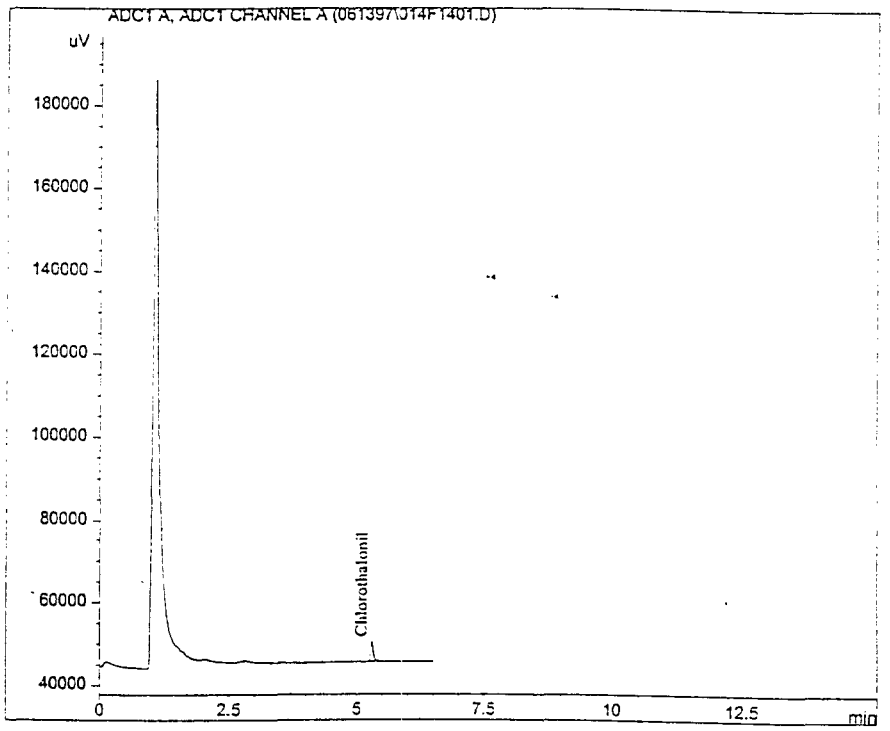
Analysis of Chlorothalonil

Run No.: 14

Sample No: NA C040397-1
Sample Info: 0.0025 µg/mL Standard, ~~C060297-7~~ 5-01-97

Injected on: 6/13/97 11:24:32 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.296	Chlorothalonil	4832.1	16862.094

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

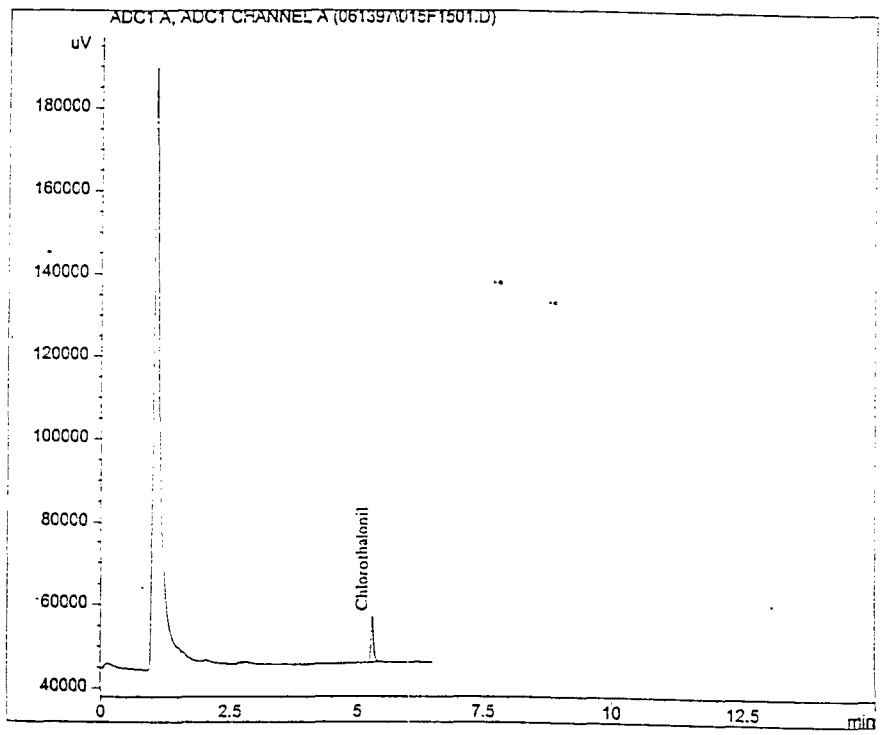
Analysis of Chlorothalonil

Run No.: 15

Sample No: NA
Sample Info: 0.005 µg/mL Standard, ~~C060297-6~~ C0 ⊃ 1097-4 8-21-97

Injected on: 6/13/97 11:42:10 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.295	Chlorothalonil	11163.8	40609.289

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

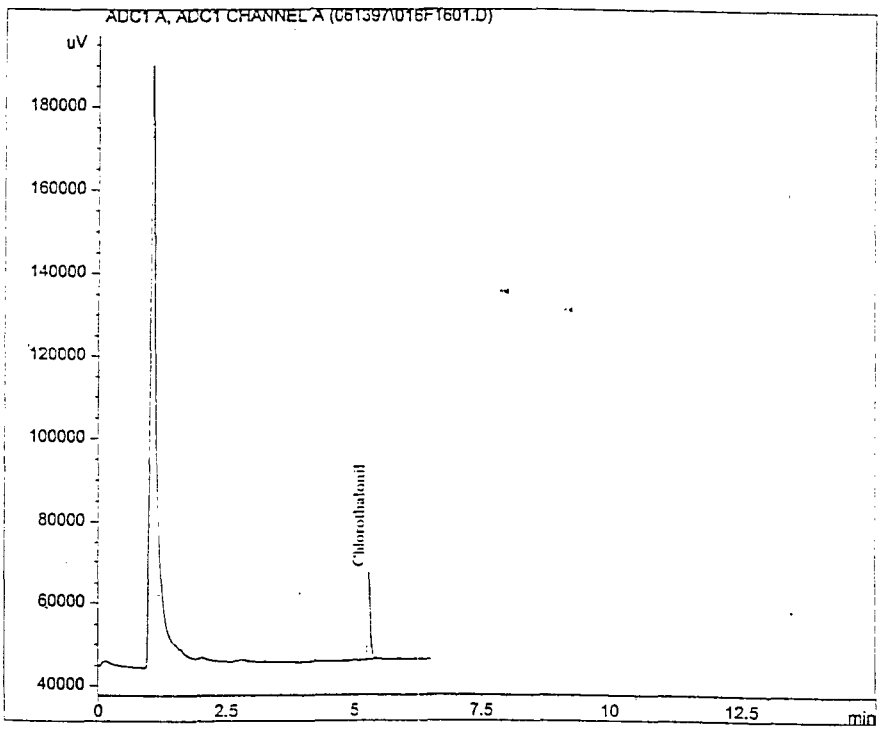
Analysis of Chlorothalonil

Run No.: 16

Sample No: NA C021097-3
Sample Info: 0.01 µg/mL Standard, ~~C060297-5~~ RESW 8-21-97

Injected on: 6/13/97 11:59:48 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.293	Chlorothalonil	21116.9	79227.695

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

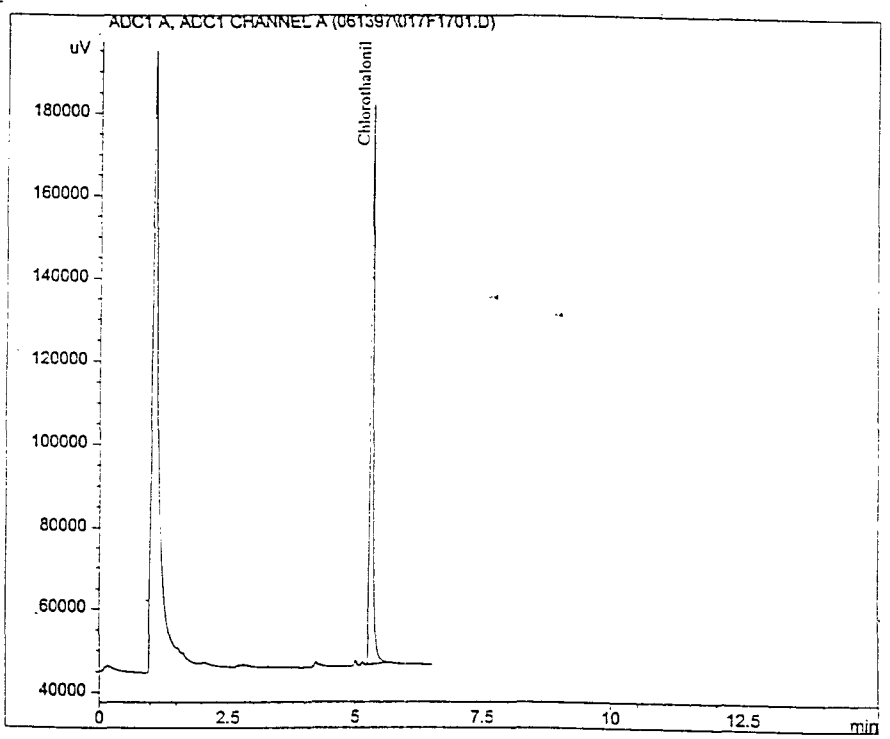
Analysis of Chlorothalonil

Run No.: 17

Sample No: NA
Sample Info: 0.05 µg/mL Standard, ~~C060297-4~~ C021097-2 RE SW 8-21-97

Injected on: 6/14/97 12:17:24 AM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
5.292	Chlorothalonil	135716.2	552534.063

CAL Study Number: 017-01
ARTF Study Number: ARF004

Operator: Julie B. Petit

Attachment 1

ARTF-8D/0 Standard Operating Procedure

ARTF-8D/0
Standard Operating Procedure

Section D: Whole Body Sampling - Outer Dosimeters
Chapter 8: MATRIX SAMPLES
Effective Date: June 6, 1997

David R Johnson APPROVAL	6/6/97 DATE
R. Chester APPROVAL	25th June 1997 DATE

1.0 PURPOSE AND SCOPE

1.1 This Standard Operating Procedure (SOP) provides a description of procedures for collecting pesticide residues from whole body dosimeters worn by workers (test subjects) during the Agricultural Reentry Task Force (ARTF) exposure studies.

1.2 The outer dosimeter will be representative of a worker's normal, outer work clothing. The outer dosimeter will be worn directly over the inner dosimeter. Both dosimeters will be collected in the same manner to measure potential exposure to pesticide residues.

2.0 MATERIALS REQUIRED

2.1 The following materials are required for using and collecting whole body outer dosimeter samples from each worker/replicate:

a. 100% cotton long-sleeved work shirt

b. 100% cotton pants

c. Scissors

d. Cleaning solutions (*i.e.*, alcohol (methanol, isopropanol), alcohol/water mixture, acetone, etc.)

e. Heat sealable or other suitable sample bags

f. Aluminum foil wrap

g. Heat sealer, if appropriate

h. Disposable gloves (*i.e.*, latex)

3.0 Use of Whole Body Dosimeter

3.1 The test subject(s) will be given clean, new outer dosimeters before initiation of each study replicate. The workers will be allowed to change in a clean "privacy" area. Disposable gloves should be worn, when handling the dosimeter, by the test subject and field personnel to minimize contamination.

3.2 Care should be taken to provide clothing of adequate fit. Shirts should be tucked into the pants during the exposure replicate. The inner dosimeter arm and pant cuffs should not extend beyond the outer dosimeter cuffs (wrists and ankles).

4.0 Collection Procedure

4.1 The test subject will be taken to a designated clean "privacy area" for removal of exposed clothing.

4.2 A disposable paper or plastic mat, or aluminum will be placed on the floor of the changing area after the worker has removed his/her shoes. The mat will help to reduce cross-contamination between the floor and the dosimeters. The mat will be changed after the processing of each worker.

4.3 The field personnel collecting samples will always wear disposable gloves when handling any clothing dosimeters. Gloves will be changed between outer and inner dosimeter collection.

4.4 The test subject will wear clean, fresh disposable gloves while removing shoes and socks. A new pair of disposable gloves will be worn by the worker to remove the outer dosimeter, and again for the inner dosimeter.

4.5 Ensure that the scissors have been decontaminated with solvent before use. Scissors must be cleaned between each replicate. Separate pairs of scissors will be used for both outer and inner dosimeter collection.

4.6 Carefully remove the outer dosimeter, taking care to prevent unnecessary contamination of the inner dosimeter. Also ensure that the outer dosimeter does not come in contact with any source of contamination (*e.g.*, floor workers' shoes).

4.7 Cut the shirt into four (4) sections:

a. Right and left upper arms (shoulder to elbow)

b. Right and left lower arms (elbow to cuff)

c. Front torso - cut at side seams

d. Rear torso - cut at side seams

4.8 Cut the pants into two (2) sections:

a. Right and left upper legs (waist to knee)

b. Right and left lower legs (knee to cuff)

4.9 Discard any buttons from clothing.

4.10 Place each sample section on a piece of aluminum foil wrap (sufficient size to completely wrap the dosimeter) and then immediately into a labeled sample bag. Do not allow samples to contact any surface before placement onto the foil. Ensure that the edges of the foil wrap are folded together to prevent loss of test material. Be sure that the correct sample label is on the bag. Seal all bags and place into frozen storage (on dry ice or in a freezer) for transport.

4.11 Refer to SOP ARTF-8E for inner dosimeter collection.

4.12 There will be six (6) outer dosimeter samples per replicate.

5.0 SAMPLING INTERVALS

5.1 Outer dosimeters will be collected at the end of each monitoring replicate, unless otherwise directed by the protocol.

Attachment 2

ARTF-8E/0 Standard Operating Procedure

ARTF-8E/0
Standard Operating Procedure

Section E: Whole Body Sampling - Inner Dosimeters
Chapter 8: MATRIX SAMPLES
Effective Date: June 6, 1997

David P Johnson APPROVAL	6/6/97 DATE
APPROVAL	DATE

1.0 PURPOSE AND SCOPE

1.1 This Standard Operating Procedure (SOP) provides a description of procedures for collecting pesticide residues from whole body dosimeters worn by workers (test subjects) during the Agricultural Reentry Task Force (ARTF) exposure studies.

1.2 The inner dosimeter will be used as a surrogate for the worker's skin. The inner dosimeter will be worn over the test subject's own undergarments and directly underneath the work clothing.

2.0 MATERIALS REQUIRED

2.1 The following materials are required for using and collecting whole body dosimeter samples from each worker/replicate:

a. 100% cotton, white, long underwear (inner) – with long sleeves, round neckline and no elastic.

b. Disposable gloves (*i.e.*, latex)

c. Scissors

d. Cleaning solutions (*i.e.*, alcohol (methanol, isopropanol), alcohol/water mixture, acetone, etc.)

e. Heat-sealable bags or other suitable bags

f. Aluminum foil wrap

g. Heat sealer, if appropriate

3.0 Use of Whole Body Dosimeter

3.1 The test subject(s) will be given a clean, new inner dosimeter prior to initiation of each study replicate. The workers will be allowed to change in a clean "privacy" area. Disposable gloves should be worn by the test subject and the field personnel to minimize contamination.

3.2 Care should be taken to provide clothing of adequate fit. The inner dosimeter arm and pant cuffs should not extend beyond the work clothing cuffs (wrists and ankles).

4.0 Collection Procedure

4.1 The test subject will be taken to a designated clean "privacy area" for removal of exposed clothing.

4.2 A disposable paper or plastic mat, or aluminum will be placed on the floor of the changing area after the worker has removed his/her shoes. The mat will help to reduce cross-contamination between the floor and the dosimeters. The mat will be changed after the processing of each worker.

4.3 The field personnel collecting samples will always wear disposable gloves when handling any clothing dosimeters. Gloves will be changed between outer and inner dosimeter collection.

4.4 The test subject will be given clean, fresh disposable gloves to wear while removing shoes and socks. A new pair of disposable gloves will be worn by the worker to remove the work clothes, and again for the inner dosimeter.

4.5 Ensure that the scissors have been decontaminated with solvent prior to use. Scissors must be cleaned between each replicate. Use one pair of scissors to section the inner dosimeters and a separate pair of scissors to section the outer dosimeters.

4.6 Carefully remove the outer garments, taking care to prevent unnecessary contamination of the inner dosimeter. Also ensure that the outer dosimeter (if used) does not come in contact with any source of contamination (*e.g.*, floor, worker's shoes).

4.7 Cut the inner dosimeter into six (6) sections:

a. Right & left upper arms (shoulder to elbow)

b. Right & left lower arms (elbow to cuff)

c. Front torso (above the waist*)

d. Rear torso (above the waist*)

e. Right & left upper legs (waist to knee)*

f. Right and left lower legs (knee to cuff)

* Cut at just below the second button from the bottom to separate the torso from the lower section. Cut along the seams to separate the front torso from the rear torso. Refer to Attachment 8-E-1.

4.8 Discard any Buttons from clothing.

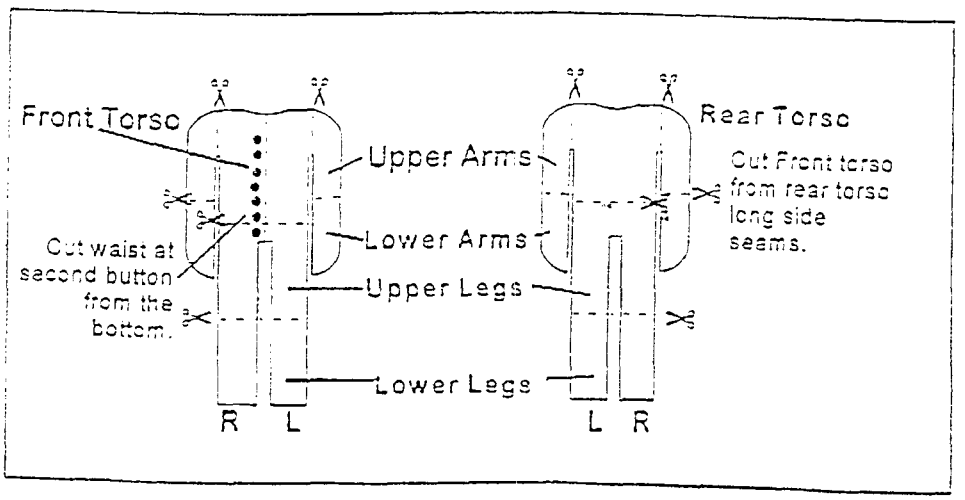
4.9 Place each sample section on a piece of aluminum foil wrap (sufficient size to completely wrap the dosimeter) and then immediately into a labeled heat-sealable bag. Do not allow samples to contact any surface before placement onto the foil. Ensure that the edges of the foil wrap are folded together to prevent loss of test material. Be sure that the correct sample label is on the bag. Heat seal all bags and place into frozen storage (on dry ice or in a freezer) for transport.

4.10 There shall be six (6) inner dosimeter samples per replicate.

5.0 Sampling Intervals

5.1 Inner whole body dosimeters will be collected at the end of each monitoring replicate, unless otherwise instructed by the protocol.

Diagram of Inner Dosimeter



INTRODUCTION

Analytical method 6445-95-0086-CR-001, developed by Ricerca, Inc., was modified by Centre Analytical Laboratories, Inc., at the request of the Agricultural Re-entry Task Force (ARTF). The enclosed method, ARTF-003, is the revised method from Centre Analytical Laboratories, Inc.

DETERMINATION OF CHLOROTHALONIL IN OVS AIR SAMPLING TUBES

Analytical Method: ARTF-003

Authors:
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Date of Issue: October 17, 1997

1.0 PRINCIPLE

Tetrachloroisophthalonitrile (common name - chlorothalonil) is extracted from OVS air sampling tubes with toluene and an extract is analyzed by electron-capture gas chromatography. The method is applicable to samples containing residue levels ranging from 0.01 µg/section to 10 µg/section. The limit of quantitation (LOQ) is 0.01 µg/section.

2.0 EQUIVALENCE STATEMENT

During the conduct of this analysis, equivalent apparatus, solvents, glassware, or techniques (such as sample concentration) may be substituted for those specified in this method, except where otherwise noted. Use of equivalent techniques or equipment will be documented, when appropriate.

3.0 APPARATUS AND EQUIPMENT

Gas Chromatograph: Hewlett-Packard (HP) gas chromatograph Model 5890 Series II equipped with a ^{63}Ni electron capture detector, HP Model 7673 autosampler and HP ChemStation data system.

Scintillation vials: 20 mL, Borosilicate glass, VWR catalog # 66022-081

Vacuum manifold: Vacmaster, IST catalog # 121-2016

Vacuum pump: 115 V/60 Hz, IST catalog # 121-9115

Sorbent Tube: Chromosorb-102, 2 section, SKC, Inc.

4.0 REAGENTS AND MATERIALS

Chlorothalonil:	Tetrachloroisophthalonitrile
Toluene:	Residue grade or equivalent
Ethyl Acetate:	Residue grade or equivalent

5.0 SAMPLE PREPARATION

OVS air sampling tube samples consist of two sections, front and back, each section representing one analytical sample.

6.0 STANDARD PREPARATION

6.1 Stock Solution:

Correcting for purity, prepare a stock standard solution of chlorothalonil by weighing an appropriate amount into a volumetric flask, dissolving with ethyl acetate, and diluting to the mark. For example, weigh 0.1 g of chlorothalonil into a 100-mL volumetric flask, dissolve in ethyl acetate, and dilute to the mark with ethyl acetate. The concentration of the stock solution is approximately 1000 µg/mL. The stock solution is stored frozen (≤ -10°C) and remade at one year intervals.

If necessary, prepare serial dilutions from the stock solution of chlorothalonil in other solvents (such as toluene) for GC analysis.

6.2 Fortification Solutions:

Dilute the stock solution and/or the appropriate fortification solution(s) with ethyl acetate to generate 500-µg/mL, 50-µg/mL, 10-µg/mL, and 1-µg/mL fortification

solutions. Other concentrations may be prepared as needed. Suggested preparation is as follows:

Standard Solution Concentration (µg/mL)	Aliquot (mL)	Final Volume (mL)	Final Concentration (µg/mL)
5000	10	100	500
5000	1	100	50
50	20	100	10
10	10	100	1

6.3 Instrument Calibration Solutions:

Dilute the appropriate fortification/calibration solution(s) with toluene to make instrumentation (calibration) solutions in a range appropriate for the expected residue levels. Suggested preparation is as follows:

Standard Solution Concentration (µg/mL)	Aliquot (mL)	Final Volume (mL)	Final Concentration (µg/mL)
50	1	100	0.5
0.5	20	100	0.1
0.5	10	100	0.05
0.1	20	100	0.02
0.1	10	100	0.01
0.05	10	100	0.005
0.01	10	100	0.001

All fortification and calibration standards are stored frozen (≤ -10°C) and should be remade at one year intervals.

7.0 FORTIFICATION

7.1 Laboratory Fortifications:

Prepare laboratory fortifications by applying the appropriate amount of fortification solution to the front of the air tube before the sections are separated via Hamilton syringe or equivalent. The volume of spiking solution applied to the

sample should be kept to a minimum to avoid translocation of the compound to the back section, but should be large enough to allow accurate measurement with the existing laboratory equipment (~125 µL maximum is suggested). Allow the fortification solution to dry and apply a vacuum for ~10 min.

8.0 SAMPLE EXTRACTION AND CLEANUP PROCEDURES

8.1 Extraction:

OVS air sampling tubes are extracted in two separate sections, front and back. Divide the air sampling tube, transferring each section (front and back) to separate 20-mL scintillation vials. Label the scintillation vials to indicate the front and back air sampling tube sections. Rinse the empty air sampling tube with 2.0 mL of toluene and collect in the front sample vial only. Add a total of 3.5 mL of toluene to each sample vial. Seal the vials with Teflon® lined caps and shake by hand for ~2 minutes. Collect an aliquot of the toluene extract for GC analysis. Dilute samples with toluene, if necessary.

9.0 QUANTITATION BY ELECTRON CAPTURE GAS CHROMATOGRAPHY

The following columns and conditions are suggested and may be modified, within reason, to attain optimum chromatography.

Analytical conditions:

Instrument:	Hewlett Packard Gas Chromatograph, model 5890 Series II
Column:	RTX-5, fused silica capillary, 30 m x 0.53-mm i.d., 0.5-µm film thickness (available from Restek, Bellefonte, PA 16823)
Detector:	^{63}Ni Electron Capture Detector
Temperature:	160 °C for 1 min then 20 °C/min to 240 °C. Hold at 240 °C for 2 min, then 25 °C/min to 270 °C, hold for 6 min
Injection Port Temperature:	270 °C
Detector Temperature:	300 °C
Carrier Gas:	High purity helium, 8 mL/min
Make-up Gas:	High purity nitrogen, 30 mL/min
Injection Volume:	1 µL

Approximate Retention Time: 4.5 minutes

Total Run Time: ~ 15 minutes

10.0 CALIBRATION

Calibrate the gas chromatograph by injecting a minimum of four standard solutions in the concentration range of 0.001 µg/mL to 0.1 µg/mL. Prepare a calibration curve by plotting standard concentration versus response. This calibration curve also serves as the standard curve used for calculation purposes.

11.0 CALCULATIONS

11.1 Calculations for instrumental analysis are conducted using Micorsoft Excel® software to create a standard curve based on linear regression. These regression functions are used to calculate a best fit line (from a set of standard concentrations in µg/mL versus peak response) and to determine concentration of the analyte found during sample analysis from the calculated best fit line.

The equation used for the least squares fit is:

$$y = mx + b$$

where,

y = peak response (height or area)

x = µg/mL found

m = slope

b = y-intercept

11.2 The amount of chlorothalonil measured in each section is calculated according to the following equation:

$$\mu g/\text{section} = \frac{(\mu g/mL) \times (mL \text{ final volume}) \times (\text{dilution factor})}{\text{section (front or back)}}$$

Where,

µg/section = total µg of analyte present per section of sample analyzed

µg/mL	=	concentration of analyte derived from the standard curve based on peak response from the sample injected utilizing the linear regression equation of y = mx + b
section (front or back)	=	amount of sample taken through the extraction process
mL final volume	=	volume of final extract submitted to instrumentation (3.5 mL)
dilution factor	=	dilution of sample extract required to produce an analyte response bracketed by standards

11.3 To determine the µg found in each air tube sample the µg found in each section is added:

µg/tube = (µg/front section + µg/back section)

11.4 The percent recovery for fortified control samples is calculated as follows:

$$\% \text{ Recovery} = \frac{\mu g/\text{tube found in fortified control}}{\mu g/\text{tube added to fortified control}} \times 100$$

12.0 REFERENCES

Ricerca, Inc. Report / SDS-2787, 6445-95-0086-CR-001

APPENDIX I

Recoveries for Chlorothalonil in OVS Air Sampling Tubes

NOTE: For the purpose of validating this method, both the front and back sections were fortified separately. Therefore the µg/section found were not added to obtain the µg/tube found, as described in the method.

Determination of Chlorothalonil in OVS Air Sampling Tubes with Chromosorb 102

Extraction Date: 2/26/97 **Analysis Date:** 3/5/97 **Matrix:** OVS Tubes w/Chromosorb 102

STANDARD CURVE:

Conc. (µg/mL)	Peak Height	Conc. (µg/mL)	Peak Height
0.05	288418	0.005	40465
0.01	65422	0.05	352963
0.005	37015	0.01	79620
0.001	9213	0.005	42675
0.05	313008	0.001	10563

Linear Calibration Equation: y = mx+b
m= 7657
b= 6218160
Correlation Coefficient = 0.9931

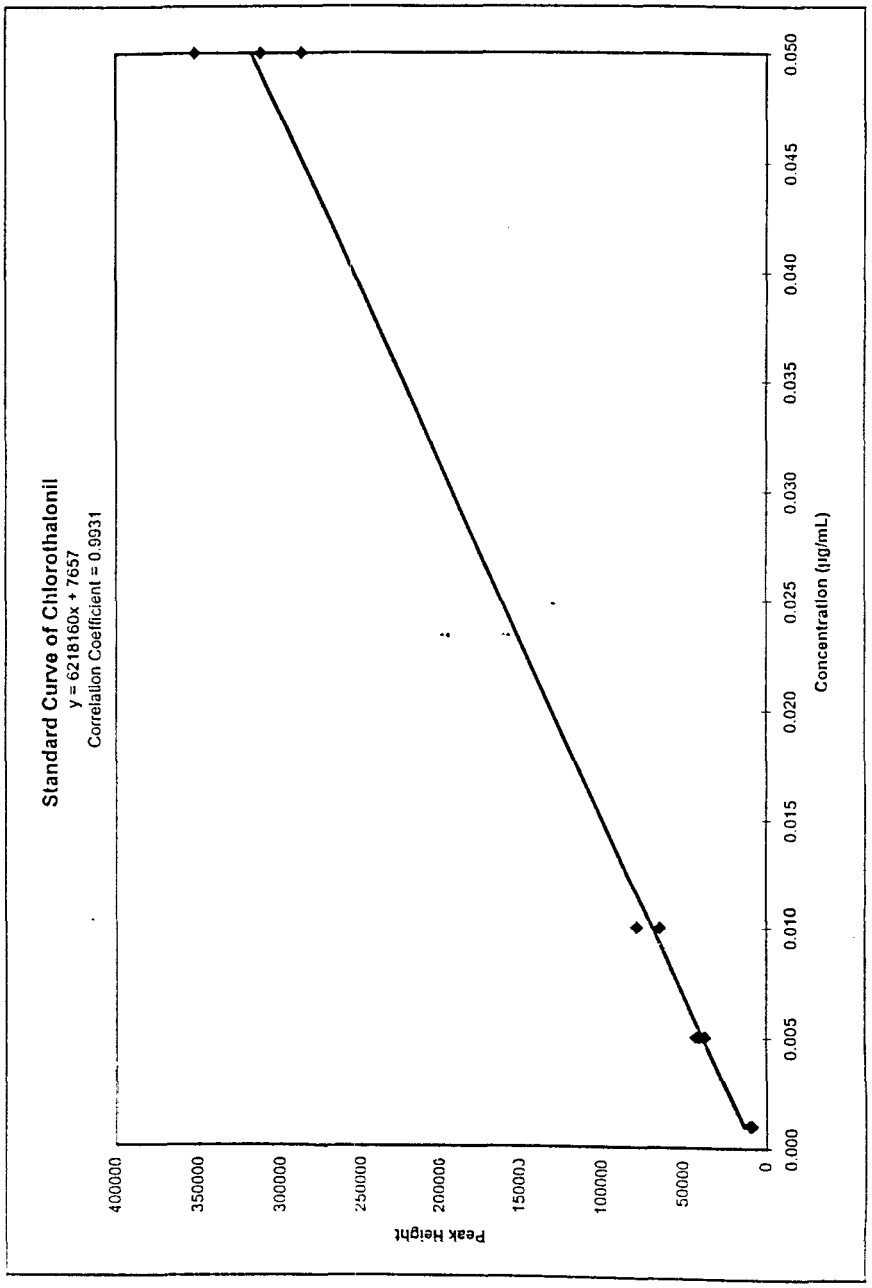
DATA:

CAL ID#	Client ID	Compound Found	Peak Height	Peak Height Corrected	µg/mL Compound Found	Final Volume (mL)	Dilution Factor	µg/Dosimeter Found	µg Compound Added	Percent Recovery
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
970986 Blk, Front	NA	Chlorothalonil	0	0	0.0000	3.5	1	0.0	na	na
970986 Blk, Rear	NA	Chlorothalonil	0	0	0.0000	3.5	1	0.0	na	na
970987 Spk A Front	NA	Chlorothalonil	97501	97501	0.0144	3.5	1	0.051	0.05	101%
970988 Spk B Front	NA	Chlorothalonil	97766	97766	0.0145	3.5	1	0.051	0.05	101%
970989 Spk C Front	NA	Chlorothalonil	51790	51790	0.0071	3.5	10	0.248	0.25	99%
970990 Spk D Front	NA	Chlorothalonil	50579	50579	0.0069	3.5	10	0.242	0.25	97%
970991 Spk E Front	NA	Chlorothalonil	53892	53892	0.0074	3.5	50	1.30	1.25	104%
970992 Spk F Front	NA	Chlorothalonil	48988	48988	0.0066	3.5	50	1.16	1.25	93%
970987 Spk A Rear	NA	Chlorothalonil	97210	97210	0.0144	3.5	1	0.050	0.05	101%
970988 Spk B Rear	NA	Chlorothalonil	101819	101819	0.0151	3.5	1	0.053	0.05	106%
970989 Spk C Rear	NA	Chlorothalonil	53261	53261	0.0073	3.5	10	0.257	0.25	103%
970990 Spk D Rear	NA	Chlorothalonil	50343	50343	0.0069	3.5	10	0.240	0.25	96%
970991 Spk E Rear	NA	Chlorothalonil	49197	49197	0.0067	3.5	50	1.17	1.25	94%
970992 Spk F Rear	NA	Chlorothalonil	52975	52975	0.0073	3.5	50	1.28	1.25	102%
									Average (n=12):	100%
									Standard Deviation:	4.1%

APPENDIX II

Calibration Curve and Example Chromatograms

Analysis Date: 3/5/97



BB 3/5/97

CAL Study No. 017-01

Extraction Date: 2/26/97

ARTF Study No. ARF004

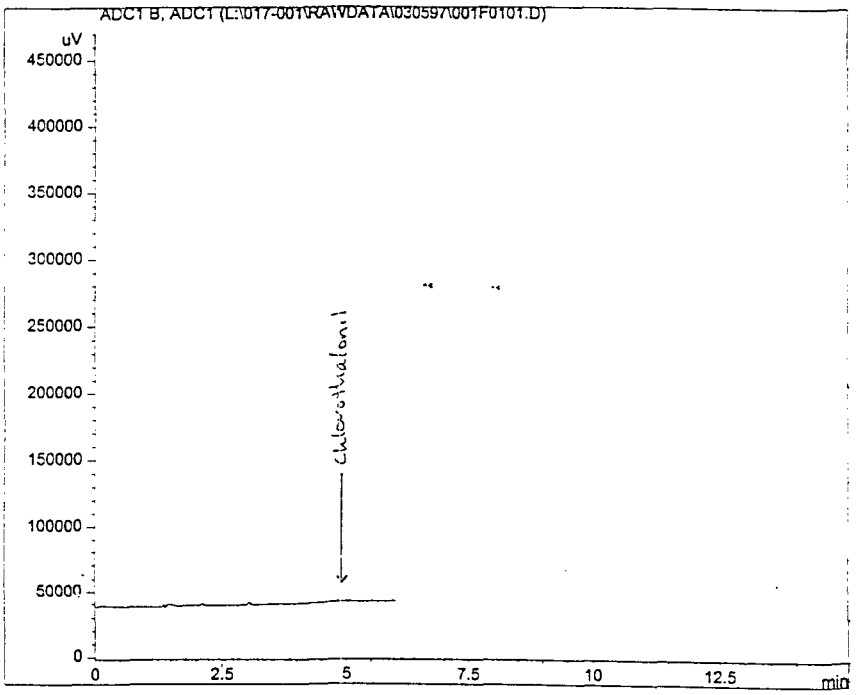
Analysis of Chlorothalonil

Run No.: 1

Sample No: NA
Sample Info: Solvent Blank

Injected on: 3/5/97 12:44:40 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

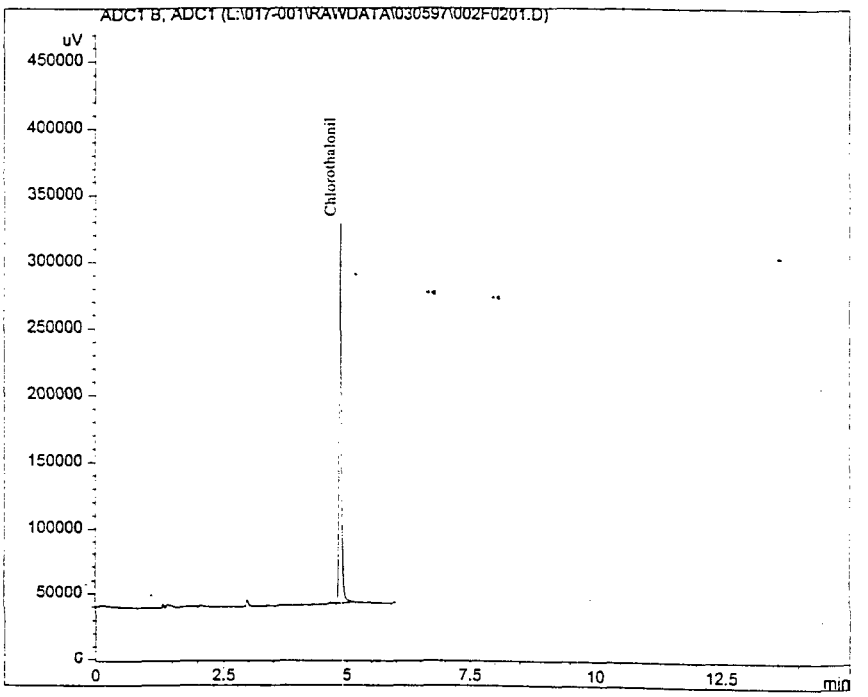
Analysis of Chlorothalonil

Run No.: 2

Sample No: NA
Sample Info: 0.05 µg/mL Standard, C021097-7

Injected on: 3/5/97 1:01:23 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.861	Chlorothalonil	288418.3	948187.500

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

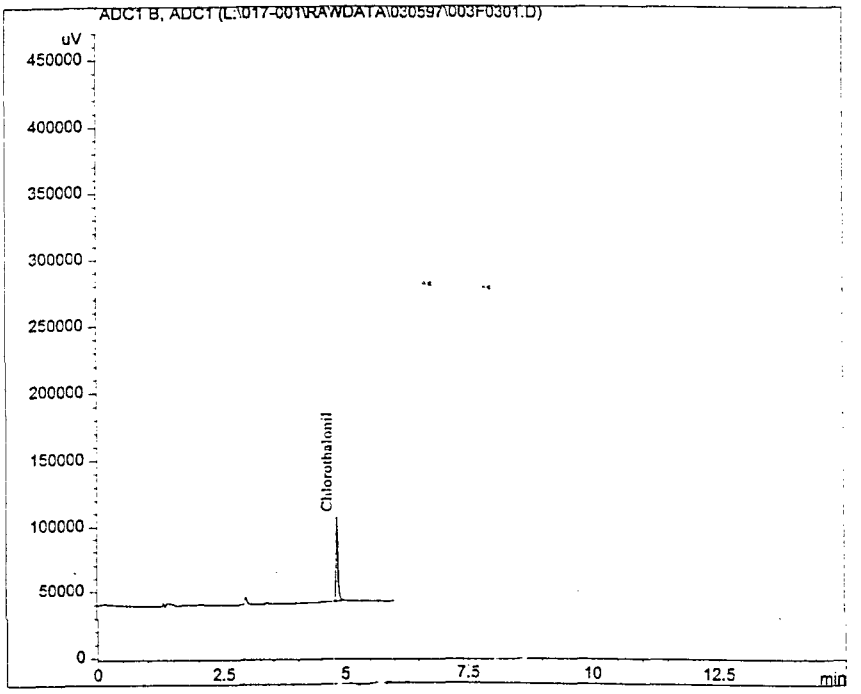
Analysis of Chlorothalonil

Run No.: 3

Sample No: NA
Sample Info: 0.01 µg/mL Standard, C021097-8

Injected on: 3/5/97 1:18:09 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.836	Chlorothalonil	65422.4	201252.547

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

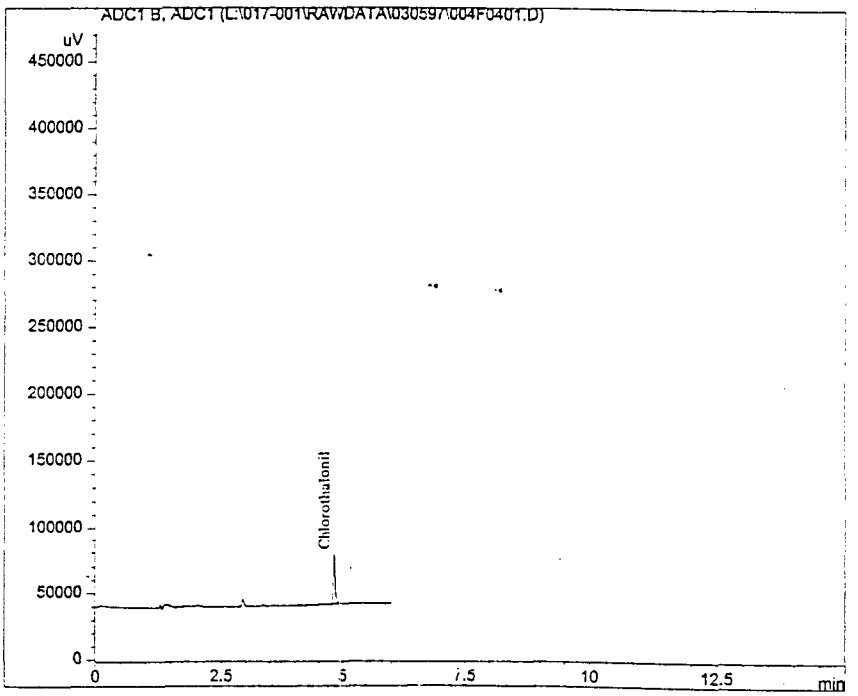
Analysis of Chlorothalonil

Run No.: 4

Sample No: NA
Sample Info: 0.005 µg/mL Standard, C021097-9

Injected on: 3/5/97 1:34:53 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.822	Chlorothalonil	37015.2	110432.227

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

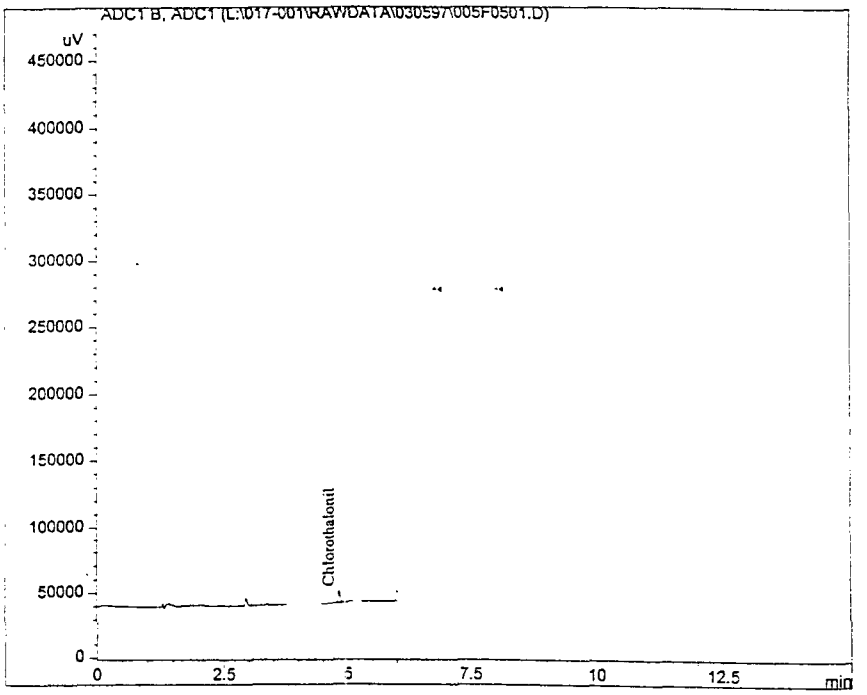
Analysis of Chlorothalonil

Run No.: 5

Sample No: NA
Sample Info: 0.001 µg/mL Standard, C021097-10

Injected on: 3/5/97 1:51:38 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.826	Chlorothalonil	9213.2	25773.492

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

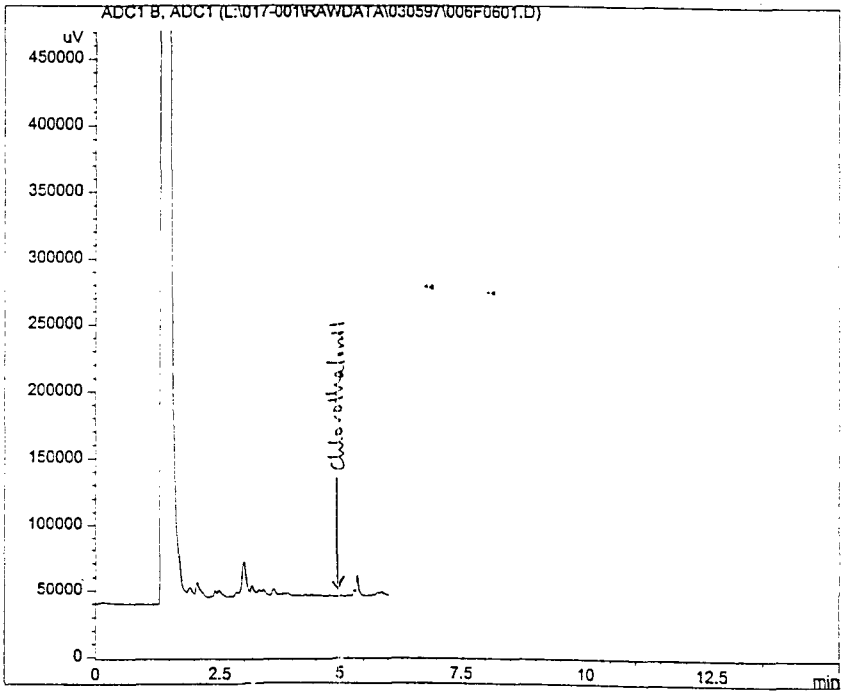
Analysis of Chlorothalonil

Run No.: 6

Sample No: CAL 970986 Blk
Sample Info: Control, Front, Final Volume = 3.5 mL

Injected on: 3/5/97 2:08:24 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

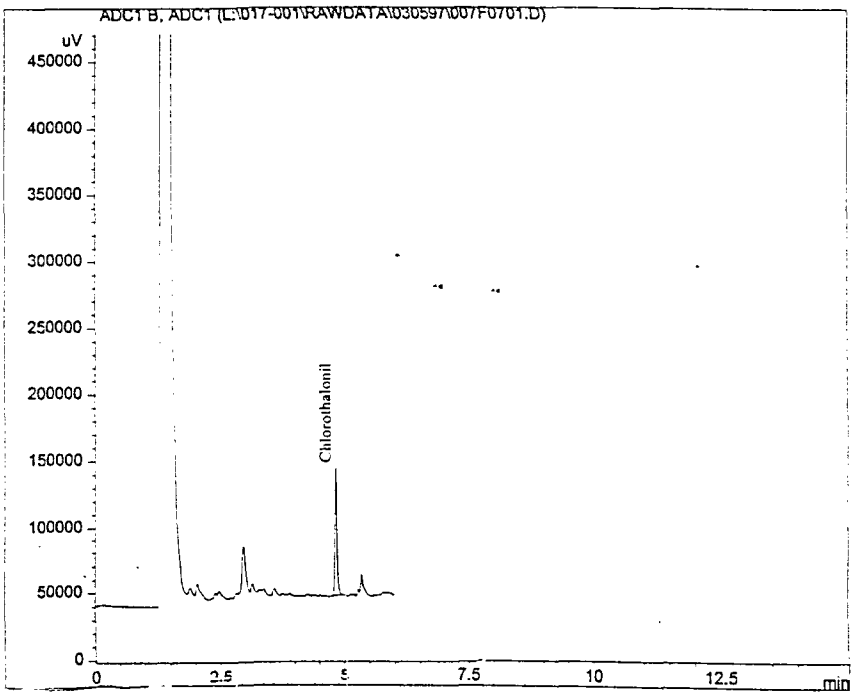
Analysis cf Chlorothalonil

Run No.: 7

Sample No: CAL 970987 Spk A
Sample Info: Control Fortified at 0.05 µg, Front
Final Volume = 3.5 mL

Injected on: 3/5/97 2:25:10 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.840	Chlorothalonil	97501.0	291594.094

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

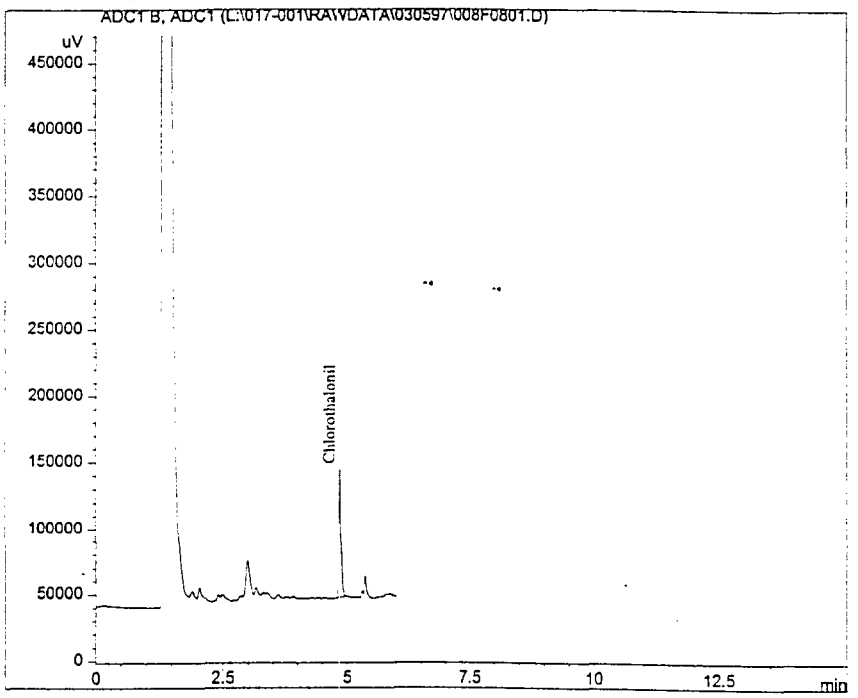
Analysis of Chlorothalonil

Run No.: 8

Sample No: CAL 970988 Spk B
Sample Info: Control Fortified at 0.05 µg, Front
Final Volume = 3.5 mL

Injected on: 3/5/97 2:41:51 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.847	Chlorothalonil	97766.2	294961.094

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

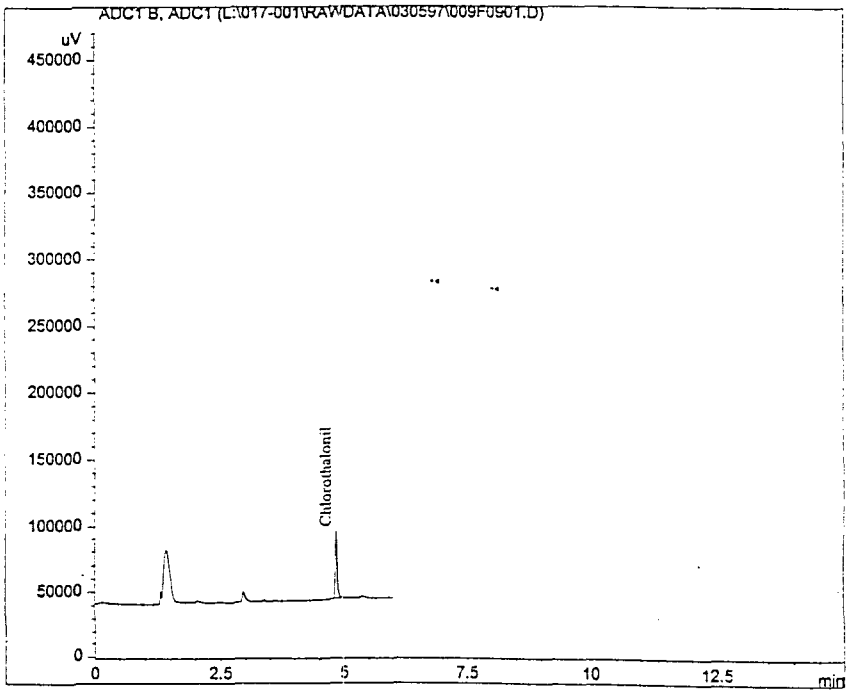
Analysis of Chlorothalonil

Run No.: 9

Sample No: CAL 970989 Spk C
Sample Info: Control Fortified at 0.25 µg, Front
Final Volume = 3.5 mL, Dilution Factor = 10

Injected on: 3/5/97 2:58:34 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.839	Chlorothalonil	51789.9	155227.844

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

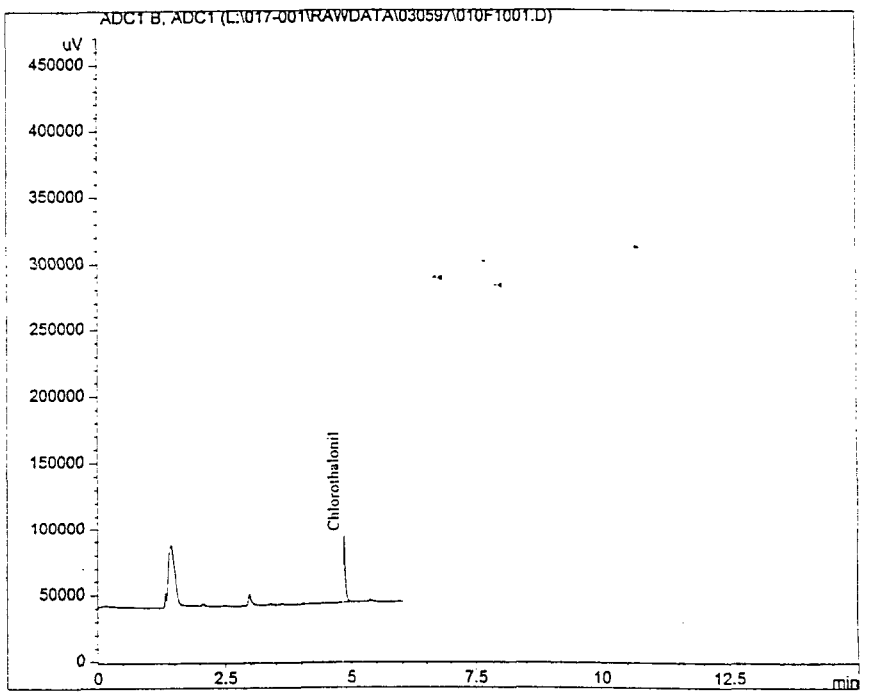
Analysis of Chlorothalonil

Run No.: 10

Sample No: CAL 970990 Spk D
Sample Info: Control Fortified at 0.25 µg, Front
Final Volume = 3.5 mL, Dilution Factor = 10

Injected on: 3/5/97 3:15:17 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.847	Chlorothalonil	50578.8	151294.141

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

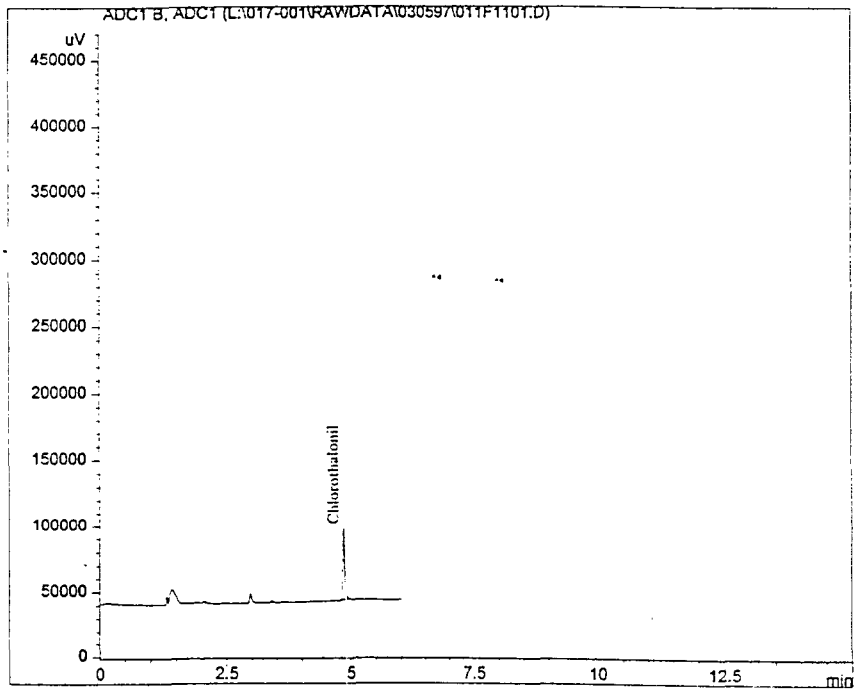
Analysis of Chlorothalonil

Run No.: 11

Sample No: CAL 970991 Spk E
Sample Info: Control Fortified at 1.25 µg, Front
Final Volume = 3.5 mL, Dilution Factor = 50

Injected on: 3/5/97 3:32:04 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.850	Chlorothalonil	53891.8	158925.391

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

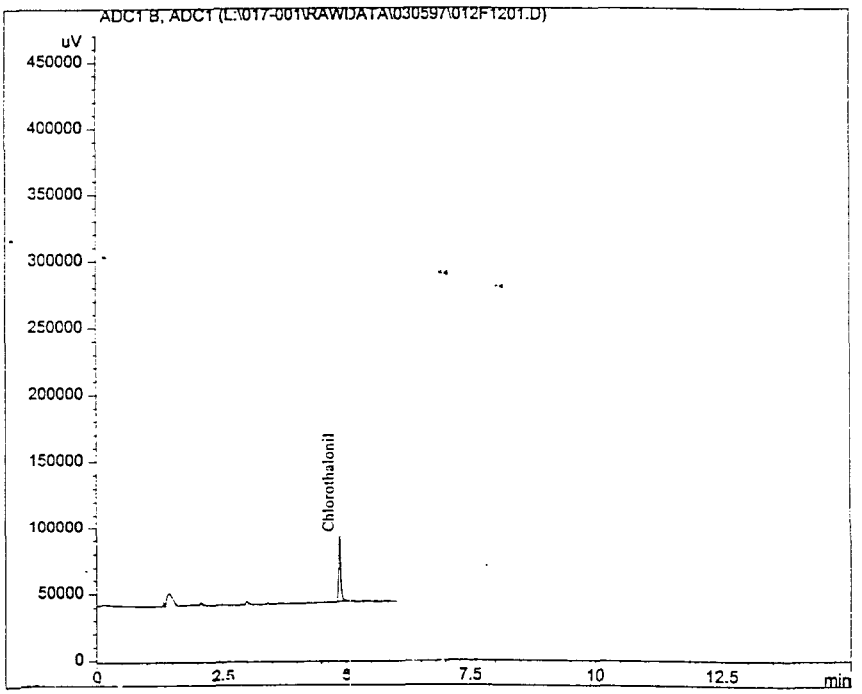
Analysis of Chlorothalonil

Run No.: 12

Sample No: CAL 970992 Spk F
Sample Info: Control Fortified at 1.25 µg, Front
Final Volume = 3.5 mL, Dilution Factor = 50

Injected on: 3/5/97 3:48:47 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.857	Chlorothalonil	48988.2	146643.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

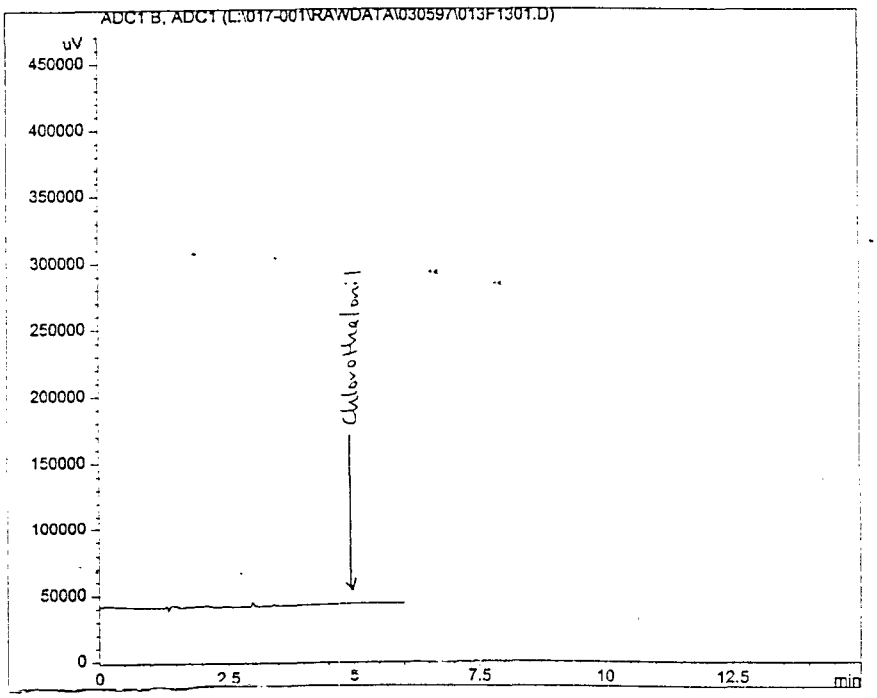
Analysis of Chlorothalonil

Run No.: 13

Sample No: NA
Sample Info: Solvent Blank

Injected on: 3/5/97 4:05:32 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

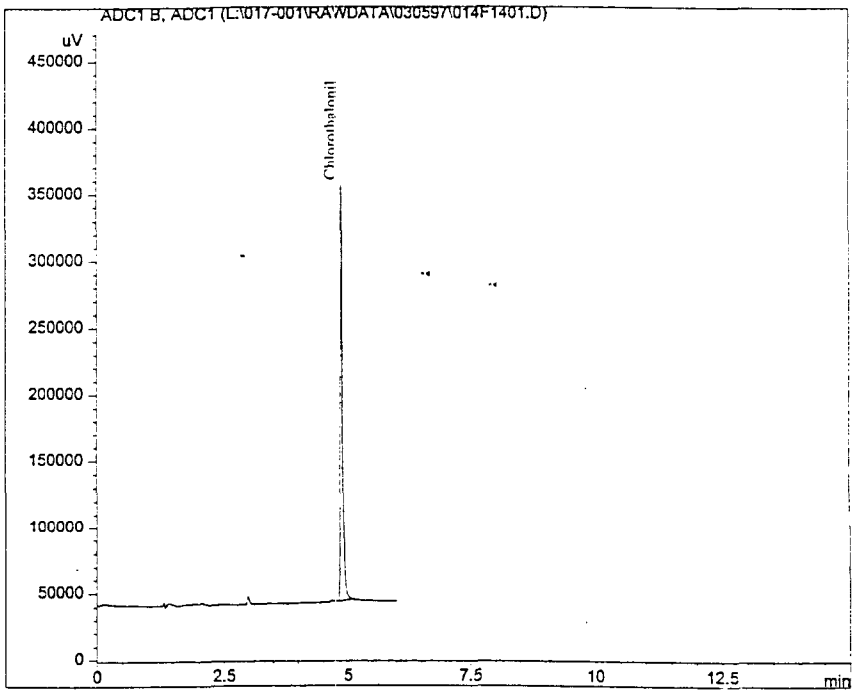
Analysis of Chlorothalonil

Run No.: 14

Sample No: NA
Sample Info: 0.05 µg/mL Standard, C021097-7

Injected on: 3/5/97 4:22:14 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.855	Chlorothalonil	313007.9	1.046e+006

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

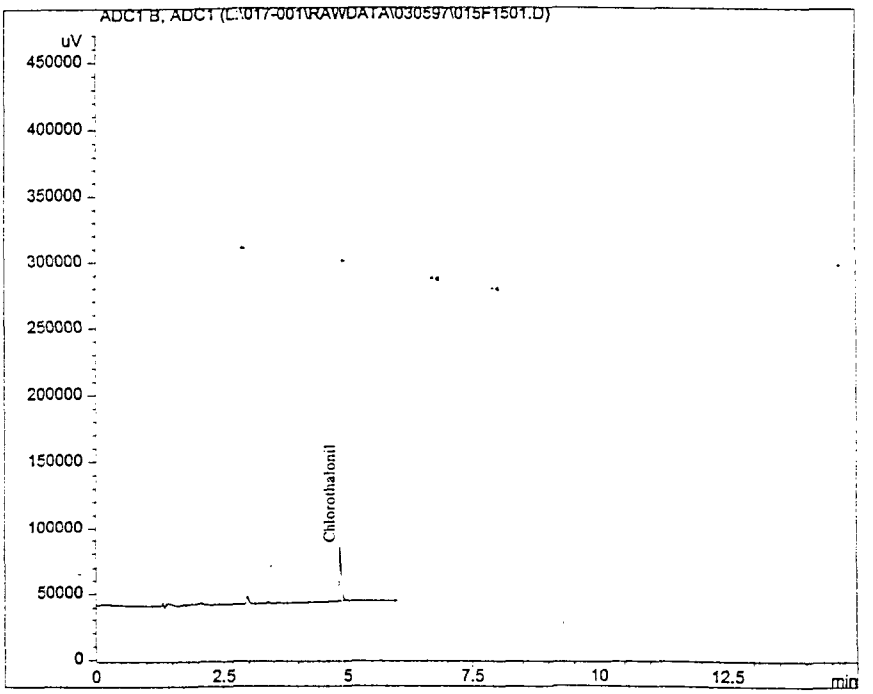
Analysis of Chlorothalonil

Run No.: 15

Sample No: NA
Sample Info: 0.005 µg/mL Standard, C021097-9

Injected on: 3/5/97 4:38:59 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.842	Chlorothalonil	40465.2	120890.320

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

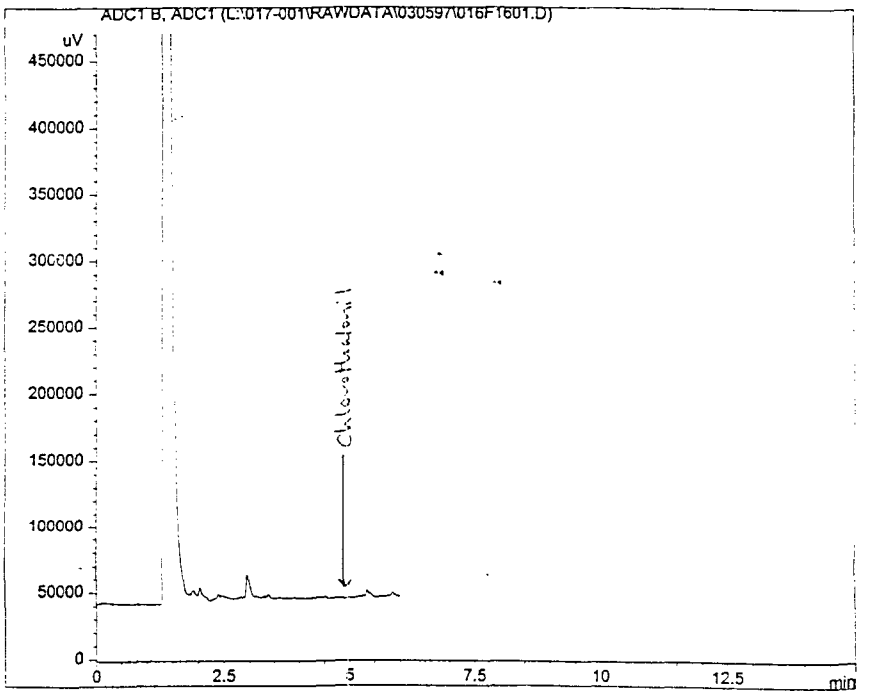
Analysis of Chlorothalonil

Run No.: 16

Sample No: CAL 970986 Blk
Sample Info: Control, Rear, Final Volume = 3.5 mL

Injected on: 3/5/97 4:55:42 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

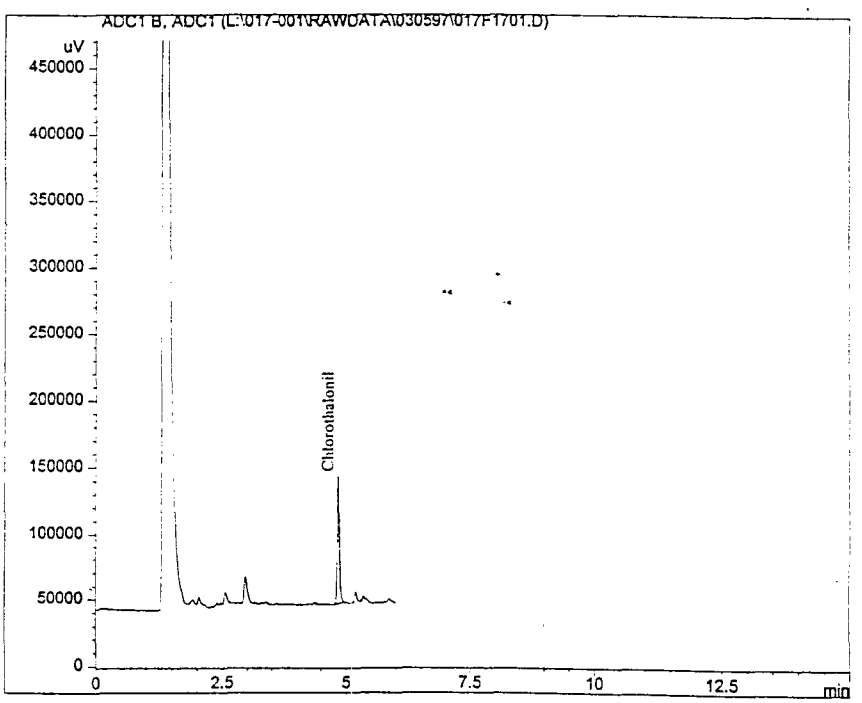
Analysis of Chlorothalonil

Run No.: 17

Sample No: CAL 970987 Spk A
Sample Info: Control Fortified at 0.05 µg, Rear
Final Volume = 3.5 mL

Injected on: 3/5/97 5:12:24 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.837	Chlorothalonil	97210.0	296316.500

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

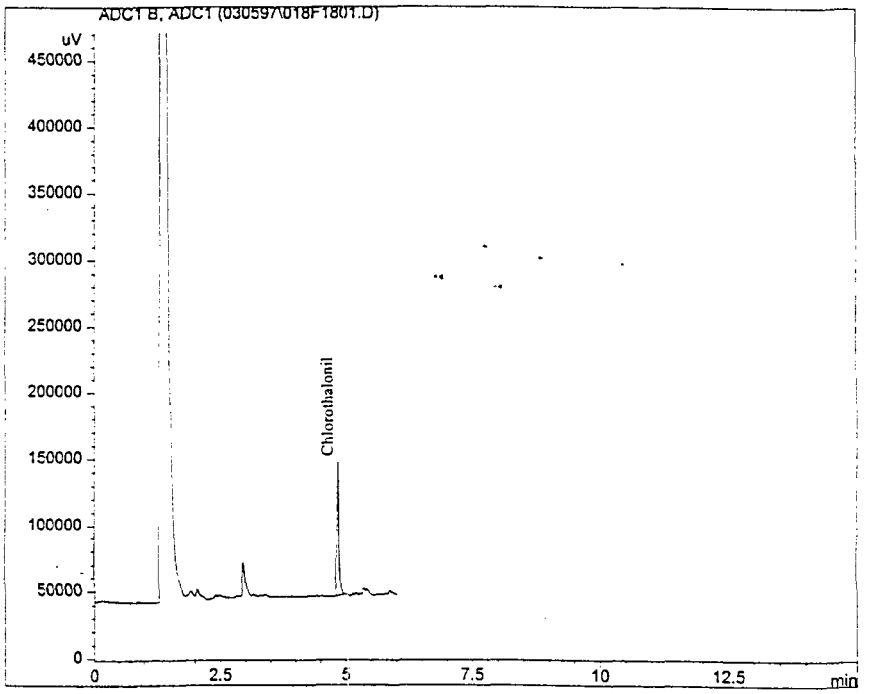
Analysis of Chlorothalonil

Run No.: 18

Sample No: CAL 970988 Spk B
Sample Info: Control Fortified at 0.05 µg, Rear
Final Volume = 3.5 mL

Injected on: 3/5/97 5:29:03 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.834	Chlorothalonil	101818.9	306645.719

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

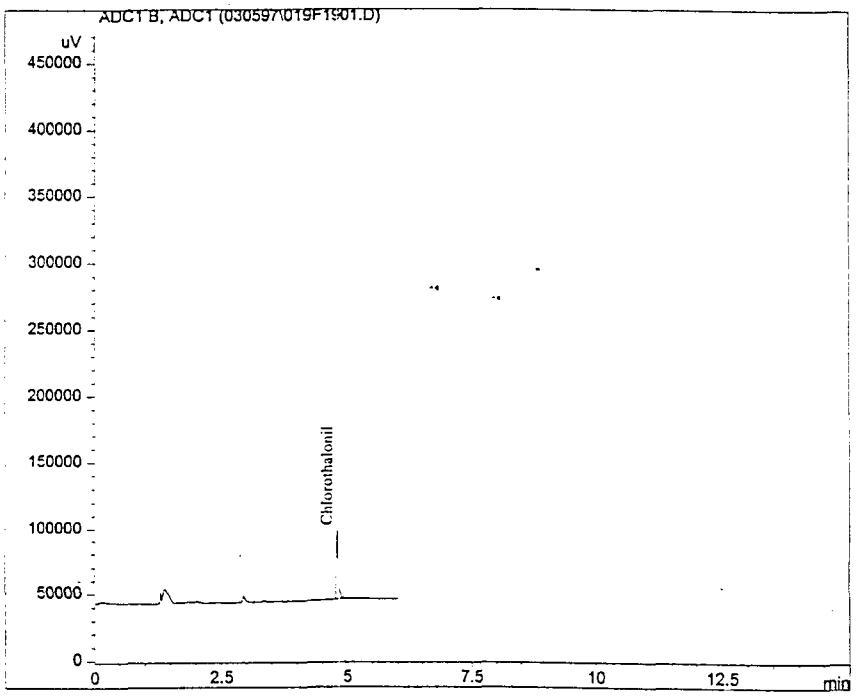
Analysis of Chlorothalonil

Run No.: 19

Sample No: CAL 970989 Spk C
Sample Info: Control Fortified at 0.25 µg, Rear
Final Volume = 3.5 mL, Dilution Factor = 10

Injected on: 3/5/97 5:45:46 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.793	Chlorothalonil	53261.0	159798.750

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

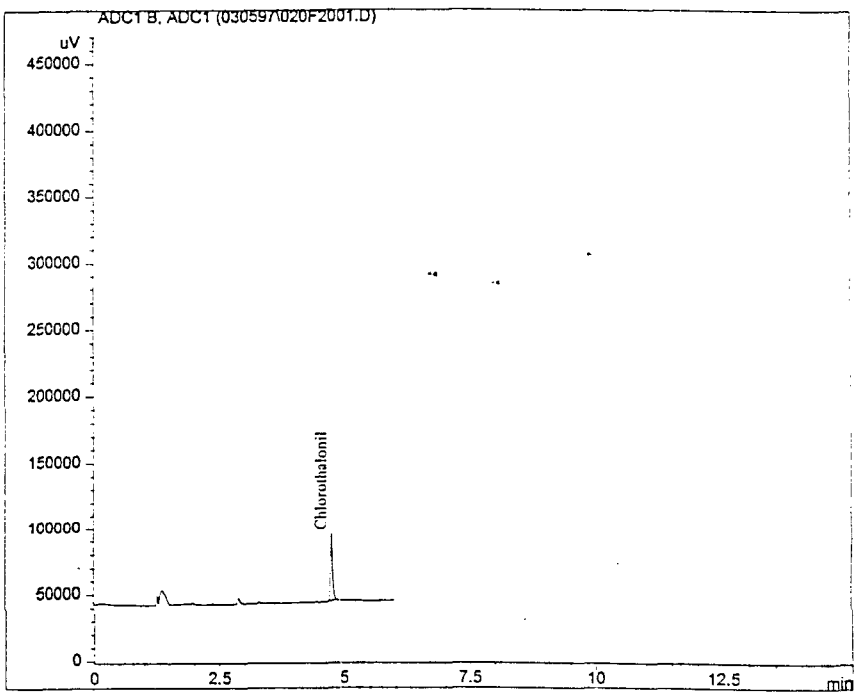
Analysis of Chlorothalonil

Run No.: 20

Sample No: CAL 970990 Spk D
Sample Info: Control Fortified at 0.25 µg, Rear
Final Volume = 3.5 mL, Dilution Factor = 10

Injected on: 3/5/97 6:02:29 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.756	Chlorothalonil	50342.6	150798.859

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

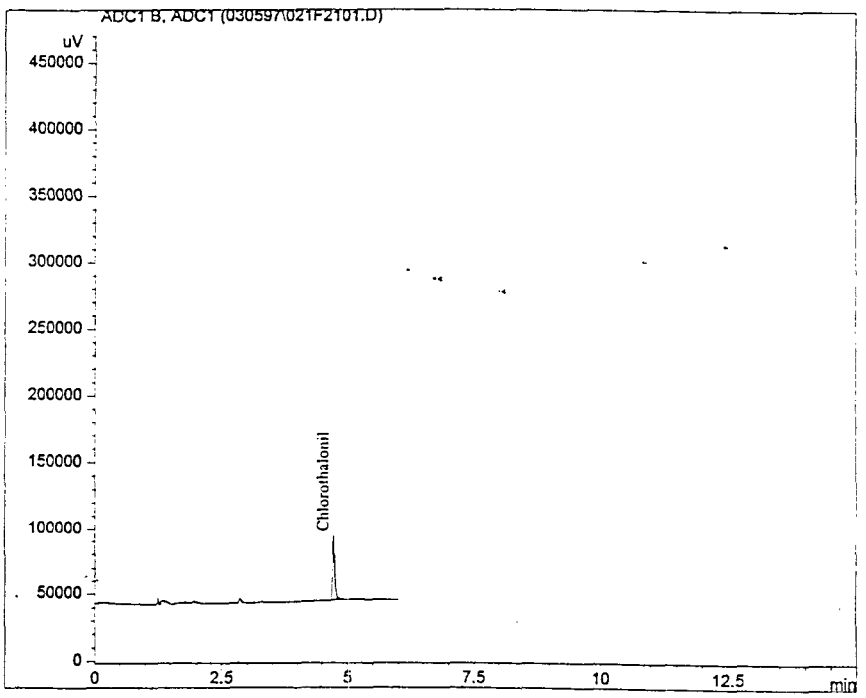
Analysis of Chlorothalonil

Run No.: 21

Sample No: CAL 970991 Spk E
Sample Info: Control Fortified at 1.25 µg, Rear
Final Volume = 3.5 mL, Dilution Factor = 50

Injected on: 3/5/97 6:19:14 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.720	Chlorothalonil	49196.5	148375.797

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

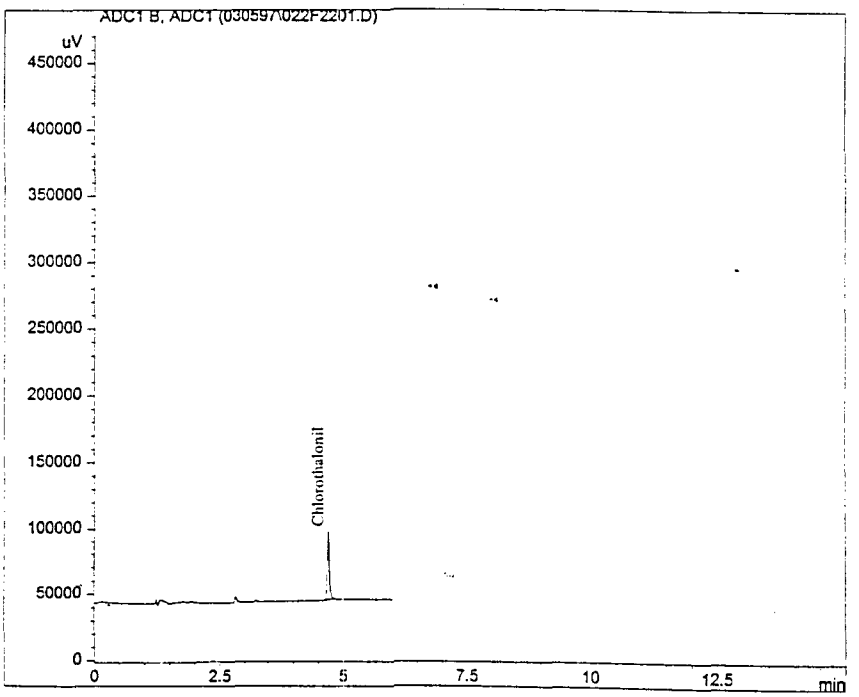
Analysis of Chlorothalonil

Run No.: 22

Sample No: CAL 970992 Spk F
Sample Info: Control Fortified at 1.25 µg, Rear
Final Volume = 3.5 mL, Dilution Factor = 50

Injected on: 3/5/97 6:35:56 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.695	Chlorothalonil	52975.1	159234.875

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

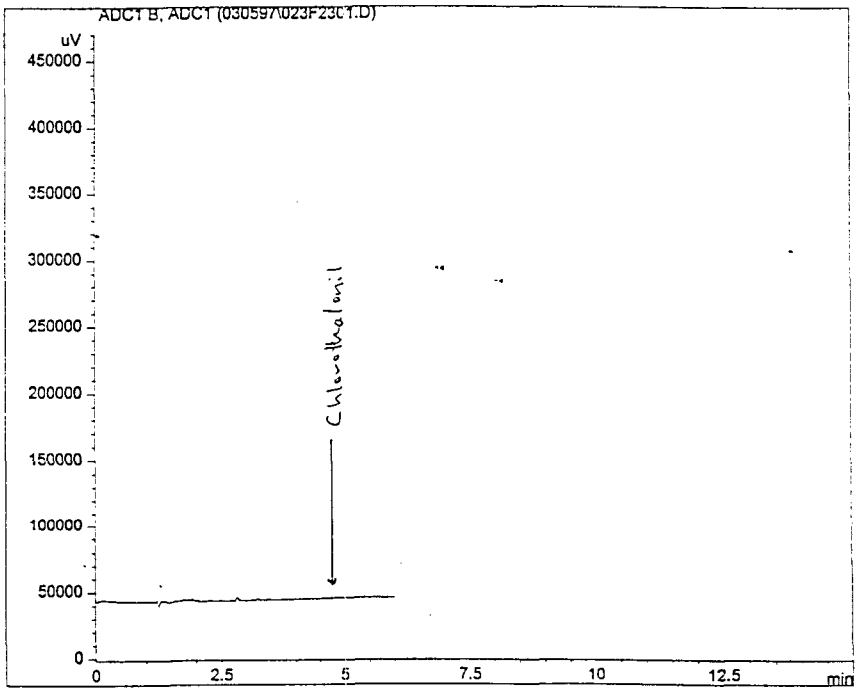
Analysis of Chlorothalonil

Run No.: 23

Sample No: NA
Sample Info: Solvent Blank

Injected on: 3/5/97 6:52:39 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

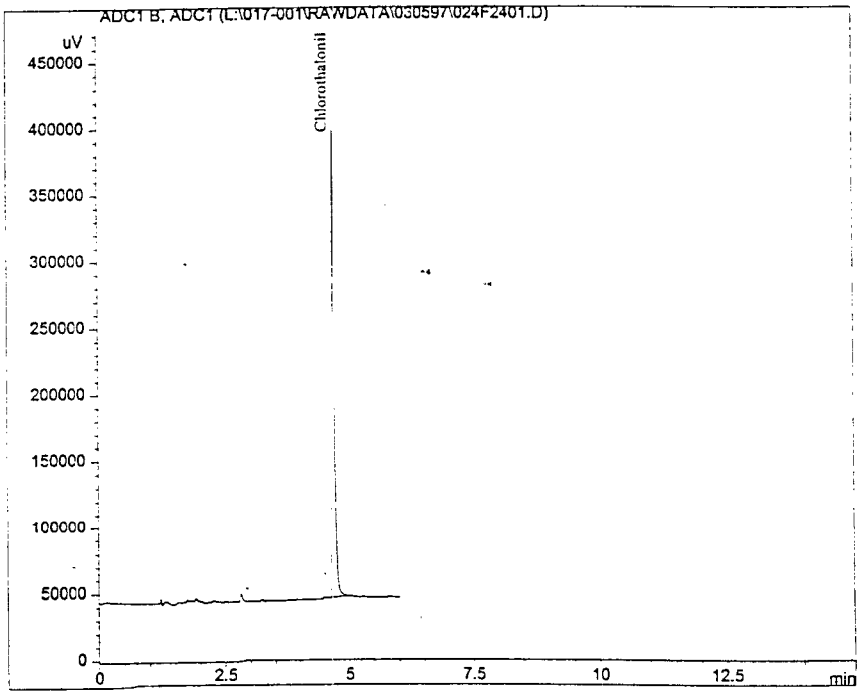
Analysis of Chlorothalonil

Run No.: 24

Sample No: NA
Sample Info: 0.05 µg/mL Standard, C021097-7

Injected on: 3/5/97 7:09:20 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.669	Chlorothalonil	352963.1	1.192e+006

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

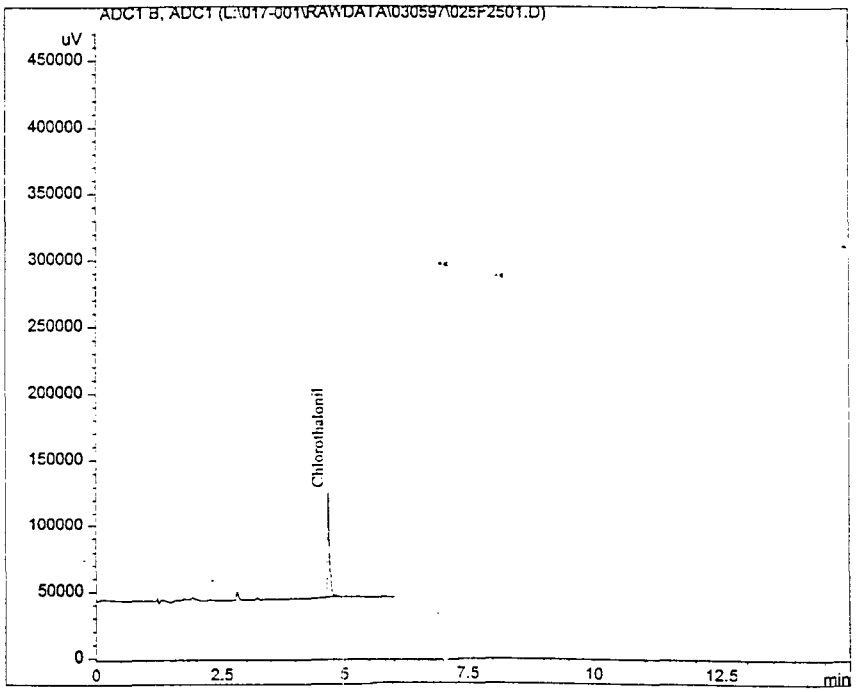
Analysis of Chlorothalonil

Run No.: 25

Sample No: NA
Sample Info: 0.01 µg/mL Standard, C021097-8

Injected on: 3/5/97 7:26:03 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.662	Chlorothalonil	79620.4	250838.953

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

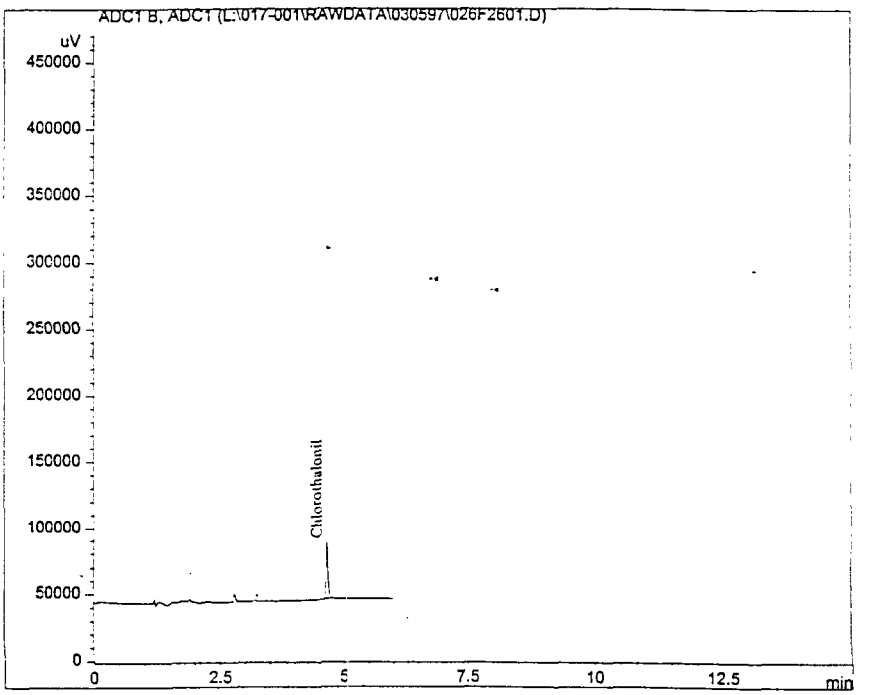
Analysis of Chlorothalonil

Run No.: 26

Sample No: NA
Sample Info: 0.005 µg/mL Standard, C021097-9

Injected on: 3/5/97 7:42:46 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.655	Chlorothalonil	42674.6	128222.500

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

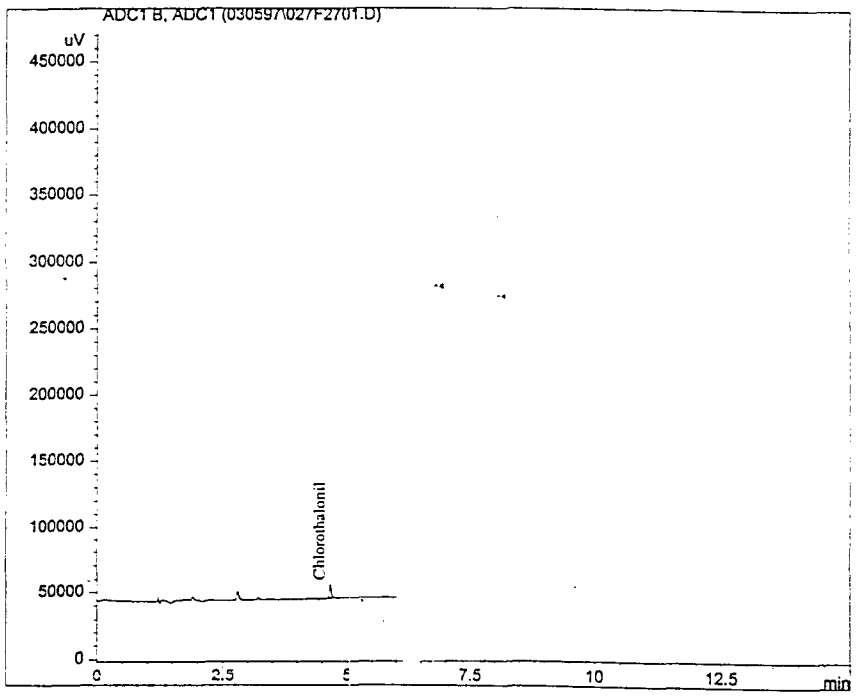
Analysis of Chlorothalonil

Run No.: 27

Sample No: NA
Sample Info: 0.001 µg/mL Standard, C021097-10

Injected on: 3/5/97 7:59:30 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.649	Chlorothalonil	10563.1	29462.918

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

INTRODUCTION

Analytical method 6445-95-0086-CR-001, developed by Ricerca, Inc., was modified by Centre Analytical Laboratories, Inc., at the request of the Agricultural Re-entry Task Force (ARTF). The enclosed method, ARTF-004, is the revised method from Centre Analytical Laboratories, Inc.

DETERMINATION OF CHLOROTHALONIL IN FACIAL/NECK WIPES

Analytical Method: ARTF-004

Authors:
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Fax: 814/231-1580

Date of Issue: October 17, 1997

1.0 PRINCIPLE

Tetrachloroisophthalonitrile (common name - chlorothalonil) is extracted from facial/neck wipe samples with ethyl acetate and analyzed by electron-capture gas chromatography. The method is applicable to samples containing residue levels ranging from 1 µg to 5000 µg. The limit of quantitation (LOQ) is 1 µg.

2.0 EQUIVALENCE STATEMENT

During the conduct of this analysis, equivalent apparatus, solvents, glassware, or techniques (such as sample concentration) may be substituted for those specified in this method, except where otherwise noted. Use of equivalent techniques or equipment will be documented, when appropriate.

3.0 APPARATUS AND EQUIPMENT

I-Chem 250 mL wide-mouthed jars with Teflon® lined caps, VWR, Catalog # IR241-0250.

Gas Chromatograph: Hewlett-Packard (HP) gas chromatograph Model 5890 Series II equipped with a ^{63}Ni electron capture detector, HP Model 7673 autosampler and HP ChemStation data system.

Laboratory Platform Shaker (reciprocating): Eberbach Model 6000. (Eberbach Corp., Ann Arbor, MI)

Standard laboratory glassware: beakers, pipettes, etc.

Facial/Neck Wipes: Cotton gauze sponges, 4" x 4" - 8-ply, (Johnson & Johnson Medical Inc.)

4.0 REAGENTS AND MATERIALS

Aerosol OT® Solution:	Residue grade or equivalent
Chlorothalonil:	Tetrachloroisophthalonitrile
Ethyl acetate:	Residue grade or equivalent

5.0 REAGENTS AND MATERIALS TO BE PREPARED

Solution	Reagent Volumes[1]
0.01% Aerosol OT® solution	Dilute 0.1 mL Aerosol OT® solution to 1 L with Type I Water

[1]The absolute volumes of the reagents may be varied by the analyst provided the correct proportions are maintained.

6.0 SAMPLE PREPARATION

One analytical sample consists of one pack of two facial/neck wipes (cotton gauze sponges, 4" x 4" - 8-ply). Wet each sample with 8 mL of 0.01% Aerosol OT® solution.

7.0 STANDARD PREPARATION

7.1 Stock Solution:

Correcting for purity, prepare a stock standard solution of chlorothalonil by weighing an appropriate amount into a volumetric flask, dissolving with ethyl

acetate, and diluting to the mark. For example, weigh 0.1 g of chlorothalonil into a 100-mL volumetric flask, dissolve in ethyl acetate, and dilute to the mark with ethyl acetate. The concentration of the stock solution is approximately 1000 µg/mL. The stock solution is stored frozen (≤ -10°C) and remade at one year intervals.

If necessary, prepare serial dilutions from the stock solution of chlorothalonil in other solvents (such as toluene) for GC analysis.

7.2 Fortification Solutions:

Dilute the stock solution and/or the appropriate fortification solution(s) with ethyl acetate to generate 500-µg/mL, 50-µg/mL, and 10-µg/mL fortification solutions. Other concentrations may be prepared as needed. Suggested preparation is as follows:

Standard Solution Concentration (µg/mL)	Aliquot (mL)	Final Volume (mL)	Final Concentration (µg/mL)
5000	25	250	500
5000	1	100	50
50	20	100	10

7.3 Instrument Calibration Solutions:

Dilute the appropriate fortification/calibration solution(s) with ethyl acetate to generate instrumentation (calibration) solutions in a range appropriate for the expected residue levels. Suggested preparation is as follows:

Standard Solution Concentration (µg/mL)	Aliquot (mL)	Final Volume (mL)	Final Concentration (µg/mL)
10	10	100	1
1	10	100	0.1
0.1	50	100	0.05
0.1	20	100	0.02
0.1	10	100	0.01
0.01	50	100	0.005

All fortification and calibration standards are stored frozen (≤ -10°C) and should be remade at one year intervals.

8.0 FORTIFICATION

8.1 Laboratory Fortifications:

Prepare laboratory fortifications by applying the appropriate amount of fortification solution to the wetted facial swab sample via Hamilton syringe or equivalent. Distribute the solution evenly over the facial swab.

9.0 SAMPLE EXTRACTION AND CLEANUP PROCEDURES

9.1 Extraction:

Transfer the wetted facial swab sample into a 250-mL jar. Fortify the appropriate samples before placing into the jar. Add a total extraction volume of 100 mL of ethyl acetate to the jar and place on a shaker for ~30 minutes.

NOTE: Add the foil containing the field samples to the jar.

9.2 Final Volume:

Collect an aliquot of the ethyl acetate extract for GC analysis. Dilute samples with ethyl acetate, if necessary.

10.0 QUANTITATION BY ELECTRON CAPTURE GAS CHROMATOGRAPHY

The following columns and conditions are suggested and may be modified, within reason, to attain optimum chromatography.

Analytical conditions:

Instrument:	Hewlett Packard Gas Chromatograph, model 5890 Series II
Column:	RTX-5, fused silica capillary, 30 m x 0.53-mm i.d., 0.5-µm film thickness (available from Restek, Bellefonte, PA 16823)
Detector:	^{63}Ni Electron Capture Detector

Temperature:	160 °C for 1 min then 20 °C/min to 240 °C. Hold at 240 °C for 2 min, then 25 °C/min to 270 °C, hold for 6 min
Injection Port Temperature:	270 °C
Detector Temperature:	300 °C
Carrier Gas:	High purity helium, 8 mL/min
Make-up Gas:	High purity nitrogen, 30 mL/min
Injection Volume:	1 µL
Approximate Retention Time:	4.5 minutes
Total Run Time:	~ 15 minutes

11.0 CALIBRATION

Calibrate the gas chromatograph by injecting a minimum of four standard solutions in the concentration range of 0.005 µg/mL to 0.1 µg/mL. Prepare a calibration curve by plotting standard concentration versus response. This calibration curve also serves as the standard curve used for calculation purposes.

12.0 CALCULATIONS

12.1 Calculations for instrumental analysis are conducted using Microsoft Excel® software to create a standard curve based on linear regression. These regression functions are used to calculate a best fit line (from a set of standard concentrations in µg/mL versus peak response) and to determine concentration of the analyte found during sample analysis from the calculated best fit line.

The equation used for the least squares fit is:

$$y = mx + b$$

Where,

y = peak response (height or area)
x = µg/mL found
m = slope
b = y-intercept

12.2 The amount of chlorothalonil measured in each sample is calculated according to the following equation:

$$\mu g/sample = \frac{(\mu g/mL) \times (mL\ final\ volume) \times (dilution\ factor)}{(sample)}$$

Where,

µg/sample	=	total µg of analyte present per sample analyzed
µg/mL	=	concentration of analyte derived from the standard curve based on peak response from the sample injected utilizing the linear regression equation of y = mx + b
sample	=	One sample consists of one pack of two facial/neck wipes (cotton gauze sponges, 4" x 4" - 8-ply)
mL final volume	=	volume of final extract submitted to instrumentation (100 mL)
dilution factor	=	dilution of sample extract required to produce an analyte response bracketed by standards

12.3 The percent recovery for fortified control samples is calculated as follows:

$$\%\ Recovery = \frac{\mu g/sample\ found\ in\ fortified\ control}{\mu g/sample\ added\ to\ fortified\ control} \times 100$$

13.0 REFERENCES

Ricerca, Inc. Report / SDS-2787, 6445-95-0086-CR-001

APPENDIX I

Recoveries for Chlorothalonil in Facial/Neck Wipes

Analytical Data and Recoveries for CAL Study # 017-01:
Determination of Chlorothalonil in Cotton Facial/Neck Wipes

Extraction Date: 2/25/97 **Analysis Date:** 2/26/97 **Matrix:** Cotton Facial/Neck Wipes

STANDARD CURVE:

Conc. (µg/mL)	Peak Height
0.10	468037
0.05	240121
0.01	49337
0.005	27899
0.10	479839
0.05	252906
0.01	54475
0.005	27994

Linear Calibration Equation: y = mx+b

m= 4703022

b= 6076

Correlation Coefficient = 0.9995

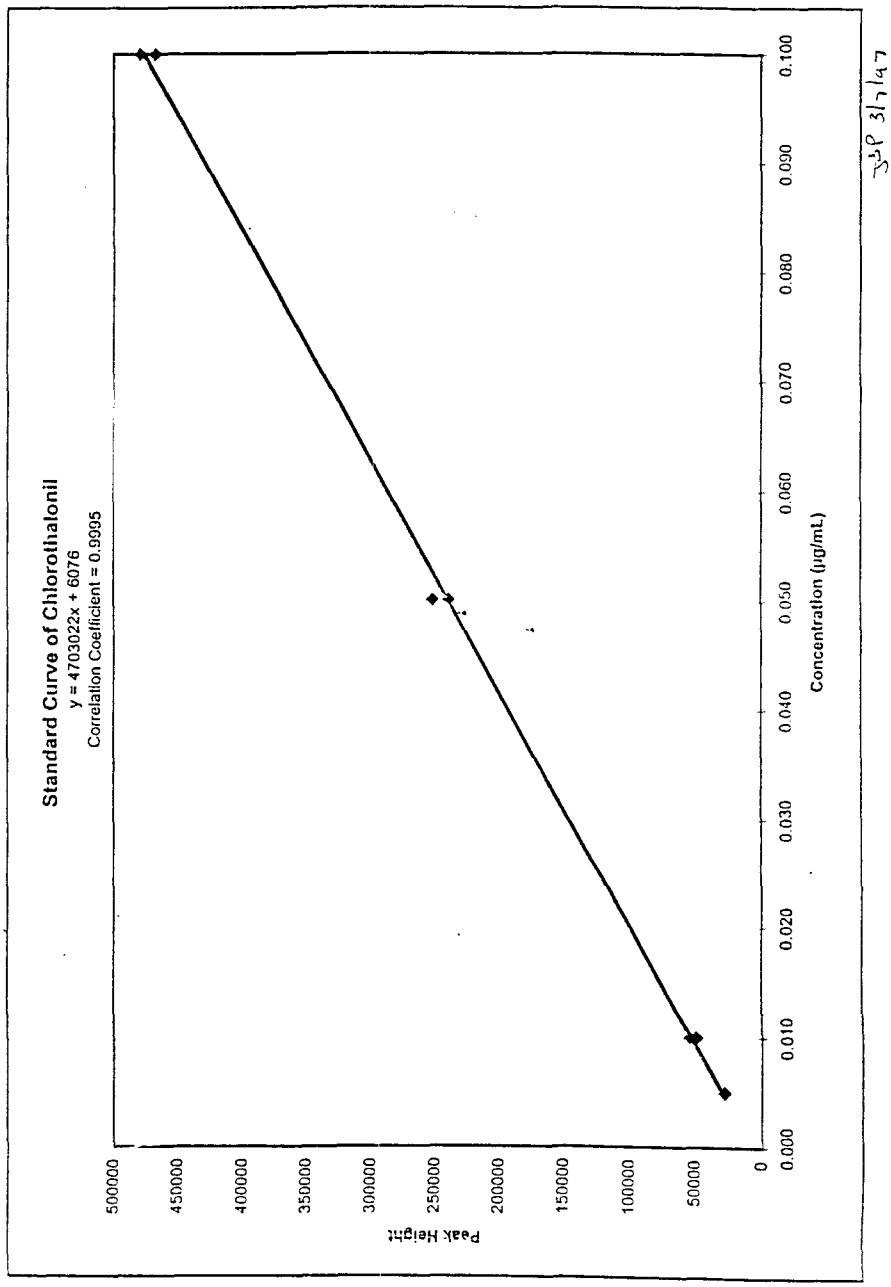
DATA:

CAL ID#	Client ID	Compound Found	Peak Height	Peak Height Corrected	µg/mL Compound Found	Final Volume (mL)	Dilution Factor	µg/Dosimeter Found	µg Compound Added	Percent Recovery
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
Solvent Blank	NA	Chlorothalonil	0	0	0.0000	na	1	0.0	na	na
970177 Blk	NA	Chlorothalonil	0	0	0.0000	100	1	0.0	na	na
970178 Spk A	NA	Chlorothalonil	222496	222496	0.0460	100	1	4.60	5	92%
970179 Spk B	NA	Chlorothalonil	232255	232255	0.0481	100	1	4.81	5	96%
970180 Spk C	NA	Chlorothalonil	126258	126258	0.0256	100	10	25.6	25	102%
970181 Spk D	NA	Chlorothalonil	129942	129942	0.0263	100	10	26.3	25	105%
970182 Spk E	NA	Chlorothalonil	127641	127641	0.0258	100	50	129	125	103%
970183 Spk F	NA	Chlorothalonil	130991	130991	0.0266	100	50	133	125	106%
									Average (n=6):	101%
									Standard Deviation:	5.6%

APPENDIX II

Calibration Curve and Example Chromatograms

Analysis Date: 2/26/97



CAL Study No. 017-01

Extraction Date: 2/25/97

ARTF Study No. ARF004

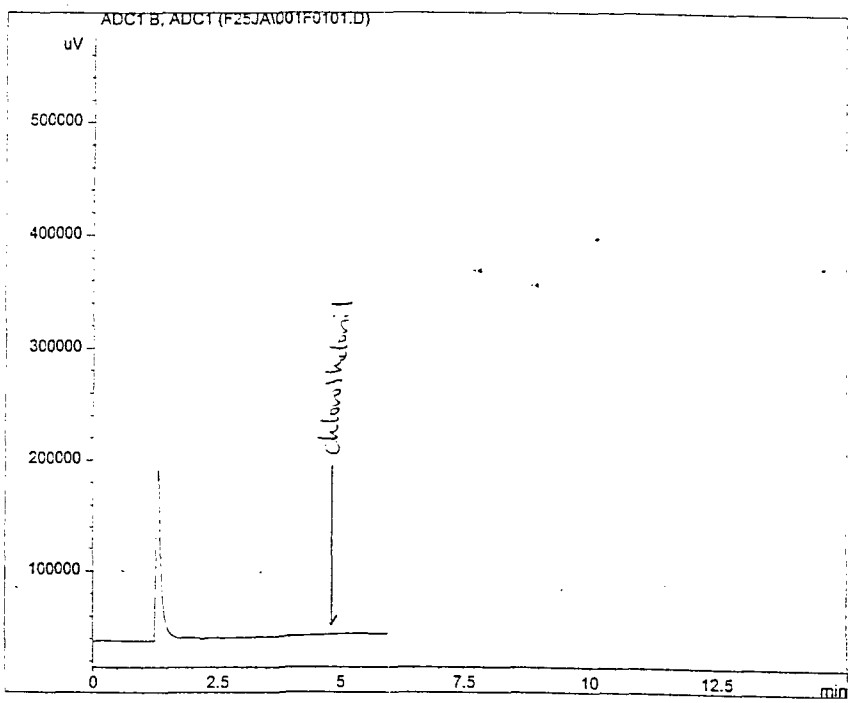
Analysis of Chlorothalonil

Run No.: 1

Sample No: NA
Sample Info: Solvent Blank

Injected on: 2/26/97 6:05:38 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

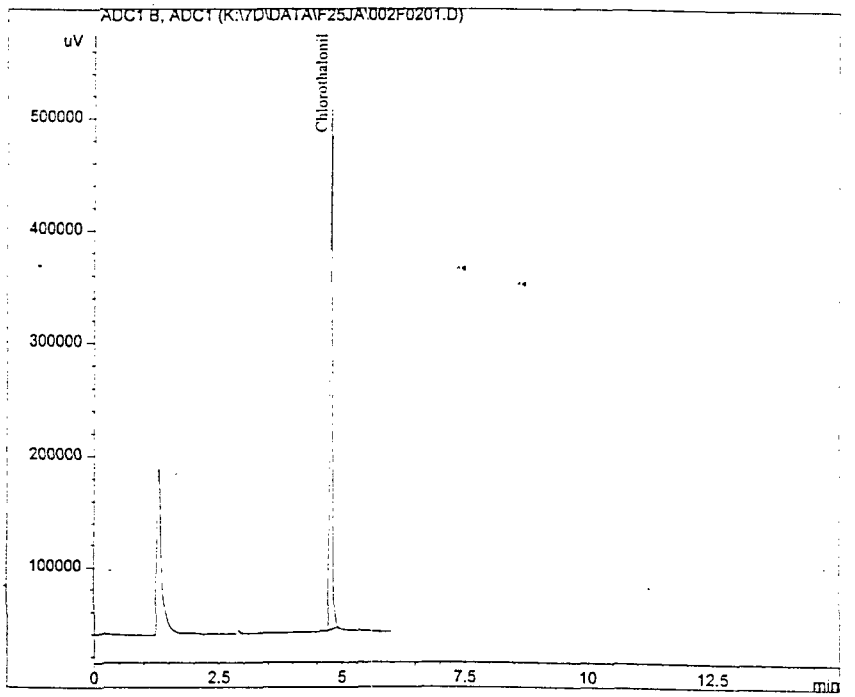
Analysis of Chlorothalonil

Run No.: 2

Sample No: NA
Sample Info: 0.1 µg/mL Standard, C021097-1

Injected on: 2/26/97 6:17:53 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.759	Chlorothalonil	468036.5	1.564e+006

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

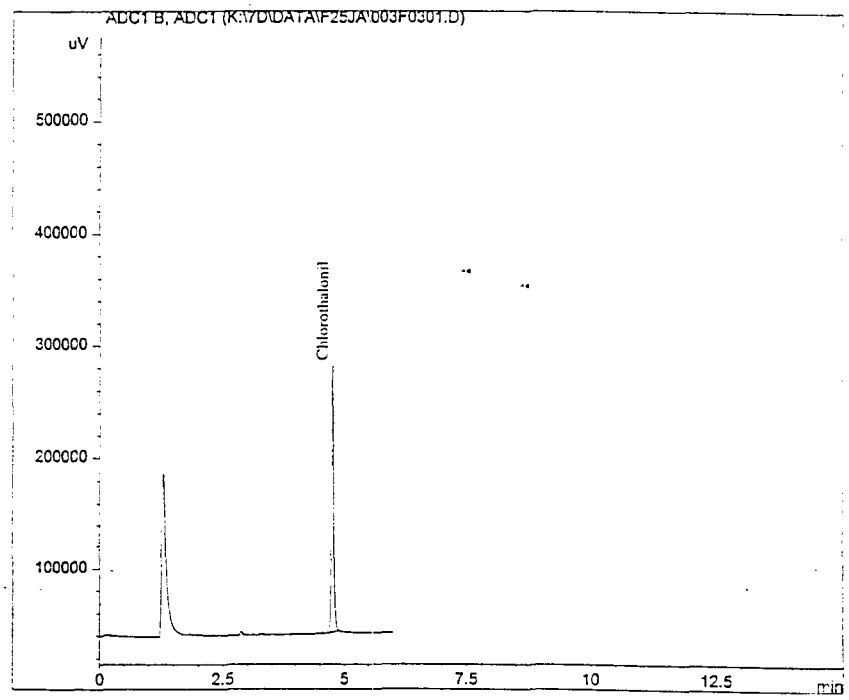
Analysis of Chlorothalonil

Run No.: 3

Sample No: NA
Sample Info: 0.05 µg/mL Standard, C021097-2

Injected on: 2/26/97 6:30:05 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.738	Chlorothalonil	240120.9	788084.250

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

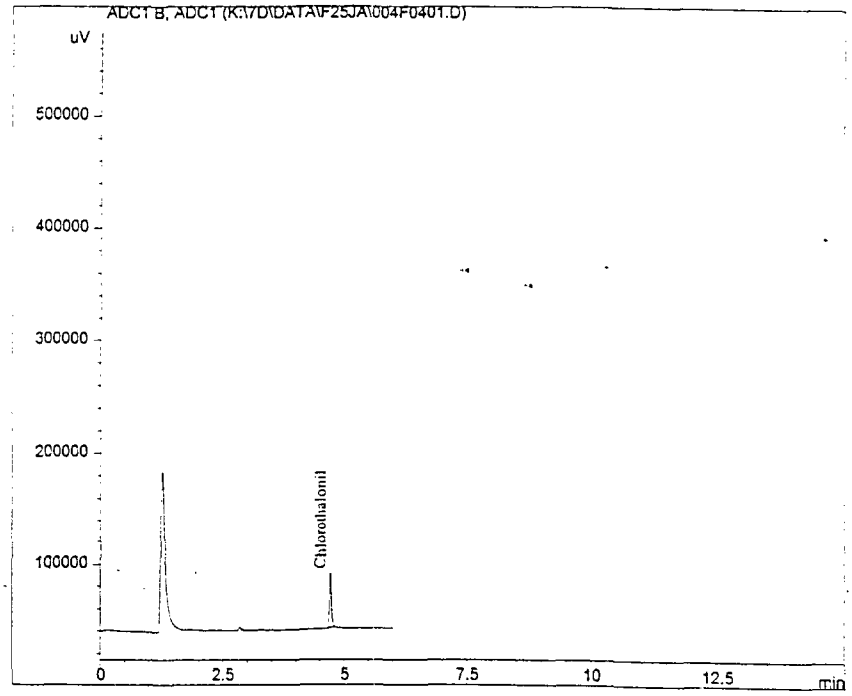
Analysis of Chlorothalonil

Run No.: 4

Sample No: NA
Sample Info: 0.01 µg/mL Standard, C021097-3

Injected on: 2/26/97 6:42:20 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.712	Chlorothalonil	49336.9	147453.719

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

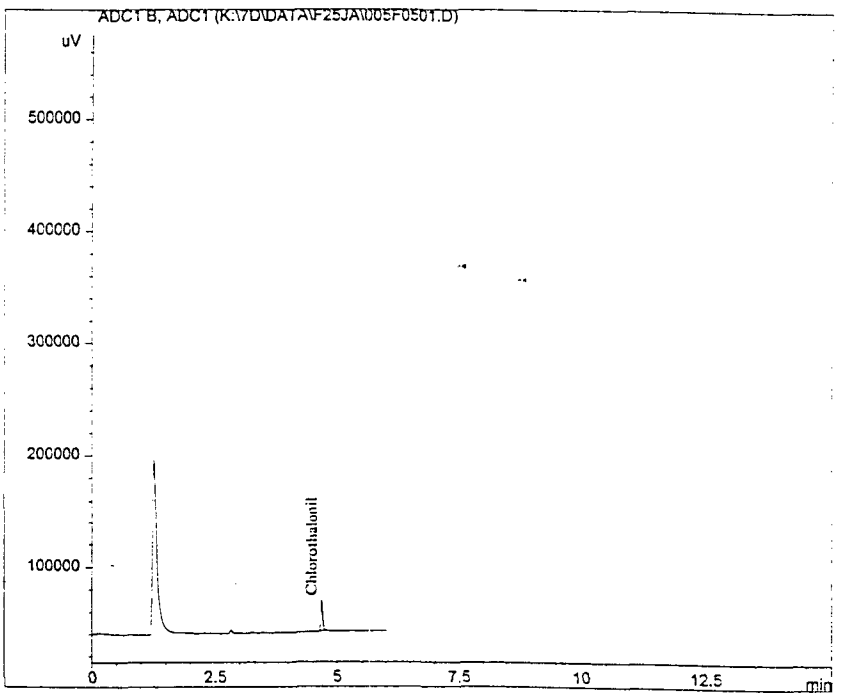
Analysis of Chlorothalonil

Run No.: 5

Sample No: NA
Sample Info: 0.005 µg/mL Standard, C021097-4

Injected on: 2/26/97 6:54:32 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.684	Chlorothalonil	27899.1	77637.523

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

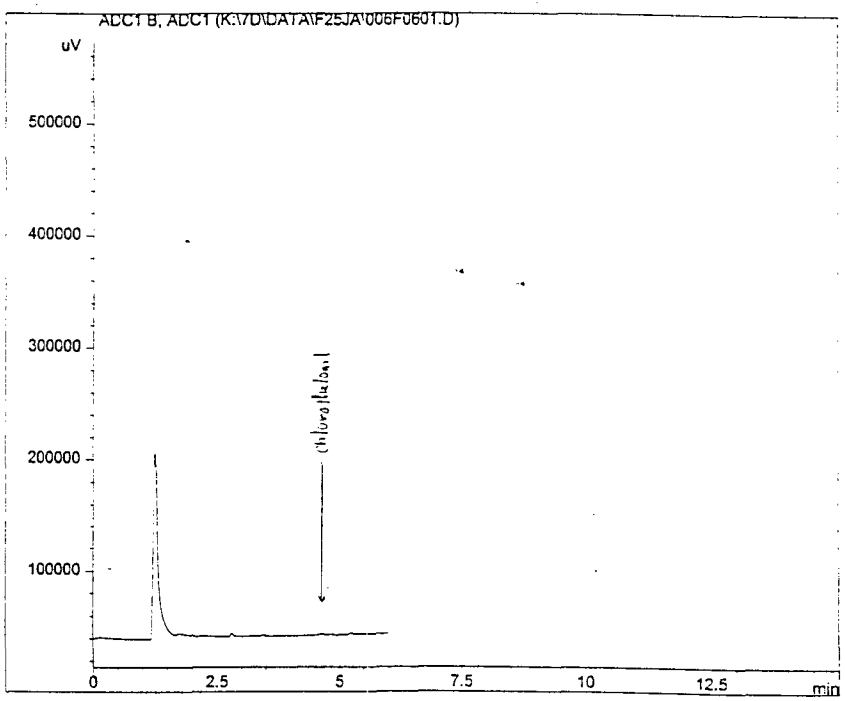
Analysis of Chlorothalonil

Run No.: 6

Sample No: CAL 970177 Blk
Sample Info: Control, Final Volume = 100 mL

Injected on: 2/26/97 7:06:47 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

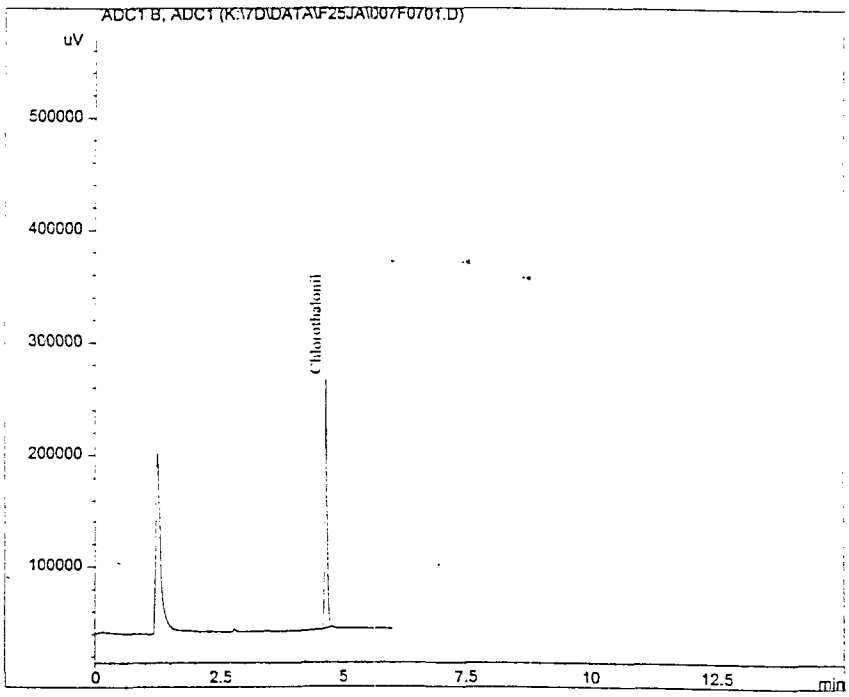
Analysis of Chlorothalonil

Run No.: 7

Sample No: CAL 970178 Spk A
Sample Info: Control Fortified at 5 µg, Final Volume = 100 mL

Injected on: 2/26/97 7:19:00 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.643	Chlorothalonil	222495.5	752778.938

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

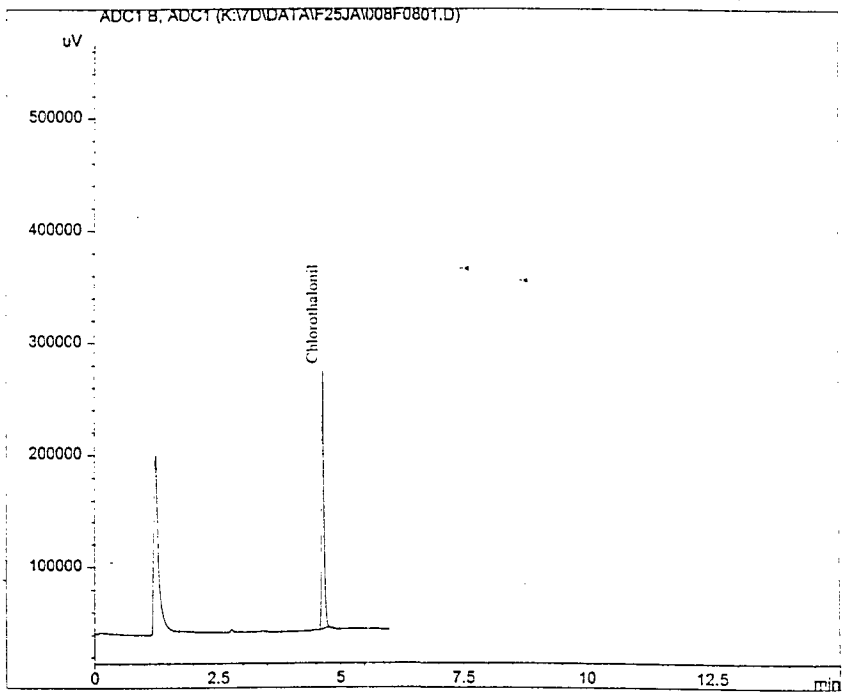
Analysis of Chlorothalonil

Run No.: 8

Sample No: CAL 970179 Spk B
Sample Info: Control Fortified at 5 µg, Final Volume = 100 mL

Injected on: 2/26/97 7:31:13 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.627	Chlorothalonil	232254.8	771053.563

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

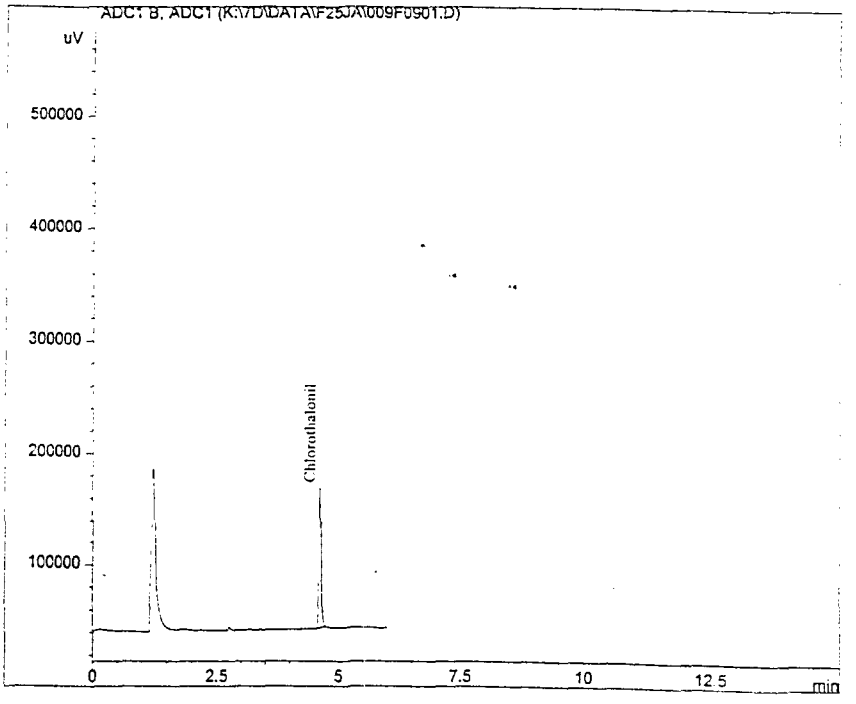
Analysis of Chlorothalonil

Run No.: 9

Sample No: CAL 970180 Spk C
Sample Info: Control Fortified at 25 µg, Final Volume = 100 mL
Dilution Factor = 10

Injected on: 2/26/97 7:43:25 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.609	Chlorothalonil	126257.9	404558.719

CAL Study Number: 017-01
ARTF Study Number: ARF004

Operator: Julie B. Petit

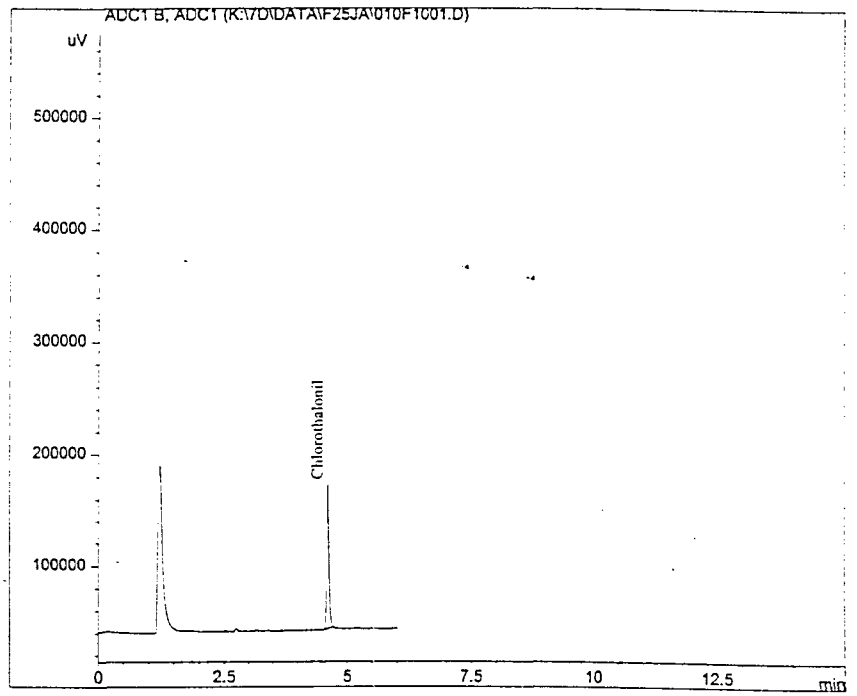
Analysis of Chlorothalonil

Run No.: 10

Sample No: CAL 970181 Spk D
Sample Info: Control Fortified at 25 µg, Final Volume = 100 mL
Dilution Factor = 10

Injected on: 2/26/97 7:55:39 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.595	Chlorothalonil	129942.0	414797.656

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

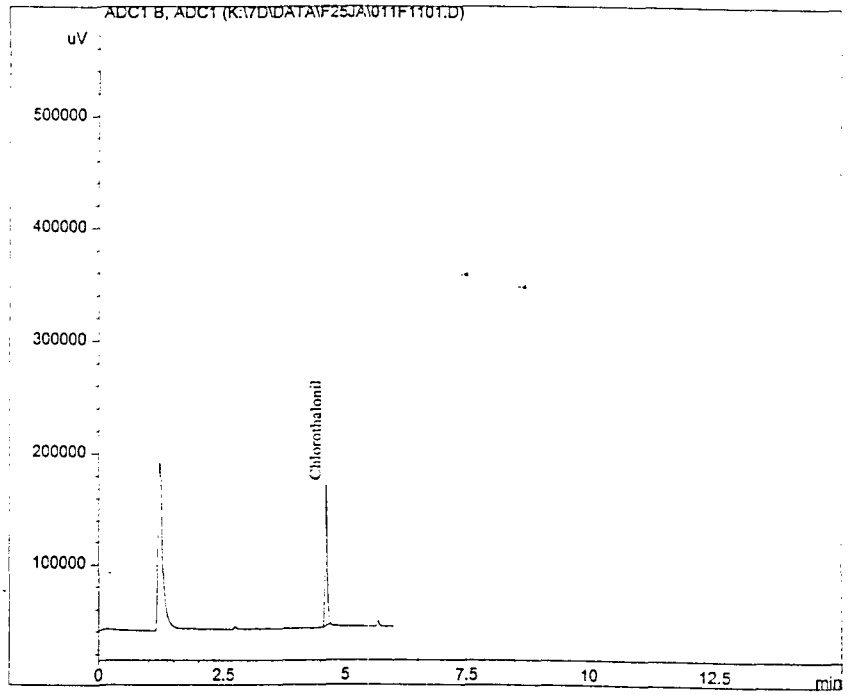
Analysis of Chlorothalonil

Run No.: 11

Sample No: CAL 970182 Spk E
Sample Info: Control Fortified at 125 µg, Final Volume = 100 mL
Dilution Factor = 50

Injected on: 2/26/97 8:07:53 PM

Is chromatogram used? Yes/No: (Y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.589	Chlorothalonil	127640.8	404530.969

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

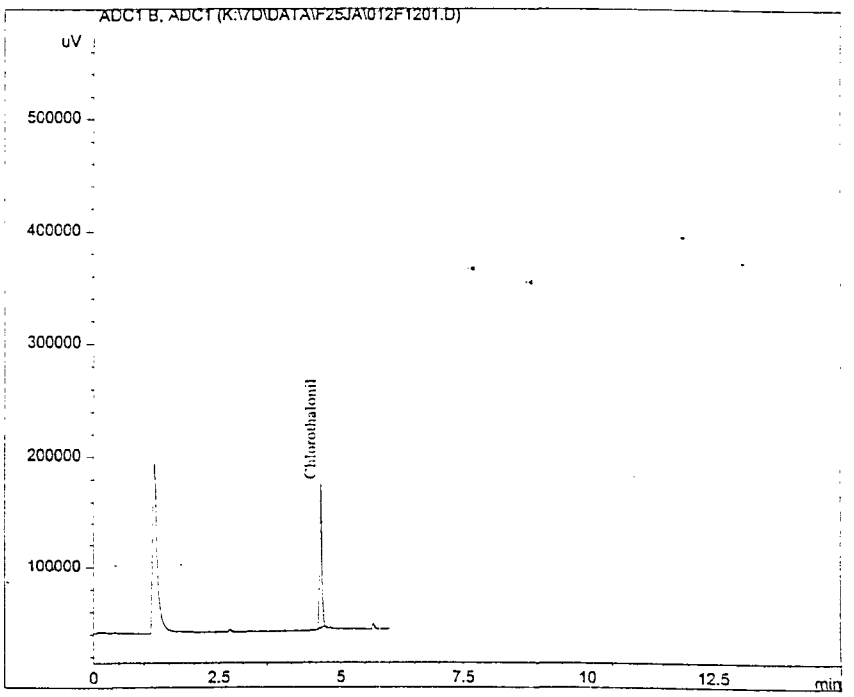
Analysis of Chlorothalonil

Run No.: 12

Sample No: CAL 970183 Spk F
Sample Info: Control Fortified at 125 µg, Final Volume = 100 mL
Dilution Factor = 50

Injected on: 2/26/97 8:20:08 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.583	Chlorothalonil	130990.8	413400.656

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

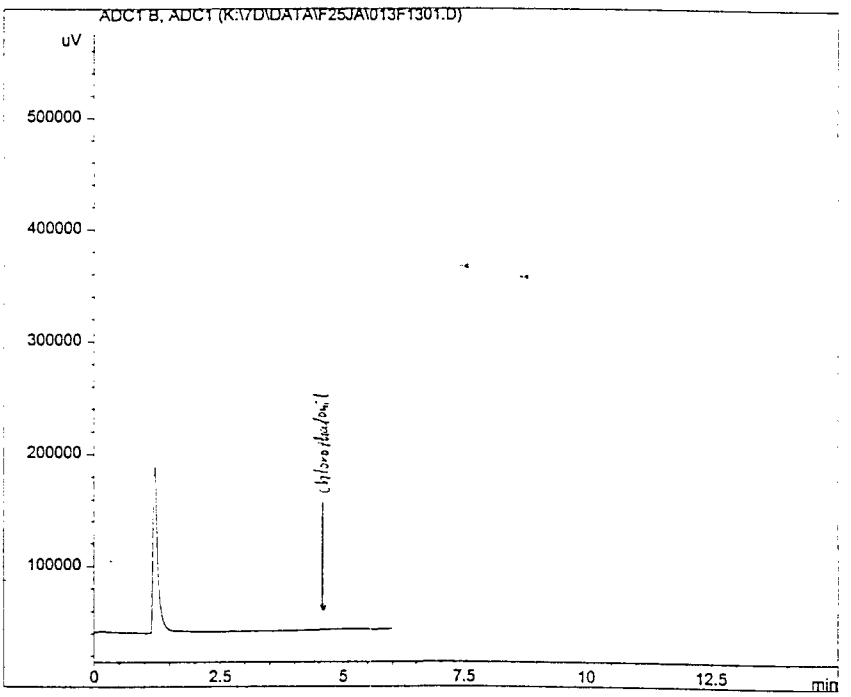
Analysis of Chlorothalonil

Run No.: 13

Sample No: NA
Sample Info: Solvent Blank

Injected on: 2/26/97 8:32:19 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
0.000	Chlorothalonil	0.0	0.000

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

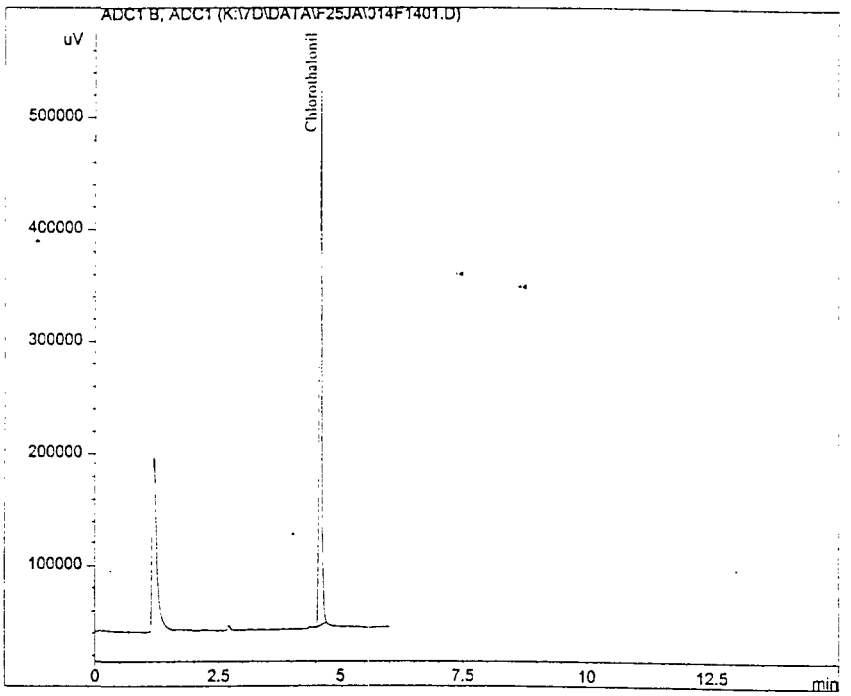
Analysis of Chlorothalonil

Run No.: 14

Sample No: NA
Sample Info: 0.1 µg/mL Standard, C021097-1

Injected on: 2/26/97 8:44:32 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.566	Chlorothalonil	479838.9	1.688e+006

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

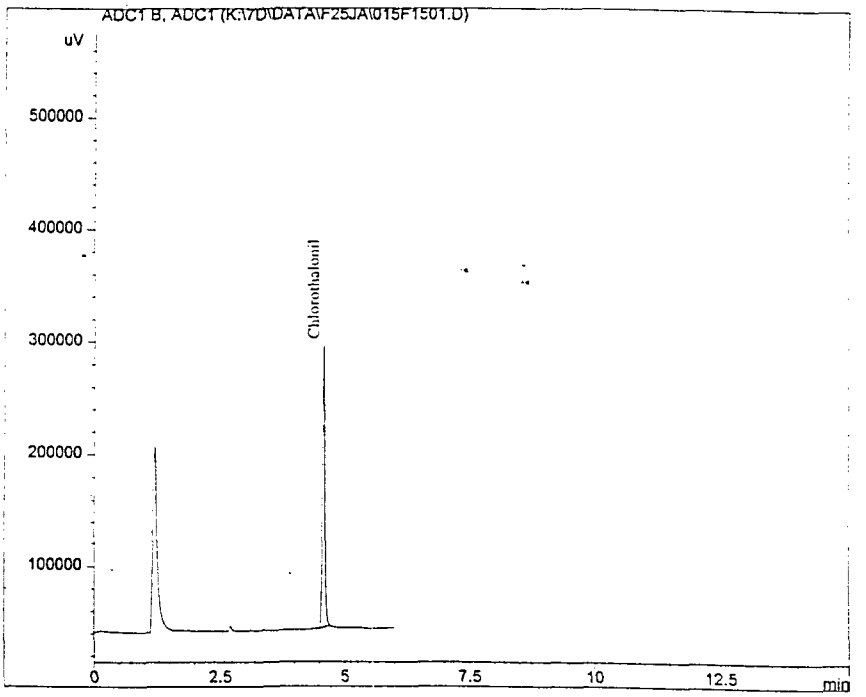
Analysis of Chlorothalonil

Run No.: 15

Sample No: NA
Sample Info: 0.05 µg/mL Standard, C021097-2

Injected on: 2/26/97 8:56:45 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.563	Chlorothalonil	252906.0	856545.938

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

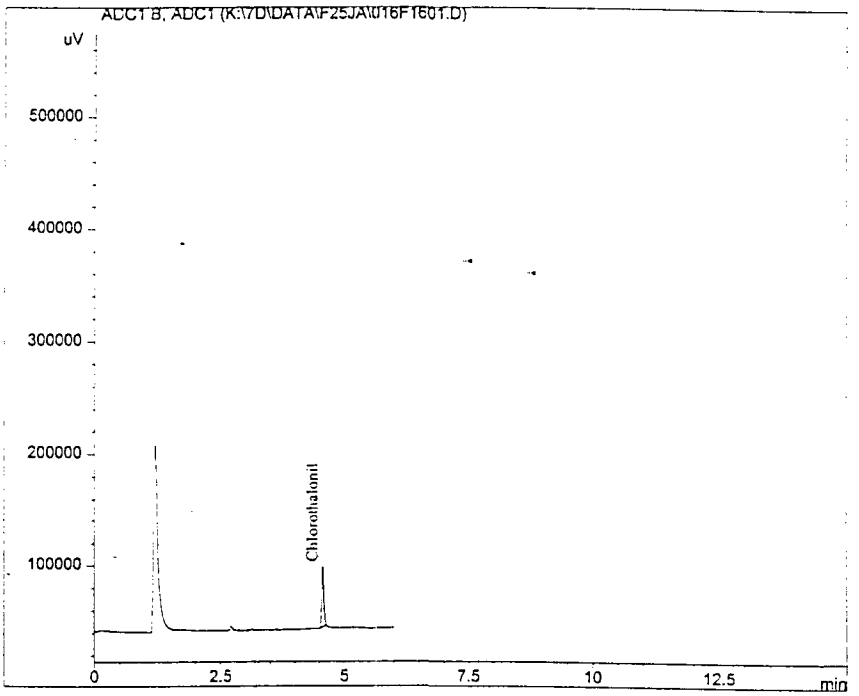
Analysis of Chlorothalonil

Run No.: 16

Sample No: NA
Sample Info: 0.01 µg/mL Standard, C021097-3

Injected on: 2/26/97 9:08:59 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.565	Chlorothalonil	54475.2	161617.063

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

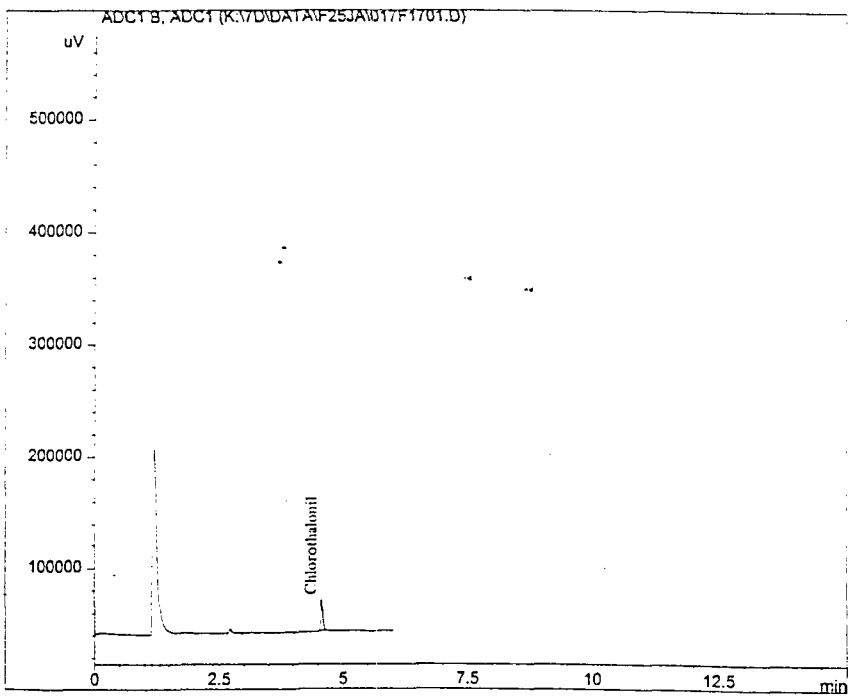
Analysis of Chlorothalonil

Run No.: 17

Sample No: NA
Sample Info: 0.005 µg/mL Standard, C021097-4

Injected on: 2/26/97 9:21:10 PM

Is chromatogram used? Yes/No: (y), if no, why?



Meas. Ret. (Min)	Compound Name	Peak Height (µV)	Peak Area (µV*s)
4.570	Chlorothalonil	27993.8	80244.539

CAL Study Number: 017-01 Operator: Julie B. Petit
ARTF Study Number: ARF004

APPENDIX II

ANALYSIS PROCEDURE FOR DETERMINATION OF

CHLOROTHALONIL IN RESPIRATORY AND DERMAL DOSIMETERS

INTRODUCTION

Residues of chlorothalonil will be extracted from samples of respiratory filters, sorbent tubes, handwash, facial swabs, socks and whole-body dosimeter into an organic solvent. Samples of field spiking solution will be extracted with petroleum ether. Residues of chlorothalonil will be quantitated by electron-capture gas chromatography.

MATERIALS

Chemicals

Acetone, pesticide grade, or equivalent

Aerosol OT-75 (w/w) solution, Fisher Scientific Company, Cat. No. A345-500

Alumina (aluminum oxide, Alumina A-Super 1), activated at 115 ± 5 °C at least 24 hours before use, Fisher Scientific Company, Cat. No. 05-719-832

Chlorothalonil (tetrachloroisophthalonitrile, SDS-2787-1501), 99.6%

Deionized water

Diethyl ether, anhydrous, A.C.S. reagent grade or equivalent

Ricerca, Inc. II-3
6445-95-0086-CR-000
Report/SDS-2787

Ethyl acetate, pesticide grade or equivalent

"Keeper" solution, consisting of 2 mL light mineral oil in 100 mL petroleum ether

Methylene chloride, pesticide grade or equivalent

Mineral oil, light, technical grade

N_2, high purity

Petroleum ether, pesticide grade, or equivalent

Sodium chloride (NaCl), A.C.S. certified, or equivalent

Sodium sulfate (Na_2SO_4), anhydrous

Sulfuric acid (H_2SO_4), 10 N, A.C.S. reagent grade or equivalent

Toluene, pesticide grade, or equivalent

Equipment

✓ Bottles, 2 oz. and 4 oz. with polyseal lined caps, Fisher Scientific Company, Cat. Nos. 03-326-5B and -5C

✓ Chromatographic glass columns, 200 mm x 9 mm, Kontes Co., Cat. No. K420100-23

✓ Filters, glass fiber, 1 µm pore size, 37 mm diameter, type AE, available from SKC, Inc., Cat. No. 225-7

Ricerca, Inc. II-4
6445-95-0086-CR-000
Report/SDS-2787

Foil, aluminum

Gas chromatograph equipped with a ^{63}Ni electron capture detector, autosampler and data system. Analytical conditions:

Column 1: 30 m DB-5 (or SE-54) capillary column, 0.25 mm i.d., 0.25 µm film thickness (available from J & W Scientific, Folsom, CA 95630)

Column 2: 30 m x 0.32 mm i.d. DB-608 capillary column, 0.50 µm film thickness (available from J & W Scientific, Folsom, CA 95630)

Column 3: 6' x 1/4" o.d. x 2 mm i.d. glass column filled with 3% Dexsil 300 on 100/120 mesh Supelcoport, available from Supelco, Inc., Bellefonte, PA 16823

Column 4: 6' x 1/4" o.d. x 2 mm i.d. glass column filled with 3% OV-210 on 80/100 Supelcoport, available from Supelco, Inc., Bellefonte, PA 16823

Column 5: 6' x 1/4" o.d. x 2 mm i.d. glass column filled with 3% OV-7 on 100/120 mesh Supelcoport, available from Supelco, Inc., Bellefonte, PA 16823

Temperature: Column 1 and 2: 220-240 °C
Column 3 and 4: 180-200 °C

Injection Port Temperature: 270-320 °C

Detector Temperature: 300-350 °C

Carrier Gas: Column 1 and 2: High purity helium
Column 3 and 4: High purity nitrogen

Make-Up Gas: High purity nitrogen or ultra high purity 5-10% methane in argon.

Injection Volume: 1-4 µL

Gauze pads, Johnson and Johnson

Glass jars, 6 oz, 8 oz and 2 liter with Teflon lined caps, Fisher Scientific Company, Cat. Nos. 03-320-11G and 03-321-1E, or equivalent

Reciprocating shaker

Socks, 80% cotton, 15% polyester, 5% elastic from K-Mart Corporation

Sorbent tube, Chromosorb-102, 50/100 mg 2-section, 8 x 70 mm, SKC, Inc., Cat. No. 226-104

Sorbent tube, Chromosorb-102, 50/100 mg 2-section, 8 x 110 mm, SKC, Inc. Cat. No. 226-107

Standard laboratory glassware: beakers, flasks, separatory funnels, etc.

Support pads, Millipore, Cat. No. AP10 03700

Water bath, maintained at a maximum temperature of 37 °C

Whole-body dosimeter, 100% cotton underwear, (J. C. Penny, Sears or equivalent)

Vials, 20 mL scintillation

PREPARATION OF STANDARD SOLUTIONS

Prepare a standard solution of chlorothalonil by weighing 0.1 g chlorothalonil to the nearest 0.1 mg into a tared weighing pan. Transfer the chlorothalonil quantitatively to a 100-mL volumetric flask using ethyl acetate. Dilute to volume with ethyl acetate to produce a stock solution of 1000 µg/mL. Dilute this stock solution serially with ethyl acetate to result in calibration standards in the range of 0.001 to 0.10 µg/mL for the quantitation of chlorothalonil. Use serial dilutions in ethyl acetate to amend control samples for recoveries in the operating range of interest.

If necessary, prepare serial dilutions in other solvents such as acetone from the 1000-µg/mL stock solution of chlorothalonil for the GC analysis of some of the matrices.

PREPARATION AND EXTRACTION OF SAMPLES

Handwash

The field fortifications will consist of 250 mL of handwash solution in a glass jar or bottle. Thaw the frozen samples by having them set out at room temperature or by immersing them in warm water.

Ricerca, [redacted]
6445-95-[redacted]-000
Report/[redacted]

[redacted]-7

Recovery [redacted] generated by amending lab controls consisting of 250 mL of 0.01% Aerosol OT-75 (v/v) in a separatory funnel.

Transfer the solution quantitatively to a 500-mL separatory funnel with 50 mL of 1:1 petroleum ether/diethyl ether (v/v). Add 10 mL of 20% NaCl (w/w) solution and 2 mL of 10 N H_2SO_4. Vent and shake the funnel for two minutes. Allow phase separation and drain the lower aqueous phase back into the beaker. Pour the ether phase through the top of the separatory funnel into an appropriately sized bottle. Care must be taken so that no water is transferred with the ether.

Repeat the extraction with another 50-mL portion of the ether mix. Combine the ether extracts and add 0.4 mL of keeper. Concentrate the ether to approximately 2 mL in the water bath. Evaporate the remaining solvent just to dryness with nitrogen only. CAUTION: The use of the nitrogen stream after the solvent has evaporated can result in low recovery of chlorothalonil. Dissolve the residue in 10 mL ethyl acetate. Transfer a 2-mL aliquot to a GC vial for analysis or dilute appropriately. If chromatographic peak interferences prevent accurate quantitation, proceed to COLUMN CLEANUP (OPTIONAL).

Facial Swabs

The field fortifications will consist of two gauze pads (7.5 cm x 7.5 cm) wrapped in foil and sealed in a 6 oz glass jar. The samples will be removed from the freezer. The foil will be cut into strips and returned to the jar.

Recovery samples will be generated by amending two gauze pads in an 8-oz. jar. A piece of foil, similar to the size used for the field fortifications, will be cut into strips and placed in the jar.

An aliquot of 100 mL of ethyl acetate will be added to the sample jar. The jar will be sealed with a Teflon lined cap and put on a shaker for 30 minutes. The ethyl acetate extract will be quantitated for chlorothalonil.

Whole-Body Dosimeter/Socks

The field spike samples will consist of a sock or a 20 cm x 20 cm piece of underwear wrapped in foil and heat sealed in a Kapak bag. The sample bags will be removed from the freezer. The field spike sample will be placed in an 8-oz. jar. The foil wrapped around the underwear will be cut into pieces and put in the jar.

Recovery samples will be generated by amending an underwear sample or sock in the jar. Underwear and sock samples used for recoveries will be similar in size to the field spikes.

A 100 mL aliquot for underwear and 500 mL aliquot for socks of ethyl acetate will be added to the sample jar. The jar will be sealed with a Teflon lined cap and placed on a shaker for 30 minutes. The ethyl acetate extract will be quantitated for chlorothalonil.

Respiratory Filters and Sorbent Tubes

The field fortification samples will consist of the glass fiber filters with support pads in cassettes and sealed sorbent tubes. The cassette will be removed from the freezer, and the filter and support pad will be transferred to a 20-mL scintillation vial. The sorbent tube will be removed from the freezer and divided into two samples. The "front tube" sample will consists of the front packing along with the front and middle pieces of glass wool. The "rear tube" sample will consist of the rear packing and rear piece of glass wool. The two samples from the sorbent tube will be placed in separate 20-mL scintillation vials.

Filter recovery samples will be generated by amending a control glass fiber filter with support pad in a scintillation vial. Sorbent tube recovery samples will be generated by amending control "front of tube" and "back of tube" sections, as described above, in 20-mL scintillation vials.

An aliquot of 10 mL of toluene will be added to each filter with support pad and 3.5 mL to each sorbent tube sample. The vials will be sealed and shaken by hand for approximately 2 minutes. The toluene extract will be quantitated for chlorothalonil.

Field Fortification Solutions

Samples of aqueous chlorothalonil field spiking solutions will be received either as a measured aliquot in a vial, or as the left over spiking solution in a bottle. The solutions will be removed from the freezer and allowed to thaw.

The entire contents of the vial or subsample of the shaken bottle of solution will be quantitatively transferred to a 250-mL separatory funnel using acetone. Add 20 mL of deionized water and 50 mL of petroleum ether. Vent and shake the funnel for two minutes. Allow phase separation and drain the lower aqueous phase into a beaker. Pour the ether phase through the top of the separatory funnel into an appropriately sized bottle. Care must be taken so that no water is transferred with the ether.

Repeat the extraction with another 50 mL portion of petroleum ether. Combine the extracts and add 0.4 mL of keeper. Concentrate the ether extract to approximately 1 mL in the water bath. Evaporate the remaining solvent to dryness with a dry air stream. CAUTION: The use of the air stream after the solvent has evaporated can result in low recovery of chlorothalonil. Dilute the sample extract in an appropriate volume of ethyl acetate for quantitation of chlorothalonil by gas chromatography.

COLUMN CLEANUP (OPTIONAL)

A glass chromatogaphic column, 200 mm x 9 mm, will be packed bottom to top with a 0.5-cm bed of glass wool, 3 g of the activated alumina and 1 cm anhydrous sodium sulfate. The column will be washed with approximately 10 mL of methylene chloride. After the methylene chloride has entered the column, a 2-oz glass bottle will be placed under the column. Two mL of the sample in methylene chloride will be quantitatively transferred to the column. After the sample has moved into the column bed, chlorothalonil will be eluted from the column with 40 mL methylene chloride.

Add a 0.4-mL portion of Keeper solution to each bottle. Place the bottle in the water bath and concentrate the solvent to approximately 0.5 mL using a gentle stream of dry nitrogen directed on the surface of the solvent to aid evaporation. Remove the bottle from the water bath and evaporate the contents to dryness using a stream of dry air. Dilute the samples in ethyl acetate for quantitation of chlorothalonil.

QUANTITATION BY ELECTRON CAPTURE GAS CHROMATOGRAPHY

GC conditions are listed in the Equipment section of this protocol. Approximate 1.0-mL portions of sample extracts and calibration standard are sealed in vials for use with the gas chromatograph. Sample volume, peak retention time, calibration standard concentration and other data are typed into the microprocessor.

Samples are analyzed based on external standard calibration using the following calculations:

$$\text{Calibration Factor} = \frac{\text{Std. Concentration (mg/mL)} \times 10{,}000^{1}}{\text{Standard Area or Peak Height}}$$

$$\mu\text{g chlorothalonil} = \frac{\text{Calibration Factor X Vol. for GC X Sample Area or Peak Height}}{10{,}000^{1}}$$

A series of varying concentration standards is prepared to establish a linear operating range. The non-detect level is established by the concentration of the calibration standard, or one of the other standards in the linear operating range.

If necessary, quantitation will be done manually using standard area or peak height.

[1]The factor of 10,000 is used by a Varian data system.