



Monitoring and Laboratory Division  
Air Quality Surveillance Branch

**Protocol for the Application  
Air Monitoring of Dicofol**

June 18, 2008

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The following protocol has been reviewed and approved by staff of the Air Resources Board (ARB). Approval of this protocol does not necessarily reflect the views and policies of the ARB, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

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## **1.0 Introduction**

At the request of the California Department of Pesticide Regulation (DPR), (January 4, 2008 Memorandum, Warmerdam to Goldstene) the Air Resources Board (ARB) staff will determine airborne concentrations of Dicofol in Fresno or Merced county. This application monitoring study will be performed prior to, during and after an application of dicofol. Dicofol application monitoring is requested by DPR to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5, Section 14022(c)) which requires the ARB "to document the level of airborne emissions.... of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. Monitoring is being conducted to coincide with the use of dicofol as a selective pesticide on cotton.

The draft laboratory analysis method titled "Standard Operating Procedure Sampling and Analysis of 222-trichloro-1,1-bis(4-chlorophenyl)ethanol (Dicofol)" dated May 19, 2008, is included as Appendix A.

## **2.0 Project Goals and Objectives**

The goal of this monitoring project is to measure the concentrations of dicofol in the ambient air prior to, during, and after an application.

To achieve the project goal, the following objectives should be met:

1. Identification of monitoring sites that mutually satisfies criteria for ambient air sampling and DPR's requirements.
2. Appropriate application of sampling/monitoring equipment to determine ambient dicofol concentrations.
3. Application of relevant field quality assurance/quality control practices to ensure the integrity of field samples.
4. At the conclusion of the project, MLD will provide DPR with a final report containing all relevant information and data of this project.

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## 4.0 Study Location and Design

Dicofol applications are performed throughout the San Joaquin Valley. DPR has identified that June and July are the peak use periods for dicofol applications.

### Application Monitoring

Samples will be collected by passing a measured volume of ambient air through XAD-4 resin tubes that are mounted on a sampling tree as shown in **Figure 2, Air Sampler Tree with Pump**. The exposed XAD-4 resin tubes (SKC #CPM090904-001) will be stored in an ice chest (on dry ice) or in a freezer until extracted in the laboratory with organic solvent. The tubes will be protected from direct sunlight and supported about 1.5 meters above the ground during application monitoring sampling periods. At the end of each sampling period, the tubes will be placed in culture tubes with an identification label affixed. Subsequent to sampling, the sample tubes will be transported on dry ice, as soon as reasonably possible, to the ARB Sacramento Monitoring and Laboratory Division laboratory for analysis. The samples will be stored in the freezer or extracted/analyzed immediately.

In addition, two additional samplers will be installed in parallel on opposite sides of the application perimeter that will incorporate a particulate pre-filter, inline and prior to the XAD-4 resin tube. See **Figure 3, Filter Cassette and Filter Holder Assembly**. The exposed filters will be placed in Petri dishes with identification labels attached. They will be stored and transferred identical to the XAD-4 resin tubes described in the previous paragraph. These parallel inline XAD-4 resin tubes will be handled identical to the other resin tubes described in the previous paragraph.

A rotometer is used to control sample flow rates. On the predominately downwind sample tree, two rotometers will be located on a collocated sampling tree. The first rotometer is to control flow to the primary sample. The second rotometer is to control flow through the collocated/parallel sample. The rotometers are scaled from 0-5 LPM. The flow rates are set to 2.0 LPM, as measured using a calibrated digital mass flow meter (MFM) scaled from 0-5 LPM. The flow rate is checked, using the MFM, at the beginning and the end of each period. Samplers will be leak checked prior to each sampling period with the sampling tubes installed. The sample field log sheet will be used to record start and stop times, start and stop flow rates, start and stop counter readings, sample identifications and all other significant information.

The following recommendations were obtained from DPR's, "Use Information and Air Monitoring Recommendations for the Pesticide Active Ingredient Dicofol", dated April 2008 (Appendix B).

The use maps for dicofol suggest that application monitoring should occur in Fresno, Merced, Madera, Kings or Tulare Counties during the months of June through July. Growers in Fresno County used the most dicofol in both 2005 and 2006, however use in 2007 dropped to less than 50 pounds. Merced County

showed consistent use over both 2005 and 2006, however use in 2007 dropped significantly. MLD Staff has investigated planned dicofol usage for 2008 and to date, only one Merced County cotton grower, is planning to apply dicofol. The majority of applications occurred during June and July to treat cotton.

DPR recommendation state:

*“Considering two thirds of dicofol is used on cotton in California, DPR recommends ARB to choose an application on cotton field at application rate of 1.5 pounds per acre”.*

After contacting Fresno, Tulare, Kings and Merced County Department of Agriculture personnel, MLD Staff have determined that all current dicofol applications are 1.5 pounds per acre or less.

DPR recommendation state:

*“Application sites for these commodities ranged from 3 to 238 acres treated with an average of 94 acres (DPR PUR Database). However, entries in the PUR database may reflect multiple applications to the same site, resulting in high reported usage. DPR therefore recommends that the selected monitoring site be 94 to 238 acres”.*

During the air monitoring of the application, samples are collected according to the Table 1A Guidelines for Daytime Application and Sampling Schedule or Table 1B Guidelines for Nighttime Application and Sampling Schedule.

**TABLE 1A. GUIDELINES FOR DAYTIME APPLICATION SAMPLING SCHEDULE**

<b>Sample period begins:</b>	<b>Sample duration time</b>
Background (pre-application)	Minimum 18 – 24 hours
Application	Start of application until 1 hour after end of application
End of application (post-application)	End of application until 1 hour before sunset
1 hour before sunset	Overnight <sup>1</sup> until 1 hour after sunrise
1 hour after sunrise	Daytime until 1 hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise
1 hour after sunrise	Daytime until 1 hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise

<sup>1</sup>All overnight samples must include the period from one hour before sunset to one hour after sunrise.

Background air sampling will be accomplished a minimum of 18 – 24 hours prior to the application. Sampling will be completed from the start of the application to one hour after the application ends. The next sample period will begin one hour after the application ends to one hour after sunrise. The following sample period will begin one hour after sunrise and end one hour before sunset (same for second or more application days). Refer to Table 1B, Guidelines for Nighttime Application and Sampling Schedule.

**TABLE 1B. GUIDELINES FOR NIGHTTIME APPLICATION SAMPLING SCHEDULE**

<b>Sample period begins:</b>	<b>Sample duration time</b>
Background (pre-application)	Minimum 18 – 24 hours
Application	Start of application until 1 hour after end of application
End of application (post-application)	End of application until 1 hour after sunrise
1 hour after sunrise	Daytime until 1 hour before sunset
1 hour before sunset	Overnight <sup>1</sup> until 1 hour after sunrise
1 hour after sunrise	Daytime until 1 hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise
1 hour after sunrise	Daytime until 1 hour before sunset

<sup>1</sup>All overnight samples must include the period from one hour before sunset to one hour after sunrise.

A minimum of eight samplers will be positioned around the application perimeter. One sampler located at approximately the midpoint of each side of the field and one at each corner. A ninth sampler will be collocated at the downwind side or corner. Two additional parallel samples will be collected using a particulate filter inline and before the XAD-4 resin tube. The particulate samples will be collected during the background, application, and post-application periods. Field spike samples will be collected using the same ambient monitoring procedures (e.g., air flow rates, sample transportation and storage), and will be located in parallel to the ambient air samplers. The recommended 24-hour target quantification limit is 0.2 ng/m<sup>3</sup> (Warmerdam, 2008), outlined in Appendix B.

## 5.0 Sampling and Analysis Procedures

Special Purpose Monitoring Section (SPM) personnel will hand-carry unexposed samples from MLD's laboratory in Sacramento, to and from the sampling location and then return the exposed samples back to MLD's Sacramento laboratory. The samples will not be exposed to extreme conditions or subjected to rough handling that might cause loss or degradation of any sample.

At each sampling site, the operator will assure that at the end of each sampling period, the XAD-4 resin tube is capped on both ends. Record all sample period information identification on a label and affixed to the XAD-4 resin tube, and record all sample information on the field sample log sheet. After each sampling period, the samples are placed in a glass tube and stored in a cooler at 4° C or less until returned to the laboratory. The sample tubes will be transported on dry ice, as soon as reasonably possible, to the ARB Sacramento Monitoring and Laboratory Division laboratory for analysis. These samples will be stored in the freezer or extracted/analyzed immediately. Samples are collected in the field with a flow rate of three (3) liters per minute (LPM).

The exposed particulate pre-filters will be placed in an individual petri dish immediately following the completion of each sampling period. All sampling information will be recorded on the petri dish's label and the field sampling log sheet. The filters will be handled similarly to the XAD-4 resin cartridges detailed in the paragraph. The parallel inline XAD-4 resin cartridges will be handled identically to those detailed in the previous paragraph.

All reported sampling times, including meteorological data, will be reported in Pacific Standard Time (PST).

The Northern Laboratory Branch (NLB) will supply SPM with XAD-4 resin tubes and filters. NLB will perform analyses for dicofol on collected application samples and report results to SPM.

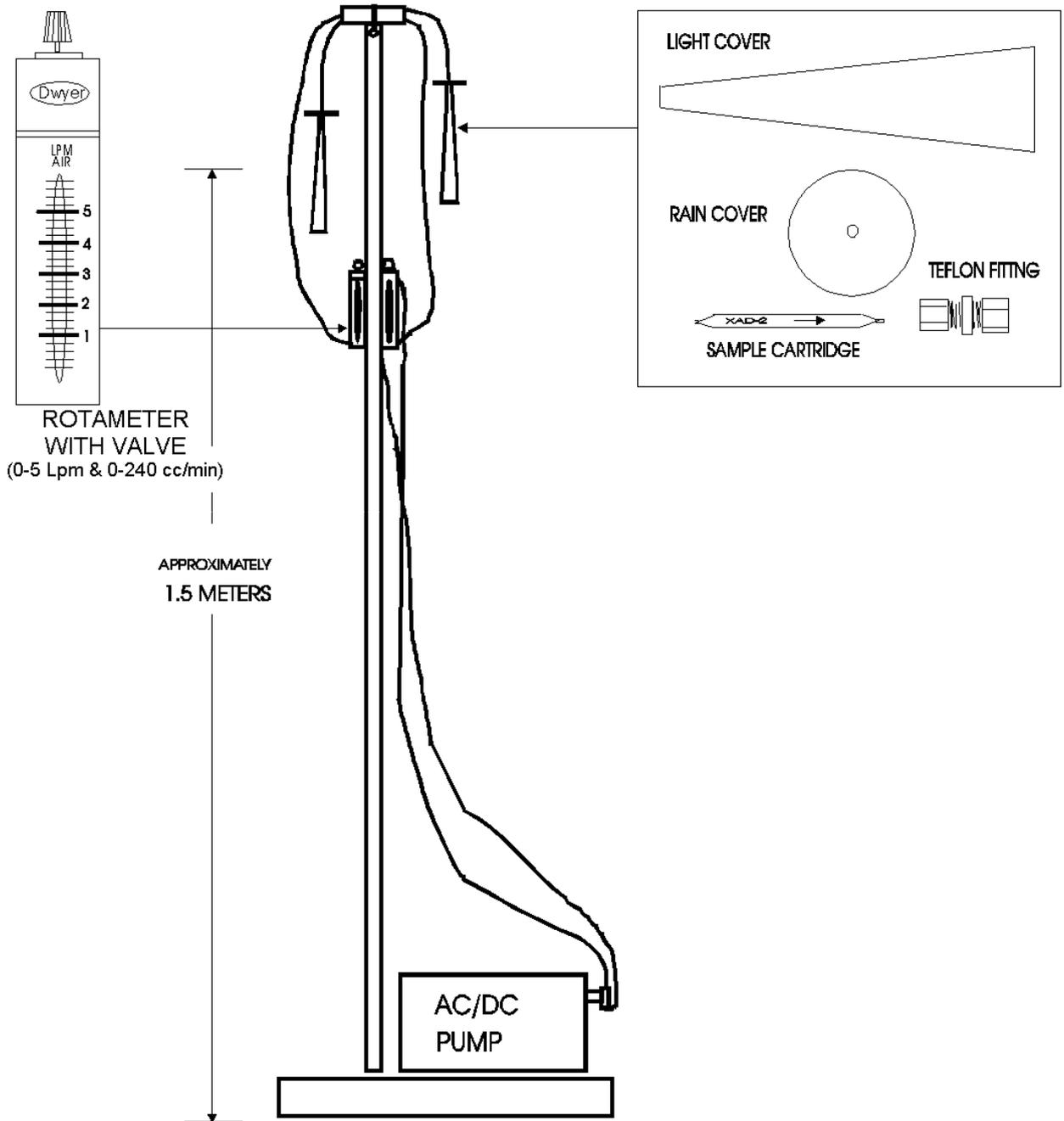
Laboratory analyses will be performed in accordance with applicable standard operating procedures (Standard Operating Procedure for Analysis of 222-trichloro-1,1-bis(4-chlorophenyl)ethanol (Dicofol)) in Appendix A.

The following XAD-4 resin tube and particulate filter validation and analytical quality control criteria should be followed during pesticide analysis.

1. **Sample Hold Time:** Sample hold time criteria will be established by the Laboratory. Samples not analyzed within the established holding time will be invalidated by the Laboratory.
2. **Duplicate Analysis:** Laboratory to establish relative percent difference (RPD) criteria for duplicate analysis. Lab to provide duplicate analytical results and RPD.
3. **Method Detection Limit (MDL):** MDL sample analytical results less than the MDL shall be reported as a less than numerical value. This less than numerical value shall incorporate any dilutions/concentrations.
4. **Analytical Linear Range:** Any analytical result greater than the highest calibration standard shall be reanalyzed within the calibrated linear range.

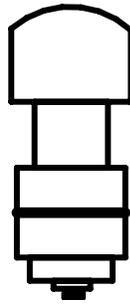
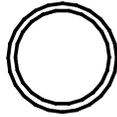
## 6.0 List of Field Equipment

<u>Quantity</u>	<u>Item Description</u>
(1)	Met-One Auto met portable meteorology system having calibrated sensors to measuring 1 minute averages for wind speed, direction, ambient temperature, and relative humidity w/built-in data logger.
(1)	Measuring Wheel.
(1)	A 200 ft measuring tape.
(1)	Tripod and compass.
(1)	Global Positioning System (GPS) with backup batteries and carrying case.
(1)	Digital Camera with backup batteries and carrying case.
(2)	Alborg mass flow meter 0-5 LPM.
(8)	Sampling trees/pumps.
(100)	XAD-4 resin tubes (11 backgrounds, 11 applications, 66 post application, 4 field spikes, 4 trip spikes, 1 trip blank, 1 field blank and 2 spare).
(3)	Filter Holder Assembly (one each for two opposite sides of the field) and 1 spare.
(20)	Filter Cassette (16 post application, 4 field spikes, 4 trip spikes, 1 trip blank, 1 field blank and 2 spare).
(9)	Sample trees/pumps (1 spare).
(50)	Batteries.



**Figure 1**  
**Air Sampler Tree with Pump**

52mm Filter Cassette  
w/ 47mm Quartz Filter



Filter Holder Assy

**Figure 2**  
**Filter Cassette and Filter Holder Assembly**

Figure 2, Filter Cassette and Filter Holder Assembly, displays a particulate sampler consisting of a Filter Cassette and Filter Holder Assembly with a filter disk (CAT No. 1851047) used in front of the XAD-4 resin tube to monitor particulates. Samples will be collected at one upwind and one downwind sampling location during each sample period. A sample line will be attached from the inlet of the XAD 4 sample tube to the filter holder assembly. The flow rate will be set to 3.0 LPM.

## 7.0 Quality Control

Quality control procedures will be observed to ensure the integrity of samples collected in the field. National Institute of Standards and Technology (NIST) traceable transfer standards will be used to calibrate meteorological sensors and measure sample flow rates.

The metrological sensors will be calibrated and aligned following the procedures outlined in the standard operating procedures on the Air Monitoring Web Manual at the following link:

<http://arb.ca.gov/airwebmanual/amwmn.php?c=5&t=sop>

Each XAD-4 resin tube and particulate filter will be assigned a field sample number that provides for identification of site, sample ID number, operator, and sample information as well as sample transfer information.

**Field Spike (FS):** A field spike will be prepared by the laboratory by injecting a XAD-4 resin tube with a laboratory determined amount of dicofol. The background, application, and post-application field spikes (4 total) will be installed onto the secondary position of one of the samplers. It will be removed and handled identically to the other samples.

**Trip Spike (TS):** A trip spike will be prepared by the laboratory by injecting a XAD-4 resin tube at the same level as the field spike. The trip spike will be transported and analyzed along with the field spike. The trip spike is treated the same as a field spike with exception that it is not installed onto a sampler.

**Field Blank (FB):** A field blank will be a XAD-4 resin tube opened in the field and returned but not installed onto a sampler.

**Trip Blank (TB):** A trip blank will be a XAD-4 resin tube transported to the field and returned capped, but unopened.

**Collocated (CO):** Collocated (side-by-side) air samplers will operate at the predominantly downwind sample site throughout the application period.

## Site/Sample Identification

The dicofol application sampling sites will be named accordingly for the background, application, and post application as follows:

### Site Naming Examples:

N-BK = Northside background  
W-BK-CO = collocated west side  
Background  
E-1 = East side period 1  
S-2-PF = filter at south side during  
period 2  
S-2-PX = XAD-4 tube at south side  
during period 2

### Letter Abbreviations as follows

N = North Side  
NWC = NW Corner Sample  
W = West Side  
SWC = SW Corner Sample  
S = South Side  
SEC = SE Corner Sample  
E = East Side  
NEC = NE Corner Sample  
CO= Co-located  
BK= Background Sample  
PF= Parallel filter  
PX= Parallel XAD-4  
A= Application  
A#=Sample after application  
FS = Field Spike  
TS = Trip Spike  
TB = Trip Blank  
FB = Field Blank

Following the quality control procedures listed above will ensure the quality and integrity of the samples collected in the field and will ensure accurate field and lab data collection.

## **8.0 Deliverables**

### **8.1 Air Quality Surveillance Branch Deliverables**

Within 90 days from receipt of the final results report from the Northern Laboratory Branch (NLB), AQSB will provide DPR with a report containing the following topics:

- 1) Sampling Protocol.
- 2) Personnel Contact List.
- 3) Site Maps.
- 4) Site Photographs.
- 5) Site Descriptions and Measurements  
Site, sampler, GPS coordinates, inlet height, distance to roads, site-specific comments, and total pounds of methomyl applied per acre.
- 6) The distance and direction of the sampler to the treated or potentially treated fields.
- 7) A map of the monitoring site locations.
- 8) Sample Summary Table.
- 9) Field Sample Log.
- 10) Laboratory Analysis Reports with calculations in electronic format.
- 11) Meteorological data and supporting documentation.
- 12) Transfer Standards' Certification Reports.
- 13) Disk containing electronic files of 1-minute averaged Meteorological Data.
- 14) Disk containing electronic files of Report.

In addition, the Special Purpose Monitoring Section (SPM) will prepare a project binder containing the above information. This binder will remain with SPM though available for viewing and review as requested.

## 8.2 Northern Laboratory Branch (NLB) Deliverables

Within 90 days from the last day of analysis, The NLB will provide SPM with a report that will include the following topics:

- 1) Table(s) of sample to include:
  - a. Sample identification (name).
  - b. Date sample received from field.
  - c. Date sample analyzed.
  - d. Dilution ratio.
  - e. Analytical results.
- 2) All equations used in calculating analytical results.
- 3) Table of duplicate results including calculated relative percent difference (RPD).
- 4) Table of collocated results.
- 5) Table of analytical results from all field, trip and laboratory spikes including percent recoveries.
- 6) Table of analytical results from all trip blanks.
- 7) Table of analytical results from all laboratory blanks, standards and control checks performed, including dates performed and relative percent recoveries if applicable.
- 8) Copy or location of analytical method or Standard Operating Procedures (SOP) used for analysis.
- 9) Section or provision listing or reporting any and all deviations from analytical SOP and this protocol.



**APPENDIX A:  
Standard Operating Procedure Analyses for Dicofol**

The Special Analysis Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for dicofol collected by the XAD-4 resin tube and particulate filter methods. This analytical procedure is entitled, Standard Operating Procedure for Analysis of 2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol (Dicofol).

California Environmental Protection Agency

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**Standard Operating Procedure for  
Sampling and Analysis of 2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol (Dicofol)  
in Application and Ambient Air using Gas Chromatography/Mass Selective  
Detector**

**Special Analysis Section  
Northern Laboratory Branch  
Monitoring and Laboratory Division**

Revision 2  
6/10/09

Approved by:

Russell Grace, Manager  
Special Analysis Section

DISCLAIMER: Mention of any trade name or commercial product in this Standard Operating Procedure does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

## 1. SCOPE

The current method is for the analysis of 2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol (Dicofol) using a gas chromatograph/mass selective detector. The procedure is for the analysis of application and ambient air monitoring of Dicofol using XAD-4 resin tubes and quartz fiber filters. The Department of Pesticide Regulation (DPR) asked the Air Resources Board (ARB) to analyze for Dicofol during agricultural application and ambient monitoring with an estimated quantitation limit of 0.2  $\mu\text{g}/\text{m}^3$ .

## 2. SUMMARY OF METHOD

Resin tubes, XAD-4, are placed on the sampler for 24 hours at a flowrate of 3.0 liters per minute (LPM). During application and ambient air monitoring, select samplers will have a quartz fiber filter loaded in front of the XAD-4 cartridge to check for particulates. The samples are stored in an ice chest or refrigerator until extracted with dichloromethane (DCM). A gas chromatograph with a mass selective detector in the selected ion monitoring (SIM) mode is used for analysis.

## 3. INTERFERENCES/LIMITATIONS

Interferences may be caused by contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. A method blank, including both solvent and resin, must be analyzed with each batch of samples to detect any possible interferences.

## 4. EQUIPMENT AND CONDITIONS

### A. Instrumentation

Hewlett-Packard 6890 Series gas chromatograph  
Hewlett-Packard 5973 Network mass selective detector  
Hewlett-Packard 6890 Enhanced Parameters ALS

MS Transfer line: 280°C

Injector: 125°C, Pulsed Splitless, Liner 4 mm straight liner with glass wool

Column: Agilent 19091J-413 HP-5 5% Phenyl Methyl Siloxane, 30 meter, 320  $\mu\text{m}$  i.d., 0.25  $\mu\text{m}$  thickness, or equivalent

GC Temperature Program: Oven initial 90°C, hold 1 min. Ramp to 300°C @ 20°C/min., hold 3.0 min.

Retention time: Dicofol 6.502 min.

Splitter open @ 1.0 min.

Flows: Column: He, 3.0 ml/min, 11.32 psi. (velocity: 64cm/sec)

Splitter: 50 ml/min.

Mass Spectrometer: Electron Ionization

Selective Ion Monitoring: Dicofol: 138.9 (quant. ion 100%), 250.9 (qual. ion 83.5%), 252.9 (qual ion 83.5%); Tuning: PFTBA on masses 69, 219, 502

#### B. Auxiliary Apparatus

1. Precleaned vials, 8 ml capacity with teflon caps
2. Silanized Glasswool
3. Disposable syringes, 3 ml
4. Sonicator
5. GC vials with septum caps

#### C. Reagents

1. Dichloromethane, Pesticide grade or better
2. Dicofol, Chem Service PS-82, 93% p,p'-Dicofol, 2% o,p-Dicofol
3. XAD-4 resin sorbent tubes, 400/200mg, SKC, Fullerton, CA
4. Whatman Quartz fiber filters QM-A, 47 mm

### 5. ANALYSIS OF SAMPLES

1. A daily manual tune shall be performed using PFTBA. The instrument is tuned using masses: 69, 219, 502. The criterion for the tune are the peak widths at  $\frac{1}{2}$  the peak height,  $0.60 \pm 0.05$ , and the criteria for relative abundance: 69:100%, 219:90-120%, and 502: 5-12%.
2. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample that may result in possible carry-over contamination.
3. A five-point calibration curve shall be analyzed with each batch of samples. The calibration will be 0.10-1.00  $\mu\text{g/ml}$  for both the application and ambient studies.
4. A calibration check sample is run after the calibration, after every ten samples and at the end of the sample batch. The value of the calibration check must be within  $\pm 3\sigma$  (the standard deviation) or  $\pm 25\%$  of the expected value whichever is greater. If the calibration check is outside this limit, then those samples in the batch after this calibration check need to be reanalyzed.

5. With each batch of XAD-4 and/or filter samples analyzed, a laboratory blank and a laboratory control spike will be run concurrently. A laboratory blank is XAD-4 and /or filter extracted and analyzed the same way as the samples. A laboratory control spike is XAD-4 and/or filter spiked with a known amount of standard. The laboratory control sample is extracted and analyzed the same way as the samples. Laboratory control samples should have recoveries that are greater than or equal to 70% of the theoretical spiked value.
6. For XAD-4 analysis, score and snap the sample resin tube, transfer the front bed of the resin tube into an 8-ml vial. (Save the back-up bed for future analysis if necessary.) Rinse the tube with 3.0 ml of DCM into the extraction vial. Cap and place the vial in the sonicator for one hour. Filter the samples using silanized glasswool plugged 3-ml syringe directly into a GC vial and cap securely.
7. For quartz filter analysis, remove the filter from the holder and transfer to a 12-ml extraction vial. Add 10 ml of DCM to the vial. Cap and place the vial in the sonicator for one hour. Transfer filter samples directly into a GC vial and cap securely.
8. The atmospheric concentration of the XAD-4 samples is calculated according to:

$$\text{Conc } (\mu\text{g}/\text{m}^3) = \text{Extract Conc } (\mu\text{g}/\text{ml}) \times 3 \text{ ml} / \text{Air Volume Sampled } (\text{m}^3)$$

The atmospheric concentration of the filter samples is calculated according to:

$$\text{Conc } (\mu\text{g}/\text{m}^3) = \text{Extract Conc } (\mu\text{g}/\text{ml}) \times 10 \text{ ml} / \text{Air Volume Sampled } (\text{m}^3)$$

## 6. QUALITY ASSURANCE

### A. Instrument Reproducibility

The reproducibility of the instrument and analytical method was established by analyzing five (5) 1.0  $\mu\text{l}$  injections of Dicofol standard at three concentrations (low, mid, and high). The low, mid and high concentrations were 0.10, 0.5 and 1.0  $\mu\text{g}/\text{ml}$ , respectively.

### B. Calibration

A four-point calibration curve is made ranging from 0.10  $\mu\text{g}/\text{ml}$  to 1.0  $\mu\text{g}/\text{ml}$ .

### C. Calibration Check

A calibration check sample is run after the calibration, after every ten samples and at the end of the sample batch to verify the system is in calibration. The value of the check must be within  $\pm 3\sigma$  (the standard deviation) or  $\pm 25\%$  of the expected value whichever is greater. If the calibration check is outside the limit, then those samples in the batch after this calibration check need to be reanalyzed.

### D. Laboratory Control Sample

A laboratory control sample (LCS) is included with each analytical batch. The LCS stock standard should come from a different source or lot than the daily calibration standards. If a different source is not available, then a separate preparation is made from the calibration stock. The analytical value of the LCS must be within three standard deviations of its historical mean. If the LCS is outside these limits then the samples in the analytical batch must be reanalyzed.

### E. Minimum Detection Limit

The detection limit is based on US EPA MDL calculation. Using the analysis of seven (7) replicates of a low-level matrix spike, the method detection limit (MDL) and the estimated quantitation limit (EQL) for Dicofol is calculated by:  $MDL = 3.14 * (\text{std dev values})$ , where std dev = the standard deviation of the concentration calculated for the seven replicate spikes. For Dicofol the MDL is  $0.117 \mu\text{g/sample}$  ( $0.039 \mu\text{g/ml}$ ). EQL, defined as  $5 * MDL$ , is  $0.585 \mu\text{g/sample}$  ( $0.195 \mu\text{g/ml}$ ) based on a 3.0 ml extraction volume. Results below the EQL but greater than or equal to the MDL are reported to one significant figure. Results less than MDL are reported as the calculated MDL to one significant figure.

### F. Collection and Extraction Efficiency (Recovery)

Dicofol at low and high-end concentrations was spiked on XAD-4 tubes (two at each concentration). The spiked tubes are placed on field samplers with airflows of 3 LPM for 24 hours. The samples are extracted with DCM and prepared as described in section 5, #6. The average percent recovery of Dicofol should be  $\pm 20\%$  of the expected value. The average percent recovery of the low spikes and high spikes was greater than 80%.

### G. Storage Stability

A storage stability was conducted which ran for 21 days with cartridges and filters being tested at 0, 7, 14, and 21 days. Three (3) XAD-4 tubes and three quartz fiber filters will be spiked  $1.0 \mu\text{g/ml}$ . The tubes and filters were stored in the

freezer until analyzed. The average percent recovery and standard deviation for each XAD cartridge group was  $101 \pm 14.0\%$ ,  $208 \pm 15.0\%$ ,  $168 \pm 18.5\%$ , and  $144.3 \pm 57.1\%$ , respectively. The average percent recovery and standard deviation for each quartz fiber filter group was  $110 \pm 10.8\%$ ,  $102 \pm 13.0\%$ ,  $99 \pm 12.0\%$ , and  $72 \pm 3.2\%$ , respectively. Dicofol, spiked at  $1.0 \mu\text{g}$  on XAD-2 cartridges and quartz fiber filters, was stable for up to 21 days when stored at  $-20^\circ \text{C}$ .

#### H. Breakthrough

A breakthrough study was conducted using XAD-4 tubes spiked with low and high concentrations of Dicofol. The spiked tubes were placed on field samplers with airflows of 3 LPM for 24 hours. Dicofol was not detected in the secondary section of the XAD-4 cartridges.

#### I. Safety

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure.

**TABLE 1**  
**REPRODUCIBILITY STUDY**  
**DICOFOL**

<b>Target Concentration</b>	<b>Low Level</b>	<b>Mid Level</b>	<b>High Level</b>
<b>Sample Number</b>			
1	0.12	0.60	1.10
2	0.10	0.63	1.09
3	0.10	0.61	1.12
4	0.10	0.64	1.14
5	0.10	0.63	1.08
<b>Average</b>	<b>0.10</b>	<b>0.62</b>	<b>1.10</b>
<b>SD</b>	<b>0.01</b>	<b>0.01</b>	<b>0.03</b>
<b>RSD</b>	<b>7.06</b>	<b>2.39</b>	<b>2.32</b>

**APPENDIX B:**  
**USE INFORMATION AND AIR MONITORING RECOMMENDATIONS FOR THE PESTICIDE**  
**ACTIVE INGREDIENT DICOFOL**

[http://www.cdpr.ca.gov/docs/emon/pubs/tac/recomm/dicofol\\_final\\_recmd\\_08.pdf](http://www.cdpr.ca.gov/docs/emon/pubs/tac/recomm/dicofol_final_recmd_08.pdf)