

APPENDIX B

Sampling Protocol



Monitoring and Laboratory Division
Air Quality Surveillance Branch

**Protocol for Air Monitoring Around a Field Application of Sodium
Tetrathiocarbonate**

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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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APPENDIX A: STANDARD OPERATING PROCEDURE, SAMPLING AND
ANALYSIS OF SODIUM TETRATHIOCARBONATE IN SILCO
CANISTERS.....21

1.0 Background

At the request of the California Department of Pesticide Regulation (DPR) (October 4, 2005 Memorandum, Warmerdam to Witherspoon), the Air Resources Board (ARB) staff will conduct air monitoring for hydrogen sulfide and carbon disulfide which are byproducts from the application of the fumigant sodium tetrathiocarbonate. Monitoring is scheduled during the week of November 13 -17, 2006. This monitoring will be performed to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) 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.

The Special Purpose Monitoring Section (SPMS) staff will assure that pesticide sampling follows the procedures outlined in this protocol.

The Special Analysis Section (SAS) of the Northern Laboratory Branch will analyze collected samples as per their procedures titled "Standard Operating Procedure Sampling and Analysis of Carbon Disulfide In Silco Treated Canisters (Version 1, March 13, 2002)" (Appendix A).

2.0 Project Goals and Objectives

The primary goal of this monitoring project is to measure ambient air concentrations of carbon disulfide and hydrogen sulfide surrounding an application of sodium tetrathiocarbonate to a 39 acre vineyard. Carbon disulfide and hydrogen sulfide are the byproducts of the pesticide sodium tetrathiocarbonate. These results will be used by DPR to determine if present rules controlling the pesticide sodium tetrathiocarbonate are adequate.

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. Determination by DPR of season of peak use.
3. Appropriate application of sampling/monitoring equipment to determine ambient carbon disulfide and hydrogen sulfide concentrations.
4. Application of relevant quality assurance/quality control practices to ensure the representativeness and integrity of field samples.
5. At the conclusion of the project, the ARB will provide the DPR with a final report or memorandum containing all relevant information, data and results gathered in the course of ARB's activities during the planning and execution of this project. As available, electronic versions of these documents, data and results will also be included.

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4.0 List of Field Equipment

<u>Quantity</u>	<u>Item Description</u>
(1)	Met-One Auto met portable meteorology system having sensors for measuring wind speed and direction, ambient temperature, relative humidity and barometric pressure with built-in data logger.
(71)	Evacuated Silco treated stainless-steel canister, each equipped with a vacuum/pressure gauge and a field data sheet/report, and carrying case (8 background, 9 application, 45 post application and 9 spare).
(4)	Field spike canister
(4)	Trip spike canister
(2)	Trip blank canister
(11)	Restek passive Siltek treated flow controller equipped with 12-hour orifice (two spare).
(10)	Siltek treated stainless-steel sample probe, 0.23 meters long, ¼ inch diameter (one spare)
(1)	Arizona Instruments Jerome 631-X H ₂ S Analyzer
(10)	Tripod with PVC tubing to mount canisters at appropriate heights (one spare).

5.0 Study Location

In California, eighty eight percent of sodium tetrathiocarbonate (sold under the name of Enzone) is applied to grapevines. Sodium tetrathiocarbonate applications are more commonly in Kern County than any other county in the state. For this reason, a vineyard in Kern County was chosen for monitoring.

Monitoring sites are arranged with the voluntary cooperation of growers and applicators. ARB staff investigated contacts until a grower was found and an appropriate site was selected. Permission to conduct sampling will be obtained from property owner and any neighboring adjacent land owners where samplers may be located. SPMS initially worked through the County Agricultural Commissioner's office in Kern County and was able to obtain the name and number of the technical representative for Arysta Life Science, the chief retailer of sodium tetrathiocarbonate. Through the retailer, SPMS was able to obtain a field near 33787 Cecil Avenue, east of Delano in northern Kern County.

6.0 Sampling

A. Carbon Disulfide

Integrated ambient air samples will be collected for carbon disulfide using passive air sampling into evacuated six liter Restek Silcosteel® canisters (Figure 1). The critical flow controller used to regulate sample flow into the canister is the Silcosteel treated Veriflo SC423XL. The Silcosteel flow controllers will be configured at 5.6 to 5.9 sccpm using a certified 0-10 sccpm mass flow meter.



Figure 1: Canister Sampler Overview



Figure 2: Air Sampler With Passive Flow Controller

The canister sampling system will operate continuously. The sampling time for each canister will be recorded in the “Canister Field Log Sheet” (Figure 3) and in the “Restek SilcoCan Pesticide Data/Sample Tracking Sheet” (Figure 4). The canister vacuum reading of each sample will be recorded at the start and end of each sampling period.

The laboratory will measure and record the canister vacuum using a certified gauge before and after field transport. The laboratory gauge will be used to determine if samples collected meet the validation criteria of -10 to -5 inches of Hg. If the pressure of a sampled canister lies outside the pressure criteria, the sample will be invalidated.

At the end of each sampling period, the canisters will be placed in shipping containers with its respective tracking sheet. At the completion of the study, the shipping containers will be delivered to the Special Analysis Section’s laboratory.

Restek SilcoCan Pesticide Data/Sample Tracking Sheet

Veriflo
Controller

Project Name: Sodium Tetrathiocarbonate Pesticide Air Monitoring in Kern County

Site/Sample Name: _____

Operator & Agency: _____

Lab I.D.: _____

	Date	Time (PST)	CANISTER		LABORATORY	MFM Reading	SAMPLER	
			LAB	FIELD			Vacuum	
Set-Up								
Start								
Stop					LAB**			
Final								

Type of Sample: Regular Collocated Field Spike Trip Spike Blank Other

Field Log Number: _____ Canister ID Number: _____ Sampler ID Number: _____

Observed Unusual Wind-Blown Sand/Dust Rain Farming Nearby

Sampling Condition: Construction Nearby Fire Nearby Other _____

INVALID SAMPLE INFORMATION
Reason for Sample Invalidation

Vacuum lower than -10"Hg Vacuum higher than -5"Hg

Sampling period out of range (<23 or >25 hours) Other reasons: _____

Sampling equipment malfunction _____

Field Comments: _____

Sample Tracking

Action	Transfer Method (Check one)		Name	Date/Time
	Carrier	Person		
Released by Lab				
Received by Field				
Released by Field				
Received by Lab				

===FOR LABORATORY USE ONLY===

Lab Comments: _____

** = Calibrated Guage Pressure or Vacuum

08/18/06

Figure 4: Data/Sample Tracking Sheet

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An outline of the sampling procedures is as follows:

1. Determine a sampling equipment access route that will meet the 12 hour +/- one hour post sampling recovery time. The generation of any airborne dust will be kept to a minimum.
2. The Auto Met trailer will be installed at a minimum of 20 meters from the edge of the field. Meteorological sensors will be at the following heights; WS & WD at 22.5', Ambient Temperature and Relative Humidity at 19' and Barometric Pressure at 3' above the ground.
3. To setup a canister sample, the operator will install the flow controller with inlet probe on to the canister.
4. Flow will be checked/set with a certified mass flow meter (MFM).
5. Canister flow readings and start times are recorded in the canister log and tracking sheet.
6. Sampler inlets are typically placed two (2) meters above the ground, but may vary due to nearby obstructions.
7. When the sampling period is over, the sample flow is measured.
8. Ending flow rate, time and canister vacuum reading are recorded.
9. Post sampled canisters are removed from the sampling tripod and its flow controller is disconnected. It is essential that the controller be kept clean throughout the application monitoring study.
10. Background sampling will occur during the 12 hours immediately preceding the scheduled application. Two canisters will be placed at each corner of the field. At each corner, one (1) of the two (2) sample canisters will be spiked at 5 $\mu\text{g}/\text{m}^3$ and both will be installed one (1) to four (4) meters apart from each other.
11. During application and post application sampling, a 12 hour canister sample system will be located at each corner and at each mid point of the field. An additional collocated canister will be located one (1) to four (4) meters away from the expected downwind position of the field. The number of canister sampling systems used during each sampling period equals nine (eight samplers plus one collocated), with a total of six 12 hour sampling periods (one application and five post application periods).

12. Table 1 below lists sampler siting criteria referenced from ARB's Quality Assurance Manual, Volume II.

Item/Influence	Requirements
Height of Sample Inlet	2 to 7 meters above the ground
Spacing Between Inlets (Collocated)	Within 4 meters, but at least 1 meter apart.
Obstacles	Distance between samplers and obstacles must be at least 2 times the height the obstacle protrudes above the sampler.
Tree Drip Line	Inlet must be at least 10 meters from the drip line if tree represents an obstruction.
Air Flow Arc	Unrestricted 270 degree arc that must include predominant wind direction for seasonal high Pollutant; samplers located on the side of a building require 180 degree clearance.
Traffic	No specific requirement for pesticide monitoring.

*From 40 CFR Part 58, Appendix E, and ARB Quality Assurance Manual, Vol. II, Section 2.0.4 (Feb. 2000)

Table 1: Siting Criteria

B. Hydrogen Sulfide

Hydrogen Sulfide (H₂S) will be measured using a portable Jerome 631-X Hydrogen Sulfide Analyzer at each sampling location. A minimum of two H₂S measurements will be performed each time the canisters are changed and mid-way through the application. If values higher than 1 ppm are measured, additional H₂S measurements will be performed for confirmation. All H₂S values, including their respective location name, date, time, operator and comments, will be entered on the Hydrogen Sulfide Field Log Sheet (Figure 5).

The principle of operation of the instrument is that hydrogen sulfide reacts with a thin gold film by increasing the electrical resistance in proportion to the mass of hydrogen sulfide present. The procedures described in the operational manual supplied by the manufacturer will be followed for field sampling. The Jerome Analyzer will be verified in Sacramento before and after the field test. The Jerome Analyzer inlet flow rate is 150cc/min. The manufacturer's specifications list the instruments sensitivity at 0.003 ppm, a precision of 5% relative standard deviation and an accuracy range from 0.003 to 50 ppm.

Prior to the recovery of each canister, the sampler will be regenerated and zeroed as per manufacturer recommendations. The Jerome Analyzer regeneration process takes approximately 10 minutes and the manufacturer recommends an additional 30 minute wait for temperature equilibration prior to sampling.

C. Sampling Schedule

The DPR requested sampling periods of 12 hours each which consist of daylight sampling from one hour after sunrise to one hour before sunset, and night sampling from one hour before sunset to one hour after sunrise. Table 2 below shows the application sampling schedule.

Application Sampling Schedule

<u>Sample period begins</u>	<u>Sample duration time</u>
Background (pre-application)	12 hours just prior to application
During application and post-application	Start of application (until the 1800 hour)
1800 hour	Overnight (until the 0600 hour)
0600 hour	Daytime (until the 1800 hour)
1800 hour	Overnight (until the 0600 hour)
0600 hour	Daytime (until the 1800 hour)
1800 hour	Overnight (until the 0600 hour)

Table 2: Application Sampling Schedule

The field selected for the fumigant drip application is 39 acres in size. The crop type for the application study will be grapes. The DPR requests “that ARB monitor a flood or furrow application at the highest allowed rates of use (500 ppm a.i. for an established vineyard or 950 ppm a.i. as a preplant application)”. As less than 1% of all sodium tetrathiocarbonate applications are flood or furrow applications, the DPR agreed that a drip irrigation application of 1,000 ppm will be monitored.

For the carbon disulfide canister samples there will be two sampler setup configurations. The first canister setup configuration (background) will consist of two paired canisters placed near each of the field’s four corners (totaling eight canisters). For each pair of canisters, one canister is a field spike. After the twelve hour background sampling period, a second canister configuration will consist of one canister located near each corner and one canister located at each mid point. A ninth canister will be collocated at the expected downwind position.

If the canisters are placed at the requested 20 meter distance from the application area, dirt and paved roads will lie between the canisters and the application area on all four sides of the field. Because of these roads and access sampling equipment access limitations, the DPR has agreed to changes in canister placement. The corner samplers will be placed adjacent to the field as close to the road as possible, and the samplers located at the mid point between the corners will be placed approximately 20 meters from

the field (roads running between the field and the samplers). Conditions at each site will dictate the exact placement of the samplers.

The monitoring report will include the following field data:

1. A record of each location of the monitoring equipment with respect to the field.
2. Field drawing, field dimensions, orientation to true north, meteorological equipment location, trees, buildings, and other obstacles.
3. Meteorological data collected at one-minute intervals including wind speed and direction, humidity, air temperature.
4. The elevation of each sampling station with respect to the field.
5. The start and end time of the fumigant application.
6. The product used and the application rate.
7. CS₂ and H₂S log sheets.

7.0 Analysis

The draft method for the sampling and analysis of carbon disulfide is included as Attachment 3. The Analytical Standard Operating Procedures (SOP) and method validation results will be included in the laboratory sample report. The procedures are based on EPA Method TO-15 and consist of cryogenic pre-concentration of an aliquot of the whole air sample followed by GC/MS analysis. The canisters arrive from the field at sub-ambient pressure and are pressurized (diluted) in the laboratory before analysis. The analyses will be performed by the ARB laboratory in Sacramento. The DPR recommended a target 24-hour EQL of 0.5 ug/m³ for carbon disulfide. The attached SOP specifies an EQL of 7.16 ug/m³ for carbon disulfide.

The following canister validation and analytical quality control criteria should be followed during pesticide analysis.

1. **Sample Hold Time:** The laboratory will develop sample hold time criteria for CS₂ in air. This criteria will be used to validate study samples.
2. **Duplicate Analysis:** The laboratory shall establish relative percent difference (RPD) criteria for duplicate analysis along with providing the 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. All values at or above the MDL shall be reported as a numeric value.
4. **Analytical Linear Range:** Any analytical results greater than the highest calibration standard shall be reanalyzed within the linear range.

8.0 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 sample flow rate of the passive flow controllers will be measured using a mass flow meter having a current calibration certification and a range of 0-10 cubic centimeters per minute.

The following certified transfer standards and equipment will be used to calibrate and align the meteorological sensors:

Meteorological Standards and Calibration Equipment

TEMPERATURE	RELATIVE HUMIDITY	WIND DIRECTION	WIND SPEED
DigiSense RTD	Rotronic 10% Salt Std	Brunton 5008	RM Young
93410-50	“ 35% “ “	Pocket Transit	Torque Disk 18310
	“ 50% “ “	Met One 040	Anemometer 18810
	“ 80% “ “	Degree Fixture	

Table 3: Meteorological Standards and Calibration Equipment

Each sample canister will be assigned a tracking sheet that provides for identification of site, sampler, operator, and sample information as well as sample chain-of-custody transfer information.

The following Quality Control checks will be performed during the study:

Field Spike (FS): The laboratory will prepare four field spikes at a concentration level of approximately 5 ug/m³ of carbon disulfide. The field spikes will be located next to the four background samplers on each corner of the field.

Trip Spike (TS): A trip spike will be prepared by the laboratory by injecting a canister with 5 ug/m³ of carbon disulfide and should be the same level as the field spikes. The trip spike will be transported and analyzed along with the field spikes. The trip spike canister accompanies the sample canisters from the lab to the field and returns, but is not installed onto a sampler.

Trip Blank (TB): The laboratory will prepare a trip blank. The trip blank canister accompanies the sample canisters from the lab to the field and back, but is not installed onto a sampler.

Collocated (C): Collocated (side-by-side) air samplers will operate at one site during the application period. This collocated sampler will be located at the expected downwind location of the field.

The naming format for this study will consist of one of the eight cardinal directions (N, NE, E, SE, S, SW, W, NW) followed immediately by whether it is a side or corner location (S or C). After inserting a dash the letters for Carbon Disulfide or Hydrogen Sulfide (CD or HS) shall be entered and after another dash will come the run number. Additional letters will be added for QC canisters and background runs as listed below in the examples.

Examples:

SEC-CD-B	=	Southeast Corner – Carbon Disulfide – Background
SEC-CD-B-FS	=	SE Corner – Carbon Disulfide – Background – Field Spike
CD-TS1	=	Carbon Disulfide – Trip Spike 1, There are 4 ea. Trip Spikes
CD-TB1	=	Carbon Disulfide – Trip Blank 1, There are 2 ea. Trip Blanks
SS-CD-1	=	South Side – Carbon Disulfide – Run One, The application
SS-HS-1	=	South Side – Hydrogen Sulfide – Run One

9.0 Deliverables

9.1 Northern Laboratory Branch (NLB) Deliverables

Within 60 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. Post analysis canister pressure.
 - f. Analytical results.
2. All equations or algorithms used in calculating analytical results.
3. Table of duplicate analytical 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 RPD 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.

9.2 Air Quality Surveillance Branch Deliverables

Within 60 days from receipt of the final results report from the Northern laboratory Branch (NLB), AQSB will provide DPR with a final report containing or covering the following sections:

1. Sampling Protocol
2. Personnel Contact List
3. Site Maps
4. Site Photographs
5. Site Descriptions and Measurements (site, sampler and met locations/GPS coordinates, inlet height, distance to roads or obstructions, site-specific comments, and sodium tetrathiocarbonate application rate).
6. Sample Summary Table
7. Canister Field Log Sheets and Restek SilcoCan Pesticide Data/Sample Tracking Sheets
8. Laboratory Analysis Reports w/calculations in electronic format
9. Met Station and Sampler Calibration Reports
10. All protocol deviations
11. Compact Disk (CD) containing electronic files of final report, 5-minute averages of Meteorological Data, wind roses, photos, tables, maps and any additional pertinent information

In addition, the Special Purpose Monitoring Section will prepare a project binder containing the above information. This binder will remain with SPMS.

APPENDIX A: STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF CARBON DISULFIDE IN AMBIENT AIR BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

The Special Analysis Section of MLD's Northern Laboratory Branch will perform the analyses for carbon disulfide collected by the canister method. This analytical procedure is entitled, "Standard Operating Procedure for the Determination of Carbon Disulfide in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry" and may be found in its entirety at:

http://www.arb.ca.gov/aaqm/sop/sop_066.pdf