California Environmental Protection Agency
AIR RESOURCES BOARD

Monitoring and Laboratory Division
Air Quality Surveillance Branch

Protocol for Ambient Air Monitoring for Methyl Bromide and 1,3-Dichloropropene In Ventura County During Summer, 2006

June 12, 2006

Prepared by:

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Signatures:

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Air Resources Board

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

I. STANDARD OPERATING PROCEDURE FOR THE SAMPLING AND ANALYSIS OF BROMOMETHANE AND TELONE BY GC/MS USING A VARIAN CRYOGENIC SAMPLER AND SILCO™ 6 LITER CANISTERS……...24-34

Protocol for the Ambient Air Monitoring
for Methyl Bromide and 1,3-Dichloropropene
In Ventura County During Summer, 2006

I.0 Introduction

At the request of the California Department of Pesticide Regulation (DPR) (December 28, 2005 Memorandum, Warnerdam to Witherspoon), the Air Resources Board (ARB) will conduct ambient air monitoring for the pesticides methyl bromide and Telone (cis-1,3-dichloropropene and trans-1,3-dichloropropene). Designed to coincide with the primary use of these fumigants prior to planting strawberries, monitoring will occur in Ventura County over an eight-week period planned for June 14, 2006 through August 6, 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 ARB first performed monitoring in Ventura County for these pesticides from August 22, 2005 through September 30, 2005. The DPR requested that the ARB repeat this monitoring in 2006 because the latest 2004 pesticide-use data supplied by DPR indicates a shift from previous use data (Fall 2003) to an earlier growing season and numerous technical problems were encountered during analyses of samples collected in 2005. The 2006 sampling and analysis will follow the procedures outlined in this protocol.

The Special Analysis Section (SAS) of the Northern Laboratory Branch (NLB) will analyze collected samples using, "Standard Operating Procedures for the Sampling and Analysis of Bromomethane and Telone by GC/MS using a Varian Cryogenic Sampler and Silco™ Canisters". This analytical method is included as **Appendix I** (May 2001 Version) of this protocol and will be used as the analytical method for methyl bromide (bromomethane) and Telone.

Silco™, and its derivatives such as Silcosteel and SilcoCan, is a Trade Name given to a proprietary surface treatment applied to stainless-steel that is available from the canister and passive flow controller vendor, the Restek Corporation. This treatment purportedly provides a chemically inert and impermeable surface for enhanced sample stability and is the preferred method for collection and short-term storage of ambient Volatile Organic Compounds and pesticide samples.

2.0 Project Goal and Objectives

The goal of this monitoring project is to measure the concentrations of methyl bromide and Telone in the ambient air at various locations within Ventura County during a season of peak use in 2006.

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 methyl bromide and 1,3-dichloropropene concentrations.

4. Application of relevant quality assurance/quality control practices to ensure the representativeness and integrity of field samples.

5. Adherence to established and approved field and laboratory practices, procedures and methods as well as provisions contained in this protocol.

6. At the conclusion of the project, the ARB will provide the DPR with a final report 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.

3.0 Contacts

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4.0 Study Locations

Staff from the Special Purpose Monitoring Section (SPMS) selected six sampling sites in Ventura County for the 2005 monitoring study based upon historical use of Methyl Bromide and 1,3-dichloropropene as indicated by the then most currently available (Fall 2003) DPR-supplied use-maps. These same sites will be used again for the 2006 monitoring study with the exception of the 2005 background site at Lincoln School. The latest (2004) use-maps indicated usage near the school and as a consequence DPR has requested a different background site. A new background site for 2006 has been identified by SPMS as the Ventura County APCD air monitoring site at Thousand Oaks High School in Thousand Oaks, Ventura County. During a visit to this site by SPMS staff, it was determined that the site is suitable and verbal approval for its use was obtained from Jim McElroy of VCAPCD. The DPR subsequently approved of the new background site.

Site locations, as indicated on the map presented in **Figure 1**, were selected for their proximity to agricultural fields, the presence of residents or students, and with additional considerations for both accessibility and security of the sampling equipment. The ARB understands that the DPR staff will verify and quantify the usage of these fumigants during the study period when the information becomes available.

Six (6) locations in Ventura County will be used for the 2006 monitoring including the new background-designated site at Thousand Oaks High School.

Thousand Oaks High School, 2323 Moorpark Road, Thousand Oaks, CA, 91360 (805) 497-0167
GPS: Pending
Approval Contacts: James McElroy, Supervisor, Ventura County APCD (805) 662-6958

CA Dept. of Transportation (CALTRANS) Station, 4821 Adohr Lane, Camarillo, CA 93012
GPS: N 34º 12.407' W 119º 00.414'
Approval Contact: Mr. Vic Korzan, Manager, CA Dept. of Transportation, District 07 – West Region, 4821 Adohr Lane, Camarillo, CA, 93012, (805) 389-1106

Ventura County Fire Dept. Maintenance Facility, 2451 Latigo Road, Oxnard, CA 93030
GPS: N 34º 12.675' W 119º 08.595'
Approval Contacts: Chief Ralston, Ventura County Fire Dept., 165 Durley Avenue, Camarillo, CA, 93010; Mr. Brett Wreesman, Senior Fire Mechanic, Support Division, 2451 Latigo Ave., Oxnard, CA, 93030, 805.278-5200

United Water Conservation District, 3561 Rose Avenue, Oxnard, CA 93030
GPS: N 34º 15.160' W 119º 08.193'
Approval Contact: Mr. Tony Blankenship, Operations Superintendent, United Water Conservation District, 106 N. 8th Street, Santa Paula, CA, 93060, 805.485-5114 ext. 11

4.0 **Study Locations** (continued)

Laguna Vista Elementary School, 5084 Etting Road, Oxnard, CA 93033
GPS: N 34º 09.695' W 119º 05.645'
Approval Contacts: Ms. Nancy J. Carroll, Ph.D., Superintendent, Ocean View School District, 2382 Etting Road, Oxnard, CA 93033; Ms. Suzanne S. Lange, Principal, Laguna Vista Elementary School, 5084 Etting Road, Oxnard, CA, 93033, 805.488-3638

CA Dept. of Forestry / CA Youth Authority, 2800 Wright Road, Camarillo, CA 93010
GPS: N 34º 14.702' W 119º 06.457'
Approval Contacts: Chief Parker, CA Dept. of Forestry, 2800 Wright Road, Camarillo, CA, 93010, (805) 983-3960; Mr. Ruben Nunez, Superintendent, CA Dept. of Corrections, 3100 Wright Road, Camarillo, CA, 93010, (805) 485-7951 ext. 3700

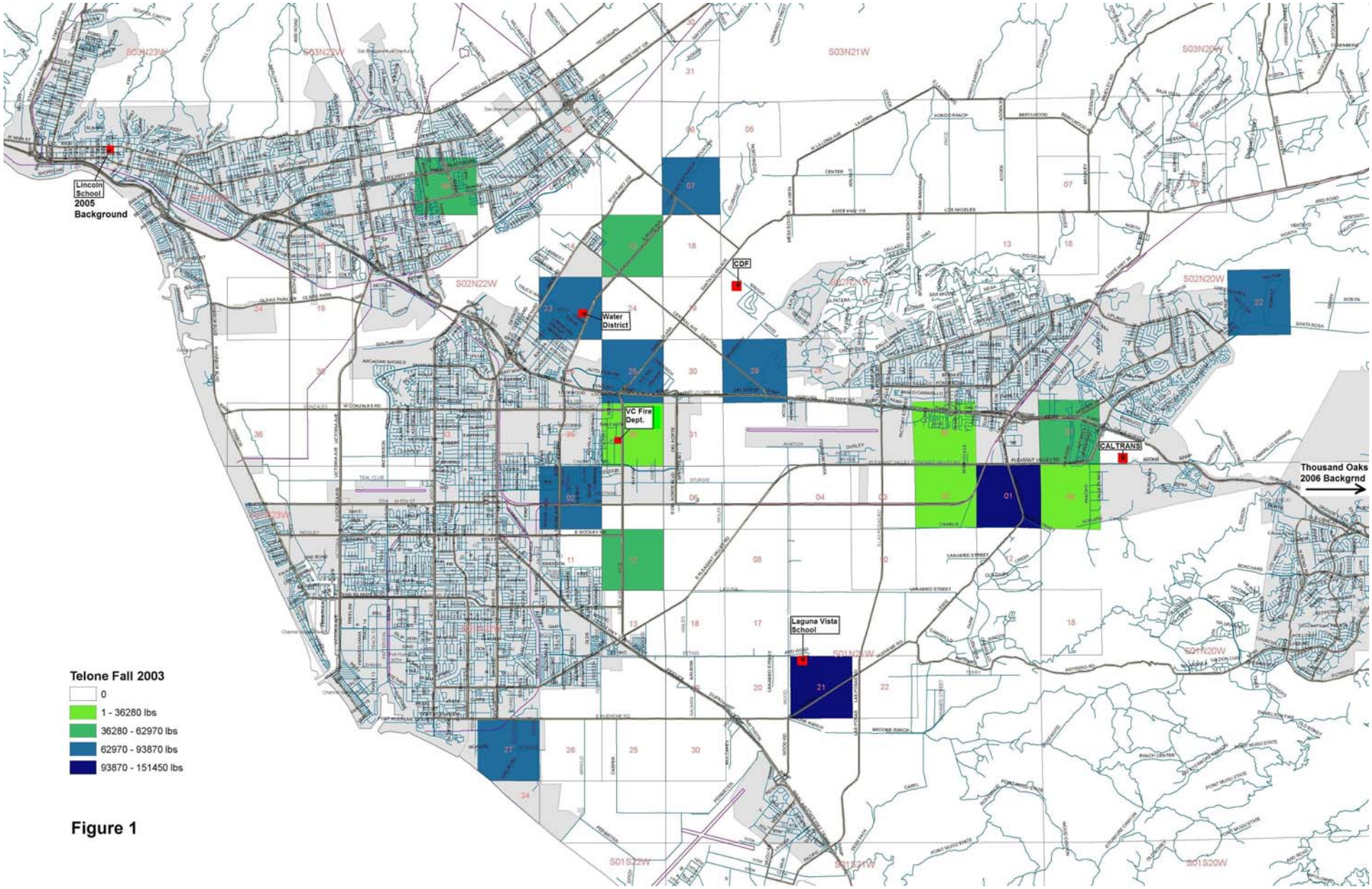
Lincoln School 2005 Background
CDF
Water District
VC Fire Dept.
CALTRANS
Laguna Vista School
Thousand Oaks 2006 Backgrnd
Telone Fall 2003
0
1 - 36280 lbs
36280 - 62970 lbs
62970 - 93870 lbs
93870 - 151450 lbs

Figure 1

5.0 Study Design

The collection media used for sampling of methyl bromide and Telone will be Silcosteel® treated canisters sampled through Restek passive flow controllers. An image of these samplers deployed during the 2005 Ventura Study is presented in **Figure 2.** Individual air samples will consist of 24-hour sample collection periods (typically 7 A.M. to 7 A.M. the following day), four days per week, Monday through Friday, for the duration of the eight-week study.

Note: In addition to sampling Monday through Friday, weekend sampling consisting of collecting Saturday and Sunday samples has been requested by DPR. This weekend sampling has been scheduled to occur at the ends of Weeks l, 4, and 8, at those sites where weekend access is permitted. Tentative approval for weekend access has been obtained for the Thousand Oaks background site, the Department of Forestry site, and the Water District site. Requests and approvals for the remaining sites are ongoing.

Twenty-four hour (24-hour) time-Integrated ambient air samples will be collected using evacuated, six-liter Silcosteel® canisters (Restek Corporation). The target sample flow rate of 3 standard cubic centimeters per minute (scc/m) will be set and regulated using a passive flow controller and verified by a certified battery-operated mass flow meter (0-10 scc/m Aalborg). The sampling system will be operated continuously for 24 hours with the exact operating interval recorded on both the Restek SilcoCan Pesticide Data/Sample Tracking Sheet presented in **Figure 3** and the Canister Field Log Sheet presented in **Figure 4**. The canister vacuum reading will be recorded at the start and end of each sampling period using the –30 to 0 inches of Mercury (in Hg) passive flow controller (sampler) gauge. The start and end canister vacuum readings will be approximately -30 in Hg and -5 to -8 in Hg respectively as indicated by the sampler gauge. The canister vacuum reading will also be measured using a more accurate gauge in the lab before and after transport to/from the field (the sampler's pressure/vacuum gauge is not calibrated for accuracy). The laboratory gauge readings will be used to calculate the sample volume collected. The 3 scc/m sampling rate will yield a sample volume of 4.3 liters over the 24-hour sampling period. The estimated quantitation limit (EQL) for MeBr is 0.036 ug/m^3 (target EQL was 0.4 ug/m^3) and the EQLs for cis and trans 1,3-dichloropropene are 0.015 and 0.03 ug/m^3 respectively (target EQL for Telone was 0.01 ug/m^3).

The passive flow controllers (Silcosteel-treated Veriflo SC423XL), equipped with new frits, will be attached to the valve fitting on the canister using a Silcosteel treated swagelock connector. A six foot section of new or adequately cleaned 1/8 inch O.D, Silcosteel tubing will be attached to the inlet end of the flow controller. The inlet end of the tubing will be bent into a U shape (to prevent rain from entering) and supported about six feet above the building rooftops for the ambient monitoring (See image in **Figure 2**).

5.0 **Study Design** (continued)

At the end of each sampling period, the canisters will be placed in shipping containers with their assigned and attached Restek SilcoCan Pesticide Data/Sample Tracking Sheet (**Figure 3**). The canisters are to be transported as soon as practical to the ARB laboratory in Sacramento (typically, at the end of each sampling week). The fresh canisters will be picked-up from the lab on Friday (or the following Monday if weekend sampling week), stored in the transport vehicle and transported to Ventura the following Sunday (or Tuesday if weekend sampling week). After sampling, the canisters will be returned to the Sacramento laboratory the following Friday (or Sunday if weekend sampling week). The canisters will be transported and stored at ambient temperatures while in the field and at ambient laboratory temperature prior to analysis. These foregoing tasks will be performed by assigned SPMS staff according to the staff rotation schedule presented in **Section 10.0** of this protocol.

To ensure a steady sample flow rate and subsequent collection of a representative sample, a passive flow controller, Veriflo SC423XL, from Restek is used. This controller uses a metal diaphragm downstream of the critical orifice to regulate the flow rate as the vacuum in the canister changes. It is capable of maintaining a constant flow rate with the vacuum ranging from -30.0 in Hg to approximately -5 in Hg. An in-line filter (referred to as a “frit” by Restek), having a 2-micron pore size, prevents particles from entering and clogging the critical orifice of the flow controller. These passive flow controllers utilize volumetric principles (pressure differential) and as such are affected by ambient conditions. The manufacturer’s specifications state that there is an approximately six percent reduction in flow rate when the temperature changes from 80 °F to 125 °F. To minimize temperature changes due to solar radiation, a 6-10 inch diameter sun-shade (pie-plate) is installed immediately above the flow controller.

The canister field/lab data sheet and canister field log sheet presented in **Figures 3 and 4** respectively will be used to record start and stop times, start and stop vacuum readings, sample identifications, weather conditions, operator’s initials and other significant observations.

For each site, a target number of 40, 24-hour canister samples will be taken during the eight-week sampling period (4 samples per week per site x 8 weeks = 32 regular + 1 collocated per site x 8 weeks) not including QC samples. Collocated (duplicate) samples will be collected from each site once per week for a total collection of 8 collocated pairs per sampling location. Three (3) weekend (Friday AM to Sunday AM) collection days are also planned for Weeks 1, 4 and 8, as requested by DPR.

6.0 Laboratory Analysis

The laboratory method, "Standard Operating Procedures for the Sampling and Analysis of Bromomethane and Telone by GC/MS using a Varian Cryogenic Sampler and Silco™ Canisters," is included as **Appendix I** (May 2001 Draft Version). This method will be used as the primary analysis method for methyl bromide (bromomethane) and 1,3-dichloropropene. The procedures are based on EPA Method TO-15 which includes cryogenic pre-concentration and GC/MS analysis. The canisters arrive from the field at sub-ambient pressure and are pressurized (diluted) in the laboratory before analysis.

6.1 Sampling and Analysis Procedures

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 methyl bromide and 1,3-dichloropropene in air. This criteria will be used to validate study samples.

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. **Estimate Quality Limit (EQL)**: This EQL convention shall be eliminated. In the past, measurements falling between the MDL and five times the MDL (EQL) were reported as "detect" All values at or above the MDL shall be reported as a numeric value.

5. **Analytical Linear Range**: Any analytical result greater than the highest calibration standard shall be reanalyzed within the linear range.

Laguna Vista-View West

Figure 2: Passive Flow Control Canister Sampler (2005 Ventura deployment)

[Place data sheet inside plastic pouch]

CALIFORNIA AIR RESOURCES BOARD
Restek SilcoCan Pesticide Data/Sample Tracking Sheet

Pesticides
Veriflo
Controller

Project Name: _____

Site/Sample Name: _____

Lab I.D.:

Operator & Agency: _____

	Date	Time (PST)	CANISTER Vacuum ("Hg) LAB	CANISTER Vacuum ("Hg) FIELD	LABORAT Pressure or LAB**	SAMPLER MFC Reading		SAMPLER Vacuum	
Set-Up									
Start									
Stop									

Type of Sample: [ ] Regular [ ] Collocated [ ] Spike [ ] Blank [ ] Other

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

Observed Unusual Sampling Condition: [ ] Wind-Blown Sand/Dust [ ] Rain [ ] Farming Nearby [ ] Construction Nearby [ ] Fire Nearby [ ] Other _____

[ ] INVALID SAMPLE INFORMATION

Reason for Sample Invalidation

[ ] Vacuum lower than -10"Hg
[ ] Sampling period out of range (<___ or >___ hours)
[ ] Sampling equipment inoperative
[ ] Vacuum higher than -5"Hg
[ ] Other reasons: _____

Field Comments: _____

Sample Tracking

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

===FOR LABORATORY USE ONLY====

Lab Comments: _____

** = Calibrated Guage Pressure or Vacuum

04/20/06

Figure 3: Restek SilcoCan Pesticide Data/Sample Tracking Sheet

Log #	Sample Name	Sampler ID Number	Date & Time (PST)		Canister Vacuum Display		Mass Flow Meter Display		Corrected Average Flow	Comment Number	Weather K,P,C,F&R		Initials	
			Start	End	Start	End	Start	End			Start	End	Start	End
001	1-LS-1185													
002	1-CT-1091													
003	1-LV-1187													
004	1-FS-1172													
005	1-DF-1105													
006	1-WD-1132													
007	2-LS-1097													
008	2-LSC-1084													
009	2-CT-1137													
010	2-CTC-1111													
011	2-LV-1176													
012	2-LVC-1157													
013	2-FS-1133													
014	2-FSC-1178													
015	2-DF-1179													
016	2-DFC-1159													
017	2-WD-1071													

MFM Used #: _____ **Slope:** _____ **Intrcpt:** _____

Figure 4: Canister Field Log Sheet

7.0 List of Field Equipment

(13 = 12 + 1 spare): passive flow controllers each equipped with 24-hour orifice.

(12): sampling trains; 2-meter length sample probe/canister pier blocks assemblies.

(2 = 1 + 1 spare): Aalborg 0-10 ccm/m battery-powered mass flow meter (certified).

(1): Minimum 10 feet tall ladder (carried in vehicle)

(1): Minimum 6 feet tall ladder (stored at Laguna Vista rooftop)

(1): Set of tie-down straps for securing samplers at Caltrans site

(1): Field Binder containing Canister Sample Log Sheets and Protocol

(1): Laptop PC with Excel spreadsheet of Canister Sample Log Sheets

(1): Digital Camera and Global Positioning Sensor (GPS) for first week only

(1): Access keys to Thousand Oaks site

(1): Tool Bag or box containing common hand tools including 3 mm Allen wrench.

(1): Cell Phone and ARB Phone List

(6): Spare flow controller frits

(6): Approval Request Letters (signed) for sampling site landowners.

7.1 Field / Lab Canister Handling Procedures

- The SAS laboratory indicated that 33 canisters (full week allotment) will be ready for field deployment on Monday June 12th.
- Thirty-three (33) canisters (cans) will be deployed each week.
- 6 sites x 4 days + 6 collocated + 1 field spike + 1 trip spike + 1 trip blank
- Cans ready for deployment will be located in the lab's north/south hallway.
- Cans returning from the field (Friday, or Sunday if weekend sampling week) should be placed in the lab's north/south hallway upon return to Sacramento.
- Lab building security access code is the same as 13th & T Streets.
- Copies of Canister Field Log Sheets (**Figure 4**) should be made for the lab and SPMS. The originals remain in the field binder.

8.0 Quality Control

Quality Control for the 2006 ambient monitoring study in Ventura will include the following provisions:

A planned total of 264 canisters are expected to go into the field over the eight-week monitoring study period. It is therefore essential that each sample be identified and distinguished by assignment of unique tags. These tags will consist of a sequential Field Log Number and a Sample Identification Name assigned by SPMS staff to canisters at the time canisters are prepared for sampling. These tags will be contemporaneously recorded onto both the Restek SilcoCan Pesticide Data/Sample Tracking Sheet and the Canister Field Log sheet (**Figures 3 and 4**). Toward the end of each sampling day, this information will also be entered into an Excel spreadsheet of the Canister Field Log Sheet. Should any discrepancies be found in the field data, corrections should be made at this time.

The Field Log Number will start with #1 and progress sequentially as the study period progresses. Once a log number has been assigned to a canister sample, that number should not be used again even if the sample didn't run or is determined to be invalid.

The unique Sample Identification Name assigned to each sample canister should follow the pattern in the following example: **1-TO-C-9999**

Where: "**1**" is the number of the daily sample batch. All samples collected on the same day, including QC samples, should have the same number. Next day's samples will start with "2", etc.

"**TO**" is the site identifier abbreviation. The following abbreviations will be used:

TO – Thousand Oaks High School
CT – Caltrans Station
VC – Ventura County Fire Dept. Maintenance Facility
UD – United Water Conservation District
CF – CA Dept. of Forestry / CA Youth Authority Facility
LV – Laguna Vista Elementary School

"**C**" is the identifier for a collocated sample. Other identifiers to be similarly used include **FS** for **F**ield **S**pike, **TS** for **T**rip **S**pike and **TB** for **T**rip **B**lank.

9999 – Permanent canister number assigned by lab

8.0 **Quality Control** (continued)

1) **Field Spikes**: For 2006, field spikes will be prepared by the laboratory by injecting canisters with two different concentration levels, 10 ug/m3 and 50 ug/m3 of methyl bromide, cis-1,3-dichloropropene, and trans-1,3-dichloropropene. The only spike concentration used in 2005 was10 ug/m3.

   A minimum of 8 field spike samples will be collected during the eight-week study. Every week the lab will supply one field spike canister, alternating between the low and high concentrations. The field spike sample is obtained by sampling ambient air at the urban background monitoring site for a 24-hour period and collocated with collection of a background sample at the same environmental and experimental conditions.

   Field Spikes will be identified and distinguished from other samples by including the initials "FS" to the Sample Identification Name as recorded on both the Restek SilcoCan Pesticide Data/Sample Tracking Sheet (**Figure 3**) and Canister Field Log Sheet (**Figure 4**). Example: 1-TO-**FS**-9999.

2) **Trip Spikes**: A minimum of 8 trip spikes will be prepared by the laboratory at the same levels (high and low) as the field spikes. A trip spike will be transported and analyzed along with each field spike. Trip spikes are treated the same as field spikes with the exception that they are not installed onto a sampler.

   Trip Spikes will be identified and distinguished from other samples by including the initials "TS" to the Sample Identification Name as recorded on both the Restek SilcoCan Pesticide Data/Sample Tracking Sheet and Canister Field Log Sheet. Example: 1-TO-**TS**-9999.

3) **Lab Spikes**: A minimum of 8 lab spikes will be prepared by the laboratory at the same levels (high and low) as the field and trip spikes. A lab spike will be analyzed along with each of the field and trip spike pairs. The lab spike canisters remain in the custody of the laboratory.

8.0 Quality Control (continued)

4) **Trip Blanks**: A minimum of 8 trip blanks will be prepared by the laboratory. The Trip Blank canister accompanies that week's sample canisters from the lab to the field and return but is not installed onto a sampler. One trip blank will be generated for each week of sampling.

Trip Blanks will be identified and distinguished from other samples by including the initials "TB" to the Sample Identification Name as recorded on both the Restek SilcoCan Pesticide Data/Sample Tracking Sheet and Canister Field Log Sheet. Example: 1-TO-**TB**-9999.

5) **Collocated:** Collocated samples will be collected at each sampling site for eight dates during the eight-week monitoring period. Typically, collocated samples are collected at least once per week from each of the sampling sites, all on the same day. This latter procedure requires that two samplers be deployed at each site, which is typically the case unless there is a shortage of samplers. In which case, a sampler may be moved or rotated from site to site to obtain collocation collection even if not on the same day as other sites.

Collocated samples will be identified and distinguished from other samples by including the initial "C" to the Sample Identification Name as recorded on both the Restek SilcoCan Pesticide Data/Sample Tracking Sheet and Canister Field Log Sheet. Example: 1-TO-**C**-9999.

Note: All canisters that go into the field, including all QC canisters, will have unique sequential log numbers and sample names assigned to them by field staff that will be recorded onto field logs and canister data sheets.

6) **Sample Duration:** The sample collection period is 24 +/- 0.5 hours and the preferred sample start time for the first visited site is 7 A.M. PDT +/- 1 hour.

7) **Flow Checks:** The sample collection period starts when the canister Valve is manually opened and ends when the valve is closed. After opening and before closing the valve, a (NIST)-certified mass flow meter is connected to the sample intake opening of the sample probe. The indicated sample flow rate is recorded, or in the case of the start of the collection period, changed if necessary by adjusting the passive flow controller then recorded.

8.0 **Quality Control** (continued)

For the 24-hour time-integrated sampling to be performed during this study, the sample flow rate should read (as indicated by the attached mass flow meter) a corrected 3.0 standard cubic centimeters per minute (sccm) +/- 0.3 sccm. This nominal flow rate has been determined to provide the necessary volume of sample to result in a final canister vacuum of between -6 and -8 inches of mercury ("Hg) as indicated by the passive flow controller vacuum gage. If the end vacuum gauge reading is less than -6" Hg, the flow controller's ability to maintain a uniform sample flow rate may have been affected, usually indicated by end flow rate measurement outside of allowable limits. If the end vacuum reading is more than -10" Hg, the collected sample volume is less than what could have been collected.

Due to factors such as ambient conditions and accuracy of sampler gauge, the start and stop flow rate measurements, and start and stop sampler vacuum gage readings, **should not** solely be used as sample validation criteria but rather a field indication as to whether a 24-hour integrated sample is being collected and that the sample volume (as indicated by the sampler gauge) correlates with flow rate measurements.

If a canister prepared for sampling indicates a sampler vacuum gage reading of 0 to 25" Hg, that canister should not be used for sampling. If a canister indicates a sampler gage reading of 25 to 29" Hg, that canister should be set aside and not used for sampling unless a spare canister is unavailable, in which case it can be used.

If measured flow rates and/or final canister vacuums don't fall within the above guidelines, perform the following tasks in the order presented:

1) Endeavor to keep sampling duration as close as possible to 24-hours.

2) Assure that beginning and ending flow rates are 3.0 +/- 0.3 sccm. If not, adjust the passive flow controller's flow control valve.

3) If a minimum sample flow of 3.0 sccm cannot be obtained and/or end can vacuums are higher than -10", replace the flow controller's frit (in-line filter).

4) If replacing the frit does not solve problem, replace the entire passive flow controller.

5) If measured sample flow rates are within guidelines but ending vacuums are less than -5", a leak may have occurred. Collect another sample as scheduled and if this happens again to a similar degree, replace the passive flow controller.

9.0 Deliverables

9.1 Deliverables from Air Quality Surveillance Branch (AQSB)

Within 60 days from receipt of the final laboratory results report from the Northern Laboratory Branch (NLB), AQSB will provide (for comment) a comprehensive draft monitoring report in both hardcopy and electronic formats to the Department of Pesticide Regulation. This draft report will contain or cover 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)
6) Sample Summary Table
7) Canister Field Log Sheets
8) Laboratory Analysis Results Report including concentration calculations in electronic (preferred) format
9) Transfer Standards' Certification Reports
10) Section or provision listing or reporting all deviations from this protocol and/or established procedures.
11) Compact Disk containing electronic file of draft monitoring report

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

9.0 Deliverables (continued)

9.2 Deliverables from Northern Laboratory Branch (NLB)

Within 60 days from last date of analysis, the NLB will provide (for comment) the AQSB with a draft analysis results report in electronic format. This draft report will contain or cover the following topics:

1) Table(s) of sample data to include:

   - Sample identification (name)
   - Date sample received from field
   - Date sample analyzed
   - Dilution ratio
   - 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 calculated 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 analyses.

9) Section or provision listing or reporting any and all deviations from analytical SOP and this protocol.

10.0 Staff Rotation Schedule

SPMS STAFF ROTATION SCHEDULE FOR THE

2006 VENTURA AMBIENT PESTICIDE STUDY

Dated: June 8, 2006

These Special Purpose Monitoring Section (SPMS) staff rotation schedules for the 2006 Ventura County ambient pesticide study are based upon a Primary June 14 through August 6 study period. If a delay in starting date should occur, the Alternate target study period is the following week, June 21 through Aug 13. The two schedules that follow are for these Primary and Alternate study periods:

Note: Monday though Friday sample collection periods require travel on Sundays and Fridays. Wednesday through Sunday sample collection periods (weekend sampling) require travel on Tuesdays and Sundays. This weekend schedule requires an enroute transfer of Field Log Sheet binder, field PC, MFM's, etc. on a Sunday between the person coming from and the person going to Ventura.

*Wednesday thru Sunday (weekend) sampling scheduled for Weeks 1, 4 and 8.

/ Setup and teardown days require 2 persons that day only.

Italicized name in table denotes a partial week assignment.

Note: Day / Dates in table refer to sample collection periods, not travel dates.

Primary: June 14 – August 6		
Wee	**Day / Dates**	**Staff**
1*	Wed 6/14–Su 6/18	Andy ***/*** *Jack*
2	Mo 6/19 – Fr 6/23	Jack
3	Mo 6/26 – Fr 6/30	Jack
4*	Wed 7/5 – Su 7/9	Aston
5	Mo 7/10 – Fr 7/14	Andy
6	Mo 7/17 – Fr 7/21	Rider
7	Sun 7/24–Fr 7/28	Aston
8*	Wed 8/2 – Sun 8/6	Andy ***/*** *Jack*

- Thousand Oaks will be last visited sampling site.
- First site sampling will start at 6 A.M. PST +/- 1 hour.

Appendix I

Draft

Standard Operating Procedure for the Sampling and Analysis of Bromomethane, and Telone by GC/MS using a Varian Cryogenic Sampler and Silco™ 6 liter Canisters

California Environmental Protection Agency

Air Resources Board

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

Draft

Standard Operating Procedure for the Sampling and Analysis of Bromomethane, and Telone by GC/MS using a Varian Cryogenic Sampler and Silco™ 6 liter Canisters

version
May, 2001

Approved by:

1. SCOPE

This method is for the sampling and analysis of bromomethane (Methyl Bromide) and telone (cis-1,3-dichloropropene and trans-1,3-dichloropropene) in ambient air using 6 liter Silco™ canisters for sample collection. Collected samples are analyzed by gas chromatography/mass spectrometry using a Varian Stand Alone cryogenic sampler.

2. SUMMARY OF METHOD

Ambient air is collected into evacuated 6-liter Silco™ canisters. Field sampling uses a sub-atmospheric pressure collection mode. Sample canisters are pressurized in the laboratory to facilitate laboratory sampling. Samples are analyzed by Gas Chromatography / Mass Spectrometry (GC/MS) using a cryogenic concentrator to prepare the air sample. Samples are analyzed in the Selected Ion Monitoring (SIM) mode using deuterated bromomethane (bromomethane-d3) and toluene (toluene-d8) as internal standards.

3. INTERFERENCES/LIMITATIONS

Interferences may result from improperly cleaned canisters. Analysis of samples containing high concentrations of method analytes may cause significant contamination of the analytical equipment. Co-eluting compounds trapped during sample collection may interfere.

4. EQUIPMENT AND CONDITIONS

A. Instrumentation

Hewlett Packard 6890 Series Plus gas chromatograph:
Column: Restek Rtx-200, 60 meter, 0.32mm I.D., 1.50 micron film thickness
GC temperature program: initial -10° C, initial time 0 minutes, to 80° C @ 10° C/min, to 200° C @ 25° C/min, hold 1 minute, to 240 ^{o} C @ 25° C/min, hold 1 minute.
Carrier Gas: Helium, grade 5

Hewlett Packard 5973 mass selective detector:
Acquisition Mode: SIM
Tune File: PFTBA Autotune
Ions Monitored: 74.8, 93.8, 95.8, 96.8, 98.8, 110.0
Quant Ions: 74.8, 93.8
Solvent Delay: 5.00 min

Varian Stand Alone cryogenic concentrator:
Valve Oven: 60° C

Autosampler Oven: 60° C
Nafion Dryer: 60° C
Sample Line: 60°
Cryotrap: -180° C to 150°
Transfer Line: 150° C
Cryofocus: -180° C to 150° C
Sample Size: 15 ml to 400 ml
Internal Standard Loop: 1 ml

B. Auxiliary Apparatus

Compressed helium: grade five
Compressed air: ultra zero grade
Compressed nitrogen: grade five
Liquid nitrogen
Gas standards: certified if available
Restek, 6.0 liter Silcosteel canisters: with silcosteel valve
Pressure gauge: able to measure –30mm to 30 psig
Canister cleaning system (see appendix)

5. ANALYSIS OF SAMPLES

1) Perform a PFTBA autotune and evaluate tune criteria (Appendix 2). Place a copy of the autotune results in the autotune folder.
2) Check and record the pressure of the field sample canisters. Pressurize the field sample canisters to approximately 5 psig with ultra pure nitrogen. Record the final pressure.
3) Prepare a sample sequence for the GC/MS. The sequence should include a calibration check, a system blank and a duplicate for every 10 samples. Load the sequence into the GC/MS in the remote start mode.
4) Prepare a sample sequence for the Varian sampler. Organize the sample sequence as follows: system blank, calibration check, field samples, duplicate field sample, calibration check. If the calibration check is not within $\pm$20% of its expected value the system must be evaluated and recalibrated if necessary.
5) Attach the sample canisters to the Varian autosampler ring as per the sequence. Execute the sequence.
6) Sample analysis report will print out after each analysis.

CALCULATIONS: Sub-ambient sampling requires pressurization prior to analysis. Instrument reports will be in units of ng/m3 and must be corrected for the analysis dilution using the following calculation:

$(Fp / Ip) \times Ci = Cr$

Ip = initial canister pressure in mm Hg
Fp = final canister pressure in mm Hg
Ci = concentration from the analysis report in ng/m3
Cr = reported concentration in ng/m3

6. QUALITY ASSURANCE

A. Instrument Reproducibility

Establish the reproducibility of the instrument and analytical method as follows. Inject five replicate samples of each target compound at three concentrations (low, mid and high range). Reproducibility study results are presented in Table 1.

B. Linearity

A six-point calibration curve is made for each of the target compounds. The curve is constructed using linear regression analysis. Appendix 3 contains method calibration data.

C. Minimum Detection Limit

Detection Limit is based on US EPA MDL calculation. Using the analysis of seven replicates of a low-level spikes, the method detection limit (MDL), and the estimated quantitation limit (EQL) for method compounds are calculated by:

$$MDL = 3.14*s$$
$$EQL = 5*MDL$$

where: s = the standard deviation of the response calculated for the seven replicate spikes. The MDL and EQL are calculated as follows.

bromomethane MDL = 3.14 (0.0015 ug/m3) = 0.0047 ug/m3
EQL = 5(0.0047 ug/m3) = 0.024 ug/m3

cis-1,3-dichloropropene MDL = 3.14 (0.0007 ug/m3) = 0.0021 ug/m3
EQL = 5(0.0021 ug/m3) = 0.010 ug/m3

trans-1,3-dichloropropene MDL = 3.14 (0.001 ug/m3) = 0.0031 ug/m3
EQL = 5(0.0031 ug/m3) = 0.015 ug/m3

Assuming a 1:1.5 dilution to pressurize ambient samples:

Bromomethane EQL = 1.5 (0.024 ug/m3) = 0.036 ug/m3

cis-1,3-dichloropropene EQL = 1.5 (0.010 ug/m3) = 0.015 ug/m3

trans-1,3-dichloropropene EQL = 1.5 (0.015 ug/m3) = 0.03 ug/m3

Results are reported to 3 significant figures above the EQL. Results below EQL and above MDL are reported as det (detected). Results less than MDL are reported as less than MDL.

D. Calibration Check

A calibration check sample is analyzed at the beginning of each analytical batch and following each batch of ten samples. The value of the check must be ±20 % of the expected value. If the check is outside limits the prior batch of 10 samples must be reanalyzed.

E. Laboratory Control Sample

A laboratory control sample (LCS) is included with each analytical batch. The analysis value of the LCS must be within three standard deviations of it's historical mean (±.3 σ). If the LCS is outside of limits then the samples in the analytical batch must be reanalyzed.

F. Storage Stability

If the method storage stability of target compounds is unknown then a storage stability study should be conducted. The study should be conducted for a time period which represents the maximum hold time for field samples.

7. SAFETY PRECAUTIONS

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. All applicable safety precautions must be observed for the use of compressed gas cylinders.

8. DISCUSSION:

Table 1

REPRODUCIBILITY STUDY

Low Level	**Bromomethane (ng/m3)**	**Cis-1,3-Dichloropropene (ng/m3)**	**Trans- 1,3-Dichloropropene (ng/m3)**
1	27.7	13.1	12.0
2	28.4	12.7	10.8
3	28.7	11.7	9.5
4	28.8	11.3	9.7
5	27.8	11.4	10.9
Average	**28.3**	**12.0**	**10.6**
SD	**0.51**	**0.81**	**1.01**
RSD	**1.8%**	**6.8%**	**9.5%**
Medium Level			
1	217	118	106
2	214	113	103
3	210	116	105
4	215	109	100
5	215	111	101
Average	**214**	**113**	**103**
SD	**2.56**	**3.65**	**2.50**
RSD	**1.2%**	**3.2%**	**2.4%**
High Level			
1	827	385	355
2	830	387	355
3	851	384	358
4	853	383	355
5	838	413	382
Average	**840**	**391**	**361**
SD	**11.7**	**12.6**	**11.6**
RSD	**1.4%**	**3.2%**	**3.2%**

Notes:
m3 cubic meters
ng nanograms
RSD Relative standard deviation
SD standard deviation

Apppendix 1

CAN CLEANING PROCEEDURE

The canister cleaning procedure uses repeated cycling from –30 inches Hg to 30 pounds per square inch gauge with humidified ultra pure nitrogen. Each cycle is 24 minutes (12 minutes vacuum & 12 minutes pressure) at 80 degrees C. The procedure includes eight complete cycles.

Canister data should be logged into the canister cleaning book for each cleaning batch. When the batch is complete one canister is chosen for analysis. The canister is pressurized with ultra pure nitrogen and analyzed by the GCMS method. If target analytes are not less that two times their MDL the entire batch should be cleaned again.

Procedure:

A. Fill dewar with LN2

1. Remove dewar cover.
2. CAREFULLY place hose from LN2 tank into dewar (Orange and silver container behind oven).
3. Open LN2 tank 3 turns
4. Close tank when LN2 can be seen near top of dewar.
5. CAREFULLY remove hose and replace dewar cover.

B. Turn on the vacuum pump.

1. Switch is located on pump to the left of the can oven.

C. Open N_2 Tank

1. Open regulator on N_2 tank to the left of the can oven.

D. Load cans in oven

1. Attach cans to manifold in oven and tighten.
2. If you are cleaning less than 8 cans the unused ports must be capped.
3. Open the can valve

E. Start Timers Located on top left of can oven

1. Push Auto button on top timer and Auto light should come on. If the light is off, hit the button again and it should light.
2. Push the Run button on the bottom timer. The 1 light should light up briefly then switch to 2. On the top timer the 2 light should light.
3. Push the ADV on the top timer. The 2 light should go off and the 1 light should light. The system should also begin to evacuate.
4. Verify the system evacuates all the way by reading the gauge on the back of the oven. The gauge should go to –30 psi.

F. Fill cans and shutdown system.

1. Close all can valves except the ones you want to fill.
2. On the top timer hit the ADV button until the 2 light comes on.
3. Monitor the pressure of the cans on the gauge on the back of the oven.
4. Close can valves when filled.
5. Close N_2 Regulator
6. Turn off Vacuum pump.
7. Remove cans and place plugs on manifold ports.
8. Hit the stop button on both timers.

Appendix 2

Autotune Criteria

A standard autotune should be performed on the detector each day prior to sample analysis. The autotune report should be evaluated for the following:

1. n unusual change in the EM voltage
2. Peak width for all tune masses should be between 0.4 aAmu and 0.6 amu.
3. The relative abundance of tune mass 219.0 should be greater than 30% of tune mass 69.0.
4. Isotope abundance ratio for tune mass 70.0 should be between 0.54% and 1.6 %; isotope abundance ratio for tune mass 220.0 should be between 3.2% and 5.4%.
5. Masses 28 and 18 should be evaluated to check for air leaks in the system.

If autotune criteria are not met the system should be evaluated for problems. After the system problems are corrected the detector should be autotuned prior to sample analysis. Autotune reports should be filed in the instrument autotune folder.

Appendix 3

Calibration Standard Preparation for Bromomethane and Telone

The certified stock gas used for calibration during this study was purchased from Scott Specialty Gases and has the following specifications:

Cylinder No AAL 2013
Expiration date 8/14/01

BROMOMETHANE	13.1 PPB/M
CIS 1,3-DICHLOROPROPENE	5.05 PPB/M
TRANS 1,3-DICHLOROPROPENE	4.93 PPB/M

Working analysis standard is prepared by diluting the stock gas using the following procedure.

1. A 6 liter Silco canister is evacuated to –30 " Hg.
2. 300 ml of stock gas is transferred to the canister using a gas tight syringe.
3. 100 ul of reagent grade water is added to the canister using a syringe and syringe adapter.
4. The canister is pressurized to 29.4 psig with ultra pure nitrogen.

The canister will contain analytes at the following concentrations:

BROMOMETHANE	0.847 ug/m3
CIS 1,3-DICHLOROPROPENE	0.382 ug/m3
TRANS 1,3-DICHLOROPROPENE	0.343 ug/m3

The standard sample injection is 400 ml. A calibration curve is generated by using the cryo sampler to introduce the following volumes of working standard to the GCMS.

Volume	methylbromide	cis 1,3-DCP	trans 1,3-DCP
400 ml	0.847 ug/m3	0.382 ug/m3	0.343ug/m3
200 ml	0.423 ug/m3	0.191 ug/m3	0.171 ug/m3
100 ml	0.212 ug/m3	0.095 ug/m3	0.086 ug/m3
50 ml	0.106 ug/m3	0.048 ug/m3	0.043 ug/m3
25 ml	0.053 ug/m3	0.024 ug/m3	0.021 ug/m3
15 ml	0.032 ug/m3	0.014 ug/m3	0.013 ug/m3

Attachment III

Draft
Standard Operating Procedure
Sampling and Analysis of Bromomethane In Silco Canisters
(**higher concentration range method**)

California Environmental Protection Agency

Air Resources Board

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

Draft

Standard Operating Procedure
Sampling and Analysis of Bromomethane In Silco Canisters

version
July 26, 2000

Approved by:

1. SCOPE

This method is for the sampling and analysis of Methyl Bromide in ambient air using 6 liter Silco canisters for sample collection. Collected samples are analyzed by gas chromatography/mass spectrometry.

2. SUMMARY OF METHOD

Ambient air is collected into evacuated 6 liter Silco canisters. Field sampling uses a subatmospheric pressure collection mode. Sample canisters are pressurized in the laboratory to facilitate laboratory sampling. Samples are analyzed by Gas Chromatography / Mass Spectrometry (GC/MS) using a cryogenic concentrator to prepare the air sample. Samples are analyzed in the Selected Ion Monitoring (SIM) mode using deuterated bromomethane (bromomethane-d3) as an internal standard.

3. INTERFERENCES/LIMITATIONS

Interferences may result from improperly cleaned canisters. Analysis of samples containing high concentrations of bromomethane may cause significant contamination of the analytical equipment. Co-eluting compounds trapped during sample collection may interfere.

4. EQUIPMENT AND CONDITIONS

A. Instrumentation

Hewlett Packard 6890 Series Plus gas chromatograph:
Detector: 280° C
Injector: 220° C
Column: J&W DB-624, 60 meter, 0.25mm I.D., 1.40 micron film thickness
GC temperature program: initial 40° C, initial time 5.0 minutes, to 80° C @ 10° C/min, to 200° C @ 25° C/min
Carrier Gas: Helium, zero grade

Hewlett Packard 5973 mass selective detector:
Acquisition Mode: SIM
Tune File: PFTBA Autotune
Ions Monitored: 93.8, 95.8, 96.8, 98.8
Solvent Delay: 5.00 min

Nuteck 3550A cryogenic concentrator:
Valve Oven: 60°
Autosampler Oven: 50°
Nafion Dryer: ambient

Sample Line: 100°
Cryotrap: -160° C to 150°
Transfer Line: 150° C
Cryofocus: -175° C to 150° C
Sample Size: 400 ml
Internal Standard Loop: 2 ml

B. Auxiliary Apparatus

Compressed helium: zero grade
Compressed air: ultra zero grade
Compressed nitrogen: zero grade
Liquid nitrogen for cryogenic concentrator
Certified bromomethane standard
Restek, 6.0 liter Silcosteel canisters with silcosteel valve
Pressure gauge, -30mm to 30 psig
Canister cleaning system (Appendix 1)

6. ANALYSIS OF SAMPLES

7) Perform a PFTBA autotune and evaluate tune criteria (Appendix 2). Place a copy of the autotune results in the autotune folder.
8) Check and record the pressure in the field sample canisters. Pressurize the field sample canisters to approximately 5 psig with ultra pure nitrogen. Record the final pressure.
9) Prepare a sample sequence for the GC/MS. The sequence should include a calibration check, a system blank and a duplicate for every 10 samples. Load the sequence into the GC/MS in the remote start mode.
10) Prepare a sample sequence for the Nuteck.. The sample sequence should organized as follows: system blank, calibration check, field samples, duplicate field sample, calibration check. If the calibration check is not within 20% of it's assigned value the system must be recalibrated.
11) Attach the sample canisters to the Nuteck autosampler ring as per the sequence. Execute the Nuteck sequence.
12) Sample analysis report will print out after each analysis.

CALCULATIONS: Sub-ambient sampling requires pressurization prior to analysis. Instrument reports will be in units of ug/m3 and must be corrected for the analysis dilution using the following calculation:

$$(Fp / Ip) \times Ci = Cr$$

Ip = initial canister pressure in mm Hg
Fp = final canister pressure in mm Hg

Ci = concentration from the analysis report in ug/m3
Cr = reported concentration in ug/m3

7. QUALITY ASSURANCE

B. Instrument Reproducibility

Establish the reproducibility of the instrument and analytical method as follows. Inject five replicate samples of bromomethane standard at three concentrations (low, mid and high range). Reproducibility study results are presented in Table 1.

B. Linearity

A 6-point calibration was performed on 7/25/2000. Calibrators from 0.027 to 0.861 ug/m3 (Appendix 3) were used to construct a calibration curve by linear regression analysis.

Response Ratio = 9.56 e +001 x Amount + 2.63 e -001

R2 = 0.999

C. Minimum Detection Limit

Detection Limit is based on US EPA MDL calculation. Using the analysis of seven replicates of a low-level spikes, the method detection limit (MDL), and the estimated quantitation limit (EQL) for bromomethane is calculated by:

MDL = 3.14*s

EQL = 5*MDL

where: s = the standard deviation of the response calculated for the seven replicate spikes. Given s = 0.0015 ug/m3 for the seven samples, the MDL and EQL are calculated as follows.

MDL = 3.14 (0.0015 ug/m3) = 0.0047 ug/m3

EQL = 5(0.0047 ug/m3) = 0.024 ug/m3

Assuming a 1:1.5 dilution to pressurize ambient samples:

EQL = 1.5 (2.4 ug/m3) = 0.036 ug/m3

Results are reported to 3 significant figures above the EQL. Results below EQL

and above MDL are reported as det (detected). Results less than MDL are reported as less than MDL.

D. Storage Stability

Conduct a storage stability study of bromomethane over a 3-week period. Four (4) canisters are spiked with bromomethane at approximately 0.5 ppb. The spiked canisters are stored at ambient temperature and analyzed on storage weeks 0, 1, 2, 3. Restek conducted a stability study for methyl bromide in Silco cans and demonstrated that it is stable at 1 ppbv for at least 16 days. A Special Analysis Section stability study is currently being conducted.

E. Safety Precautions

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. All applicable safety precautions must be observed for the use of compressed gas cylinders.

DISCUSSION:

Table 1

REPRODUCIBILITY STUDY

Low Level	**Methyl Bromide (ng/m3)**	**Cis-1,3-Dichloropropene (ng/m3)**	**Trans- 1,3-Dichloropropene (ng/m3)**
1	48.59	48.47	47.90
2	47.48	42.51	41.97
3	49.49	39.05	43.09
4	47.77	38.93	40.30
5	46.06	49.49	48.05
Average	**47.88**	**43.69**	**44.26**
SD	**1.283**	**5.05**	**3.53**
RSD	**2.68**	**11.56**	**7.98**
Medium Level			
1	168.51	145.90	123.36
2	175.56	145.13	123.95
3	170.05	143.84	123.68
4	170.32	148.41	129.57
5	166.02	146.34	128.35
Average	**170.09**	**145.92**	**125.78**
SD	**3.50**	**1.68**	**2.94**
RSD	**2.06**	**1.15**	**2.34**
High Level			
1	859.54	933.33	965.97
2	873.08	938.40	965.55
3	858.87	949.98	972.94
4	841.56	933.93	961.24
5	852.66	943.24	1,004.36
Average	**857.14**	**939.78**	**974.01**
SD	**11.46**	**6.96**	**17.48**
RSD	**1.34**	**0.74**	**1.79**

Notes:

m3	cubic meters
ng	nanograms
RSD	Relative standard deviation
SD	standard deviation

Appendix

Appendix 1

CAN CLEANING PROCEEDURE

The canister cleaning procedure uses repeated cycling from –30 inches Hg to 30 pounds per square inch gauge with humidified ultra pure nitrogen. Each cycle is 24 minutes (12 minutes vacuum & 12 minutes pressure) at 80 degrees C. The procedure includes eight complete cycles.

Canister data should be logged into the canister cleaning book for each cleaning batch. When the batch is complete one canister is chosen for analysis. The canister is pressurized with ultra pure nitrogen and analyzed by the GCMS method. If target analytes are not less that two times their MDL the entire batch should be cleaned again.

Procedure:

A. Fill dewar with LN2

6. Remove dewar cover.
7. CAREFULLY place hose from LN2 tank into dewar (Orange and silver container behind oven).
8. Open LN2 tank 3 turns
9. Close tank when LN2 can be seen near top of dewar.
10. CAREFULLY remove hose and replace dewar cover.

B. Turn on the vacuum pump.

2. Switch is located on pump to the left of the can oven.

C. Open N_2 Tank

2. Open regulator on N_2 tank to the left of the can oven.

D. Load cans in oven

4. Attach cans to manifold in oven and tighten.
5. If you are cleaning less than 8 cans the unused ports must be capped.
6. Open the can valve

E. Start Timers Located on top left of can oven

5. Push Auto button on top timer and Auto light should come on. If the light is off, hit the button again and it should light.
6. Push the Run button on the bottom timer. The 1 light should light up briefly then switch to 2. On the top timer the 2 light should light.
7. Push the ADV on the top timer. The 2 light should go off and the 1 light should

light. The system should also begin to evacuate.

8. Verify the system evacuates all the way by reading the gauge on the back of the oven. The gauge should go to –30 psi.

F. Fill cans and shutdown system.

8. Close all can valves except the ones you want to fill.
9. On the top timer hit the ADV button until the 2 light comes on.
10. Monitor the pressure of the cans on the gauge on the back of the oven.
11. Close can valves when filled.
12. Close N_2 Regulator
13. Turn off Vacuum pump.
14. Remove cans and place plugs on manifold ports.

8. Hit the stop button on both timers.

Appendix 2

Autotune Criteria

A standard autotune should be performed on the detector each day prior to sample analysis. The autotune report should be evaluated for the following:

6. n unusual change in the EM voltage
7. Peak width for all tune masses should be between 0.4 aAmu and 0.6 amu.
8. The relative abundance of tune mass 219.0 should be greater than 30% of tune mass 69.0.
9. Isotope abundance ratio for tune mass 70.0 should be between 0.54% and 1.6 %; isotope abundance ratio for tune mass 220.0 should be between 3.2% and 5.4%.
10. Masses 28 and 18 should be evaluated to check for air leaks in the system.

If autotune criteria are not met the system should be evaluated for problems. After the system problems are corrected the detector should be autotuned prior to sample analysis. Autotune reports should be filed in the instrument autotune folder.

Appendix 3

Calibration Standard Preparation for Bromomethane and Telone

The certified stock gas used for calibration during this study was purchased from Scott Specialty Gases and has the following specifications:

Cylinder No ALM057764
Expiration date 11/17/00
BROMOMETHANE 5.77 PPB/M
CIS 1,3-DICHLOROPROPENE 5.45 PPB/M
TRANS 1,3-DICHLOROPROPENE 5.45 PPB/M

Working analysis standard is prepared by diluting the stock gas using the following procedure.

5. A 6 liter Silco canister is evacuated to –30 " Hg.
6. 692 ml of stock gas is transferred to the canister using a gas tight syringe.
7. 100 ul of reagent grade water is added to the canister using a syringe and syringe adapter.
8. The canister is pressurized to 29.4 psig with ultra pure nitrogen.

The canister will contain analytes at the following concentrations:

BROMOMETHANE 0.861 ug/m3
CIS 1,3-DICHLOROPROPENE 0.953 ug/m3
TRANS 1,3-DICHLOROPROPENE 0.953 ug/m3

The standard sample injection is 400 ml. A calibration curve is generated by using the cryo sampler to introduce the following volumes of working standard to the GCMS.

Volume	methylbromide	cis 1,3-DCP	trans 1,3-DCP
400 ml	0.861 ug/m3	0.953 ug/m3	0.953 ug/m3
200 ml	0.431 ug/m3	0.476 ug/m3	0.476 ug/m3
100 ml	0.215 ug/m3	0.238 ug/m3	0.238 ug/m3
50 ml	0.108 ug/m3	0.119 ug/m3	0.119 ug/m3
25 ml	0.054 ug/m3	0.060 ug/m3	0.060 ug/m3
15 ml	0.032 ug/m3	0.036 ug/m3	0.036 ug/m3

Attachment IV

Draft
Standard Operating Procedure
Sampling and Analysis of 1,3-dichloropropene (Telone) and Methyl Isothiocyanate (MITC) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector

California Environmental Protection Agency

Air Resources Board

Draft
Standard Operating Procedure
Sampling and Analysis of 1,3-dichloropropene (Telone) and Methyl Isothiocyanate (MITC) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

06/25/01 version

Approved by:

3. SCOPE

The method uses resin tubes and a gas chromatograph/mass selective detector for the determination of 1,3- dichloropropene (Telone) and methyl isothiocyanate (MITC), one of the breakdown products of Metam-Sodium, for application and ambient air sample analysis. The Department of Pesticide Regulation (DPR) asked the Air Resources Board (ARB) to do ambient and application monitoring of Telone and MITC at a requested quantitation limit of 0.5 $\mu g/m^3$ for MITC.

2. SUMMARY OF METHOD

Coconut based charcoal tubes are placed on the sampler for 24 hours at 3.0 liters per minute (LPM) flow rate. The samples are stored in an ice chest or refrigerator until extracted with 3 ml of dichloromethane (DCM). The injection volume is 1 μl. A gas chromatograph with a mass selective detector in the selected ion monitoring (SIM) mode is used for analysis.

3. INTERFERENCES/LIMITATIONS

The primary interference encountered with the previous method was the presence of the MITC near the cis-DCP. The retention time difference is only about 0.05 minutes and even operating in SIM mode, similar ions are detected by the instrument. This makes it difficult to accurately quantitate if both cis-DCP and MITC are present. The installation of a different column than that used in the previous method resolved the issue and easily separates the target compounds. As with any method, additional interferences may be caused by contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. Method blanks, both solvent and resin, must be run concurrently 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: 210 °C, Splitless, Liner 4 mm straight liner with glass wool.
Column: Restek Rtx-200, 60 meter, 320 μm i.d., 1.5 μm film thickness.

GC Temperature Program: Oven initial 40 °C, hold 4 min. Ramp to 220 °C @ 12 °C/min., hold 1 min., ramp to 240 °C @ 20 °C/min., hold 2.0 min. Retention time: cis-DCP= 11.63 min., trans-DCP= 12.10 min., MITC=12.23 min.

Splitter open @ 1.0 min.
Flows: Column: He, 1.6 ml/min, 9.1psi. (velocity: 32cm/sec)
Splitter: 50 ml/min.

Mass Spectrometer: Electron Ionization
Selective Ion Monitoring: dichloropropene: 75 (quant. ion 100%), 110 (qual. ion 30%); methyl isothiocyanate: 73 (quant. ion 100%), 72 (qual. ion 46%). Tuning: PFTBA on masses 69, 219, 502.

B. Auxiliary Apparatus

1. Precleaned vials, 8 ml capacity with teflon caps.
2. Whatman filters, 0.45 μm
3. Disposable syringes, 3 ml
4. Sonicator
5. GC vials with septum caps.

C. Reagants

1. Dichloromethane, Pesticide grade or better.
2. 1,3 -Dichloropropene (cis- and trans- mixture), Chem Service PS- 1 52, 99 (+) % or equiv.
3. Methyl Isothiocyanate, Chem Service MET-221A, 99.5%
4. Coconut charcoal sorbent tubes, SKC, Fullerton, CA #226-09.

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 ½ the peak height, 0.60 ± 0.05, and the criteria for relative abundance: 69:100%, 219:100-120%, and 502: 7-12%.

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 which may result in possible carry-over contamination.

3. A 5-point calibration curve shall be analyzed with each batch of samples. For dichloropropene the analysis is calibrated at 10, 20, 40, 60, 100 ng/ml cis and

trans. For methyl isothiocyanate the calibration is at 0.5, 1.0, 2.0, 3.0, 5.0 μg/ml.

4. With each batch of samples analyzed, a laboratory blank and a laboratory control spike will be run concurrently. A laboratory blank is an unexposed charcoal tube prepared and analyzed the same way the samples are analyzed. A laboratory control spike is a charcoal tube spiked with a known amount of standard. The control sample is prepared and analyzed the same way as the samples. Laboratory check samples should have recoveries that are at least 70% of the theoretical spiked value.

5. A DCP calibration check sample of 10 ng/ml is run after the calibration and every 10 samples and at the end of each sample batch. The calibration check for MITC is 0.75 μg/ml. The value of the check must be within $\pm 3\sigma$ (the standard deviation) or $\pm$10% of the expected value, whichever is greater. If the calibration check is outside the limit, then those samples in the batch after the last calibration check that was within the limit need to be reanalyzed.

6. Score and snap the sample tube, transfer the charcoal into a 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 1 hour.

7. Filter the samples using a 3 ml syringe and 0.45 μm filter directly into a GC vial and cap securely.

8. The atmospheric concentration is calculated according to:

Conc (ng/m^3) = Extract Conc (ng/ml) X 3 ml / Air Volume Sampled (m^3)

8. QUALITY ASSURANCE

A. Instrument Reproducibility

The reproducibility of the instrument and analytical method was established by analyzing five(5) 1.0 μl injections of dichloropropene and methyl isothiocyanate standard at three concentrations (low, mid, and high range). The low, mid and high concentrations of dichloropropene were 10, 40 and 100 ng/ml, respectively. The low, mid and high concentrations of methyl isothiocyanate were 0.5, 2.0 and 5.0 μg/ml, respectively.

B. Calibration

The five-point calibration curve is constructed for each compound using linear regression analysis. A curve cannot be used if its correlation coefficient is less than 0.995.

C. Calibration Check

A calibration check control is run after the calibration and every 10 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$10% of the expected value, whichever is greater. If the calibration check is outside the limit, then those samples preceding the out of limit check need to be reanalyzed.

D. Minimum Detection Limit

Detection limits are 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 1,3-dichloropropene is calculated by: MDL = 3.14*(std dev values), where std dev = the standard deviation of the concentration calculated for the seven replicate spikes. For dichloropropene, the MDL is 2.0 ng/ml for each isomer. EQL, defined as 5*MDL, is 10 ng/ml based on a 3 ml extraction volume. For methyl isothiocyanate, the MDL is 0.04 μg/ml with an EQL of 0.22 μg/ml. Results above the EQL are reported to 3 significant figures. Results below EQL but above the MDL are reported as DET (detected) and results less than the MDL are ND (nondetect).

E. Collection and Extraction Efficiency (Recovery)

The target compounds at a low and high level are spiked on charcoal tubes (3 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, #6-7. The average percent recovery should be $\pm$ 20% of the expected value. Normal recoveries for DCP were found to be greater than 90%. Normal recoveries for MITC are greater than 85%.

F. Storage Stability

Storage stability studies were completed in the previous analysis and not continued further here. All analyses are to be completed within 4 days of receipt.

G. Breakthrough

No breakthrough analysis was done for DCP. The breakthrough was checked for MITC since the field sampling flow rate was set to 3 LPM. The recovery of charcoal

tubes spiked at 5.0 μg/ml was greater than 85% with no MITC detected in the secondary beds.

H. 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.

Attachment V

Draft
Standard Operating Procedure
Sampling and Analysis of Methyl Isocyanate in Application and Ambient Air using High Performance Liquid Chromatography with a Fluorescence Detector

California Environmental Protection Agency

Air Resources Board

Draft
Standard Operating Procedure
Sampling and Analysis of Methyl Isocyanate in Application and Ambient Air using High Performance Liquid Chromatography with a Fluorescence Detector

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

06/25/01 version

Approved by:

4. SCOPE

The analysis of methyl isocyanate (MIC), a degradation product of the soil fumigant metam-sodium, is based on OSHA Method 54 using a high-performance liquid chromatograph with a fluorescence detector. This method analyzes application and ambient air samples for MIC using XAD-7 resin tubes coated with 1-(2-pyridyl) piperazine, a derivatizing agent. The Department of Pesticide Regulation (DPR) asked the Air Resources Board (ARB) to do ambient monitoring of MIC at a requested quantitation limit of 0.05 $\mu g/m^3$ and application monitoring at a quantitation limit of 0.1 $\mu g/m^3$.

2. SUMMARY OF METHOD

Resin tubes, XAD-7 coated with 1-(2-pyridyl)piperazine, are placed on the sampler for 24 hours at a flowrate of 75 milliliters per minute (mLPM). The samples are stored in an ice chest or refrigerator until extracted with 3 ml of acetonitrile (ACN). The injection volume is 0.01 mL. A high performance liquid chromatograph (HPLC) with a fluorescence detector is used for the 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. For this method the derivatizing agent, 1-(2-pyridyl)piperazine, is an additonal factor in possible interfences. 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:

Dionex LC20 Chromatography Module
Dionex GP50 Gradient Pump
Dionex AS40 Autosampler
Dionex RF-2000 Fluorescence Detector: 240 nm excitation, 370 nm emission. Sensitivity: medium; Gain: 1

Eluant: Acetonitrile (ACN) and 25 mM Ammonium Acetate (NH_4 AC), pH 6.1. Gradient: 5% ACN/95% NH_4 AC to 30%ACN/70% NH_4 AC in 20 minutes. Flowrate: 1.0 mL/min.

Column: Restek Ultra PFP, 4.6 mm i.d. x 250 mm, 5 μm.

B. Auxiliary Apparatus

6. Precleaned vials, 8 ml capacity with teflon caps.
7. Whatman filters, 0.45 μm
8. Disposable syringes, 3 ml
9. Sonicator
10. Dionex Polyvials with filter caps, 0.5 mL.

C. Reagants

5. Acetonitrile, HPLC/Pesticide grade or better.
6. Ammonium Acetate, 99.99%.
7. Glacial Acetic Acid, HPLC Grade or better.
8. Nanopure Water, Type I
9. 1-(2-Pyridyl)piperazine, 99.5+% or better.
10. Methyl Isocyanate, Chem Service #O-2179, 99+%.
11. XAD-7 resin sorbent tubes, coated with 1-(2-pyridyl)piperazine. Supelco ORBO 657, 80/40 mg, Bellefonte, PA.

5. ANALYSIS OF SAMPLES

9. The instrument is equilibrated for approximately one (1) hour before analysis of samples. Check that the volume in the eluant reservoirs is sufficient for the sample batch.

10. It is necessary to analyze a solvent blank and a resin blank with each batch of samples to ascertain the presence of possible interferences.

11. A 6-point calibration curve is analyzed with each batch of samples. For the ambient and application studies the calibration will be 0.013 to 0.260 μg/mL of the purified MIC derivative. (See section 6.0 B for the preparation of the purified derivative.)

12. A calibration check sample of 0.078 μg/ml is run after the calibration and every 10 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$10% of the expected value, whichever is greater. If the calibration check is outside this limit then those samples in the batch after the last calibration check that was within limits need to be reanalyzed.

13. With each batch of samples analyzed, a laboratory resin blank and a laboratory control spike will be run concurrently. A laboratory blank is XAD-7 extracted and

analyzed the same way as the samples. A laboratory control spike is XAD-7 spiked with a known amount of MIC. The laboratory control sample is extracted and analyzed the same way as the samples.

14. Score and snap the sample resin tube, transfer the resin into an 8 ml vial. (Save the second tube for future analysis if necessary.) Rinse the tube with 3.0 ml of ACN into the extraction vial. Cap and place the vial in the sonicator for 1 hour.

15. Filter the samples using 0.45 μm filter attached to a 3 ml syringe directly into a Dionex sampling vial and cap securely. Cap and refrigerate the remaining solution vial if necessary for further analysis.

16. The atmospheric concentration is calculated according to:

Conc ($\mu g/m^3$) = Extract Conc ($\mu g/ml$) X 3 ml / Air Volume Sampled (m^3)

9. QUALITY ASSURANCE

A. Instrument Reproducibility

The reproducibility of the instrument has been established by analyzing five (5) injections of MIC-derivative standard at three concentrations (low, mid, and high). The low, mid, and high concentrations were 0.013, 0.078 and 0.260 μg/ml, respectively.

B. Purified Derivative and Calibration

1. The purified MIC derivative is prepared as described in OSHA Method 54, section 3.3.1. A stock standard is prepared by dissolving the MIC derivative into ACN. The derivative is expressed as free MIC by multiplying the amount of MIC urea weighed by the conversion factor 0.2590. (See OSHA Method 54, section 3.3.2)

2. A six (6)-point calibration curve is made at 0.013, 0.026, 0.052, 0.078. 0.134, and 0.260 μg/ml of the MIC derivative.

C. Calibration Check

A calibration check sample is run after the calibration, after every 10 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$10% of the expected value, whichever is larger. If the calibration check is outside the limit, then those samples

in the batch after the last calibration check that was within the limit need to be reanalyzed.

D. Minimum Detection Limit

The detection limit is based on US EPA MDL calculation. The method detection limit (MDL) and the estimated quantitation limit (EQL) for methyl isocyanate is calculated by the analysis of seven (7) replicates of a low-level matrix spike. The MDL = 3.14*(std dev values), where std dev = the standard deviation of the concentration calculated for the seven replicate spikes. For MIC the MDL is 0.009 μg/sample (0.003 μg/mL). EQL, defined as 5*MDL, is 0.045 μg/sample (0.015 μg/mL) based on a 3 ml extraction volume. Results above the EQL are reported to 3 significant figures. Results below EQL but above the MDL are reported as DET (detected) and results less than the MDL are reported as ND (nondetect).

E. Collection and Extraction Efficiency (Recovery)

Methyl isocyanate at a low and high level are spiked on XAD-7 tubes. The spiked tubes are placed on field samplers with airflows of 75 mLpm for 24 hours. The samples are extracted with ACN and prepared as described in section 5, #6-7. The recovery of MIC for this method is low, ranging 50% to 70%. At concentrations above 1.0 μg/mL the recovery is greater than 70%.

F. Storage Stability

Storage stability will be run concurrent with analysis of samples.

H. Breakthrough

A low sample flow rate is required for this method and optimization of the bed weights with the derivatizing agent is necessary to capture the MIC and minimize interference.

H. 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.

Attachment VI

Draft
Standard Operating Procedure
Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector

California Environmental Protection Agency

Air Resources Board

Draft
Standard Operating Procedure
Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

06/25/01 version

Approved by:

5. SCOPE

The current method is for the analysis of trichloronitromethane (TCNM) using a gas chromatograph/mass selective detector. The procedure is for the analysis of application and ambient air monitoring of TCNM using XAD-4 resin tubes. The Department of Pesticide Regulation (DPR) asked the Air Resources Board (ARB) to analyze for TCNM during agricultural/structural application with a requested quantitation limit of 1.0 $\mu g/m^3$ and ambient monitoring with a quantitation limit of 0.1 $\mu g/m^3$.

2. SUMMARY OF METHOD

Resin tubes, XAD-4, are placed on the sampler for 24 hours at a flowrate of 0.1 liters per minute (LPM or 100 mLPM). The samples are stored in an ice chest or refrigerator until extracted with 3 ml of dichloromethane (DCM). The injection volume is 1 μl. 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: 210°C, Splitless, Liner 4 mm straight liner with glass wool.
Column: Restek Rtx-200, 60 meter, 320 μm i.d., 1.5 μm film thickness.

GC Temperature Program: Oven initial 40°C, hold 4 min. Ramp to 220°C @ 12°C/min., hold 1 min., ramp to 240°C @ 20°C/min., hold 2.0 min.
Retention time: TCNM 11.93 min.

Splitter open @ 1.0 min.
Flows: Column: He, 1.6 ml/min, 9.1psi. (velocity: 32cm/sec)
Splitter: 50 ml/min.

Mass Spectrometer: Electron Ionization
Selective Ion Monitoring: trichloronitromethane: 117 (quant. ion 100%), 119 (qual. ion 98%); Tuning: PFTBA on masses 69, 219, 502.

B. Auxiliary Apparatus

11. Precleaned vials, 8 ml capacity with teflon caps.
12. Whatman filters, 0.45 μm
13. Disposable syringes, 3 ml
14. Sonicator
15. GC vials with septum caps.

C. Reagants

12. Dichloromethane, Pesticide grade or better.
13. Trichloronitromethane, Chem Service PS-4, 98.8%
14. XAD-4 resin sorbent tubes, 400/200mg. SKC, Fullerton, CA.

5. ANALYSIS OF SAMPLES

17. 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 ½ the peak height, 0.60 ± 0.05, and the criteria for relative abundance; 69:100%, 219:100-120%, and 502: 7-12%.

18. 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 which may result in possible carry-over contamination.

19. A 5-point calibration curve shall be analyzed with each batch of samples. For the ambient studies the calibration will be 0.5-50.0 ng/mL and for the application studies 50.0-500 ng/mL.

20. A calibration check sample of 7.5 ng/ml is run after the calibration and every 10 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 ±10% of the expected value whichever is greater. If the calibration check is outside this limit, then those samples in the batch after the last calibration check that was within limits need to be reanalyzed.

21. With each batch of samples analyzed, a laboratory blank and a laboratory control spike will be run concurrently. A laboratory blank is XAD-4 extracted and analyzed the same way as the samples. A laboratory control spike is XAD-4 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.

22. Score and snap the sample resin tube, transfer the front bed of the resin tube into a 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 1 hour.

23. Filter the samples using 0.45 μm filter attached to a 3 ml syringe directly into a GC vial and cap securely.

24. The atmospheric concentration is calculated according to:

Conc (ng/m^3) = Extract Conc (ng/ml) X 3 ml / Air Volume Sampled (m^3)

10. QUALITY ASSURANCE

A. Instrument Reproducibility

The reproducibility of the instrument and analytical method was established by analyzing five (5) 1.0 μl injections of trichloronitromethane standard at three concentrations (low, mid, and high). The low, mid and high concentrations were 5, 20 and 50 ng/ml, respectively.

B. Calibration

A five-point calibration curve is made ranging from 5.0 ng/ml to 50.0 ng/ml for ambient and 50 ng/ml to 500 ng/ml for application.

C. Calibration Check

A calibration check sample is run after the calibration, after every 10 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$10% of the expected value whichever is larger. If the calibration check is outside the limit, then those samples in the batch after the last calibration check that was within the limit need to be reanalyzed.

D. 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 trichloronitromethane is calculated by: MDL = 3.14*(std dev values) where std dev = the standard deviation of the concentration calculated for the seven replicate spikes. For TCNM the MDL is 3.96 ng/sample (1.32 ng/mL). EQL, defined as 5*MDL, is 19.8 ng/sample (6.60 ng/mL) based on a 3 ml extraction volume. Results 4are reported to 3 significant figures. Results below EQL but above the MDL are reported as DET (detected) and results less than the MDL are reported as ND (nondetect).

E. Collection and Extraction Efficiency (Recovery)

Trichloronitromethane at a low and high level are spiked on XAD-4 tubes (3 at each concentration). The spiked tubes are placed on field samplers with airflows of 100 mLpm for 24 hours. The samples are extracted with DCM and prepared as described in section 5, #6-7. The average percent recovery of trichloronitromethane should be ± 20% of the expected value. The recoveries both for the low and high levels are greater than 80.0%.

F. Storage Stability

Storage stability was set up for a 4-week study. Three (3) XAD-4 tubes each were spiked at the low and high-end concentrations. The tubes were stored in the freezer until analyzed. At the low-end concentrations (5 ng/ml), the recovery for the three spikes averaged 106.8 percent, ranging from 103.68 to 113.68 percent. The average percent recovery peaked after fourteen days and was at the lowest after 28 days. At the high end (50 ng/ml), the recovery for the three spikes averaged 90.237 percent, ranging from 88.904 to 91.996 percent. The average percent recovery peaked at 14 days and was at the lowest at 20 days.

I. Breakthrough

The previous analysis of trichloronitromethane (ARB #A5-169-43) was for 4 hour sampling at 1.0 LPM in September/October, 1986. The current study for ambient monitoring for 24 hours will require a low sample flow rate to meet the requested EQL. A breakthrough analysis study was conducted. The flow rates tested were 1.0, 0.5, 0.2 and 0.1 Lpm. To meet the EQL and minimize breakthrough possibility, the flow rate for the field sampling will be at 100 mLpm.

H. 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.

Attachment VII

Pesticide Ambient Sampling Procedures
For Canisters

Pesticide Ambient Sampling Procedures
For Canisters

Overview:

-Collect samples for 24 hour periods; Four sampling periods per week per site; Five sampling sites plus an urban background site (e.g., ARB Bakersfield station).

-Start the collocated sample at each site on the second or third sampling period per week.

-Submit 1 trip blank per week (unused, evacuated can, carry on route for 1 day, log-in and ship back with the others).

-With the trip blank there normally will be 31 samples shipped per week.

-4 field spikes will be run at the ARB site (time collocated exactly with the ambient sample. The field spikes will be distributed over the monitoring period (e.g., 1 per week every other week). A trip spike will also accompany each field spike. These field and trip spikes will be delivered to the laboratory with the rest of the samples.

-The field log sheet is filled out as the sampling is conducted. The originals stay in the field binder. Please include a copy with sample shipments. All QA samples must be logged onto the log sheet.

-The canister Data Sheet forms are started by the lab staff before can shipment to the field (beginning pressures, dates, etc. are recorded). The field staff fills out the appropriate portions during sampling and before shipment. The lab staff completes the Data Sheet upon receipt of the samples.

-(Disregard if samples are driven back to Sacramento) The samples are shipped by UPS, regular ground, to 13th and T (e.g., to John Roll but to the attention of Jim Omand/Mike Orbanosky). This is normally done each day, Monday thru Thursday (e.g., along with the PAMS samples from Bakersfield). Review the Data Sheets and log sheet to insure that all documentation is correct and that the appropriate QA samples have been included. A custody seal is filled out and placed on each shipping container.

Sampling Procedure:

Materials that will be needed on the roof to conduct the sampling include:

- -Clip board with log sheets
- -pencils/pens
- -9/16 inch open end wrench
- -allen wrench
- -sample cans with data sheets

-0 to 10 sccpm mass flow meter (MFM) with battery

Figure out your route for sampling the six locations and try to keep this the same throughout the study. In general, try to make each sampling period exactly 24 hours; e.g., if start time is 11:10 then end time should be 11:10. (round off to the nearest 5 minutes.) Due to field logistical issues, the sample period may not always be exactly 24 hours; but that is the target time frame.

Sample Start:
On the way to the first site, plug the MFMs into the batteries. It takes the MFMs about 10 minutes to warm up before they can be used. Leave the MFMs plugged in until the last sample for the day is taken; then unplug for the night to minimize drop in battery charge. Recharge the batteries once per week.

Upon arrival at the site, check in if needed. I suggest a backpack (big enough to hold a canister) and fanny-pack to carry the sampling gear to the roof.

a) check to make sure that the canister valve is closed,
b) remove the ¼ inch brass cap from the inlet of the can,
c) securely attach the canister to the passive sampler, tighten the ¼ inch swagelock fitting,
d) open the canister valve,
e) record the canister pressure; if the can vacuum is **less than –29 ”Hg** (e.g., -25) then replace with a new can (and return the bad one with appropriate comments made on the data sheet). Sometimes the cans will read beyond the scale, e.g., -31 or –32 ”Hg; this is OK. When in doubt use the spare gauge to verify the vacuum reading.

Using the 0 to 10 sccpm MFM measure the flow rate; should be 3.0 sccpm; if the reading is **between 2.95 and 3.05** then record the value on the data sheet. If outside of this range then record the value and adjust the flow back to 3.0 sccpm using an allen wrench. If you have to adjust the flow then note it on the log sheet.

Fill out the Data Sheet and field log sheet, including: log #, start date, time, beginning vacuum reading, any comments, samplers initials, and the general weather conditions (e.g., sunny, cloudy, raining, etc.).

Sample collection and Shipment:
Measure (do not re-set) the flow rates at the end of the sampling period with the MFM; record the end data on the log sheet and data sheet. **Close the can valve! (Do not use excessive force when closing the valve. When the knob stops turning the valve is closed.)** Detach the can from the sampler and put a ¼ inch brass swagelock cap on the can inlet **and tighten**. Put the can back into a shipping container.

Start the collocated (duplicate) samples. These should be started and stopped at the

same times as the regular samples.

Log-in a trip blank (TB), once per week. It doesn't matter which site (or which day) but you can note it in the comment section of the log sheet. Log the TB into the log sheet.

After samples are collected and before shipment, store in the Bakersfield office (i.e., at room temp).

Attachment VIII

Pesticide Ambient Sampling Procedures
For Adsorbent Tubes

Pesticide Ambient Sampling Procedures
For Adsorbent Tubes

Overview:

-Collect samples for 24 hour periods; Four sampling periods per week per site; Five sampling sites plus an urban background site (e.g., ARB Bakersfield station).

-Collect a collocated sample from each site on the second or third sampling period per week.

-Submit 1 trip blank per week, per cartridge type.

-With the trip blank there normally will be 31 samples shipped per week, per cartridge type.

-4 field spikes will be run at the ARB site (time collocated exactly with the ambient sample. The field spikes will be distributed over the monitoring period (e.g., 1 per week every other week). A trip spike will also accompany each field spike. These field and trip spikes will be logged in and shipped along with the regular samples. The field and trip spikes will be kept on dry ice during transport to and storage in the field.

-All samples are stored either in an ice-chest on dry ice or in a freezer.

-The field log sheet is filled out as the sampling is conducted. The originals stay in the field binder. Please include a copy with sample shipments. All QA samples must be logged onto the log sheet.

-The chain of custody (COC) forms are filled out prior to sample shipment; the originals are shipped with the samples; make and retain copies if desired (not necessary).

-(Disregard if samples are driven back to Sacramento) The samples are shipped by UPS, next day delivery, to 13th and T. This is normally done each Monday. The original chain of custody sheets must accompany the samples. The samples are shipped on 5 pounds of dry ice. Review the COCs and log sheet to insure that all documentation is correct and that the appropriate QA samples have been included.

Sampling Procedure:

Materials that will be needed on the roof to conduct the sampling include:

- -Clip board with log sheets
- -pencils/pens
- -sample labels
- -sample cartridges
- -end caps
- -plastic test tubes
- -0 to 100 ccpm mass flow meter (MFM) with battery
- -0 to 5 Lpm mass flow meter (MFM) with battery

Figure out your route for sampling the six locations and try to keep this the same throughout the study. In general, try to make each sampling period 24 hours; e.g., if start time is 11:10 then end time should be 11:10. (round off to the nearest 5 minutes.) The sample period may not always be exactly 24 hours; but that is the target time frame.

Preparation and Set-up

On the way to the first site, plug the MFMs into the batteries. It takes the MFMs about 10 minutes to warm up before they can be used. Leave the MFMs plugged in until the last sample for the day is taken; then unplug for the night to minimize drop in battery charge. Recharge the batteries once per week to be on the safe side.

Upon arrival at the site, check in if needed. Fill out the sample labels for that site. I suggest a backpack and/or fannypacks to carry the stuff to the roof.

Securely attach one adsorbent sample cartridge to the sampling tree. MAKE SURE THE ARROW ON THE CARTRIDGE IS POINTING TOWARDS THE SAMPLE LINE.

Set the rotameter roughly to the appropriate flow rate. Perform the leak check on each sample line by placing a plastic tube cap over the inlet of the cartridge (with the pump on). The rotameter ball should fall to zero. The leak check should be performed before setting the flows with the MFMs.

Using the MFMs set the flow rates exactly to 2.5 Lpm, 90 ccpm and 75 ccpm for the different cartridges.

Make sure that the rain/sun cover is pulled down over the sample tube.

Fill out the log sheet, including: log #, start date, time, start counter reading, leak check OK, any comments and the weather conditions.

Sample collection and Shipment

Measure (do not re-set) the flow rates at the end of the sampling period with the MFMs; leak check the sample lines; record the end data on the log sheet.

Remove the sample cartridge and cap the ends. Attach the sample label like a flag on the secondary end of the tube. Make sure that the label does not cover the glass wool separating the primary and secondary beds in the cartridge.

Place the cartridge in the plastic test tube shipping container.

Place all the samples for each day (6) in a zip-lock bag and place on dry ice in a cooler or in a freezer. While driving the route the collected samples need to be kept on dry ice.

Collect the collocated (duplicate) samples from each site on the second or third sampling period per week. These should be started and stopped at the same times as the regular samples.

Collect a trip blank (TB) for each method, once per week, while at one of the field sites. It doesn't matter which site (or which day) but note it in the comment section of the log sheet. The TB is collected by breaking the ends off of a tube, capping and labeling as usual and storing along with the rest of the samples. Log the TB into the log sheet.

Attachment IX

Canister Field Log Sheet and
Canister Field Data Sheet

Attachment X

Adsorbent Tube Sampling Field Log Sheet