State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

Protocol for the Ambient Air Monitoring for Methyl Bromide, 1,3-Dichloropropene, Chloropicrin and Breakdown Products of Metam Sodium In Kern, Monterey and Santa Cruz Counties During Summer/Fall, 2001

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This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Protocol for the Ambient Air Monitoring for Methyl Bromide, 1,3-Dichloropropene, Chloropicrin and Breakdown Products of Metam Sodium In Kern, Monterey and Santa Cruz Counties During Summer/Fall, 2001

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR) (June 28, 2000 Memorandum, Helliker to Lloyd), the Air Resources Board (ARB) staff will conduct ambient air monitoring for the pesticides methyl bromide, 1,3-dichloropropene (Telone), chloropicrin and two breakdown products of metam sodium (methyl isothiocyanate and methyl isocyanate). Monitoring will occur in Kern County over an eight week ambient monitoring period, tentatively scheduled from June 30, 2001 to August 30, 2001 and also in Monterey and Santa Cruz Counties over an eight week ambient monitoring period, tentatively scheduled from September 10, 2001 to November 8, 2001. This is the second consecutive year the DPR has requested monitoring for methyl bromide and 1,3-dichloropropene at these locations. This monitoring will be done 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. Monitoring is being conducted to coincide with the primary use of these fumigants prior to planting carrots in Kern County and prior to planting strawberries in Monterey and Santa Cruz Counties.

The sampling and analysis will follow the procedures outlined in this protocol as well as the quality assurance guidelines described in the "Quality Assurance Plan for Pesticide Air Monitoring" (May 11, 1999 version)(Attachment I).

The draft 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 Attachment II (May 2001 Version). This method will be used as the primary analysis method for methyl bromide (bromomethane) and 1,3-dichloropropene. Samples with concentrations above the calibration range of the primary method will be analyzed on a secondary method, "Standard Operating Procedure Sampling and Analysis of Bromomethane In Silco Canisters", included as Attachment III.

The draft ARB method, "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 (06/25/01 Version)," is enclosed as Attachment IV.

The draft ARB method, "Standard Operating Procedure, Sampling and Analysis of

Methyl Isocyanate in Application and Ambient Air using High Performance Liquid Chromatography with a Fluorescence Detector (06/25/01 Version)," is enclosed as Attachment V.

The draft ARB method, "Standard Operating Procedure, Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector (06/25/01 Version)," is enclosed as Attachment VI.

II. Sampling

The collection media used for monitoring of methyl bromide and 1,3-dichloropropene will involve Silcosteel® canister sampling. The media used for chloropicrin will be *XAD-4* sampling cartridges. The media used for methyl isocyanate (MIC) will be *XAD-7* sampling cartridges. The media used for methyl isothiocyanate (MITC) will be charcoal sampling cartridges (1,3-dichloropropene results from the charcoal samples will also be reported). Individual samples will be collected for 24-hour periods. For pesticide ambient monitoring conducted in 2000, 24-hour samples were collected four days per week, Monday through Friday. However, for the 2001 monitoring the DPR has requested that: "At each site, 4 samples per week should be collected randomly over the full seven-day week during the sampling period". To accommodate this request the sampling schedule will be arranged, generally in groups of four consecutive sampling periods separated by one, two or three off-days, to add sampling days during most of the weekends during the eight week monitoring studies.

Caution should be used during field monitoring, transportation, storage, and lab analysis to minimize exposure of samples to sunlight in order to prevent photo degradation of chloropicrin, MIC and MITC.

Chloropicrin, MIC and MITC Sampling:

The sampling methods for three of the compounds require passing measured quantities of ambient air through adsorbent sampling tubes. For chloropicrin, the tubes are 8 mm x 150 mm, XAD-4, with 400 mg in the primary section, and 200 mg in the secondary section (SKC special order). For MIC, the tubes are 6 mm x 90 mm, XAD-7, 1-(2-pyridyl)piperazine coated, with 80 mg in the primary section, and 40 mg in the secondary section (Supelco special order). Two tubes will be used in sequence for the MIC sampling. For MITC, the tubes are 8 mm x 110 mm, coconut shell charcoal with 400 mg in the primary section, and 200 mg in the secondary section (SKC catalogue #226-09). (The coconut base charcoal tube samples will also be analyzed for 1,3-dichloropropene to be compared with the canister results).

Sample collection for chloropicrin is at a flow rate of 90 standard cubic centimeters per

minute (sccpm); at 75 sccpm for MIC; and at 2.5 standard liters per minute (slpm) for MITC. All samples are 24 hours in duration. Subsequent to sampling, the tubes are capped, labeled, placed in a culture tube and stored and transported to the ARB laboratory in Sacramento in an insulated container with dry ice. The DPR recommended target 24-hour estimated quantitation limits (EQLs) were 0.1 ug/m^3, 0.05 ug/m^3 and 0.5 ug/m^3 for chloropicrin, MIC, and MITC, respectively. The ARB 24-hour EQLs are 0.15 ug/m^3, 0.42 ug/m^3 and 0.18 ug/m^3 for chloropicrin, MIC, and MITC, respectively. The MIC EQL is approximately 8 times higher than requested. The DPR directed that the monitoring for MIC should be conducted as planned even with the higher than requested quantitation limit.

Each sample train consists of an adsorbent tube, Teflon fittings and tubing, rain/sun shield, rotameter, train support and a 115 volt AC vacuum pump (Figure 1). Tubes are prepared for use by breaking off the sealed glass end and immediately inserting the tube into the Teflon fitting. The tubes are oriented in the sample train according to a small arrow printed on the side indicating the direction of flow. A 0-5 lpm rotameter is used to control sample flow for the MITC sampling and 0-240 ccpm rotameters will be used to control the flow for the chloropicrin and MIC sampling. The flow rates will be set using a calibrated digital mass flow meter (MFM) before the start of each sampling period. A MFM scaled from 0-5 slpm is used for MITC and a 0-100 sccpm MFM is used for the chloropicrin and MIC samplers. The flow rate is also checked and recorded, using the MFM, at the end of each sampling period. Samplers will be leak checked prior to each sampling period with the sampling tubes installed. Any change in flow rates will be recorded in the field logbook. The pesticide ambient sampling procedures for adsorbent tubes are attached as Attachment VIII. The adsorbent tube sampling field log sheet is enclosed as Attachment X.

Methyl Bromide (MeBr) and 1,3-Dichloropropene Sampling

Integrated ambient air samples will be collected using passive air sampling into evacuated six liter, Silcosteel® canisters (from Restec Corporation). The flow rate of 3 sccpm will be set using a battery operated mass flow meter. The sampling system will be operated continuously for 24 hours with the exact operating interval recorded on the log and field data sheets (see Attachment IX). The canister vacuum reading will be recorded at the start and end of each sampling period using the –30 to 0 inHg gauge on the passive sampler. The start and end canister vacuum readings will be approximately -30 inHg and -8 inHg, respectively. 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 laboratory gauge readings will be used to calculate the sample volume collected. The 3 sccpm sampling rate will yield a sample volume of 4.32 liters over the 24 hour sampling period. The 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 critical orifice flow controllers (Silcosteel treated Veriflo SC423XL) will be attached to the valve fitting on the canister using a Silcosteel treated swagelock connector (Figure 2). A six foot section of 1/8 inch O.D, Silcosteel tubing will be attached to the inlet end of an in-line, 7 micron filter, which 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 roof tops for the ambient monitoring. At the end of each sampling period, the canisters will be placed in shipping containers, with a sample identification/chain of custody sheet, and will be shipped as soon as reasonably possible to the ARB Monitoring and Laboratory Division laboratory for analysis. The samples will be stored at ambient laboratory temperature prior to analysis.

When using a critical orifice flow restrictor for passive integrated sampling, the potential decrease in flow rate as the vacuum in the canister changes must be taken into account. This condition is resolved by using the Veriflo SC423XL flow controller. The controller uses a metal diaphram downstream of the critical orifice to regulate the flow as the pressure the canister changes. It is capable of maintaining a continuous low flow with vacuum ranges from -29.9 to approximately -5 inHg. The in-line filter prevents particles from entering the critical orifice of the flow controller, which could clog the critical orifice and affect the flow through the controller. The outside temperature can also affect the flow rate. For example, there could be an approximately six percent flow drop when the temperature changes from 80 °F to 125 °F (according to manufacturer's specifications).

The pesticide ambient sampling procedures for canisters are enclosed as Attachment VII. The canister sampling field log sheet and canister data sheet are enclosed as Attachment IX. These forms will be used to record start and stop times, start and stop vacuum readings, sample identifications, weather conditions, sampler's initials and any other significant data.

Ambient Monitoring

The DPR has directed that monitoring site selection in Kern County should focus on 1,3-dichloropropene and metam sodium, but that samples be collected and analyzed for all five compounds. The historical use patterns for 1,3-dichloropropene and metam sodium suggest that monitoring should occur over a two-month period during July and August in Kern County. As was done in 2000, five sampling sites will be selected in relatively high-population areas or in areas frequented by people. At each site, a target of 32 discrete 24-hour sampling periods will be monitored during the study. Collocated (field duplicate) samples will be collected for 1 day/week at each sampling location.

The DPR has directed that monitoring site selection in Monterey and Santa Cruz Counties should focus on methyl bromide and chloropicrin, but that samples be collected and analyzed for all five compounds. In Monterey and Santa Cruz Counties,

historical use patterns indicate that monitoring for methyl bromide and chloropicrin should take place during September and October. As was done in 2000, five sampling sites will be selected in relatively high-population areas or in areas frequented by people (e.g., schools or school district offices, fire stations or other public buildings). Also, samples will again be collected in an urban area in Salinas. At each site, a target of 32 discrete 24-hour samples will be taken during the sampling period. Collocated (duplicate) samples will be collected for eight dates at each sampling location. Samples will also be collected for a one-week period in an area which is distant to fumigant applications. The location of this 'background' sampling site will be determined after consultation with the County Agricultural Commissioner's offices.

The sites were selected by ARB personnel from the areas of Kern County where carrot (and roses for one site) farming is predominant and from areas of Monterey and Santa Cruz Counties where strawberry farming is predominant. Sites were selected for their proximity to the fields and the presence of residents or students, with considerations for both accessibility and security of the sampling equipment. The sites are near areas of historical use of methyl bromide, 1,3-dichloropropene, chloropicrin and metam sodium. ARB understands that DPR staff will verify and quantify the actual use of these fumigants that takes place during the study when the information becomes available.

III. Analysis

The draft 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 Attachment II (May 2001 Version). This method will be used as the primary analysis method for methyl bromide (bromomethane) and 1,3-dichloropropene. Samples with concentrations above the calibration range of the primary method will be analyzed on a secondary method, "Standard Operating Procedure Sampling and Analysis of Bromomethane In Silco Canisters" (Attachment III), using a higher calibration range. The procedures are based on EPA Method TO-15 and consist of cryogenic pre-concentration of an aliquot of the whole air sample followed by GC/MS analysis. The canisters arrive from the field at sub-ambient pressure and are pressurized (diluted) in the laboratory before analysis. The analyses will be performed by the ARB laboratory in Sacramento.

The ARB method, "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 (06/25/00 Version)," is enclosed as Attachment IV. The exposed charcoal tubes are stored in an ice chest or refrigerator until desorbed with 3 ml of dichloromethane. The attached SOP specifies that a gas chromatograph with a mass selective detector is used for analysis. The analyses will be performed by the ARB laboratory in Sacramento.

The draft ARB method, "Standard Operating Procedure, Sampling and Analysis of Methyl Isocyanate in Application and Ambient Air using High Performance Liquid Chromatography with a Fluorescence Detector (06/25/01 Version)," is enclosed as Attachment V. As outlined in the SOP, the sampling efficiency/recovery is low using this method, ranging from 50% to 70% at low levels. The sampling stability study will be run concurrently with analyses of samples. The analyses will be performed by the ARB laboratory in Sacramento.

The draft ARB method, "Standard Operating Procedure, Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector (06/25/01 Version)," is enclosed as Attachment VI. The analyses will be performed by the ARB laboratory in Sacramento.

IV. Quality Assurance

Field Quality Control for the ambient monitoring will include the following for each of the sampling methods (and for each of the sampling regions).

1) Field Spikes: For the 2000 ambient monitoring, field spikes were prepared (spiked) at approximately 0.6 ug/m^3 for both methyl bromide and 1,3-dichloropropene. The 2000 field spikes were collocated with samples collected at the urban sampling sites of Bakersfield and Salinas for the two respective studies. However, the pesticide levels observed in the collocated ambient samples were significantly higher than the spike levels, causing poor results in the recovery calculation. For 2001, the field spikes will be prepared (spiked) at levels of approximately 10 ug/m^3 each for methyl bromide and cis and trans 1,3-dichloropropene in the canister samples.

   The spike levels for MIC, MITC and chloropicrin in the adsorbent tube samples have not yet been determined.

   The four field spikes will be obtained by sampling ambient air at the urban background monitoring site for 24 hour periods (i.e., collocated with a background sample at the same environmental and experimental conditions). The four field spikes will be collected over the eight-week monitoring period. For example, one each of the field spikes will be collected every other week.

   For the 2001 Monterey/Santa Cruz Counties study, a field spike sample will also be collected at a site (to-be-determined) distant to methyl bromide applications. Levels of methyl bromide at this 'background' site are expected to be lower than in Salinas.

2) Four trip spikes will be prepared at the same level as the field spikes. A trip spike will be transported and analyzed along with each of the field spikes.

3) Four lab spikes will be prepared at the same level as the field and trip spikes. A lab spike will be analyzed along with each of the field and trip spike sets.

4) Collocated samples will be taken for eight dates at each sampling location.

5) A trip blank will be obtained each week of sampling.

V. Personnel

ARB sampling personnel will consist of staff from the ARB Air Quality Surveillance Branch. Laboratory personnel will consist of staff from the ARB Northern Laboratory Branch.

FIGURE 1. SAMPLE TREE

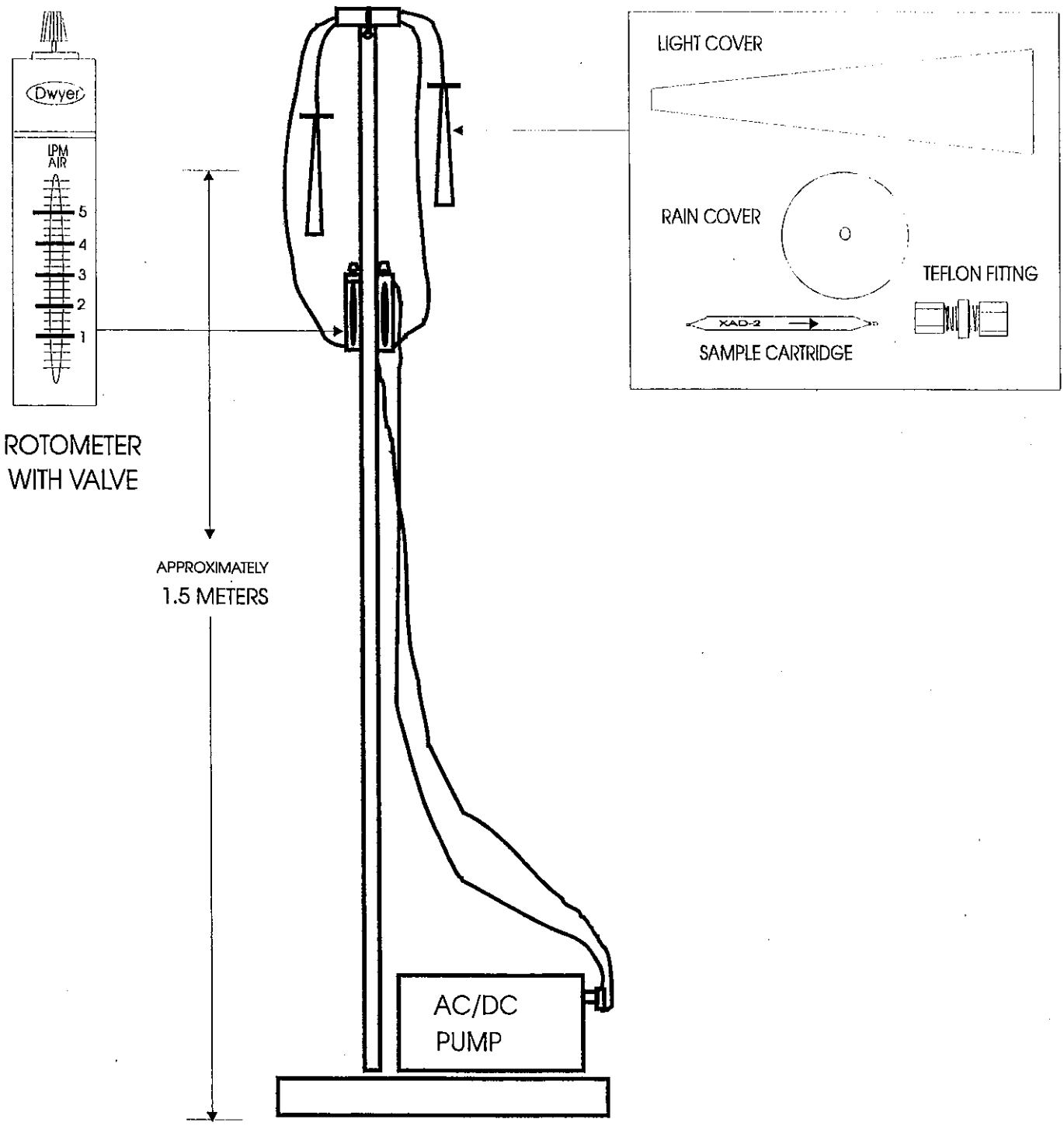
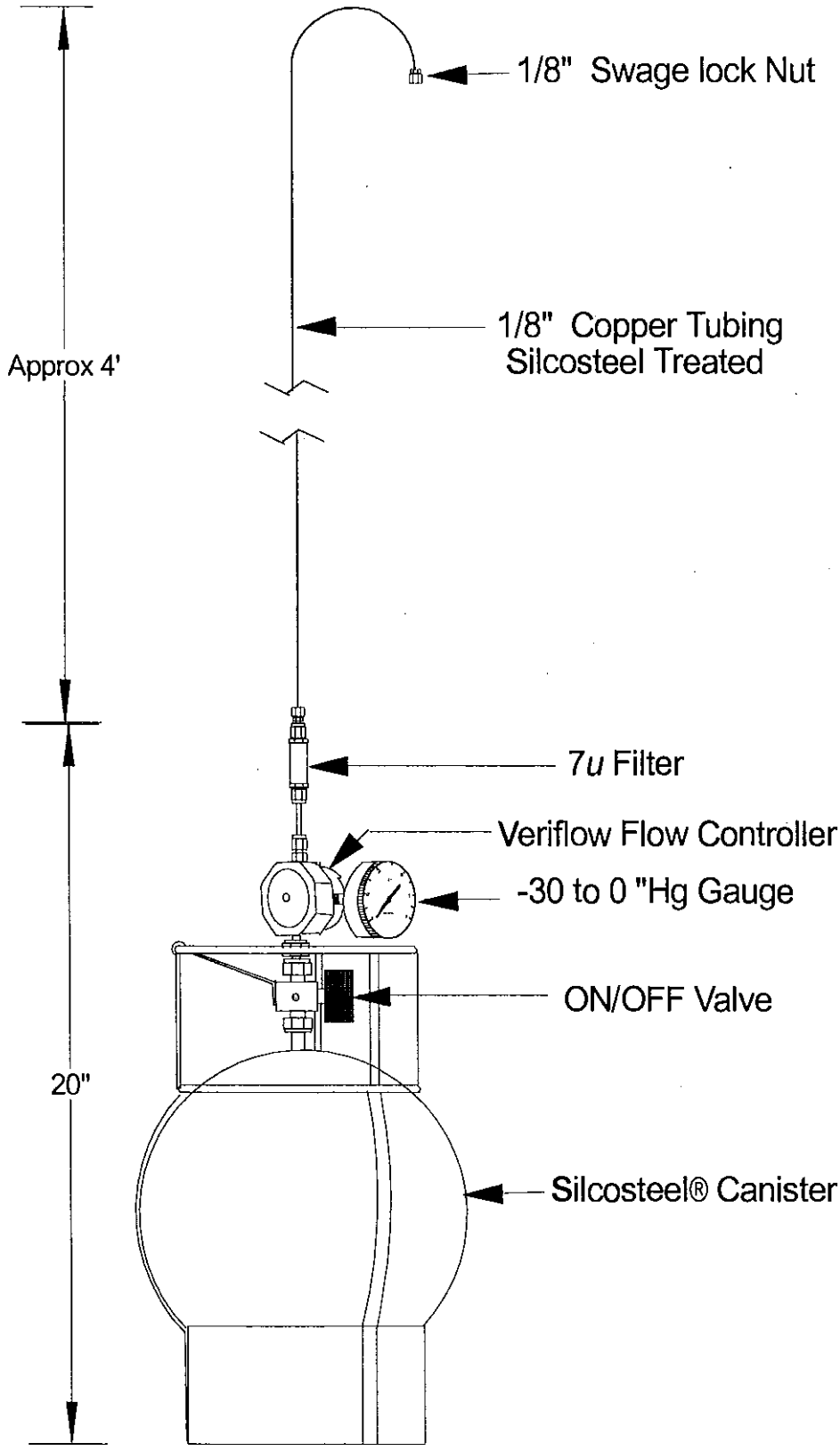


Figure 2

Passive Canister Sampling Train



Attachment I

Quality Assurance Plan for Pesticide Air Monitoring

State of California
California Environmental Protection Agency
Air Resources Board

QUALITY ASSURANCE PLAN FOR PESTICIDE AIR MONITORING

Prepared by the

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This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) staff determines the airborne concentrations of specified pesticides following monitoring recommendations established by the DPR. This air monitoring is conducted 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 documentation of airborne concentrations is usually accomplished through two types of monitoring. The first consists of five to eight weeks of **ambient** monitoring in the general area of, and during the season of, peak use of the specified pesticide. The second is monitoring around the perimeter of a field during and for 72 hours after an **application** has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, ambient and application are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

A. Quality Assurance Policy Statement

It is the policy of the ARB to provide DPR with accurate, relevant and timely air monitoring measurements of airborne pesticide concentrations. The goal of this document is to identify procedures that ensure the implementation of this policy.

B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are as follows.

(1) to establish the necessary quality control activities relating to site selection, method validation, analytical standard operating procedures (SOP), sample collection, sampling and analysis protocol, data reduction and final reports, and;
(2) to assess data quality in terms of precision, accuracy and completeness, and;
(3) to design air monitoring strategies to meet the pesticide target (estimated) quantitation levels as provided by the DPR.

II. Air Monitoring

All sampling will be coordinated through communication with the County Agricultural Commissioner's Office. The local Air Quality Management District (AQMD) or Air Pollution Control District (APCD) will be notified prior to any monitoring. Sample collection will be conducted by staff of the Testing Section or staff of the Air Quality Surveillance Branch of the ARB, or an approved ARB contractor.

A. Siting

The location and time-frame for **ambient** and **application** monitoring are based on direction provided by the DPR in their "Use Information and Air Monitoring Recommendation for Pesticide Active Ingredient" documents. These recommendations are based on historical trends (normally 2 to 3 years prior) and are submitted to the ARB by the DPR approximately 1 year in advance of intended monitoring. The recommendations direct ARB to monitor for a pesticide in specific counties during specific use periods. Pesticide use maps (historical) and histograms are used along with close coordination with staff of the County Agricultural Commissioner's Office to predict areas (and times) of use for the pesticide for the upcoming use year. Approximately one month prior to the scheduled monitoring DPR will reevaluate the historical use trends using the most recent pesticide use data available.

For selection of **ambient** monitoring sites, ARB staff work through authorized representatives of school districts, private companies or city, county or state government agencies. The probe (sampler) siting criteria for **ambient** pesticide monitoring were obtained from the U.S. EPA "Ambient Air Quality Surveillance" criteria (40 CFR, Part 58) and are listed in TABLE 1. As per the DPR monitoring recommendations, three to five sites are chosen. The monitoring objective in choosing these sites is to estimate population exposure in relatively high-population areas or in areas frequented by people (e.g., schools or school district offices, fire stations, or other public buildings). Sampling sites should be located near (in regions of) specific agricultural crops as recommended by the DPR. One additional site is chosen and designated to be an urban area "background" site which is located away from any expected applications. Information will be collected for each site and reported to DPR regarding; 1) the proximity of the each sampler to treated or potentially treated fields, including the distance and direction, and 2) the distance the sampler is located above the ground. Normally the **ambient** samplers will be located on the roof of a one-story building (e.g., at schools) with the sample cartridge located about 1.5 meters above the roof.

Probe siting criteria for placement of samplers around a pesticide **application** are the same as for **ambient** monitoring tests (TABLE I). A minimum of four samplers are positioned, one on each side of the field. A fifth sampler is collocated at one position, normally the downwind side (based on prevailing breezes). Once monitoring has begun, the sampling stations are not moved, even if the wind direction has changed. Ideally, samplers should be placed at a minimum distance of 20 meters from the perimeter of the field and should be equidistant from the field. *These requirements are nearly impossible to meet because of the physical limitations of most application sites. Twenty meters from a potential application field invariably places the sampler on another landowner's property, in another field where tractors and other equipment must operate, or into another orchard where the siting criteria cannot be met. Fences, canals, roads, ditches, railroad tracks, brush, trees, houses, barns, livestock, parked equipment, uncooperative neighbors, etc. are common obstacles. Monitors are placed as far as possible, up to 20 meters, from the field. Attempts are always made to center the samplers on the face of a side of the field. The sampler is placed to maximize the distance from the field and to avoid obstructions bordering the field. Conditions at the site will dictate the actual placement of monitoring stations.* Information is collected and reported to DPR regarding; 1) an accurate record of the positions of the monitoring equipment with respect to the field, including the exact distance that

the sampler is positioned from the field; 2) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees buildings and other obstacles; 3) the elevation of each sampling station with respect to the field and the orientation of the field with respect to North (identified as true or magnetic North). Determination of an appropriate site for an **application** test is based on the "recommendations" provided by the DPR. Parameters used to choose the site are:

1. crop type,
2. minimum field area of 10 acres,
3. minimum application rate (as directed by the DPR),
4. type of application (normally no preference by the DPR),
5. availability of sites on all four sides of the field which meet the criteria in Table 1 and can be sited 20 meters from the perimeter of the field (quite often this is not possible, i.e., normally 4 sites are chosen but they may not all meet the criteria), and
6. accessibility and security of the sampling sites/equipment.

Monitoring sites (fields) are arranged through communication with, and the voluntary cooperation of, applicators, growers or owners for **application** monitoring. Normally, representatives of the County Agricultural Commissioner's Office will make initial contact with the applicators/growers or will at least provide a list of possible candidates.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

Height Above Ground (Meters)		2-15
Minimum Distance from Supporting Structure (Meters)	Vertical	1
	Horizontal	1
Other Spacing Criteria		1. Should be 20 meters from trees.
		2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler.
		3. Must have unrestricted air flow 270° around sampler.
		4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

B. Schedule

Samples for **ambient** pesticide monitoring will generally be collected over 24-hour periods on a schedule of 4 samples per week (Monday through Friday) for 5 to 7 weeks. Occasionally the normal schedule will be interrupted due to holidays and make-up samples may be collected over weekends.

Individual **application** monitoring schedules will vary based on the type and length of application but will follow the schedule guidelines outlined below in TABLE 2. Ideally, the

monitoring study will include samples taken before, during and for approximately 72 hours following application.

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

Sample period begins:	Sample duration time
Background (pre-application)	Minimum of 12 hours
During application	Length of application time
End of application	1 hour (or up to 1 hour before sunset) [1]
1 hour post-application	2 hours (or up to 1 hour before sunset) [1]
3 hour post-application	3 hours (or up to 1 hour before sunset) [1]
6 hour post-application	6 hours (or up to 1 hour before sunset) [1]
1 hour before sunset	Overnight[2] (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	24-hour (until 1 hour after sunrise)

1 These sample duration times will be adjusted depending on length of application and time of sunset.
2 All overnight samples must include the period from one hour before sunset to one hour after sunrise. If the application extends beyond "1 hour before sunset" then the overnight sample will be started at the end of application.

Occasionally, a pesticide application may occur all day long and over the course of two or more days. In these instances samples are collected during the first daily application, followed by a sample from end of application to 1 hour before sunset, followed by an overnight sample ending at either the start of application or 1 hour after sunrise the next morning (same for second or more application days). Following the end of the application, samples are collected according to the above schedule, starting with the 1-hour sample.

C. Meteorological Monitoring

Data on wind speed and direction, barometric pressure, relative humidity and air temperature will be collected during **application** monitoring by use of an on-site meteorological station. The meteorological data will be acquired using a data logger at a minimum of 15 minute intervals (averages). Meteorological systems will be calibrated as specified in the ARB manual, "Air Monitoring Quality Assurance, Volume II, Standard Operating Procedures for Air Quality Monitoring." Meteorological data are not collected for the **ambient** monitoring programs.

III. Method Validation

A. Method Detection Limit

The method detection limit (MDL) is defined as the lowest concentration at which individual measurement results for a specific analyte are statistically different from a blank (that may be zero) with a specified confidence level for a given method and matrix.

MDL is defined as 3.14 x s; where s is equal to the standard deviation of seven replicate spiked samples (e.g., XAD sample cartridges). The spiked samples are prepared and analyzed in the same way as actual samples. The spikes should be prepared at a concentration that is between one to five times the estimated MDL.

B. Estimated Quantitation Limit

The estimated quantitation limit (EQL) is the recommended lowest level for quantitative decisions based on individual measurements for a given method and representative matrix. This EQL is defined as 5 x MDL.

C. Reproducibility

The reproducibility of the method should be determined by performing five replicates at three different concentrations. The lowest level should be at or near the EQL. The average and standard deviation of each set of replicates should be determined and reported.

D. Extraction Efficiency

Extraction efficiency is defined as the amount of pesticide recovered from a spiked sample. Three replicates at two levels and blank should be extracted with the average and standard deviation determined for the replicates. The average amount divided by the amount added multiplied by 100 will give the percent recovery. Recommended recoveries should be between 70-130%.

E. Sampling Efficiency

Sampling efficiency is determined by spiking a sample with a known amount of pesticide. The spiked sample is placed in a sampler and set to the same flow rate and time that samples are collected. At a minimum three replicate spiked samples at a concentration two times the EQL of the method and a collocated background are collected. The samples are extracted and average recovery and standard deviation of the spike samples are determined.

F. Breakthrough

Breakthrough is determined by using a two stage sampling media (usually a filter or resin). The front stage is spiked with a known quantity of the pesticide. The breakthrough study samples are normally spiked at a relatively high level, e.g., at a level that might be observed

during an application study. If time and resources permit, both low and high level spike studies are run. The backup will be the same filter or resin type and placed in series with the front filter or resin. Air is passed through the sampler at the same flow rate and sample time as a real sample (minimum sample time of 24 hours). The front and backstage are recovered and extracted separately. If breakthrough is observed then the sampling strategy must be reviewed, modified and retested before the start of a sampling project.

G. Freezer Storage Stability

Spiked samples should be stored under the same conditions as the samples and for the anticipated time that the samples are stored. Recoveries are determined. A high (either at a level expected during the application study or at the high end of the calibration curve) and a low (1 to 2 times the EQL) concentration set should be studied. A set consists of three replicate spikes each for 3 time intervals.

IV. Field Sampling Quality Control Procedures

Monitoring programs will include the following quality control procedures:

A. Sample Labels

Sample labels will be affixed either directly to the sampling cartridge or will be placed in the individual sample container (e.g., culture tube or zip-lock bag). The sample labels will include at least the following information.

1. Pesticide name and the ARB project number.
2. Log number
3. Sample I.D.
4. Monitoring Location
5. Sampling end date
6. General comments

B. Log Sheets

Field data log sheets will be used to record the sampling log number, sample I.D., start and stop dates, start and stop times, start and end flow rate, initials of individuals conducting sampling, malfunctions, leak checks (at the beginning and end of each sampling period, see Appendix I), weather conditions (e.g., rain) and any other pertinent data which could influence sample results. Refer to Appendix I for a recommended log sheet format.

C. Chain of Custody Forms

Attached as Appendix II is a recommended format for chain of custody (COC) sheets. A COC sheet must accompany any/all samples during transport, transfer or storage. All exchanges of sample possession must be recorded. The laboratory will keep copies of the COCs and

forward the originals to the project engineer. The original COC sheets must be retained in the pesticide project file.

D. Flow Controller Calibration and Audit

Field flow controllers (rotameter, electronic flow controller or critical orifice) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard (e.g., digital bubble flowmeter or electronic digital mass flowmeter) must be verified, certified or calibrated with respect to a primary standard at least once per year by the Quality Management and Operations Support Branch (QMOSB) of ARB. Appendix V shows an example of a form to document the flow controller calibration results.

A flow audit of the field air samplers will be conducted by the QMOSB before each pesticide monitoring project. If results of this audit indicate a difference from the calibrated values of more than 10%, then the field flow controllers should be rechecked until they meet this objective. A written report of the QMOSB audit results will be included as an appendix in the final monitoring report.

Sampling flow rates should be checked in the field and noted before and after each sampling period. A separate, certified flow meter (i.e., not the one used in the sample train to control flow) will be used to check the flow. The flow rates should be checked after the initial sampling system leak check and before the "end" sampling system leak check.

E. Background Sampling

A background sample will be taken at all sites (4 sides) prior to an **application** test. The duration of the background sample should be sufficient to achieve the pesticide target 24-hour EQL, as directed by the DPR prior to the test, and must be a minimum of twelve hours and up to 24 hours if scheduling permits. This sample will establish if any of the pesticide being monitored is present in the air prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for **ambient** monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site. Detectable levels of some pesticides may be found at an urban area background site if they are marketed for residential as well as commercial/agricultural use. An example of an urban area background site is the ARB air monitoring station in downtown Fresno.

F. Collocated Samples

For both ambient and application monitoring, the method precision will be demonstrated in part by collecting samples from collocated samplers (replicate analysis of samples also relates to method precision). An additional **ambient** sampler will be collocated at each of the sampling

sites. Normally, collocated samples will be collected at each **ambient** site every Wednesday for each week of sampling. The samplers should be located at least two meters apart if they are high volume samplers (>20 Lpm) in order to preclude airflow interference. This consideration is not necessary for low flow samplers. The collocated sampler for **application** monitoring should be positioned at the downwind sampling site where the highest concentrations are expected. The collocated site is not changed after the study starts.

G. Trip Blanks

A trip blank should be included with each batch of samples submitted for analysis. This will usually require one trip blank for an **application** monitoring study and one trip blank per week for an **ambient** monitoring program. Trip blanks are prepared by opening a sampling cartridge (e.g., breaking the ends of an XAD glass tube) in the field followed by normal labeling and sample transport (i.e., along with the samples).

H. Laboratory, Trip and Field Spikes

The *laboratory, trip and field* spikes are prepared, extracted and analyzed at the same time and they are generally all spiked at the same level. The *laboratory* spikes are immediately placed in the laboratory refrigerator (or freezer) and kept there until extraction and analysis. The *trip* spikes are kept in the freezer until transported to the field. The trip spike samples are kept on dry ice in an ice chest (the same one used for the samples) during transport to and from the field and at all times while in the field except for trip spike sample log-in and labeling. The *field* spikes are stored and transported in the same way as the trip spikes. However, field spikes are obtained by sampling ambient air through the spiked cartridge at the same environmental and experimental conditions as those occurring at the time of the study.

Ambient field spikes are collocated (same location, flow rate and sampling period) with a sample collected at the urban background sampling site (to minimize background concentrations). **Ambient** field spikes are normally prepared at a level of approximately 2 times the EQL, or at a level representative of ambient concentrations.

Application study field spikes are collocated with the background samples collected at the four sides of the application site (i.e., one background and one field spike per side). **Application** field spikes are normally prepared at a level close to expected air concentrations. Field spike results are corrected by subtracting the amount of pesticide residue found in the collocated, unspiked sample before calculation of residue recoveries.

I. Transportation of Samples

All samples will be capped, placed in a sample container (e.g., culture tube or zip-lock bag) and placed in an ice chest on dry ice immediately following sample collection and labeling. The samples will remain on dry ice until transferred to the laboratory and will then be stored in the lab refrigerator or freezer. Any special handling procedures will be identified during the method validation and will be outlined in the SOP.

J. Meteorological Station Calibration

Meteorological station calibration procedures will be performed as specified by the ARB manual, "Air Monitoring Quality Assurance, Volume II, Standard Operating Procedures for Air Quality Monitoring."

K. Preventive Measures

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

V. Analysis

Method development and analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, a systems audit may be performed, upon request, by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis per a pesticide project. After a history of competence is demonstrated, an audit prior to each pesticide project is not necessary. However, during each pesticide project, the spiked samples discussed above should be provided to the laboratory to demonstrate accuracy and precision. These spiked samples will be prepared by qualified ARB laboratory staff.

If using GC/MS, isotope dilution is the recommended method for quantitation. Isotope dilution is where the isotope analog of the target compound is spiked to the sample prior to sample preparation. The internal standard goes through the same sample and analytical steps that the target analyte does thus compensating for losses during sample preparation and instrument variability during analysis. When no isotope is available an internal standard is recommended. An internal standard is spiked to the sample just prior to analysis. The internal standard compensates for instrument variability. If no suitable internal standard is found then an external standard method may be used.

VI. Analytical Quality Control Procedures

A. Mass Spectrometer Tuning (if MS is used)

A daily tune shall be performed using perfluorotributyl amine (PFTBA). The MS should be calibrated to optimize the MS for the mode of operation and type of pesticide analyzed. Documentation and performance criteria shall be specified in the standard operating procedure. A record of the tune for each batch should kept on file. A daily tune must be performed prior to the analysis of an analysis sequence and every 24 hours during an analysis sequence. If longer intervals between tunes are used, then the stability of the MS must be demonstrated during the method development phase and approved prior to the sample analysis.

B. Calibration

Initial Calibration

At the beginning of method development an initial multi-point calibration curve is performed to demonstrate the calibration range of the pesticide analyzed. A typical multi-point calibration consists of 5 different concentrations with a single replicate at each concentration. The calibration range usually should not exceed 40:1 with the lowest level standard at the EQL unless there is no need to measure values as low as the EQL. Depending on the linear range of the analyte, multi-points with other than 5 levels may be used although a multi-point with less than 3 levels is not permitted. Typically a linear calibration is preferred although a dynamic range using a quadratic is acceptable. For quadratic calibration curves quantitation can only be performed within the calibration range. Sample above the calibration curve must be diluted into the calibration range and reanalyzed.

Daily Calibration

Prior to the analysis of a set of samples a calibration must be performed. This calibration is called the daily calibration. The daily calibration is either a multi-point calibration or a mid-point calibration. The mid-point calibration consists of a single calibration at the mid-point of the initial multi-point calibration curve. If the mid-point is within a prescribed range (i.e., within +/- 20% of the original calibration) as determined from the initial calibration then the original initial calibration is still considered valid and the response is replaced. If the mid-point calibration is outside that range then another multi-point calibration must be performed. A calibration check at the same level is also run. If the mid-point calibration and the midpoint calibration check are within a prescribed range (i.e., +/-20%) of each other then analysis can begin. If the calibration check is outside the specified range then the problem must be rectified before analysis can begin.

C. Reagent Blanks.

A reagent (solvent) blank is performed at least for every batch of reagent used. The reagent blank uses the same solvent that was used for the sample preparation. The blank should be free of interferences. If low level contamination of the pesticide residue is found in the reagent blank (as may happen when using isotope dilution), then a reagent blank will be performed before analysis of each batch of samples. A reagent blank must be analyzed after any sample which results in possible carry-over contamination.

D. Laboratory Control Blank.

A laboratory blank is run with each batch of samples. A laboratory control blank (blank sampling media, e.g., resin cartridge or filter) is prepared and analyzed by the same procedures as used for field samples. Laboratory blank results must be no higher than 20% of the lowest value reported.

E. Laboratory Control Spike.

A laboratory control spike (LCS) is a resin cartridge spiked (at the level of the midpoint of the daily calibration runs) with a known amount of standard. The LCS is prepared and analyzed the same way as the samples. Two LCS are performed for each batch of samples. Laboratory control spikes need to be within 40% (100*difference/average) of each other and have recoveries that are +/-30% of the theoretical spiked value. If in the method development stage it is found that the differences or recoveries are larger, then they must be approved by ARB before the analysis can begin.

F. Calibration Check Samples.

A calibration check sample (CCS) is a mid-point standard run after every tenth sample in an analysis set. The purpose of the CCS is to ensure sample drift is within specified values. The CCS sample must be within +/- 25% of its theoretical value. If the standard is outside this range, then the samples associated with that calibration check sample must be reanalyzed. If in the method development stage it is found that the CCS variation is greater than 25%, then the percent variation limit used for the method must be approved by the ELB Branch Chief before the analysis can begin.

G. Duplicate Analysis.

A duplicate analysis is a sample analyzed in duplicate as a measure of analytical precision. Every tenth sample of an analysis set must be run in duplicate.

H. Standard Operating Procedures

Analytical methods must be documented in a Standard Operating Procedure (SOP) before monitoring begins. The recommended format for the SOP is provided in Appendix III. The SOP will include a discussion of all of the procedures outlined above in this section. The SOP will also include a summary of method development results as outlined in Section III above.

VII. Sampling and Analysis Protocol

Prior to conducting any pesticide monitoring, a sampling and analysis protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.

2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).

3. Specification of sampling periods and flow rates.

4. Description of the analytical method (SOP included if possible).

5. Tentative test schedule and expected test personnel.

6. Safety information specific to the pesticide monitored.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Procedures which apply to all sampling projects include: (1) sample log sheets (APPENDIX I), (2) chain of custody forms (APPENDIX II), (3) sunlight and rain shields for sample protection during monitoring, (4) sample storage in an ice chest on dry ice until delivery to the laboratory, (5) trip blanks and, (6) laboratory, trip and field spikes. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

VIII. Final Reports and Data Reduction

The mass of pesticide found in each sample should be reported along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as ug/m^3 (microgram per cubic meter) or ng/m^3 (nanogram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units at conditions of 1 atmosphere and 25 °C. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume.

The final report should indicate the dates of sampling as well as the dates of laboratory receipt, extraction and analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring studies are sent to the Department of Pesticide Regulation, the Office of Environmental Health Hazard Assessment, the Department of Health Services, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering and Laboratory Branch.

A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building)

including the locations Range/Township/ Section. A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described. Information will be collected for each site and reported to DPR regarding; 1) the proximity of the each sampler to treated or potentially treated fields, including the distance and direction, and 2) the distance the sampler is located above the ground.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average ("detected" results are factored in as (MDL+EQL)/2, <MDL results are factored in as MDL/2), total number of samples, number of samples above the estimated quantitation limit (EQL), number of samples "detected" and the number of samples below the MDL. For this purpose, collocated samples are averaged and treated as a single sample.

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX IV). Meteorological data will be reported in 15 minute averages for the application site during the monitoring period. Meteorological and pesticide air concentration data will also be summarized as wind roses for each application sampling period. The raw meteorological data file will also be transferred to DPR on 1.44 mb floppy disk.

C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, collocated etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

APPENDIX I

SAMPLE FIELD LOG BOOK

SAMPLE FIELD LOG BOOK
Project: Pesticide Air Monitoring
Project #:

Log #	Sample ID	Date On/Off	Time On/Off	Start Flow	End Flow	Start Leak Check	End Leak Check	Comments	Weather o=overcast pc=partly c=cloudy k=clear	Techn. Initial

APPENDIX II

CHAIN OF CUSTODY FORM

CHAIN OF CUSTODY FORM
CALIFORNIA AIR RESOURCES BOARD
MONITORING AND LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812
PESTICIDE
CHAIN OF CUSTODY

SAMPLE RECORD

Job #: _____ Date: _____
Sample/Run #: _____ Time: _____
Job Name: _____
Sample Location: _____
Type of Sample: _____
Log #'s: _____

ACTION	DATE	TIME	INITIALS		METHOD OF STORAGE freezer, ice or dry ice
Sample Collected					
			GIVEN BY	TAKEN BY	
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					

LOG #	ID #	

RETURN THIS FORM TO: _____

APPENDIX III

ANALYTICAL STANDARD OPERATING PROCEDURE FORMAT

ELEMENTS TO BE INCLUDED IN LABORATORY STANDARD OPERATING PROCEDURES FOR PESTICIDE AIR ANALYSIS

Engineering and Laboratory Branch
Air Resources Board
April 1999

I. SCOPE

A. Description of scope and detection limits of pesticide(s) to be analyzed.
B. Documents and references upon which method is based.
C. Definitions of any special terms must be given.

II. SUMMARY OF METHOD

A. General description of sampling and analytical procedure. Enough information should be included for an experienced analyst to readily recognize the principles of operation.

III. INTERFERENCES AND LIMITATIONS

A. Comments made here should cover both analytical and sampling problems, known and potential.

IV. EQUIPMENT AND CONDITIONS

A. INSTRUMENTATION: As specific a description as possible. Any modifications or improvements of the basic system must have an accompanying schematic. For chromatographic analysis list columns, flow rates, temperatures, detectors, amplifier ranges and attenuations, sample volumes, etc.
B. AUXILIARY APPARATUS: Provide a description of the function and operating conditions. Include a description of the sampling equipment if the equipment is specific to this method. For example, "Vacuum pump, ACME Model 62, capable of maintaining a 1 CFM Air Flow at 10" vacuum."

V. REAGENTS AND MATERIALS

A. Provide a list of all reagents used and specify purity and/or grade.
B. Describe preparation of any special reagents for analysis and sampling.
C. Specify composition, preparation, and concentrations of stock, intermediate, and working standards.
D. Describe in detail any necessary safety precautions for handling and disposition of chemicals.

VI. PROCEDURES

A. FIELD SAMPLING TECHNIQUES

1. Refer to appropriate Field Sampling S.O.P. for exact details of sampling, chain of custody and sample identification procedures.
2. Describe equipment used.
3. List sampling conditions: materials, flow rates, etc.
4. Describe any potential problems and limitations, with means of controlling such problems.
5. Describe any methods used to split samples for other types of analyses, if necessary.

B. LABORATORY SAMPLE PREPARATION/PRETREATMENT TECHNIQUES

1. Describe (or refer to an appropriate section of a Laboratory Quality Control Manual) a protocol for sample log-in procedures, including document control and sample examination for damage. Any possible hazards due to toxic or flammable chemicals must be clearly identified. Any sample storage requirements, such as immediate refrigeration or protection for light must be noted.
2. Describe any methods used for preconcentration, dilution clean-up filtration, extraction, concentration, etc., after the sample is received from the field.

C. ANAYSIS

1. Describe as clearly as possible the exact instrument configuration and set-up techniques
2. Describe analysis blank and calibration procedure with associated limits on precision and accuracy. Describe analysis of Control Samples and limits of the resulting data. Describe steps taken in an "out-of-control" situation. Specify the format and location of recorded calibration and Control Sample data.
3. Describe sample analysis. Description must include an example of expected data (for example, a sample chromatogram with all components of interest labeled).
4. Give calculation procedures for results. Describe data recording and data submittal.

VII. PERFORMANCE CRITERIA

A. Describe frequency of duplicate analyses, spikes, field blanks, and acceptable limits of each.

B. Describe frequency of multiple standard analyses to check method linearity and detection limit.

C. If confirmatory method is used, refer to specific S.O.P.

VIII. METHOD VALIDATION

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, method detection limit and estimated quantitation limit. Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time internals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain. The following data will be included in the SOP.

A. A table describing linearity (correlation coefficients), accuracy (method bias), precision (standard deviations at all levels analyzed), and detection.
B. Data on sampling efficiencies, stability, pertinent breakdown products, break through volumes and desorption efficiencies.
C. Data on storage stability and conditions for samples and standards.
D. References to quality assurance information derived from published and/or interlaboratory sources if available.

APPENDIX IV

APPLICATION CHECKLIST

APPLICATION CHECKLIST

1. Pesticide:
2. County:
3. Crop:
4. Field Address:
5. Field Location (R/T/S):
6. Field Size (acres):
7. Contact Person:
8. Background Monitoring Period:
9. Target EQL Met?:
10. Product Applied:
11. Application Rate:
12. Comments on Tank Mix:
13. Method of Application (ground, air, irrigation, injection, tarping etc.):
14. Start of Application:
15. End of Application:
16. Pattern of Application: (e.g., east to west):
17. Weather Conditions:
18. Met Station Location (and elevation):
19. Any Other Applications in Area:
20. Sampler Elevations:

___ Camera pictures of each sampler from all 4 directions
___ Camcorder video of each sampler in relation to field and surroundings
___ Rotameter #s logged
___ Check dimensions of field with known acreage (43560 ft^2/acre) & compare sides
___ Crops around field labeled on diagram

APPENDIX V

FLOW CONTROLLER CALIBRATION FORM

FLOW CONTROLLER; 1-POINT FLOW CALIBRATION SHEET

Project: Pre: _____ Post: _____ **Project #:** _____ **Date:** _____

Desired Flow Rate: _____ **Calib. by:** _____ (name)

BUBBLEMETER READINGS

Controller ID:					
Controller Set:					
-Readings:					
-Readings:					
-Readings:					
Average:					
Deviation:					
Controller ID:					
Controller Set:					
-Readings:					
-Readings:					
-Readings:					
Average:					
Deviation:					

Average of Averages _____ : _____

PROCEDURE

1. Set-up sampler as if to collect sample, including filled sample cartridge.
2. Set flow controller to achieve desired flowrate and record controller setting.
3. Observe and record Bubblemeter flow (on form or direct to floppy - Change File name).
4. Reset to zero. Then repeat step 3 two more times.
5. Calculate the average of 3 readings.
6. Repeat steps 1 thru 5 for each Rotameter.
7. Average of Averages and Deviation automatically calculated. Replace any Rotameters that deviate by 10% or more from the Average of Averages.
8. QA Section will get a copy for comparison with their results for the same setups.

Attachment II

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 (**low concentration range method**)

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° 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:

$(Fp / Ip) X Ci = Cr$

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

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

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.

$$\text{Response Ratio} = 9.56\ e\ +001 \times \text{Amount} + 2.63\ e\ -001$$

$$R2 = 0.999$$

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 ±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 (μg/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 ±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 $\pm$ 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

SAMPLE FIELD LOG SHEET FOR CANISTERS

Project # P-01-004

Ambient Monitoring for MeBr/Telone

Kern County

Sample Log Number	Sample Name	Sample Start				Sample Stop				Sampler ID Number	Silco Canister Number	Comments Including Weather Status	Sampler's Initials
		Date	Time (PST)	Flowrate Initial / Start	Guage ("Hg)	Date	Time (PST)	Flowrate (sccm)	Guage ("Hg)			Start / Stop	Start / Stop

Weather Codes: K = Clear, P = Partly Cloudy, C = Cloudy, F = Foggy, & R = Raining.

Page _____ of _____

Place data sheet inside plastic pouch. Questions? Call Steve Rider @ 916-327-4719.

PESTICIDES

CALIFORNIA AIR RESOURCES BOARD
MeBr/Telone Canister Data Sheet
Kern County, Project # P-01-004

Sample Name: _____ Sample Log #: _____

Station Operator: _____ Sampling Start Date: _____

Lab I.D. : Canister I.D. #: _____

	Date	Time (PST)	Vacuum ("Hg)	MFM Reading
Lab-pre*				
Sample Start				
Sample Stop				
Lab-post*				

*Calibrated Gauge Pressure

SAMPLE TYPE: [ ] Regular [ ] Collocated [ ] Episode [ ] Other:

SAMPLER ID NUMBER: _____ SHIP DATE TO LAB: _____ SHIPPED BY: _____

SHIP TIME: _____

SAMPLING CONDITIONS:
- [ ] No unusual conditions
- [ ] Construction nearby
- [ ] Farm operations nearby
- [ ] Fire nearby
- [ ] Rain
- [ ] Wind-blown sand/dust
- [ ] Other :_____

FLAGGED SAMPLE? [ ]NO or [ ]YES

Reason for sample flag (Valid vacuum range -5.0 to -10 inHg)
- [ ] Low canister pressure
- [ ] High canister pressure
- [ ] Sampling equipment inoperative
- [ ] Damaged sampling media
- [ ] Other reasons: _____

FIELD COMMENTS:

FOR LABORATORY USE

Shipped to field by:	Date:	Received in lab by:	Date:	Time:

Custody Seal Intact: Yes____ No _____ (If No: comment)	LAB COMMENTS:

Attachment X

Adsorbent Tube Sampling Field Log Sheet

SAMPLE FIELD LOG SHEET

Project: MITC Ambient Air Monitoring

Project # : P-01-004

Log #	Sample ID	Date On/Off	Time On/Off	Start Flow ( )	End Flow ( )	Start Leak Check	End Leak Check	Start Count	End Count	Comments	Weather k = clear p = partly c = cloudy r = rain	Initials