

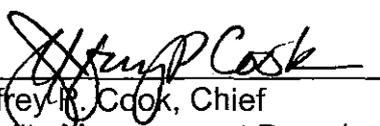
State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

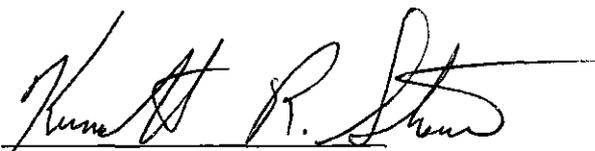
**Protocol for Air Monitoring
Around a Drip Irrigation Application of Metam Sodium
During Spring 2002**

Prepared by
Operations Planning and Assessment Section
Quality Management Branch
Monitoring and Laboratory Division

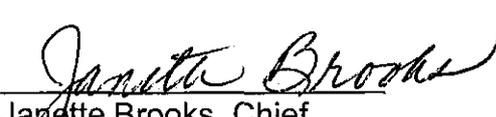
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APPROVED:


Jeffrey R. Cook, Chief
Quality Management Branch
Monitoring and Laboratory Division


Ken Stroud, Chief
Air Quality Surveillance Branch
Monitoring and Laboratory Division


Michael Poore, Chief
Northern Laboratory Branch
Monitoring and Laboratory Division


Janette Brooks, Chief
Air Quality Measures Branch
Stationary Source Division


William V. Loscutoff, Chief
Monitoring and Laboratory Division

This protocol has been reviewed by the staff of the California Air Resources Board and is 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 Air Monitoring
Around a Drip Irrigation Application of Metam Sodium
During Spring 2002**

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 application site air monitoring for the pesticide metam sodium (as the breakdown products methyl isothiocyanate, methyl isocyanate, hydrogen sulfide, and carbon disulfide). Monitoring is tentatively scheduled to occur in Spring 2002. 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.

The pesticide 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) and the following ARB methods:

"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)" (Attachment 1)

"Standard Operating Procedure, Sampling and Analysis of Methyl Isocyanate (MIC) in Application and Ambient Air using High Performance Liquid Chromatography with a Fluorescence Detector (06/25/01 Version)" (Attachment 2).

"Standard Operating Procedure Sampling and Analysis of Carbon Disulfide In Silco™ Canisters (Version 1, March 13, 2002)" (Attachment 3).

II. Sampling

Monitoring for methyl isocyanate (MIC) and methyl isothiocyanate (MITC) will be conducted with sampling tubes. Monitoring for carbon disulfide will be conducted using Silcosteel® canisters. Monitoring for hydrogen sulfide will be conducted using a portable sampler (Jerome sampler).

MIC and MITC Sampling:

The sampling methods for two of the compounds require passing measured quantities of ambient air through adsorbent sampling tubes. For MIC, the tubes are 8 mm x 110 mm, XAD-7, 1-(2-pyridyl)peperazine coated, with 400 mg in the primary section and 200 mg in the secondary (Supelco special order). 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 (SKC catalogue #226-09).

Sample collection for MIC is at a flow rate of 75 standard cubic centimeters per minute (sccpm) and MITC is at a flow rate of 2.5 standard liters per minute (sLpm). Immediately after sampling, the tubes are capped, labeled, placed in a culture tube, and stored and transported in an insulated container with dry ice to the ARB laboratory in Sacramento.

Each sample train consists of an adsorbent tube, Teflon fittings and tubing, rain/sun shield, rotameter (or needle valve), train support, and a 12 volt DC vacuum pump. 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 rotameter (or needle valve) with a range of 0-5 Lpm is used to control sample flow for the MITC sampling and a rotameter (or needle valve) with a range of 0-240 ccpm will be used to control the flow for the MIC sampling. The flow rates will be set using calibrated digital mass flow meters (MFM) before the start of each sampling period. An MFM scaled from 0-5 sLpm is used for MITC, and a 0-100 sccpm MFM is used for the 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 on the field log sheet. The pesticide sampling procedures for adsorbent tubes are included as Attachment 5.

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 MITC and MIC.

Carbon Disulfide Sampling:

Integrated ambient air samples will be collected for carbon disulfide using passive air sampling into evacuated six liter, Silcosteel® canisters (from Restec Corporation). The flow rate of 3 sccpm will be set and measured using a 0-10 sccpm mass flow meter. The sampling system will be operated continuously with the exact operating interval recorded in the log-book and on the field data sheets (see Attachment 6). 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 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 critical orifice flow controllers (Silcosteel treated Veriflo SC423XL) will be attached, using a Silcosteel treated swagelock connector, to the valve fitting on the canister (Figure 2). A 6-foot section of 1/8 inch O.D, Silcosteel tubing will be attached to the inlet end of an in-line, 5 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). 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 canister sampling, the potential decrease in flow rate as the vacuum in the canister changes must be taken into account. The flow control device used for the study (Veriflo SC423XL, from Restek Corporation) was designed to regulate and maintain a constant flow as the vacuum in the canister decreases. The manufacturer specifications indicate that the controller is capable of maintaining a continuous low flow with vacuum ranges from -29.9 to -5 inHg. The in-line filter helps prevent particles from entering the critical orifice of the flow controller, which could clog the critical orifice and affect the flow through the controller. The manufacturer specifications indicate that the outside temperature can have a slight effect on the flow rate. For example, there could be an approximately 6% flow drop when the temperature changes from 80 °F to 125 °F.

The pesticide ambient sampling procedures for canisters are enclosed as Attachment 4. The canister sampling field log sheet and canister data sheet are enclosed as Attachment 6. These forms will be used to record start and stop times, start and stop vacuum readings, sample identifications, weather conditions, the sampler's initials and any other significant data.

Hydrogen Sulfide Sampling:

Hydrogen Sulfide will be sampled with a portable Jerome 631-X Hydrogen Sulfide Analyzer at each sampling site. A 25-second sample will be taken each time the XAD-4 cartridges are changed out and at approximately mid-way through the application. The Jerome Analyzer samples at 150cc/min and for the expected range of 0.10 to 0.99 ppm must sample for 25 seconds. The detection limit of the Jerome Analyzer is 0.003 ppm and its range is 0.001 to 50 ppm. The DPR's requested quantitation limit was 5 ug/m³ (0.004 ppm). Prior to first use and after each morning and evening recovery, the sampler will be regenerated to assure the sensor is zeroed prior to use. The principle of operation of the instrument is that hydrogen sulfide reacts with a thin gold film by increasing the electrical resistance in proportion to the mass of hydrogen sulfide present. The procedures described in the operational manual supplied by the manufacturer will be followed for field sampling. The sampler will be audited at the Sacramento ARB shops before and after the field test, using an ARB certified standard of H₂S.

Sampling Schedule:

The application sampling schedule consists of samples collected during daylight and overnight periods as shown in Table 1.

Table 1
Application Sampling Schedule

<u>Sample period begins</u>	<u>Sample duration time</u>
Background (pre-application)	24 hours if possible; minimum 12 hours (if <24 hours must meet target EQL)
During application and post –application	Start of application (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)

In the event that application occurs at night, the alternate day-night schedule will be followed, i.e., with six sampling periods following the application sampling period. If the fumigation takes two or more days, samples will be collected during the overnight period separating the applications, and the overnight/daytime schedule will be followed from the last day of application.

The exact location of the application monitoring study has not yet been determined. ARB staff will contact the County Agricultural Commissioner’s offices in the Central Coast area to coordinate the selection of a study site and the test dates. The County Agricultural Commissioner’s staff will make initial contact with, or will at least provide a list of local contacts for growers, applicators, and/or pesticide control advisers that may be willing to cooperate in conducting the study. Monitoring sites are arranged with the voluntary cooperation of growers and applicators. ARB staff will investigate contacts until a cooperative grower is found and an appropriate site is selected. Permission to conduct the study will be obtained from the application plot land-owner and owners of adjacent land where samplers will be positioned.

Candidate fields for application monitoring will be 10 acres or larger. The crop type for the application study was not specified by the DPR. The DPR has recommended that, “monitoring for metam sodium be a drip irrigation application at a site using the highest allowed rates of use (i.e., about 318 pounds AI per treated (raised bed area) acre”).

For the MIC and MITC adsorbent tube samples, 8 samplers will be positioned, one on each side of the field and one at each corner. A 9th replicate sampler will be collocated at one position (downwind). For the carbon disulfide canister samples, 4 samplers will be positioned, 1 on each side of the field. A 5th replicate sampler will be collocated at

one position (downwind) Ideally, samplers should be positioned a minimum of 20 meters from the field; however, site conditions will dictate the exact placement of samplers.

In regard to field data, the monitoring report will include: 1) a record of the positions of the monitoring equipment with respect to the field, and if necessary, how the field was divided to treat over several days; 2) a drawing of the field including precise dimensions, field size, location of the monitoring sites, and showing the precise location of the meteorological equipment, trees, buildings, and other obstacles; 3) meteorological data collected at a minimum of 15-minute intervals, including wind speed and direction, humidity, and air temperature and comments regarding degree of cloud cover; 4) the elevation of each sampling station with respect to the field, and the orientation of the field with respect to North (identified as either true or magnetic North); 5) the start and end time of the application, and 6) the product used and the application rate.

III. Analysis

The ARB method and MITC sampling and analysis is enclosed as Attachment 1. 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 DPR recommended a target 24-hour estimated quantitation limit (EQL) of 0.5 ug/m³ for MITC. The attached SOP specifies an EQL of 0.18 ug/m³ for MITC for a 24-hour sample collected at 2.5 sLpm.

The draft method for the sampling and analysis of MIC are included as Attachment 2. The MIC method will consist of HPLC analysis with fluorescence detector. The analyses will be performed by the ARB laboratory in Sacramento. The DPR recommended a target 24-hour EQL of 0.1 ug/m³ for MIC. The attached SOP specifies an EQL of 0.42 ug/m³ for MIC for a 24-hour sample collected at 75 sccpm.

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

IV. Quality Assurance

Field Quality Control for the application monitoring will include the following for each of the sampling methods:

- 1) Four field spikes will be obtained by sampling ambient air at the application monitoring site for between 12 and 24 hours during the background monitoring (i.e., collocated with a background sample at the same environmental and experimental conditions). The spike levels for MIC, MITC, and carbon disulfide have not yet been determined.
- 2) Four trip spikes will be prepared at the same level as the field spikes.
- 3) Four lab spikes will be prepared at the same level as the field and trip spikes.
- 4) Collocated (replicate) for all sampling periods (except the background period) at one sampling location (downwind).
- 5) A trip blank will be obtained for each type of sample media.

V. Sample Labeling

Samples will be labeled using the following format:

Location-Chemical-Sampling Period-Type of Sample

Where:

Location is designated as north 1, 2, or 3 (N1, N2, N3), west (W), south 1, 2, or 3 (S1, S2, S3), and east (E). These designations can be revised as necessary depending on the configuration of the field.

Chemical is designated as M (for MIC), T (for MITC), CS (for CS₂), H (for H₂S).

Sampling period is designated as B (for background) or 1 through 6.

The type of sample is designated as S (sample), C (collocated), TB (trip blank), TS (trip spike), and FS (field spike).

Examples: S2-T-B-S (South2, MITC, background, sample)
 S2-T-B-FS (South2, MITC, background, field spike)
 S2-T-1-S (South2, MITC, sampling period 1, sample)
 S2-T-1-C (South2, MITC, sampling period 1, collocated)

VI. Personnel

ARB field coordination and sampling personnel will consist of staff from the Source Test Section of MLD/ARB.

VII. Safety Recommendations

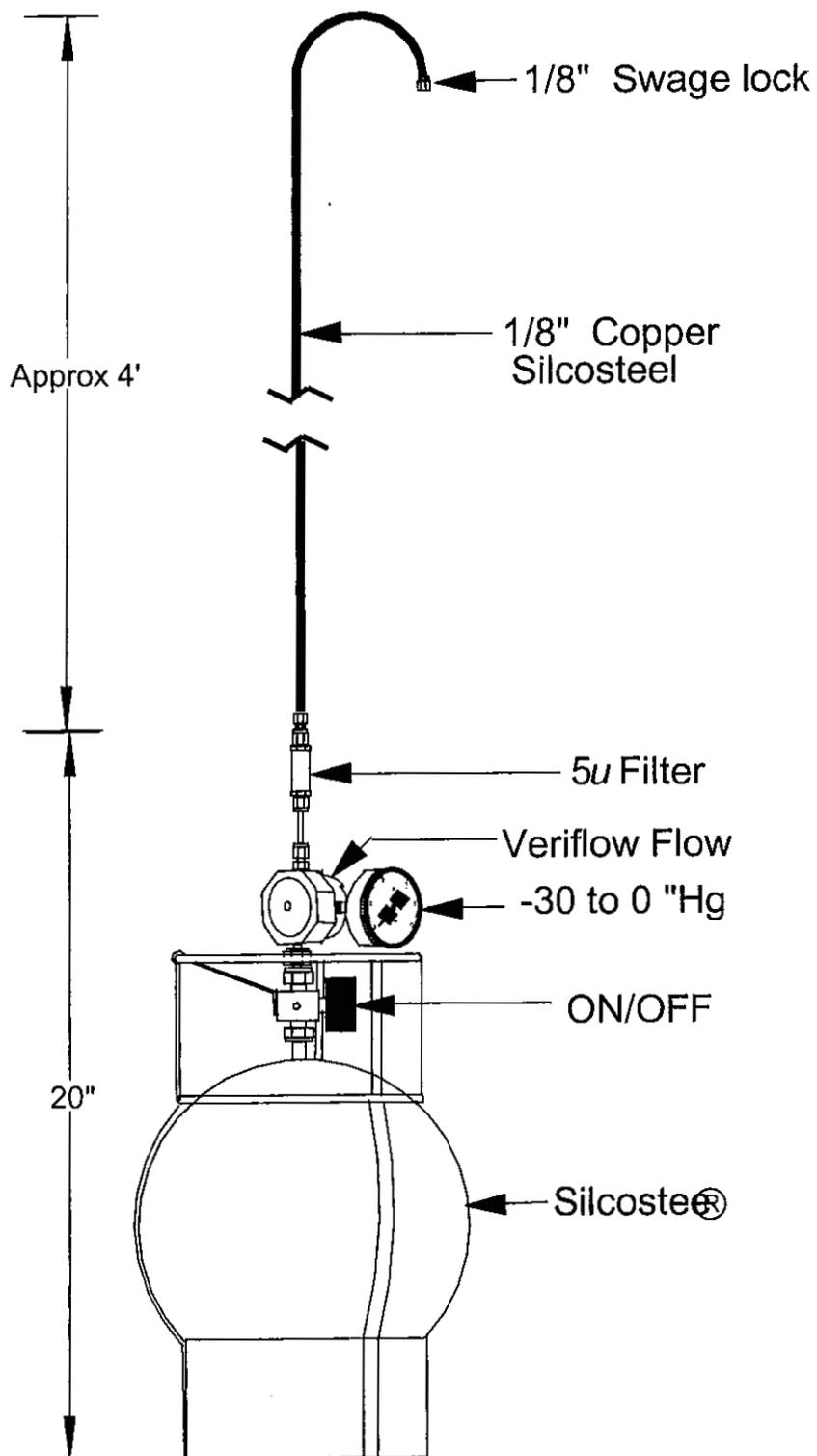
The DPR has revised the standard application study sampling schedule (Table 1) to minimize exposure to sampling personnel and states: "Due to high application rates and high volatility of these pesticides, the potential for exposure is higher than most other pesticides. However, this recommendation should not require any special safety equipment or precautions for sampling personnel."

The DPR's 'Monitoring Recommendations' also include the following safety recommendations.

"The metam sodium product labels warn that metam sodium causes skin damage and may be fatal if absorbed through the skin. Prolonged or frequent contact may cause an allergic reaction. Metam sodium is harmful if inhaled or swallowed and is irritating to eyes, nose, and throat. Monitoring personnel should use proper protective equipment to prevent exposure to the vapors or spray mist and refer to the label of the actual product used for further precautions. According to the product labels, proper protective equipment for applicators making direct contact or for applicators outside an enclosed cab includes coveralls, waterproof gloves, chemical resistant footwear plus socks, face sealing goggles, chemical resistant headgear (for overhead exposure) and apron, and a respirator with an organic-vapor removing cartridge. Concentrations should not exceed 0.5 ppm for any of the sampling intervals at the 60-foot sampling distance from the field."

Figure 1

Passive Canister Sampling



Attachment 1

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



**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:

1. 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 µg/m³ 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. Reagents

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

5. ANALYSIS OF SAMPLES

1. A daily manual tune shall be performed using PFTBA. The instrument is tuned using masses: 69, 219, 502. The criterion for the tune are the peak widths at ½ the peak height, 0.60 ± 0.05 , and the criteria for relative abundance: 69:100%, 219:100-120%, and 502: 7-12%.
2. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample which may result in possible carry-over contamination.
3. A 5-point calibration curve shall be analyzed with each batch of samples. For dichloropropene the analysis is calibrated at 10, 20, 40, 60, 100 ng/ml cis and trans. For methyl isothiocyanate the calibration is at 0.5, 1.0, 2.0, 3.0, 5.0 µg/ml.

4. With each batch of samples analyzed, a laboratory blank and a laboratory control spike will be run concurrently. A laboratory blank is an unexposed charcoal tube prepared and analyzed the same way the samples are analyzed. A laboratory control spike is a charcoal tube spiked with a known amount of standard. The control sample is prepared and analyzed the same way as the samples. Laboratory check samples should have recoveries that are at least 70% of the theoretical spiked value.
5. A DCP calibration check sample of 10 ng/ml is run after the calibration and every 10 samples and at the end of each sample batch. The calibration check for MITC is 0.75 µg/ml. The value of the check must be within $\pm 3\sigma$ (the standard deviation) or $\pm 10\%$ of the expected value, whichever is greater. If the calibration check is outside the limit, then those samples in the batch after the last calibration check that was within the limit need to be reanalyzed.
6. Score and snap the sample tube, transfer the charcoal into a 8 ml vial. (Save the back-up bed for future analysis if necessary.) Rinse the tube with 3.0 ml of DCM into the extraction vial. Cap and place the vial in the sonicator for 1 hour.
7. Filter the samples using a 3 ml syringe and 0.45 µm filter directly into a GC vial and cap securely.
8. The atmospheric concentration is calculated according to:

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

6. **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: $MDL = 3.14 * (\text{std dev values})$, 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 $\mu\text{g/ml}$ with an EQL of 0.22 $\mu\text{g/ml}$. 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 $\mu\text{g/ml}$ 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 2

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



**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:

1. 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 $0.05 \mu\text{g}/\text{m}^3$ and application monitoring at a quantitation limit of $0.1 \mu\text{g}/\text{m}^3$.

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 additional factor in possible interferences. 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 ($\text{NH}_4 \text{AC}$), pH 6.1.
Gradient: 5% ACN/95% $\text{NH}_4 \text{AC}$ to 30%ACN/70% $\text{NH}_4 \text{AC}$ 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

1. Precleaned vials, 8 ml capacity with teflon caps.
2. Whatman filters, 0.45 μm
3. Disposable syringes, 3 ml
4. Sonicator
5. Dionex Polyvials with filter caps, 0.5 mL.

C. Reagents

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

5. ANALYSIS OF SAMPLES

1. 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.
2. It is necessary to analyze a solvent blank and a resin blank with each batch of samples to ascertain the presence of possible interferences.
3. 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 $\mu\text{g/mL}$ of the purified MIC derivative. (See section 6.0 B for the preparation of the purified derivative.)
4. A calibration check sample of 0.078 $\mu\text{g/ml}$ 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.
5. 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.

6. 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.
7. 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.
8. The atmospheric concentration is calculated according to:

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

6. **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 $\mu\text{g}/\text{ml}$, 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 $\mu\text{g}/\text{ml}$ of the MIC derivative.

C. Calibration Check

A calibration check sample is run after the calibration, after every 10 samples and at the end of the sample batch to verify the system is in calibration. The value of the check must be within $\pm 3\sigma$ (the standard deviation) or $\pm 10\%$ of the expected value, whichever is larger. If the calibration check is outside the limit,

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

D. Minimum Detection Limit

The detection limit is based on US EPA MDL calculation. The method detection limit (MDL) and the estimated quantitation limit (EQL) for methyl isocyanate is calculated by the analysis of seven (7) replicates of a low-level matrix spike. The MDL = 3.14*(std dev values), where std dev = the standard deviation of the concentration calculated for the seven replicate spikes. For MIC the MDL is 0.009 $\mu\text{g}/\text{sample}$ (0.003 $\mu\text{g}/\text{mL}$). EQL, defined as 5*MDL, is 0.045 $\mu\text{g}/\text{sample}$ (0.015 $\mu\text{g}/\text{mL}$) 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 $\mu\text{g}/\text{mL}$ the recovery is greater than 70%.

F. Storage Stability

Storage stability will be run concurrent with analysis of samples.

G. 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 3

Standard Operating Procedure Sampling and Analysis of Carbon Disulfide In Silco™ Canisters

California Environmental Protection Agency

 **Air Resources Board**

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

**Standard Operating Procedure
Sampling and Analysis of Carbon Disulfide
In Silco™ Canisters Using a Varian
Stand Alone Cryogenic Sampler**

**Version 1
March 13, 2002**

Approved by:

**Russell Grace, Manager
Special Analysis Section**

This SOP has been reviewed by 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 of commercial products constitute endorsement or recommendation for use.

SCOPE

This method, which follows closely EPA Method TO-15, is for the sampling and analysis of ambient air using six-liter Silco™ canisters for sample collection. The compound, carbon disulfide (CS₂) is analyzed by gas chromatography/mass spectrometry.

2. SUMMARY OF METHOD

Ambient air is collected into evacuated six-liter Silco™ canisters using a sub-atmospheric pressure collection mode. Sample canisters are subsequently pressurized in the laboratory to approximately fifteen pounds per square inch gauge (psig) and 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 bromomethane-d₃ as the primary internal standard for quantitation, and 1,2-dichloropropane-d₆ as a secondary internal standard for quantitation. 1,2-dichloropropane-d₆ is used only if interference makes bromomethane-d₃ unusable. Estimated quantitation levels for this method range from 9.6 to 62.4 µg/m³.

3. INTERFERENCES/LIMITATIONS

Interference may result from improperly cleaned canisters. Analysis of samples containing high concentrations of early eluting pesticide components may cause significant contamination of the analytical equipment. Co-eluting compounds trapped during sample collection may interfere. Running canister blanks and system blanks should minimize contamination originating in the analytical instrument.

4. EQUIPMENT AND CONDITIONS

A. Instrumentation

Hewlett Packard 5890 Series II gas chromatograph:

Detector: 280° C

Injector: 220° C

Column: Restek Rtx-200, 60 meter, 0.32mm I.D., 1.5 micron film thickness

GC temperature program: initial -10° C, -10 to 80° C @ 10° C/min, 80° to 200° C @ 25° C/min, hold for 1 minute, 200 to 240° C @ 25° C/min

Carrier Gas: Helium, grade 5 or better

Hewlett Packard 5973 mass selective detector:

Acquisition Mode: SIM

Tune File: PFTBA Autotune, maximum sensitivity

Ions monitored: 76 m/z quant, 78 m/z qualifier

Varian Stand Alone cryogenic concentrator:

Valve Oven: 60° C

Autosampler Oven: 60° C

Nafion Dryer: ambient

Sample Line: 150° C

Cryotrap: -180° C to 150° C

Transfer Line: 150° C

Cryofocus: -180° C to 150° C

Sample Size: 100 ml

Internal Standard Loop: 1 ml

B. Auxiliary Apparatus

Compressed helium: Grade 5 or better

Compressed nitrogen: Grade 5 or better

Liquid nitrogen for cryogenic concentrator

Certified standard for carbon disulfide

Restek, 6.0 liter Silcosteel™ canisters with Silcosteel™ valve

Pressure gauge, -30 inches Mercury (Hg) to 30 pounds psig.

Canister cleaning system (Appendix 1)

5. ANALYSIS OF SAMPLES

- 1) Perform a PFTBA autotune and evaluate tune criteria. See Appendix 2. Place a copy of the autotune results in the autotune folder.
- 2) Check and record the pressure in the field sample canisters. Pressurize the field sample canisters to approximately 14.7 psig with Grade 5 or better nitrogen. Record the final pressure.
- 3) Prepare a sample sequence for the GC/MS. The sequence should include a continuing calibration check (CCV), and a blank, for every 10 field samples. A laboratory control sample (LCS) and a duplicate are run once per analytical batch not to exceed 20 samples. Load the sequence into the GC/MS in the remote start mode.
- 4) Prepare a sample sequence for the Varian. The sample sequence should be organized as follows: system blank, CCV, LCS, field samples, duplicate field sample, and CCV. If the CCV is not within $\pm 20\%$ of its assigned value the system must be recalibrated.
- 5) Attach the sample canisters to the Varian autosampler ring as per the sequence. Execute the Varian sequence, which in turn will initiate the GC sequence.
- 6) Sample quantitation reports will print out after each analysis.
- 7) Review and edit the quantitation reports as needed.

8) Calculations will require a correction for the required pressurization performed prior to analysis. Instrument reports will be in units of $\mu\text{g}/\text{m}^3$ and must be corrected for the analysis dilution using the following calculation:

$$(F_p / I_p) \times C_i = C_r$$

I_p = initial canister pressure in mm Hg

F_p = final canister pressure in mm Hg

C_i = concentration from the analysis report in $\mu\text{g}/\text{m}^3$

C_r = reported concentration in $\mu\text{g}/\text{m}^3$

6. QUALITY ASSURANCE

A. Instrument Reproducibility

Establish the reproducibility of the instrument and analytical method as follows. Inject five replicate samples of CS_2 standards at three concentrations ($0.9 \mu\text{g}/\text{m}^3$, $2.55 \mu\text{g}/\text{m}^3$, and $9.49 \mu\text{g}/\text{m}^3$). See Table 1.

B. Linearity

A 5-point calibration is performed. Calibration standards ranging from approximately 1.6 to $10.4 \mu\text{g}/\text{m}^3$ are used to calibrate the method. If ambient samples are diluted times six, the calibrated ambient sample range is approximately 9.6 to $62.4 \mu\text{g}/\text{m}^3$. The results are used to calculate calibration curves using linear or quadratic regression. See Appendix 3

C. Minimum Detection Limit

Detection limits are based on the US EPA MDL calculation. Using the analysis of seven replicates of a low-level analysis, the method detection limits (MDL) and the EQL for the pesticide components are calculated as follows:

$$\text{MDL} = 3.14*s$$

$$\text{EQL} = 5*\text{MDL}$$

Where s equals the standard deviation of the response calculated for the seven replicate spikes. The calculated MDL for CS_2 is $0.23 \mu\text{g}/\text{m}^3$. The respective EQL is $1.15 \mu\text{g}/\text{m}^3$. Assuming a 1 to 6 dilution to pressurize the ambient samples the EQL is $6.9 \mu\text{g}/\text{m}^3$ for CS_2 .

Results are reported to 3 significant figures above the EQL. Results below EQL but above MDL are reported as DET (detected). Results reported as non-detect (ND) and reported values less than the MDL are reported as less than MDL (<MDL).

D. Storage Stability

A CS₂ storage stability study will not be performed. Carbon Disulfide is included in EPA Method T0-15 and as stated in section 1.3 "under conditions of normal usage for sampling ambient air, most VOC's can be recovered from canisters near their original concentrations after storage of up to 30 days." During this program all samples will be analyzed within 21 days of collection.

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.

TABLE 1
 REPRODUCIBILITY STUDY
 CARBON DISULFIDE

Target Concentration	0.92 $\mu\text{g}/\text{m}^3$	2.55 $\mu\text{g}/\text{m}^3$	9.49 $\mu\text{g}/\text{m}^3$
Sample Number			
1	0.9	2.76	9.62
2	0.93	2.65	9.54
3	0.89	2.52	9.44
4	1.02	2.46	9.43
5	0.84	2.36	9.42
Average	0.92	2.55	9.49
SD	0.067	0.16	0.09
RSD	7.27	6.18	0.92

Appendices

Appendix 1

CAN CLEANING PROCEDURE

The canister cleaning procedure uses repeated cycling from -30 inches Hg to 30 pounds per square inch gauge with humidified ultra pure nitrogen. The procedure includes four complete cycles each 24 minutes (19 minutes vacuum and 5 minutes pressure) at 60 degrees C.

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 than their MDL the entire batch should be cleaned again.

Procedure:

A. Fill dewar with Liquid Nitrogen (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 canister oven.

C. Open Nitrogen (N₂) Tank

1. Open regulator on N₂ tank to the left of the canister oven.

D. Load canisters in oven

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

E. Start Timers Located on top left of canister 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.
3. The system should 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 canister 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 canisters 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 canisters and place plugs on manifold ports.
8. Hit the stop button on both timers.

Appendix 2

Autotune Criteria

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

1. Any unusual change in the EM voltage
2. Peak width for all tune masses should be between 0.4 amu and 0.6 amu.
3. The relative abundance of tune mass 219.0 should be greater than 25% 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 Carbon Disulfide

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

Cylinder No:	CC72058
Expiration date	May 9, 2002
Carbon Disulfide	0.985 PPM/M

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

1. A six liter Silco canister is evacuated to -30 " Hg.
2. 60 ml of carbon disulfide stock is transferred to the canister using a gas tight syringe equipped with a stopcock.
3. 100 ul of reagent grade water is added to the canister using a syringe and syringe adapter.
4. The canister is pressurized to approximately 29.4 psig with grade five or better nitrogen.

The canister will contain CS₂ at the following concentration:

Carbon Disulfide	10.39 $\mu\text{g}/\text{m}^3$
------------------	--------------------------------

The standard sample injection volume is 100 ml. Using the cryogenic sampler to introduce the following volumes of working standard to the GCMS generates a calibration curve.

<u>Volume</u>	<u>Carbon disulfide</u>
100 ml	10.39 $\mu\text{g}/\text{m}^3$
75 ml	7.79 $\mu\text{g}/\text{m}^3$
50 ml	5.20 $\mu\text{g}/\text{m}^3$
25 ml	2.60 $\mu\text{g}/\text{m}^3$
15 ml	1.56 $\mu\text{g}/\text{m}^3$

Attachment 4

Pesticide Canister Sampling Procedures
For Application Studies

Pesticide Canister Sampling Procedures For Application Studies

Overview:

- Collect samples, according to the schedule in Table 1 of this protocol.
- Collect 4 background samples, one from each of the 4 sampling positions.
- Collocate 1 field spike with each of the 4 background samples.
- Collect a collocated sample from the downwind site for all sampling periods (except the background period).
- Submit 1 trip blank.
- With the trip blank, there should be a total of 35 samples collected during the study, plus 4 trip and 4 field spikes.
- The field log sheet is filled out as the sampling is conducted. All QA samples must be logged onto the log sheet.
- The chain of custody (COC) forms are filled out prior to sample transfer; the originals are transferred with the samples. Make and retain copies if desired (not necessary).

Sampling Procedure:

Materials that will be needed 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 (make sure battery has full charge)

Figure out your route for sampling the sampling locations, and keep this the same throughout the study.

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. Unplug when not in use to minimize drop in battery charge. Recharge the batteries regularly.

- 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; it should be 3.0 sccpm. If the reading is **between 2.95 and 3.05**, then record the value on the data sheet. If it is *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.

Log-in a trip blank (TB), once per study. Log the TB into the log sheet.

Attachment 5

Pesticide Adsorbent Tube Sampling Procedures
For Application Studies

Pesticide Adsorbent Tube Sampling Procedures For Application Studies

Overview:

- Collect samples, according to the schedule in Table 1 of this protocol.
- Collect 4 background samples, one each from the corner sampling positions.
- Collocate 1 field spike with each of the 4 background samples.
- Collect a collocated sample from the downwind site for all sampling periods (except the background period).
- Submit 1 trip blank.
- With the trip blank, there should be a total of 59 samples collected during the study (for each method), plus 4 trip and 4 field spikes.
- All samples are stored after sampling either in an ice-chest on dry ice or in a freezer.
- The field log sheet is filled out as the sampling is conducted. All QA samples must be logged onto the log sheet.
- The chain of custody (COC) forms are filled out prior to sample transfer; the originals are transferred with the samples. Make and retain copies if desired (not necessary).

Sampling Procedure:

Materials that will be needed to conduct the sampling include:

- Clip board with log sheets
- pencils/pens
- sample labels
- sample cartridges
 - end caps
 - plastic test tubes
- zip-lock bags
- 0 to 100 sccpm and 0 to 5 sLpm mass flow meters (MFM) with batteries
- ice chest
- dry ice

Figure out the route for sampling the 8 locations and keep this the same throughout the study.

Preparation and Set-up

On the way to study site, plug the MFM into the battery. It takes the MFMs about

10 minutes to warm up before they can be used. Leave the MFM plugged in until the last sample is taken; unplug when not in use to minimize drop in battery charge. Recharge the batteries regularly.

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 correct setting. 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 appropriate MFM, set the flow rate exactly to 75 sccpm for MIC or 2.5 sLpm for MITC.

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, MFM Serial #, 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 MFM; 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 period in a zip-lock freezer storage bag and place on dry ice in a cooler.

Collect a trip blank (TB) 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 6

Adsorbent Tube Field Log Sheet
Canister Field Log Sheet and
Canister Field Data Sheet

PESTICIDES

CALIFORNIA AIR RESOURCES BOARD Carbon Di-Sulfide (CS2) Canister Data Sheet San Luis Obispo County, Project # P-02-001

Sample Name: _____

Sample Log #: _____

Operator: _____

Canister I.D. #: _____

Sampler I.D. #: _____

Lab I.D. :

--

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

*Calibrated Gauge Pressure

SAMPLE TYPE: Regular Colocated Spike Blank Other:

SHIPPED TO LABORATORY: Date _____ Time _____ Via _____

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 (Flow must be between 2.2 & 3.7ccm)

- Canister flow < 2.3ccm
- Canister flow > 3.7ccm
- Sampling equipment inoperative
- 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:		