



Monitoring and Laboratory Division
Air Quality Surveillance Branch

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

October 1, 2007

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

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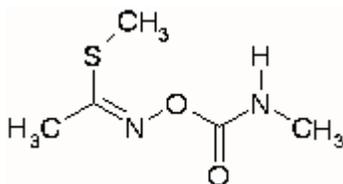
1.0 Introduction

At the request of the of the California Department of Pesticide Regulation (DPR), (January 29, 2007 Memorandum, Warmerdam to Witherspoon) the Air Resources Board (ARB) staff will determine airborne concentrations of methomyl in Fresno County. This will be done prior to, during and after an application of methomyl. This monitoring will be done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5, Section 14022(c)) which requires the ARB "to document the level of airborne emissions.... of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. Monitoring is being conducted to coincide with the use of methomyl as a selective pesticide on alfalfa and corn for human consumption.

The draft "Standard Operating Procedure Sampling and Analysis of S-methyl-N((methylcarbamoyl)oxy)thioacetimidate (Methomyl)" dated June 2007, is included as Appendix A.

2.0 Chemical Properties of Methomyl

Figure 1. Chemical structure of methomyl.



The following information on the physical/chemical properties of Methomyl (Chemical name: S-methyl-N((methylcarbamoyl)oxy)thioacetimidate; Molecular structure: $C_5H_{10}N_2O_2S$) (Figure 1) is a white crystalline solid with a slightly sulfurous odor with a solubility of 5.8 g/100 g water (DuPont 2005). It is stable under normal temperatures when dry, but thermal decomposition and combustion will produce hazardous gases including sulfur oxides, methyl isocyanate and hydrogen cyanide. Table 1 lists the physical and chemical properties of methomyl as obtained from DPR's, "Use Information and Air Monitoring, and Ambient Air Monitoring Recommendations for the Pesticide Active Ingredient Methomyl", dated June 2007 and included as Appendix B.

Chemical name	methomyl
Trade name†	Lannate
CAS Registry number	16752-77-5
Molecular formula	C ₅ H ₁₀ N ₂ O ₂ S
Molecular Weight	162.2 g/mol
Melting Point	78 – 79 °C
Vapor Pressure	5.4 x 10 ⁻⁶ mmHg (25 °C)
Specific Gravity	1.2946 (24 °C)
Water Solubility	58,000 mg/L (25 °C)
Henry's Law Constant	1.90 x 10 ⁻¹⁰ atm-m ³ /mol (25 °C)
Soil Adsorption Coefficient (K _{oc})	43.3 cm ³ /g
Field Dissipation Half-life	54 days, sandy loam soil
Octanol / Water Partition Coefficient (K _{ow})	0.60
Hydrolysis half life	30 days

Table 1.

Physical and chemical properties of methomyl (Hazardous Substances Data Bank. 2007; Crop Protection Handbook, 2007).

E.I. Du Pont De Nemours & Co. (Du Pont) currently registers two products containing methomyl — Lannate SP (soluble powder) and Lannate LV (liquid concentrate). Lannate SP contains a higher percentage of methomyl than Lannate LV (90% versus 29%) and accounts for the majority of agricultural use of methomyl in California. These products are applied directly to soil either by aerial application or ground spraying and are used as pesticides to control a wide range of insects including thrips, bugs, aphids, beetles, moths, diptera and ant-hymenoptera on a variety of commodities. (DPR Product/Label Database <http://www.cdpr.ca.gov/docs/label/>). They are restricted use pesticides.

Methomyl is an n-methyl carbamate insecticide with anticholinesterase activity and as such carries a Poison/Danger signal word on the label. It is fatal if swallowed and may be fatal if inhaled. According to the label Lannate SP, the more widely used of the formulations, is a dry powder to be dissolved in water for application by mechanical ground or air equipment only. Hand-held equipment is prohibited for applications to crops and the pesticide must not be applied through any type of irrigation system. It should not be applied by ground equipment within 25 feet, or by air within 100 feet of lakes, reservoirs, rivers, estuaries, commercial fish ponds, natural streams, marshes or natural ponds.

† Disclaimer: The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

3.0 Project Goals and Objectives

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

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

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

4.0 Contacts

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5.0 Study Location and Design

Methomyl applications are performed throughout the San Joaquin Valley. Peak use is June, through October.

Application Monitoring

Samples will be collected by passing a measured volume of ambient air through two XAD-2 resin tubes that are mounted on a sampling tree as shown in Figure 2. The exposed XAD-2 resin tubes (SKC #226-30-06) are stored in an ice chest (on dry ice) or in a freezer until extracted in the laboratory with organic solvent. The tubes will be protected from direct sunlight and supported about 1.5 meters above the ground during application monitoring sampling periods. At the end of each sampling period, the tubes will be placed in culture tubes with an identification label affixed. Subsequent to sampling, the sample tubes will be transported on dry ice, as soon as reasonably possible, to the ARB Sacramento Monitoring and Laboratory Division laboratory for analysis. The samples will be stored in the freezer or extracted/analyzed immediately

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

The following recommendations were obtained from DPR's, "Use Information and Air Monitoring, and Ambient Air Monitoring Recommendations for the Pesticide Active Ingredient Methomyl", dated June 2007 (Appendix B).

DPR recommendation stated:

The use maps for methomyl suggest that application monitoring should occur in Fresno, Kings and Tulare Counties during the months of June through October. Growers in Fresno County used the most methomyl in both 2004 and 2005. The majority of applications occurred during June, July and August to treat over 40 different crop types. Corn, tomatoes, alfalfa, onion, cantaloupe and sugarbeet accounted for 75% of methomyl use over 2004-05.

After contacting Fresno County Department of Agriculture personnel, Agricultural/Standards Specialist from six districts, nine Pest control advisors and agricultural specialist from UC Davis, MLD Staff have determined that the only usage currently found is on corn for human consumption and alfalfa.

DPR recommendation stated:

According to the product label for Lannate SP, the highest application rate of no more than 6.3 lbs a.i./acre can be applied to tomatoes, followed by cantaloupe (5.4 lbs a.i./acre), sugarbeet (4.5 lbs a.i./acre) onions and alfalfa (3.6 lbs a.i./acre), therefore DPR recommends that monitoring occur in a one of the crops with the highest application rate during the summer of 2007.

After contacting Fresno County Department of Agriculture personnel, Agricultural/Standards Specialist from six districts, nine Pest control advisors and agricultural specialist from UC Davis, MLD Staff have determined that the only usage currently found is current application rate is a half pound per acre.

DPR recommendation stated:

Application sites for these commodities ranged from 3 to 238 acres treated with an average of 94 acres (DPR PUR Database). However, entries in the PUR database may reflect multiple applications to the same site, resulting in high reported acreage. DPR therefore recommends that the selected monitoring site be 94 to 238 acres. If a site this size cannot be located, a smaller site is acceptable but should be at least 10 acres. The monitoring study will include samples taken before, during and for approximately 72 hours following the pesticide 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).

After contacting Fresno County Department of Agriculture personnel, Agricultural/Standards Specialist from six districts, nine Pest control advisors and agricultural specialist from UC Davis, MLD Staff have determined that applications of methomyl are accomplished primarily at night. This is done to limit the loss of beneficial insects such as bees.

During the air monitoring of the application, samples are collected according to the Table 2A Guidelines for Daytime Application and Sampling Schedule or Table 2B Guidelines for Nighttime Application and Sampling Schedule.

Sample period begins:	Sample duration time
Background (pre-application)	Minimum 12 – 24 hours
Application	Start of application until 1 hour after end of application
End of application (post-application)	End of application until 1 hour before sunset
1 hour before sunset	Overnight ¹ 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

TABLE 2A.
GUIDELINES FOR DAYTIME APPLICATION SAMPLING SCHEDULE

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

Many applications are accomplished by air at night. This is done to prevent the loss of beneficial's (i.e. bees). Background air sampling will be accomplished a minimum of 12 – 24 hours prior to the application. Sampling will be accomplished from the start of the application to one hour after the application ends. The next sampling will be from one hour after the application ends to one hour after sunrise. The next sampling will be from one hour after sunrise to one hour before sunset (same for second or more application days). Refer to Table 2B, Guidelines for Nighttime Application and Sampling Schedule.

Sample period begins:	Sample duration time
Background (pre-application)	Minimum 12 – 24 hours
Application	Start of application until 1 hour after end of application
End of application (post-application)	End of application until 1 hour after sunrise
1 hour after sunrise	Daytime until 1 hour before sunset
1 hour before sunset	Overnight ¹ 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

TABLE 2B.
GUIDELINES FOR NIGHTTIME APPLICATION SAMPLING SCHEDULE

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

A minimum of eight samplers will be positioned around the application perimeter. One sampler located at approximately the midpoint of each side of the field and one at each corner. A ninth sampler will be collocated at one position (downwind). Field spike samples should be collected at similar ambient conditions (e.g., temperature, humidity, exposure to sunlight) and monitoring procedures (e.g., air flow rates, sample transportation and storage) as those occurring at the time of ambient air sampling. Target 24-hour quantitation limit of 10 ng/m³ for methomyl are recommended (Warmerdam, 2007).

6.0 Sampling and Analysis Procedures

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

At each sampling site, the operator will assure that at the end of each sampling period, the XAD-2 resin tube will be placed in culture tubes with an identification label affixed with a record of the run information on the field sample report. After collection the samples are placed in a glass tube and stored in a cooler at 4° C or less until returned to the laboratory. The sample tubes will be transported on dry ice, as soon as reasonably possible, to the ARB Sacramento Monitoring and Laboratory Division laboratory for analysis. These samples will be stored in the freezer or extracted/analyzed immediately. Samples are collected in the field with a flow rate of two (2) liters per minute (lpm).

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

The Northern Laboratory Branch (NLB) will supply SPM with XAD-2 resin tubes. NLB will perform analyses for methomyl on collected application samples and report results to SPM.

Laboratory analyses will be performed in accordance with applicable standard operating procedures (Standard Operating Procedure Sampling and Analysis of S-methyl-((methylcarbamoyl)oxy)thioacetamide (Methomyl). The SOP is included in this Protocol as Appendix A.

The following XAD-2 resin tube validation and analytical quality control criteria should be followed during pesticide analysis.

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

7.0 List of Field Equipment

<u>Quantity</u>	<u>Item Description</u>
(1)	Met-One Auto met portable meteorology system having calibrated sensors to measuring 1 minute averages for wind speed, direction, ambient temperature, and relative humidity w/built-in data logger.
(1)	Measuring Wheel
(1)	200 ft measuring tape
(1)	Tripod and compass
(1)	Global Positioning System (GPS) with backup batteries and carrying case
(1)	Digital Camera with backup batteries and carrying case
(2)	Alborg mass flow meter 0-5 Lpm.
(8)	Sampling trees/pumps
(90)	XAD-2 resin tubes (9 backgrounds, 9 applications, 63 post application, 4 field spikes, 4 trip spikes, 1 trip blank, 1 field blank and 2 spare).
(9)	Sample trees/pumps
(50)	Batteries

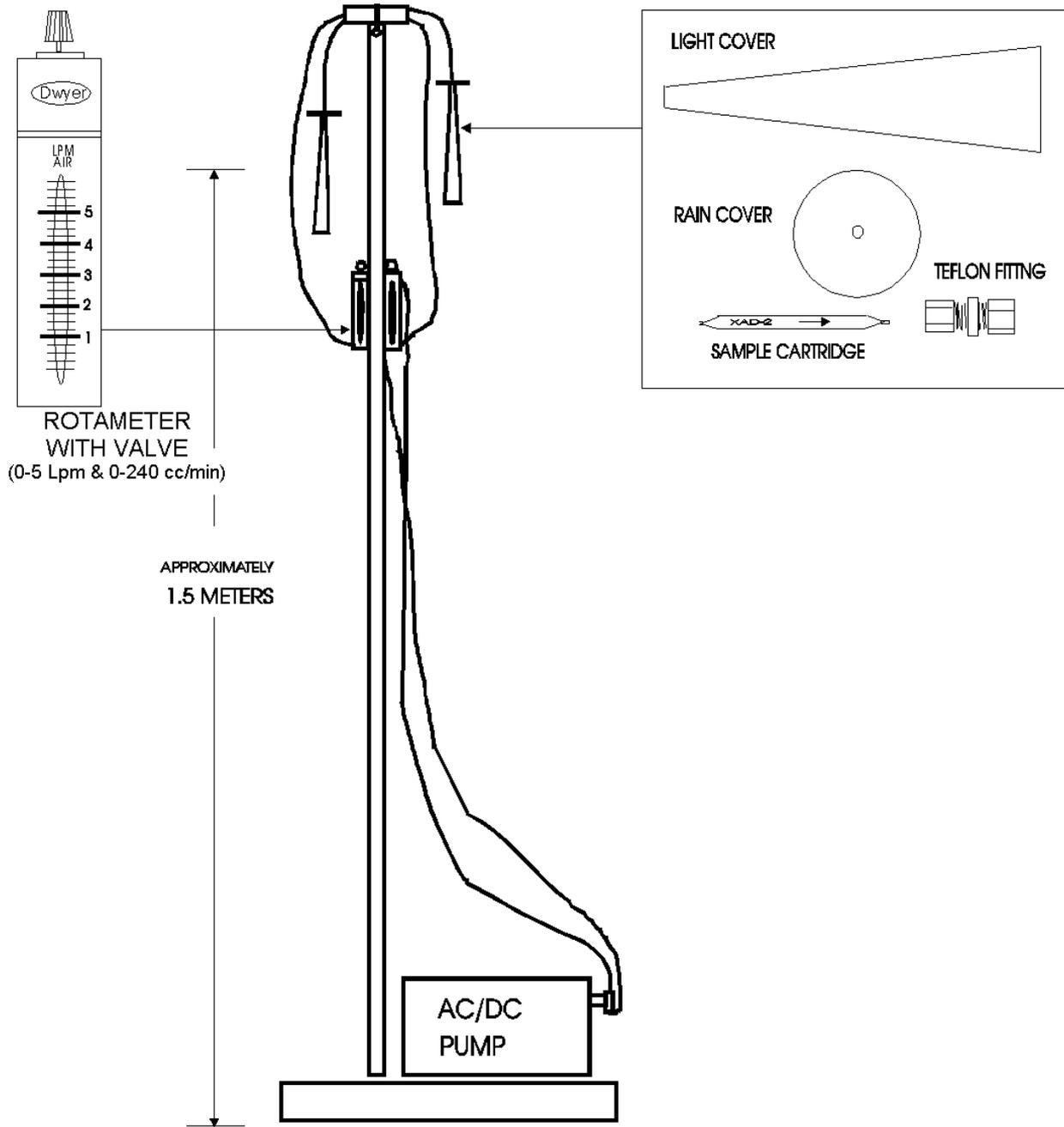


Figure 1
Air Sampler Tree with Pump

8.0 Quality Control

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

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

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

Each XAD-2 resin tube will be assigned a field sample number that provides for identification of site, sample ID number, operator, and sample information as well as sample transfer information.

Field Spike (FS): A field spike will be prepared by the laboratory by injecting a XAD-2 resin tube with 51 nanograms (ng) of methomyl. The field spike is installed onto a sampler and will be collocated next to the background sampler. The application field spike will sample for 12- 24 hours prior to the application.

Trip Spike (TS): A trip spike will be prepared by the laboratory by injecting a XAD-2 resin tube at the same level as the field spike. The trip spike will be transported and analyzed along with the field spike. The trip spike is treated the same as a field spike with exception that it is not installed onto a sampler.

Field Blank (FB): A field blank will be a XAD-2 resin tube opened in the field and return but is not installed onto a sampler.

Trip Blank (TB): A trip blank will be an unopened XAD-2 resin tube to the field and return but is not installed onto a sampler.

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

Site/Sample Identification

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

Background Site Naming:

Site-1-BKGD
Site-1CO-BKGD
Site-1-FS

Letter Abbreviations as follows

N = North Side
S = South Side
W = West Side
E = East Side
BKGD = Background Sample
FS = Field Spike
CO= Co-located
NEC = NE Corner Sample
NWC = NW Corner Sample
SEC = SE Corner Sample
SWC = SWCorner Sample
TS = Trip Spike
TB = Trip Blank
FB = Field Blank

Application Site Naming:

Site-1N Site-2NEC
Site-3E Site-4SEC
Site-5S Site-6SWC
Site-7W Site-8NWC

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

9.0 Deliverables

9.1 Air Quality Surveillance Branch Deliverables

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

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

Also provided in the application monitoring report:

- 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, etc..
- 3) Meteorological data collected at a minimum of 1 minute intervals (averages) including wind speed, wind direction, humidity, air temperature, and comments regarding degree of cloud cover.
- 4) The elevation of each sampling station with respect to the field.
- 5) The orientation of the field with respect to North (identified as either true or magnetic north). Samples collected during fog episodes will be designated as such.

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

9.2 Northern Laboratory Branch (NLB) Deliverables

Within 60 days from the last day of analysis, The NLB will provide SPM with a report that will include the following topics:

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

APPENDIX A: Standard Operating Procedure Analyses for Methomyl

The Special Analysis Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for methomyl collected by the XAD-2 resin tube method. This analytical procedure is entitled, Standard Operating Procedure Sampling and Analysis of S-methyl-((methylcarbamoyl)oxy)thioacetamide (Methomyl).

California Environmental Protection Agency

 **Air Resources Board**

DRAFT

Standard Operating Procedure

**Sampling and Analysis of S-methyl-N((methylcarbamoyl)oxy)thioacetimidate
(Methomyl)**

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

June 2007

Version 1

Approved by:

Russell Grace, Manager
Special Analysis Section

1. SCOPE

This is a high pressure liquid chromatography/mass spectrometer (LC/MS) method for the determination of S-methyl-N((methylcarbamoyl)oxy)thioacetimidate (methomyl) from application air samples.

2. SUMMARY OF METHOD

Application air samples are collected on XAD-2 cartridges. Sampled cartridges are stored at four degrees centigrade (°C) or lower prior to extraction. Sample cartridges are extracted using 50% acetonitrile and 50% water (50%ACN/H₂O) and an ultrasonic bath. Sample analysis is performed using a high performance liquid chromatograph with a mass spectrometer (LC/MS) in the selected ion-monitoring mode (SIM). Sample analysis and quantitation uses an external standard method for instrument calibration. Estimated quantitation level for this method is approximately 0.001 microgram per cubic meter ($\mu\text{g}/\text{m}^3$) prior to any sample dilution.

3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in solvents, reagents, glassware and the XAD-2 cartridges that can lead to discrete artifacts or elevated baselines. Analysis of samples containing high concentrations of early eluting pesticide components may cause significant contamination of the analytical equipment. Both a system blank and method blank must be analyzed with each batch of samples to detect any possible method or instrument interference.

4. EQUIPMENT AND CONDITIONS

A. Instrumentation

Agilent Instruments 1100 Series liquid chromatograph with LC/MSD SL analyzer (or equivalent):

Binary Pump Parameters:

Column Flow 1.0 ml/min

Stop Time 15.0 minutes

Post Time 5.0 minutes

Solvent Gradient:

25% ACN/75% H₂O at 0.0 minutes

60% ACN/40% H₂O at 10.0 minutes

80% ACN/20% H₂O at 14.0 minutes

Column:

Allure C18, 5 μm , 150 x 4.6 mm (or equivalent)

Oven Temperature at 35 degrees centigrade

Agilent LC/MSD SL Detector with Multimode Ionizer (or equivalent)

Ionization mode: MM-APCI

Polarity: Positive

Spray Chamber:

Gas (nitrogen) temperature: 350 degrees Centigrade

Vaporizer temperature: 250 degrees Centigrade

Drying Gas: 8 liters/minute

Nebulizer Pressure: 20 psig

Capillary Voltage: 2000 volts

Corona Current: 5.0 μ A

Charging Voltage: 2000 volts

Acquisition Mode: SIM

Masses: 163.10, 88.10

Fragmentor: 60, 140

Gain: 4.0

Dwell Time: 319 milliseconds

Tune File: APCI autotune

B. Auxiliary Apparatus

XAD-2 cartridges (SKC cat # 226-30-6) or equivalent

Glass amber vials, 2-ml capacity with septum caps

Sonicator

C. Reagents

Acetonitrile (B&J brand HPLC grade or equivalent)

Water Millipore 18 mohm -cm or equivalent

Methomyl 98.5% pure (Chem Service Inc. PS-1020)

D. Gases

Liquid Nitrogen at 350 psig or N₂ generator yielding 99% pure N₂ at 90 psig

5. **SAMPLE COLLECTION**

a) Samples are collected in the field with a maximum flow rate of two liters per minute (lpm).

b) After collection the samples are placed in a glass tube and stored in a cooler at 4° C or less until returned to the laboratory.

- c) Methomyl is stable for up to 28 days when kept at -20°C. See section 8F for storage stability summary.

6. **SAMPLE EXTRACTON**

- a) Prepare a method blank and laboratory control sample (LCS) cartridge with every batch of field samples not to exceed twenty (20) samples in an analytical batch.
- b) Spike the LCS with approximately 50 ng of methomyl before extraction.
- c) Carefully score and break the XAD-2 cartridge just above the glass wool plug on the primary section.
- d) Remove the glass wool plug using forceps.
- e) Pour the XAD-2 resin from the primary section into the glass vial.
- f) Retain the secondary section for later analysis to check for analyte breakthrough.
- g) Using two ml of 50% ACN/H₂O rinse the inside of the primary section into the glass vial. Cap tightly.
- h) Place all the vials in an ultrasonic bath and sonicate for 30 to 45 minutes.
- i) After sonication the extracts are ready for analysis or if not analyzed store in a refrigerator at 4° C.

7. **ANALYSIS OF SAMPLES**

- a) Transfer approximately 0.5 ml of the sample extract into a 1.5-ml autosampler vial equipped with a 0.5 ml insert. Sample extract is now ready for analysis.
- b) A 40-µl injection volume will be used for all analyses.
- c) Perform an initial calibration curve using concentrations at or near the EQL to approximately 100 times higher. At least five points must be analyzed to establish a calibration curve. Appendix 1 lists the concentrations used when the EQL is approximately 0.001 µg/m³.
- d) Prepare a sample sequence for the LC/MSD. The sequence should include a continuing calibration verification standard (CCV), and a system blank, for every ten samples analyzed. If this batch of samples includes a method blank and/or LCS, they should be run prior to field samples to verify that QC criteria have been met.
- e) Because of the nature of the XAD-2 cartridge, extraneous components will be extracted along with the analytes of interest. To minimize excessive carry over of these contaminants from one analysis to the next, a system blank should be run after every 10 to 20 samples or more frequently if indicated by sample chromatograms. In no case should a sample contaminant interfere with the peaks of interest. This will be verified by the absence of a peak in the analyte retention time window during the system blank analysis.
- f) Review and edit the quantitation reports as needed.

- g) The samples must be diluted if the analytical results are not within the calibration curve. Every attempt should be made to have the diluted results fall within the upper half of the calibration curve.
- h) The final results will be adjusted by an appropriate dilution factor and reported in µg/ml.
- i) The atmospheric concentration is calculated according to:

$$\text{Ambient Sample Conc. (}\mu\text{g/m}^3\text{)} = \frac{\text{Extract Conc. (ng/ml)} \times 2 \text{ ml}}{\text{Air Volume Sampled (m}^3\text{)} \times 1000}$$

- k) Given instrument sensitivity and a maximum sample volume of 2.9 m³ the EQL for this method will be approximately 0.001 µg/m³.

8. QUALITY ASSURANCE

A. Instrument Reproducibility

Establish the reproducibility of the instrument and analytical method as follows: analyze three different concentrations of standard (low, medium, and high levels) by injecting each five times. Table 1 lists the results for the methomyl instrument reproducibility.

TABLE 1
INSTRUMENT REPRODUCIBILITY
METHOMYL (ng/ml)

Low Level	Medium Level	High Level	
4.07	18.9	86.3	
4.02	19.3	85.4	
4.09	18.6	86.2	
3.55	18.9	85.5	
3.90	18.9	87.2	
3.93	18.94	86.14	Average
0.2196	0.2385	0.7038	Std Dev
5.588	1.259	0.817	RSD

B. Linearity

A six-point calibration is performed. Calibration standards ranging from at or near the EQL to approximately 100 times higher are used for methomyl. The results are used to calculate calibration curves using linear or quadratic regression. An r² of 0.995 or higher is required for an initial calibration to be acceptable. See Appendix 1 for an example

calibration curve. A CCV will be run at the start of each analytical batch, and after every tenth sample to verify the system linearity. The CCV quantitated value must be within 25% of the actual value.

C. Method Detection Limit

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

$$\text{MDL} = 3.143 * \text{STD}$$

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

STD equals the standard deviation of the calculated results for the seven replicate spikes. The calculated MDL for methomyl is 0.2059 ng/m³ using a two-ml extraction volume and a sample collection volume of 2.9 m³. The EQL for methomyl using a two-ml extraction volume and a sample collection volume of 2.9 m³ is 1.030 ng/m³.

D. Laboratory Control Sample

A laboratory control sample (LCS) is included with each analytical batch. The LCS stock standard should come from a different source or lot than the daily calibration standards. The analytical value of the LCS must be within three standard deviations of its historical mean. If the LCS is outside these limits then the samples in the analytical batch must be reanalyzed.

E. Collection and Extraction Efficiency (Recovery)

Collection and efficiency (recovery) data for methomyl should be established prior to sample analysis. Using three concentration levels (51, 570 and 5000 ng) the recovery for methomyl was as follows: an average recovery of 44ng with a standard deviation of 1.32 was achieved for the low level spikes, an average recovery of 532 ng with a standard deviation of 12.5 was achieved for the mid-level spikes, and an average recovery of 3900 ng with a standard deviation of 50.7 was achieved for the high level spikes. These equate to 86, 93 and 78 per cent, respectively.

F. Storage Stability

Storage stability studies were performed in triplicate using 51 ng methomyl spiked on the primary section of XAD-2 cartridges. The project was run for 28 days with cartridges being tested at 0, 7, 14, 21, and 28 days. Table 2 lists the results for the storage stability study.

Table 2
Storage Stability Study
Methomyl 2007

Day	Sample 1 %recovery	Sample 2 %recovery	Sample 3 %recovery	Average %recovery	Standard Deviation
0	107	97	97	100	5.86
7	100	99	101	100	1.13
14	89	84	83	86	3.19
21	92	94	95	94	1.75
28	88	89	89	89	0.66

G. Breakthrough

Methomyl breakthrough was evaluated at three concentrations: 51 ng, 570 ng, and 5000 ng. Three XAD-2 cartridges were spiked at each concentration level. Air was collected at approximately two lpm for 24 hours. Methomyl was not detected in the secondary sections of the XAD-2 cartridges. Average recoveries for methomyl from the primary sections were 83, 93, and 78 per cent, respectively.

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.

Appendix 1

Calibration Standard Preparation for Methomyl

The certified neat standard used for calibration was purchased from Chem Service Inc., West Chester, Pennsylvania and has the following specification:

Lot No: 344-83A
Expiration date: July 2011
Methomyl 98.5% pure (solid)

A stock standard with a concentration of approximately one-milligram (mg) per ml was prepared by weighing 25 mg of methomyl into a 25-ml volumetric flask and bringing to volume with methanol.

Using a serial dilution technique the following calibration standards were prepared in acetonitrile: 1.0, 5.0, 10.0, 20.0, 50.0, and 100.0 ng/ml.

A minimum of six standards was used to generate the calibration curve, with the standard at 1.0 ng/ml being the low point. The low point equates to approximately 0.345 ng/m³.

All standard and sample injections used a volume of 40 µl.

Initial calibration curve acceptance requires a r² of at least 0.995.

APPENDIX B:

**USE INFORMATION AND APPLICATION MONITORING RECOMMENDATIONS FOR THE PESTICIDE
ACTIVE INGREDIENT METHOMYL AND THE AMBIENT AIR MONITORING RECOMMENDATIONS FOR
METHOMYL AND CARBARYL**

http://www.cdpr.ca.gov/docs/emon/pubs/tac/recomm/methomyl_final.pdf