

California Environmental Protection Agency

 **Air Resources Board**

S-methyl-N((methylcarbamoyl)oxy)thioacetamidate (Methomyl) and 1-naphthalenylmethylcarbamate (Carbaryl) Method Development and Analytical Results for Ambient Air Monitoring Samples

**DATE: November 2008
Revision 1**

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This report 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.

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1.0 INTRODUCTION

The Department of Pesticide Regulation (DPR) requested the Air Resources Board (ARB) to conduct ambient air monitoring for S-methyl-N((methylcarbamoyl)oxy)thioacetamide (Methomyl) and 1-naphthalenylmethylcarbamate (Carbaryl). This report covers the method development and analytical and quality assurance results for methomyl and carbaryl during an ambient air study in Fresno, Tulare, and Kings Counties. DPR requested a method estimated quantitation limit (EQL) of 0.01 microgram per cubic meter ($\mu\text{g}/\text{m}^3$) for methomyl and an undefined EQL for carbaryl. The EQL achieved during this project was $0.001 \mu\text{g}/\text{m}^3$ ($1.5 \text{ ng}/\text{m}^3$) for methomyl and $0.032 \mu\text{g}/\text{m}^3$ ($32 \text{ ng}/\text{m}^3$).

2.0 METHOD DEVELOPMENT

2.1 *Overview*

XAD-2 cartridges are used to collect the air samples. After sampling, cartridges are stored at or below four (4) degrees centigrade ($^{\circ}\text{C}$) before extraction. Sample extraction is a two step process involving an initial extraction to remove the methomyl followed by the addition of more ACN to facilitate the extraction of carbaryl. Two (2) separate instrument methods are used to analyze for methomyl and carbaryl. 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 levels for this method, based on 2.9 cubic meters (m^3) of air collected, and a final extract volume of three (3) ml, is $1.5/32 \text{ ng}/\text{m}^3$ for methomyl and carbaryl respectively. Appendix A contains the standard operating procedure (SOP) for the combined extraction and analysis of methomyl and carbaryl.

2.2 *Instrument Reproducibility*

Instrument reproducibility for methomyl and carbaryl was established by analyzing both analytes at three different concentrations (low, medium and high). Both analytes were injected five (5) times at each concentration level. Forty (40) microliters (μl) of methomyl and 10 (ten) μl of carbaryl were injected. Table 1 shows the results for the three levels with the average and standard deviation for each level.

Table 1: Instrument Reproducibility

Methomyl (ng/ml)

Sample Number	Low Level	Medium Level	High Level
1	4.07	18.9	86.3
2	4.02	19.3	85.4
3	4.09	18.6	86.2
4	3.55	18.9	85.5
5	3.90	18.9	87.2
Average	3.93	18.94	86.14
SD	0.2196	0.2385	0.7038

Carbaryl (ng/ml)

Sample Number	Low Level	Medium Level	High Level
1	82.36	339.64	1531.47
2	80.35	323.68	1349.92
3	83.17	319.50	1422.17
4	86.56	324.41	1364.04
5	80.93	318.27	1441.37
Average	82.77	325.10	1421.79
SD	2.3326	8.5427	72.3076

Notes:
ml Milliliters
ng Nanograms
SD Standard deviation

2.3 Calibration Curve

Laboratory staff used standard concentrations for methomyl/carbaryl of approximately 1/16, 5/80, 10/150, 20/320, 50/700, and 100/1500 ng/ml to produce a six (6) point calibration curve. All calibrations curves performed have an r^2 (variance) greater than or equal to 0.995. Laboratory staff performed calibrations at the beginning of the monitoring program, after instrument maintenance, after remaking of external standard, and whenever the continuing calibration verification standard (CCV) did not fall within \pm 25 percent (%) of expected value.

2.4. Minimum Detection Limit (MDL)

The MDL calculation for methomyl/carbaryl follows the United States Environmental Protection Agency (USEPA) procedures for calculating MDL's. Using the analysis of seven low-level matrix spikes (5.0/80.0 ng/ml), the MDL and EQL for a three (3) ml extract is calculated as follows:

s = the standard deviation of the concentration calculated for the seven replicate spikes.

For methomyl: $s = 0.09511$ ng/ml

$$MDL = (3.14) \times (s) = (3.14) \times (0.09511) = 0.299 \text{ ng/ml.}$$

$$MDL \text{ for total ng/sample} = 0.897 \text{ ng/sample}^*$$

$$EQL = (5) \times (MDL) = (5) \times (0.2989) = 1.495 \text{ ng/ml}$$

$$EQL \text{ for total ng/sample} = 4.484 \text{ ng/sample}^*$$

For carbaryl: $s = 1.9824$ ng/ml

$$MDL = (3.14) \times (s) = (3.14) \times (1.9824) = 6.231 \text{ ng/ml.}$$

$$MDL \text{ for total ng/sample} = 18.7 \text{ ng/sample}^*$$

$$EQL = (5) \times (MDL) = (5) \times (6.231) = 31.153 \text{ ng/ml}$$

$$EQL \text{ for total ng/sample} = 93.459 \text{ ng/sample}^*$$

** assuming a 3 ml final extract volume*

Based on a total collection volume of 2.9 m³ the EQL would be 1.5/32 ng/m³ for methomyl and carbaryl. Staff report results above the EQL to two (2) significant figures. Results below the EQL but greater than or equal to the MDL are reported to one (1) significant figure. Results less than MDL are reported as less than the calculated MDL to one (1) significant figure.

2.5. Collection and Extraction Efficiency (Recovery)

Spiked XAD-2 cartridges were used to determine method field recovery. The XAD-2 cartridges were spiked with 51/300 ng, and 570/3600 ng, of methomyl/carbaryl standard. The spiked tubes were placed on field samplers and sampled at approximately two (2) liters per minute (lpm) for 24 hours at ambient temperature. The average percent recovery for methomyl/carbaryl was 86/90% with a standard deviation of 2.6/5.7% for the low level spike and 93/103% with a standard deviation of 2.2/1.4% for the high level spike.

2.6. Storage Stability

Laboratory staff completed a storage stability study which ran for 28 days with cartridges being tested at 0, 7, 14, 21, and 28 days. Methomyl and carbaryl were spiked at 52/754 ng respectively. Table 1 and 2 list 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 Dev
0	107.12	97.41	96.59	100.37	5.86
7	99.88	98.53	100.76	99.73	1.13
14	89.41	84.41	83.47	85.76	3.19
21	91.71	94.24	95.06	93.67	1.75
28	87.94	89.06	89.12	88.71	0.66

Table 3: Storage Stability Study Carbaryl 2007

Day	Sample 1 %recovery	Sample 2 %recovery	Sample 3 %recovery	Average %recovery	Standard Dev
0	79.34	78.71	72.30	76.79	3.90
7	74.30	80.53	74.63	76.49	3.50
14	56.40	70.30	58.16	61.62	7.57
21	48.12	63.58	70.27	60.65	11.36
28	69.14	61.00	71.20	67.11	5.39

2.7. Breakthrough

Three (3) XAD-2 cartridges were spiked with five (5) µg of methomyl and four (4) µg of carbaryl to evaluate analyte breakthrough. Air was collected at approximately two (2) lpm for 24 hours. Methomyl and carbaryl were not detected in the secondary (back) section of the XAD-2 cartridges. Average recovery for methomyl/carbaryl from the primary sections was $78 \pm 1.32\%$ and $103 \pm 1.41\%$ respectively.

3.0 METHOMYL AND CARBARYL AMBIENT AIR MONITORING SAMPLE RESULTS.

The laboratory received a total of 182 ambient air samples plus twelve (12) field spikes, five (5) field blank, five (5) trip blank, and five (5) trip spikes from July 7 to August 31,

2007. Table 4 presents the results for the Mendota site only. All other sites had results that were less than the MDL for both methomyl and carbaryl. The other sites were Fresno, Parlier, Rich Grove, Kettleman City, and Huron.

4.0 ANALYTICAL QUALITY CONTROL SAMPLES

4.1 System Blanks

Laboratory staff analyzes a system blank with each analytical batch, after each CCV, after every tenth sample and after samples containing high levels of methomyl, carbaryl or co-extracted contaminants. Staff defines the analytical batch as all the samples extracted together, but not to exceed twenty (20) samples. The system blank is run to insure the solvent and instrument do not contribute interferences to the analysis, and to minimize carryover from high level samples. All system blanks were less than the MDL.

4.2 Method Blanks

Laboratory staff analyzed a method blank with each analytical batch. This is an XAD-2 cartridge prepared and analyzed as described for the ambient air samples. Laboratory staff analyzed twenty (20) method blanks during this project. All method blank results were less than the MDL.

4.3 Laboratory Control Samples (LCS)

Laboratory staff analyzed a LCS with each analytical batch. The stock standard used to prepare the LCS comes from a different source or is a different lot number than the stock standard used for method calibration. A LCS is an XAD-2 cartridge spiked with 54 ng of methomyl and 757 ng of carbaryl. The LCS is extracted and analyzed as described for the samples. The LCS recoveries for methomyl and carbaryl averaged 101 and 87% with a standard deviation of 9.02 to 13.93% respectively. The acceptable LCS ranges were 74% to 128% for methomyl and 45 to 129% for carbaryl.

4.4 Continuing Calibration Verification Standards (CCV)

Following standard lab procedures, laboratory staff analyzed a CCV after every calibration curve, after every tenth (10) sample and at the end of an analytical batch. The CCV must be within $\pm 25\%$ of the expected value. If any of the CCVs are outside this limit, the affected samples are re-analyzed. The CCVs for each analytical batch are 23 and 147 ng/ml for methomyl and carbaryl respectively.

4.5 Laboratory Duplicates

No laboratory duplicates were run with this project.

5.0 FIELD, TRIP, AND LABORATORY SPIKES AND TRIP BLANKS

During the ambient air project five (5) laboratory, trip, and twelve (12) field spikes along with five (5) field blanks and five (5) trip blanks were analyzed. Laboratory staff prepared the spikes that ranged from 53.9 to 57.5 ng/sample for methomyl and from 757 to 890 ng/sample for carbaryl.

5.1 Laboratory Spikes

Table 5 presents the results of the laboratory spikes. The average recovery for methomyl and carbaryl was 103/92% with a standard deviation of 4.88/5.34% respectively. Laboratory spikes with identification number LS081707a and LS082007 were spiked at the higher range for both methomyl and carbaryl.

5.2 Trip Spikes

Table 5 presents the results of the trip spikes. The average recovery for methomyl and carbaryl was 100/93% with a standard deviation of 3.86/8.82% respectively. Trip Spikes with log numbers 37 and 106 were spiked at the higher range.

5.3 Field Spikes

Table 5 presents the results of the field spikes. Twelve (12) field spikes were analyzed during this study. Starting in week 2 of the project a pair of collocated field spikes was collected. During the collection of field spikes in week two (2) the power failed at the collection site. During week three (3) two pairs of field spikes were collected. For the weeks four, five and six a single pair of collocated spikes was collected. The spike level amounts for methomyl and carbaryl were 54 and 757 ng/sample. Recovery results for methomyl varied from 13 to 34 ng/sample and for carbaryl the results varied from 670 to 890 ng/sample. These values are not corrected for background levels. During this study all background sample results were less than the MDL. Field spikes with log numbers 35, and 36 were spiked at the higher range.

5.4 Field and Trip Blanks

Table 5 presents the results of the blanks. Six (6) each of a field and trip blank were received during this project. All results were less than the MDL.

6.0 DISCUSSION

The Laboratory received 182 ambient air field samples from six different sites. The laboratory also received 29 field quality control samples. Twelve (12) field spikes and five (5) trip spikes along with six (6) field blank and six (6) trip blank were received. Five (5) additional spikes were prepared and held at the laboratory. All results for carbaryl were less than the MDL of 18.7 ng/sample. Results for methomyl ranged from less than the MDL of 0.9 ng/sample to 28 ng/sample. Five (5) sample results were greater

then the EQL of 4.5 ng/sample. These sample results were all from the Mendota site.

Because all results reported were either less than the MDL or at the low end of the calibration curve, no back sections were analyzed.

During this study six (6) field and six (6) trip blank were analyzed. Methomyl and carbaryl were not detected in either the field or trip blanks.

Five (5) trip and five (5) laboratory spikes were analyzed during this study. Average recovery for the trip spikes was 100/93% with a standard deviation of 3.86/8.82% for methomyl and carbaryl. The laboratory spikes had an average recovery of 103/92% with a standard deviation of 4.88/5.34% for methomyl and carbaryl. No anomalous events occurred with these samples.

Twelve field spikes were analyzed during this study. All field spikes were collected from the Fresno site. Field spike recoveries overall were on the low side for methomyl which averaged 45% recovery with a range of recoveries over the six weeks study from 23% to 62%. While the recoveries for carbaryl were higher with an average of 100% and a range from 88% to 118%.

Initial breakthrough studies which were run at two liters per minute with methomyl loadings of 100 to 5000 ng resulted in recoveries ranging from 73% to 93% with no detectable breakthrough. All methomyl spikes were run at approximately 54 ng. Unlike carbaryl, methomyl may have a lower affinity for the XAD-2 resin. This is compounded by the high affinity of methomyl for water. Thus collecting methomyl in a humid environment may reduce the effectiveness of the XAD-2 and therefore lower recoveries. This is not the case for carbaryl. Carbaryl recoveries indicated that it was not affected by the ambient conditions in the field.

No other anomalous events occurred.

**Table 4: Mendota Site Ambient Air Field Data Results
Methomyl and Carbaryl 2007**

Log Number	Sample ID	Methomyl			Carbaryl		
		Date Analyzed	Sample Dilution	ng/sample	Date Analyzed	Sample Dilution	ng/sample
11	MEN1	8/13/07	1	<9E-01	8/10/07	1	<2E+01
12	MEN1CO	8/13/07	1	<9E-01	8/10/07	1	<2E+01
18	MEN2	8/17/07	1	<9E-01	8/20/07	1	<2E+01
24	MEN3	8/17/07	1	<9E-01	8/20/07	1	<2E+01
30	MEN4	8/17/07	1	<9E-01	8/20/07	1	<2E+01
46	MEN5	9/19/07	1	1.19E+01	9/18/07	1	<2E+01
47	MEN5CO	9/19/07	1	9.87E+00	9/18/07	1	<2E+01
54	MEN6	9/27/07	1	<9E-01	9/26/07	1	<2E+01
60	MEN7	9/27/07	1	<9E-01	9/26/07	1	<2E+01
66	MEN8	9/27/07	1	<9E-01	9/26/07	1	<2E+01
76	MEN9	9/28/07	1	<9E-01	9/27/07	1	<2E+01
82	MEN10	9/28/07	1	2.76E+01	9/27/07	1	<2E+01
94	MEN11	9/28/07	1	<9E-01	9/28/07	1	<2E+01
95	MEN11CO	9/28/07	1	<9E-01	9/28/07	1	<2E+01
103	MEN12	9/28/07	1	<9E-01	9/28/07	1	<2E+01
117	MEN13	9/30/07	1	<9E-01	9/29/07	1	<2E+01
118	MEN13CO	9/30/07	1	<9E-01	9/29/07	1	<2E+01
128	MEN14	9/30/07	1	<9E-01	9/30/07	1	<2E+01
134	MEN15	10/2/07	1	<9E-01	10/1/07	1	<2E+01
140	MEN16	10/2/07	1	<9E-01	10/1/07	1	<2E+01
154	MEN17	10/2/07	1	<9E-01	10/1/07	1	<2E+01
155	MEN17CO	10/2/07	1	<9E-01	10/1/07	1	<2E+01
162	MEN18	10/2/07	1	<9E-01	10/2/07	1	<2E+01
168	MEN19	10/2/07	1	<9E-01	10/2/07	1	<2E+01
174	MEN20	10/3/07	1	<9E-01	10/2/07	1	<2E+01
189	MEN21	10/4/07	1	1.24E+01	10/3/07	1	<2E+01
190	MEN21CO	10/4/07	1	1.11E+01	10/3/07	1	<2E+01
197	MEN22	10/4/07	1	<9E-01	10/3/07	1	<2E+01
203	MEN23	10/4/07	1	<9E-01	10/3/07	1	<2E+01
209	MEN24	10/4/07	1	<9E-01	10/3/07	1	<2E+01

Table 4 Notes: Ambient Air Monitoring Results 2007

If the analytical result is <MDL it is reported as less than the established method detection limit multiplied by the dilution factor. Results are reported to one significant figure. If the analytical result is ≥ MDL and <EQL it is reported in the table as the measured value to one significant figure. Levels at or above the EQL are reported as the actual measured value and are reported to two significant figures.

ng = nanogram

Sample ID (Sample Identification) numbers followed by the letters CO are collocated samples for the samples with the corresponding number.

MEN = Mendota site

**Table 5: XAD-2 Cartridge Spikes, Field and Trip Blanks
Methomyl and Carbaryl Ambient Air 2007**

Quality Control Type	Log Number	Laboratory ID	Date Analyzed	Methomyl amount (ng/sample)	Percent Recovery ¹	Carbaryl amount (ng/sample)	Percent Recovery ¹
Lab Spike		LS081707a	8/21/07	59.31	103.15*	748.65	84.12*
		LS082007	8/21/07	56.58	104.97*	732.84	96.81*
		LS082207a	9/22/07	59.25	109.93	722.61	95.46
		LS082707	9/22/07	52.35	97.12	668.19	88.27
		LS090407	9/24/07	53.91	100.02	710.52	93.86

Field Spike	35	MCA035	8/21/07	32.46	56.45*	878.49	98.71*
	36	MCA036	8/21/07	32.97	57.34*	791.94	88.98*
	70	MCA070	8/21/07	32.34	60.00	889.83	117.55
	71	MCA071	8/21/07	33.72	62.56	891.48	117.76
	97	MCA097	9/20/07	22.47	41.69	707.82	93.50
	98	MCA098	9/20/07	24.12	44.75	838.62	110.78
	122	MCA122	9/22/07	20.73	38.46	717.03	94.72
	123	MCA123	9/22/07	22.98	42.63	784.20	103.59
	144	MCA144	9/22/07	22.14	41.08	700.26	92.50
	145	MCA145	9/22/07	23.70	43.97	838.20	110.73
	179	MCA179	9/24/07	13.95	25.88	702.18	92.76
	180	MCA180	9/24/07	12.60	23.38	668.64	88.33

Trip Spike	37	MCA037	9/19/07	56.04	97.46*	785.04	88.21*
	106	MCA106	9/20/07	50.88	94.40*	723.57	95.58*
	120	MCA120	9/23/07	55.17	102.36	611.19	80.74
	156	MCA156	9/23/07	55.02	102.08	746.73	98.64
	191	MCA191	9/25/07	55.77	103.47	779.46	102.97

Trip Blank	31	MCA31	9/27/07	<0.90
	68	MCA68	9/27/07	<0.90
	104	MCA104	9/28/07	<0.90
	141	MCA141	10/1/07	<0.90
	176	MCA176	10/3/07	<0.90
	211	MCA211	10/4/07	<0.90

<18.67
<18.67
<18.67
<18.67
<18.67
<18.67

Field Blank	32	MCA32	9/27/07	<0.90
	67	MCA67	9/27/07	<0.90
	105	MCA105	9/28/07	<0.90
	119	MCA119	9/30/07	<0.90
	175	MCA175	10/3/07	<0.90
	210	MCA210	10/4/07	<0.90

<18.67
<18.67
<18.67
<18.67
<18.67
<18.67

Notes:

- 1 Field Spike levels not background subtracted.
- ID Identification
- ng Nanograms
- * Spiked at the 57.5 and 890 ng/sample for methomyl and carbaryl

Appendix A:
Standard Operating Procedure for Methomyl

California Environmental Protection Agency



Air Resources Board

DRAFT

Standard Operating Procedure

**Sampling and Analysis of S-methyl-N((methylcarbamoyl)oxy)thioacetamidate
(Methomyl) and 1-naphthalenylmethylcarbamate (Carbaryl)**

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

August 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)thioacetamide (Methomyl) and 1-naphthalenylmethylcarbamate (Carbaryl) from ambient air samples.

2. SUMMARY OF METHOD

Ambient air samples are collected on XAD-2 cartridges. Sampled cartridges are stored at 4 degrees centigrade (°C) or lower prior to extraction. Sample extraction is a two step process involving an initial extraction to remove the Methomyl followed by the addition of more ACN to facilitate the extraction of Carbaryl. Two separate instrument methods are used to analyze for Methomyl and Carbaryl. 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 and 0.032 microgram per cubic meter ($\mu\text{g}/\text{m}^3$) for methomyl and carbaryl respectively, 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 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: Methomyl

25% ACN/75% H₂O at 0.0 minutes

60% ACN/40% H₂O at 10.0 minutes

80% ACN/20% H₂O at 14.0 minutes

Solvent Gradient: Carbaryl

45% ACN/55% H₂O at 0.0 minutes
60% ACN/40% H₂O at 10.0 minutes
80% ACN/20% H₂O at 12.0 minutes

Column:

Allure C18 5um 150 x 4.6 mm (or equivalent)
Oven Temperature at 35 ° C

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

Ionization mode: MM-APCI

Polarity: Positive

Spray Chamber:

Gas (nitrogen) temperature: 350 ° C

Vaporizer temperature: 250 ° C

Drying Gas: 8 liters/minute

Nebulizer Pressure: 20 psig

Capillary Voltage: 2000 volts

Corona Current: 5.0 µA

Charging Voltage: 2000 volts

Acquisition Mode: SIM

Masses: 88.1, 145.1, 163.1, 202.1,

Fragmentor: 60, 140

Gain: 4.0

Dwell Time: 319 milliseconds

Tune File: APCI autotune

B. Auxiliary Apparatus

XAD-2 cartridges (400/200 mg) (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)

Carbaryl 99.5% pure (Chem Service Inc. PS-84)

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 (2) 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 and to a lesser extent Carbaryl is stable for up to 28 days when kept at -20°C. See section F for the 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 and 700 ng of Carbaryl 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) Carefully score and break the XAD-2 cartridge just above the glass wool plug on the secondary section.
- g) Carefully rinse the primary section glass segment with 2.0 ml of 50% ACN/H₂O into the 8 ml vial. Cap tightly.
- h) Retain the secondary section for later analysis to check for breakthrough.
- i) Place all the 8 ml vials in an ultrasonic bath and sonicate for 30 to 45 minutes.
- j) At the end of the initial sonication add 1 ml of ACN to each vial. Recap and sonicate for an additional 30 to 45 minutes.
- k) Place 8 ml vial with XAD-2 and extract into a refrigerator until analysis.

7. ANALYSIS OF SAMPLES

- a) Just prior to analysis transfer approximately 0.5 ml of the sample extract to a 1.5-ml autosampler vial equipped with a 0.5 ml insert. Sample extract is now ready for analysis.
- b) A 10 µl injection volume will be used for Carbaryl and a 40 µl injection volume for the Methomyl analyses.
- c) Perform an initial calibration curve using concentrations at or near the EQL to approximately 100 times higher. At least 5 points must be

analyzed to establish a calibration curve. Appendix 1 lists the concentrations used.

- d) Prepare a sample sequence for the LC/MSD. The sequence should include a system blank, and a calibration curve or a continuing calibration verification standard (CCV), for every 10 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 sample 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 $\mu\text{g}/\text{sample}$.
- i) The atmospheric concentration is calculated according to:

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

- k) Given instrument sensitivity and a maximum sample volume of 2.9 m^3 the EQLs for this method will be approximately $0.001 \mu\text{g}/\text{m}^3$ for methomyl and $0.032 \mu\text{g}/\text{m}^3$ for carbaryl.

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. Tables 1 and 2 list the results for the methomyl and carbaryl instrument reproducibility study.

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

TABLE 2
INSTRUMENT REPRODUCIBILITY
CARBARYL (ng/ml)

Low Level	Medium Level	High Level
82.36	339.64	1531.47
80.35	323.68	1349.92
83.17	319.50	1422.17
86.56	324.41	1364.04
80.93	318.27	1441.37

82.77	325.10	1421.79	Average
2.3326	8.5427	72.3076	Std Dev
0.02818	0.02628	0.05086	RSD

B. Linearity

A 5 or 6-point calibration is performed. Calibration standards ranging from at or near the EQL to approximately 100 times higher are used for methomyl and carbaryl. The results are used to calculate calibration curves using linear or quadratic regression. An r^2 of 0.995 or higher is required for an initial calibration to be acceptable. 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 and Carbaryl are calculated as follows:

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

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

STD equals the standard deviation of the calculated results for the seven replicate spikes. The calculated MDLs for methomyl/carbaryl are 0.2738/6.439 ng/m³ based on a 2.9 m³ sample collection volume and a 3 ml extraction volume. The EQL for methomyl/carbaryl using a three-ml extraction volume and a sample collection volume of 2.9 m³ is 1.369/32.197 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 and Carbaryl should be established prior to sample analysis. Using two concentration levels (51 and 570 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, while an average recovery of 532 ng with a standard deviation of 12.53 was achieved for the high level spikes. Carbaryl was spiked at 300ng and 3600 ng. The recovery for carbaryl was as follows: An average recovery of 270 ng with a standard deviation of 5.89 was achieved for the low level spike, while an average recovery of 3720 ng with a standard deviation of 10.6 was achieved for the high level spike.

F. Storage Stability

Storage stability studies were performed in triplicate using 52 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, 28 days. Tables 3 and 4 list the results for the storage stability study.

Table 3
Storage Stability Study
Methomyl 2007

Day	Sample 1 %recovery	Sample 2 %recovery	Sample 3 %recovery	Average %recovery	Standard Dev
0	107.12	97.41	96.59	100.37	5.86
7	99.88	98.53	100.76	99.73	1.13
14	89.41	84.41	83.47	85.76	3.19
21	91.71	94.24	95.06	93.67	1.75
28	87.94	89.06	89.12	88.71	0.66

Table 4
Storage Stability Study
Carbaryl 2007

Day	Sample 1 %recovery	Sample 2 %recovery	Sample 3 %recovery	Average %recovery	Standard Dev
0	79.34	78.71	72.30	76.79	3.90
7	74.30	80.53	74.63	76.49	3.50
14	56.40	70.30	58.16	61.62	7.57
21	48.12	63.58	70.27	60.65	11.36
28	69.14	61.00	71.20	67.11	5.39

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 liters per minute for 24 hours. Methomyl was not detected in the back section of the XAD-2 cartridges. Average recovery for methomyl from the front sections was 83, 93 and 78 per cent, respectively. Carbaryl breakthrough was evaluated at 300 and 3600 ng. As with methomyl air was collected at

two liters per minute for 24 hours. No carbaryl was detected in the back section of the XAD-2 cartridges. Average recovery for carbaryl was 90 and 103 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 and Carbaryl

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)
Carbaryl:	99.5% pure (solid)

A stock standard with a concentration of approximately 1-milligram (mg) per ml was prepared by weighing 25 mg of methomyl and 25 mg of Carbaryl 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 for methomyl and 16, 80, 150, 320, 700, 1450 ng/ml for carbaryl.

The calibration curve was generated using six standard concentrations, with the Methomyl and Carbaryl standard at 1.0/16 ng/ml being the low point. The low point equates to approximately 0.345/5.52 ng/m³ respectively.

All standard and sample injections used a volume of 40 µl for methomyl and 10 µl for carbaryl

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