Methomyl (Lannate)

Method number:	PV2114
Target concentration:	2.5 mg/m^3 (ACGIH TLV-TWA)
Procedure:	Samples are collected by drawing known volumes of air through OSHA versatile sampler (OVS-2) tubes, each containing a glass fiber filter and two sections of XAD-2 adsorbent. Samples are desorbed with acetonitrile and analyzed by high performance liquid chromatography (HPLC) using an ultraviolet (UV) detector.
Recommended air volume and sampling rate:	60 minutes at 1.0 L/min (60 Liters)
Detection limit of the overall procedure:	0.029 mg/m^3 (Based on the recommended air volume and the analytical detection limit)
Status of method:	Partially validated method. This method has been only partially evaluated and is presented for information and trial use only.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

This evaluation was undertaken to determine the effectiveness of the OVS-2 tube as a sampling device for methomyl. It follows the procedure developed for carbaryl. (Ref. 5.1)

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy).

The toxic effects of carbamate pesticides parallel those of organophosphorus pesticides. Both classes of compounds inhibit cholinesterase, thereby allowing the accumulation of large amounts of acetylcholine. The major difference being that this inhibition is reversible for carbamates and irreversible for organophosphates.

The following paragraph describing the results of this cholinesterase inhibition is excerpted from the book "OCCUPATIONAL DISEASES, A Guide to Their Recognition" and is applicable to both carbamates and organophosphates. (Ref. 5.2)

When a critical level of cholinesterase depletion is reached, usually about 20% of normal, symptoms and signs of acetylcholine accumulation poisoning become manifest. Symptoms may include blurred vision, weakness, nausea, headache, abdominal cramps, chest discomfort, and diarrhea. Signs may include miosis, muscle twitching, salivation, sweating, tearing, cyanosis, convulsions, and coma.

Carbamate pesticides can have low oral LD_{50}s but in general, their dermal LD_{50}s are higher than other cholinesterase inhibiting pesticides, such as organophosphates.

Methomyl has an acute oral LD_{50} of 25 to 40 mg/kg for rats. The acute dermal (rabbit LD_{50} is 5880 mg/kg for a 24% liquid formulation. (Ref. 5.3)

Due to these factors, methomyl has been given an exposure limit of 2.5 mg/m^3 by the ACGIH. (Ref. 5.3)

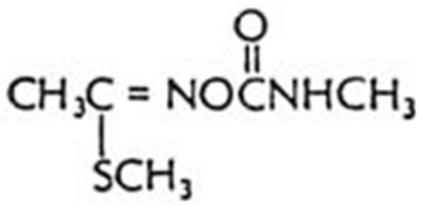
1.1.3 Potential workplace exposure

No estimate of worker exposure to methomyl could be found. Methomyl is used as an insecticide. (Ref. 5.4.)

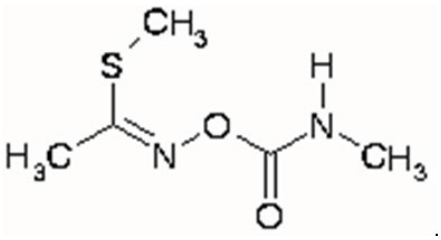
1.1.4 Physical properties (Ref. 5.3.-5.4.)

Molecular weight:	162.20
Molecular formula:	$C_5H_{10}N_2O_2S$
CAS #:	16752-77-5
IMIS #:	1644
Melting point:	78 to 79 °C
Vapor Pressure:	0.0067 Pa at 25 °C
Appearance:	white crystalline solid
Solubility:	5.8 g/100 g water, 42 g/100 g ethanol, 100 g/100 g methanol
Synonyms:	Lannate, NuBait II, Nudrin, SD 14999.
Chemical Name:	S-Methyl-N-[(methylcarbamoyl)oxy] -thioacetimidate

UV spectrum:



Structure:



1.2 Limit defining parameters

The detection limit of the analytical procedure is 8.8 ng per injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise.

2 Sampling Procedure

2.1 Apparatus

2.1.1 A personal sampling pump that can be calibrated to within ±5% of the recommended flow rate with the sampling device in line.

2.1.2 OVS-2 tubes, which are specially made 13-mm, o.d. glass tubes that taper to 6-mm o.d. They are packed with a 140-mg backup section and a 270-mg sampling section of cleaned XAD-2. The backup section is retained by two foam plugs and the sampling section is between one foam plug and a 13-mm diameter glass fiber filter. The glass fiber filter is held next to the sampling section by a polytetrafluoroethylene (PTFE) retainer.

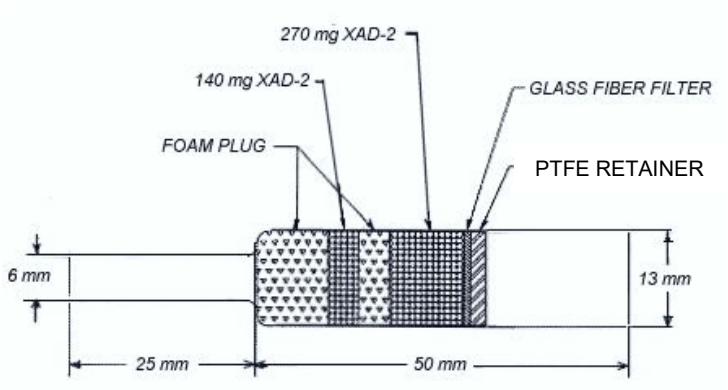


Figure 2.1.2. OVS-2 Sampling Device.

2.2 Reagents

No sampling reagents are required.

2.3 Sampling technique

2.3.1 Attach the small end of the OVS-2 sampling tube to the sampling pump with flexible, plastic tubing such that the large, front section of the sampling tube is exposed directly to the atmosphere. Do not place any tubing in front of the sampler.

2.3.2 Attach the sampler vertically (large end down) in the worker's breathing zone in such a manner that it does not impede work performance.

2.3.3 After sampling for the appropriate time, remove the sampling device and seal the tube with plastic end caps.

2.3.4 Wrap each sample end-to-end with a Form OSHA-21 seal.

2.3.5 Submit at least one blank with each set of samples. Handle the blank the same as the other samples but draw no air through it.

2.3.6 Submit any bulk samples in a separate container. Do not ship them with the air samples.

2.4 Extraction and desorption efficiencies

2.4.1 Glass fiber filter

Six 13-mm glass fiber filters were placed in separate 4-mL vials. Five of these filters were each liquid spiked with 28 µL of a 5.345 mg/mL solution of methomyl in acetonitrile. These six vials were sealed with PTFE-lined septa and stored overnight in a drawer at room temperature. They were then extracted with 2.0 mL of acetonitrile and analyzed as in Section 3.5.

Table 2.4.1
Glass Fiber Filter Extraction Study

Filter #	amount spiked, µg	amount recovered, µg	% Recovery
F1	149.66	147.56	98.6
F2	149.66	148.91	99.5
F3	149.66	149.66	100.0
F4	149.66	148.91	99.5
F5	149.66	141.13	94.3
F6	000.00	000.00	blank

average recovery = 98.4%

2.4.2 XAD-2 adsorbent

An amount of XAD-2 adsorbent equal to the sampling section (270 mg) of an OVS-2 tube was placed in each of six 4-mL glass vials which were then sealed with PTFE-lined septa. Five of these vials were then each liquid spiked with 28 µL of a 5.345 mg/mL solution of methomyl in acetonitrile by injecting the solution onto the adsorbent through the septum. After replacing the punctured septa, these vials were allowed to equilibrate overnight in a drawer at room temperature. They were then desorbed with 2.0 mL of acetonitrile and analyzed as in Section 3.5.

Table 2.4.2
XAD-2 Adsorbent Desorption Study

adsorbent #	amount spiked, μg	amount recovered, μg	% recovered
AD1	149.66	147.56	98.2
AD2	149.66	148.91	99.3
AD3	149.66	149.66	98.6
AD4	149.66	148.91	98.6
AD5	149.66	141.13	98.9
AD6	000.00	000.00	blank

average recovery = 98.7%

2.5 Retention efficiency

Six OVS-2 tubes were each liquid spiked with 28 μL of a 5.345 mg/mL solution of methomyl in acetonitrile by spiking the glass fiber filter. These tubes were then sealed with plastic end caps and placed in a drawer at room temperature. After overnight storage, 60 liters of humid air (approximately 70% relative humidity) were drawn through each tube. Three of these tubes, along with a blank tube, were then desorbed and analyzed as in Section 3. No methomyl was recovered from the backup section of these tubes.

Table 2.5
Retention Efficiency Study

tube #	amount spiked, μg	amount recovered, μg	% recovered
RET1	149.66	146.22	97.7
RET2	149.66	162.23	108.4
RET3	149.66	153.70	102.7
RET4	000.00	000.00	blank

average recovery = 102.9%

2.6 Sample storage

The remaining three spiked tubes from Section 2.5 (and a blank tube) were stored for a total of 7 days in a-drawer at room temperature. They were then desorbed and analyzed as in Section 3. No methomyl was recovered from the backup section of these tubes.

Table 2.6
Storage Study

tube #	amount spiked, μg	amount recovered, μg	% recovered
ST1	149.66	sample lost	sample lost
ST2	149.66	138.88	92.8
ST3	149.66	148.91	99.5
ST4	000.00	000.00	blank

average recovered (excluding ST1) = 96.2%

2.7 Recommended air volume and sampling rate

2.7.1 The recommended air volume is 60 L.

2.7.2 The recommended flow rate is 1.0 L/min.

2.8 Interferences (sampling)

It is not known if any compounds will interfere with the collection of methomyl. Suspected interferences should be reported to the laboratory with submitted samples.

2.9 Safety precautions (sampling)

2.9.1 Attach the sampling equipment in such a manner that it will not interfere with work performance or employee safety.

2.9.2 Follow all safety practices that apply to the work area being sampled.

3 Analytical Procedure

3.1 Apparatus

3.1.1 An HPLC equipped with a UV detector and a manual or automatic injector. A Waters 510 pump, Waters 490E UV detector and a Waters 712 autosampler were used in this evaluation.

3.1.2 An HPLC column capable of separating methomyl from any interference. A 25-cm × 4.6-mm i.d. 5 µm Chromasil C18 column was used in this evaluation.

3.1.3 An electronic integrator or other suitable means of measuring detector response. A Hewlett-Packard 3357 data system was used in this evaluation.

3.1.4 Vials, 4-mL glass with PTFE-lined septa.

3.1.5 Volumetric flasks, pipettes, and syringes.

3.2 Reagents

3.2.1 Acetonitrile, HPLC grade.

3.2.2 Water, HPLC grade. A Millipore Milli-Q system was used to prepare the water in this evaluation.

3.2.3 Methomyl. A 99+% pure standard from EPA was used in this evaluation.

3.3 Standard preparation

Prepare stock standard solutions by adding acetonitrile to preweighed amounts of methomyl in volumetric flasks. Prepare working range standards by diluting stock solutions with acetonitrile. Store stock and dilute standards in a freezer.

3.4 Sample preparation

3.4.1 Transfer the 13-mm glass fiber filter and the 270-mg sampling section of the tube to a 4-mL glass vial. Place the first foam plug and the 140-mg backup section in a separate 4-mL glass vial. A small glass funnel can be used to facilitate the transfer of the adsorbent. Discard the rear foam plug. Do not discard the glass sampling tube it can be reused.

3.4.2 Add 2.0 mL of acetonitrile to each 4-mL glass vial.

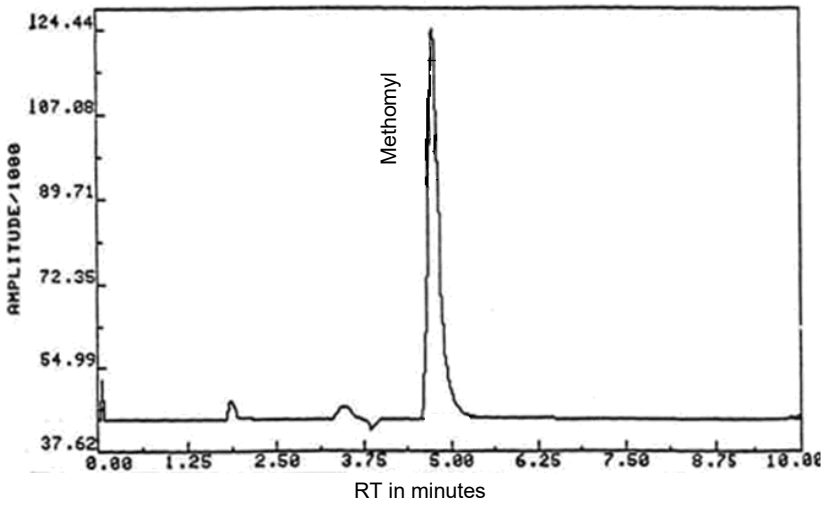
3.4.3 Seal the vials with PTFE-lined septa and allow them to desorb for one hour. Shake the vials by hand periodically during this time.

3.5 Analysis

3.5.1 Liquid chromatographic conditions

Column:	25-cm x 4.6-mm i.d., stainless steel column packed with 5 µm Chromasil C18
Mobile Phase:	(25/75) acetonitrile/water
Flow rate:	1 mL/minute
UV detector:	210 nm
Retention time:	4.7 minutes
Injection volume:	10 µL

3.5.2 Chromatogram



3.6 Interferences (analytical)

3.6.1 Any compound having a retention time similar to that of the analyte is a potential interference. Generally, chromatographic conditions can be altered to separate interferences from the analyte.

3.6.2 Retention time on a single column is not proof of chemical identity. Analysis by an alternate HPLC column, detection at another wavelength (for comparison of absorbance response ratios) and confirmation by mass spectrometry are additional means of identification.

3.7 Calculations

3.7.1 Construct a calibration curve by plotting detector response versus standard concentration (µg/mL).

3.7.2 Determine the concentration of methomyl in each sample from the calibration curve. If methomyl is found on the backup section, make blank corrections for each section separately before adding the results together.

3.7.3 Determine the air concentration by the following formula.

$$mg/m^3 = \frac{(\mu g/mL\ in\ sample)(desorption\ volume, mL)}{(air\ volume, L)(desorption\ efficiency, decimal)}$$

3.8 Safety precautions (analytical)

3.8.1 Avoid exposure to all standards.

3.8.2 Avoid exposure to all solvents.

3.8.3 Wear safety glasses and lab coats at all times while in the lab.

4 Recommendations for Further Study

4.1 Analysis at 235 nm is more sensitive (See UV spectrum). This evaluation was done at 210 nm as methomyl was being evaluated along with another carbamate pesticide, which was more sensitive at this lower wavelength.

4.2 A desorption study determining the recovery from a 13-mm glass fiber filter in combination with 270 mg of XAD-2 should be done. The resulting combined desorption efficiency is the value used in Section 3.7.3.

4.3 This method should be fully validated.

5 References

5.1 Burright, D.; Method #63, "Carbaryl"; OSHA Analytical Laboratory, unpublished, 1987.

5.2 "OCCUPATIONAL DISEASES, A Guide to their Recognition"; U.S. Department of Health, Education, and Welfare; Public Health Service, Public Health Service Publication No. 1097, U.S. Government Printing Office: Washington, D.C., 1964; p 245.

5.3 "Documentation of the Threshold Limit Values and Biological Exposure Indices", 5th ed.; American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1986; p 363.

5.4 "Farm Chemicals Handbook"; Meister Publishing Co.: Willoughby, OH, 1986; p C153.