



DIMETHOATE

Method number: PV2113

Target Concentration: 0.2 mg/m³ (0.021 ppm) Skin (Arbitrary)

Procedure: Samples are collected by drawing known volumes of air through OSHA versatile sampler (OVS-2) tubes. Each tube contains a glass fiber filter and two sections of XAD-2 adsorbent. Samples are desorbed with toluene and analyzed by gas chromatography (GC) using a flame photometric detector (FPD).

Recommended air volume and sampling rate: 480 minutes at 1.0 L/min (480 Liters)

Detection limit of the overall procedure: 0.004 mg/m³ (0.43 ppb) (Based on the recommended air volume and the analytical detection limit.)

Status of method: Partially evaluated method. This method has been 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 dimethoate. It follows the procedure developed for several other organophosphorus pesticides (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 following paragraph is excerpted from the book "OCCUPATIONAL DISEASE, A Guide to Their Recognition" (Ref. 5.2).

The organic phosphorus compounds act as irreversible inhibitors of cholinesterase, thereby allowing the accumulation of large amounts of acetylcholine. 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.

Besides being absorbed following inhalation or ingestion, organophosphorus pesticides are readily adsorbed through the intact skin (Ref. 5.2). When a particular pesticide has a low dermal LD₅₀, a skin notation should be added to the TLV or PEL.

Dimethoate has an acute oral LD₅₀ of 152 mg/Kg and acute dermal LD₅₀ of 353 mg/Kg for rats (Ref. 5.3).

Due to these factors, an arbitrary target concentration of 0.2 mg/m³, with a skin notation, was chosen for dimethoate.

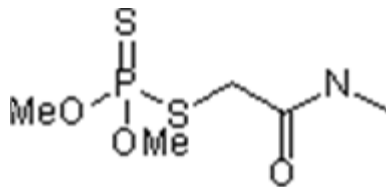
1.1.3 Potential workplace exposure

Dimethoate is a systematic insecticide/acaricide used to spray walls of farm buildings to control houseflies and in the control of insects on ornamental plants, vegetables, fruits, and farm crops. No data is available on the extent of work place exposure (Ref. 5.4).

1.1.4 Physical properties (Ref. 5.3, 5.4 and 5.5)

CAS number:	60-51-5
IMIS number:	D617
Molecular weight:	229.3
Molecular formula:	C ₅ H ₁₂ NO ₃ PS ₂
Melting point:	52 to 52.5 °C at 101.3 kPa (760 mmHg)
Solubility:	Very slightly soluble in water freely soluble in most organic solvents, except saturated hydrocarbons.
Chemical name:	Dimethoate
Synonyms:	Phosphorodithioic acid, 0,0-Dimethyl S-[2-(methylamino)-2-oxoethyl] ester; 0,0-Dimethyl S-(N-Methylcarbamoylmethyl) Phosphorodithioate; Cygon; Fostion MM; Perfekthion; Rogor; Roxion
Appearance:	White crystals

Structure:



1.2 Limit defining parameters

The detection limit of the analytical procedure, including a 12.5:1 split ratio, is 0.078 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 sample is collected by using a personal sampling pump that can be calibrated to within $\pm 5\%$ 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. tapered 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. These tubes are commercially available.

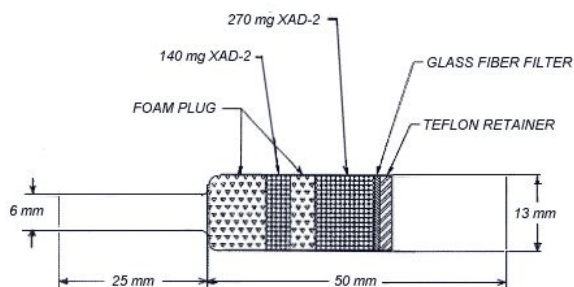


Figure 1. OVS-2 Sampling Device

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 employee'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 Record the sampling rate, time, and air volume for each sample and list any possible interference.
- 2.3.6 Submit at least one blank with each set of samples. Handle the blank in the same manner as the other samples, except that no air is drawn through it.
- 2.3.7 Submit any bulk samples for analysis in a separate container. Do not ship bulk samples with the air samples.

2.4 Desorption efficiency

A 13-mm glass fiber filter and an amount of XAD-2 adsorbent equal to the sampling section (270 mg) of an OVS-2 tube were placed in each of nine 4-ml vials. They were divided into three groups of three vials each. These groups were liquid spiked respectively with 9.5, 19, and 38 μL of 5.15 mg/mL solution of dimethoate in toluene by spiking the glass fiber filter. These amounts represent 0.5 \times , 1.0 \times , and 2.0 \times the target concentration. They were then sealed with PTFE-lined septa and allowed to equilibrate overnight in a drawer at room temperature. The tubes, along with a blank tube, were desorbed with 2.0 mL of the desorbing solution, and analyzed as in Section 3. The average desorption efficiency was 97.1%. The results are listed in Table 2.4.

Table 2.4
Desorption Efficiency

sample #	amount spiked, μg	amount found, μg	% recovered
D1	48.9	46.8	95.7
D2	48.9	47.9	98.0
D3	48.9	50.2	102.3
Average of 0.5x PEL = 98.7%			
D4	97.9	93.5	95.5
D5	97.9	92.8	94.8
D6	97.9	98.2	100.3
Average of 1.0x PEL = 96.9%			
D7	195.7	186.1	95.1
D8	195.7	189.0	96.6
D9	195.7	187.3	95.7
D10	0.0	0.0	Blank
Average of 2.0x PEL = 95.8%			

2.5 Retention efficiency

Four OVS-2 tubes were each liquid spiked with 19 μL (1 \times PEL) of 5.15 mg/mL solution of dimethoate in toluene by spiking the glass fiber filter. These were allowed to equilibrate overnight in a drawer at room temperature and then 480 L of humid air (~80% relative humidity) were drawn through each tube at 1.0 L/min. The tubes, along with a blank tube, were desorbed with 2.0 mL of desorbing solution, and analyzed as in Section 3. No analyte was observed in the backup sections. The results are listed in Table 2.5.

Table 2.5
Retention Efficiency

sample #	amount spiked, μg	amount found, μg	% recovered
R1	97.9	92.3	94.3
R2	97.9	95.3	97.3
R3	97.9	95.2	97.2
R4	97.9	98.0	100.1
R5	00.0	0.0	blank
			average = 97.2%

2.6 Sample storage

Eight OVS-2 tubes were each liquid spiked with 19 μL ($1\times$ PEL) of 5.15 mg/mL solution in toluene by spiking the glass fiber filter. These tubes were allowed to equilibrate overnight in a drawer at room temperature and then 480 L of humid air ($\sim 80\%$ relative humidity) were drawn through each tube at 1.0 L/min. The eight tubes were divided into two groups of four tubes each. The first group was stored in a drawer at ambient temperature, the second group was stored in a freezer (-5°C). After seven days, they were extracted and analyzed as in Section 3. No analyte was observed on the backup sections. The results are given in Tables 2.6.1, and 2.6.2.

Table 2.6.1
Ambient Storage

days stored	amount spiked, μg	amount found, μg	% recovered
7	97.9	94.1	96.1
7	97.9	96.3	98.4
7	97.9	97.2	99.3
7	97.9	97.0	99.0
7	00.0	00.0	blank
			average = 98.2%

Table 2.6.2
Freezer Storage

days stored	amount spiked, μg	amount found, μg	% recovered
7	97.9	96.7	98.8
7	97.9	98.7	100.8
7	97.9	96.4	98.5
7	97.9	99.2	101.3
			average = 99.9%

2.7 Recommended air volume and sampling rate

2.7.1 The recommended air volume is 480 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 dimethoate. Any 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 A GC equipped with an FPD. A Hewlett-Packard 5890A (capillary GC equipped with both an FPD operating in the phosphorus mode and a Hewlett-Packard 7673A Autosampler was used in this evaluation.

3.1.2 A GC column capable of separating dimethoate from any interference. A 30-m × 0.32-mm i.d. (0.5 µm d_r DB-210) capillary column was used in this evaluation.

3.1.3 An electronic integrator or some other suitable means to measure detector response. Waters 860 Networking Computer System was used in this evaluation.

3.1.4 Volumetric flasks, pipettes, and syringes for preparing standards, making dilutions and performing injections.

3.1.5 Glass vials 2-mL and 4-mL, with PTFE-lined caps.

3.1.6 Mechanical shaker.

3.2 Reagents

3.2.1 GC grade Hydrogen, air, and nitrogen.

3.2.2 Dimethoate. A 99% pure standard from EPA was used in this evaluation.

3.2.3 Toluene. The toluene used in this evaluation was purchased from Burdick and Jackson.

3.2.4 Tributyl phosphate. The tributyl phosphate was used as the internal standard and was purchased from Aldrich Chemical Company Inc.

3.2.5 Desorbing solution. If an internal standard procedure is used, the desorbing solution is prepared by adding 8 µL of tributyl phosphate to 100 mL of toluene. Otherwise, toluene is used alone.

3.3 Standard preparation

Prepare stock standards by adding either toluene or the desorbing solution (toluene plus internal standard) to preweighed amounts of dimethoate. Prepare working range standards by diluting stock solutions with either toluene or the desorbing solution. 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 after it has been cleaned by surfactant or solvent washing.
- 3.4.2 Add 2.0 mL of either toluene or the desorbing solution (toluene plus internal standard) to each vial and seal with a PTFE-lined cap.
- 3.4.3 Shake the vials on a mechanical shaker for half an hour.
- 3.4.4 If necessary, transfer aliquots of the samples to the vials used in GC analysis. In this evaluation, the samples were transferred to 2-mL glass vials, sealed with PTFE-lined septa, and loaded on the automatic sampler.

3.5 Analysis

3.5.1 Instrument conditions

Column 30 m × 0.32 mm i.d., (0.5 µm d_f DB-210)

Instrument temperatures

Injector temperature: 200 °C
Detector temperature: 250 °C
Column temperature: 160 °C
Temperature program: hold initial temp 1 min, increase temp at 16 °C/min to 200 °C, hold final temp. 7 min

FPD conditions

Hydrogen flow rate: 200 mL/min
Airflow rate: 100 mL/min
Nitrogen flow rate: 30 mL/min
Head Pressure: 7.5 psi

Injection volume

1 µL

Split ratio

12.5:1

Retention time

4.5 min (tributyl phosphate)
7.5 min (dimethoate)

3.5.2 Chromatogram

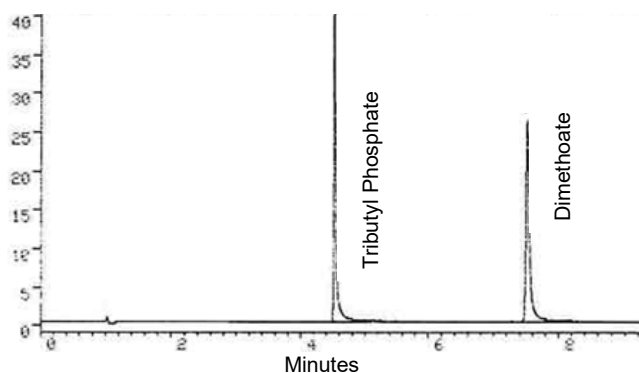


Figure 2. Chromatogram of Dimethoate at the target level.

3.5.3 Measure detector response using a suitable method such as electronic integration.

3.6 Interferences

3.6.1 Any collected compound which produces an FPD response and has a similar retention time as dimethoate is a potential interference.

3.6.2 GC conditions may generally be varied to circumvent interferences.

3.6.3 Retention time on a single column is not proof of chemical identity. Analysis by an alternate GC column, high performance liquid chromatograph (HPLC), and confirmation by GC/Mass Spectrometry are additional means of identification.

3.7 Calculations

3.7.1 An internal standard (ISTD) calibration method was used. A calibration curve was constructed by plotting concentration of analyte per mL versus ISTD-corrected response of standard concentration ($\mu\text{g/mL}$) of dimethoate. Bracket the samples with prepared analytical standards over a range of concentrations.

3.7.2 Determine the $\mu\text{g/mL}$ of dimethoate in both sections of each sample and blank from the calibration curve. If dimethoate is found on the backup section, it is added to the amount found on the front section. Blank corrections should be performed before adding the results together.

3.7.3 Determine the air concentration by using the following formula.

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

$$\text{ppm} = \frac{(\text{mg} / \text{m}^3)(24.46)}{(229.3)}$$

Where: 24.46 = molar volume (liters) at 101.3 kPa (760 mmHg) and 25 °C
229.3 = molecular weight of dimethoate

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and air exposure to dimethoate.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses and a lab coat in the laboratory.

4 Recommendation for Further Study

This method should be fully validated.

5 References

5.1 Burright, D.; Methods #62, "Chlorpyrifos, DDVP, Diazinon, Malathion, and Parathion"; OSHA Analytical Laboratory, unpublished, 1986.

- 5.2 "OCCUPATIONAL DISEASE, 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 Sax, N. Irving, Dangerous Properties of Industrial Materials. Van Nostrand Reinhold Company, 1981; p 608.
- 5.4 "Farm Chemicals Handbook"; Meister Publishing Co.: Willoughby, OH, 1986; p C113.
- 5.5 Windholz, M., Budavari, S., Blumetti, RF., and Otterbein, E., The Merck Index, 10th ed., Merck & CO., Inc., Rahway, N.J., 1983; p469.