Method number:	PV2099
Target concentration:	0.25 mg/m^3 Skin (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 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 L)
Detection limit of the overall procedure	0.0073 mg/m^3 (based on the recommended air volume)
Status of method:	Partially validated method. This method has only 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 dicrotophos. 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 DISEASES, 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 absorbed through the intact skin (Ref 5.2). When a particular pesticide has a low dermal LD_{50}, a skin notation should be added to the TLV or PEL.

Dicrotophos has an acute oral LD_{50} of 16 to 21 mg/kg for rats and an acute dermal LD_{50} of 42 to 43 mg/kg for rats. (Ref. 5.3)

Due to these and other factors, the ACGIH has established a TLV-TWA of 0.25 mg/m^3, with a skin notation, for dicrotophos. (Ref. 5.4)

In March 1989, OSHA adopted this same value as its PEL. Editorial Note: These March 1989 PELs were vacated on July 7, 1992 and ceased to be enforceable on March 23, 1993 (FR 58:35338-35351, 6/30/1993).

1.1.3 Potential workplace exposure

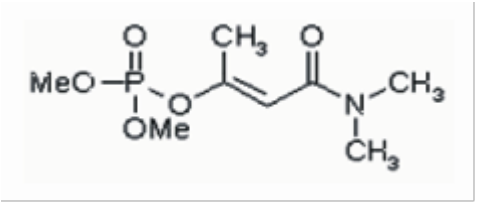
No estimate of worker exposure to dicrotophos could be found. Dicrotophos is used as a contact and systemic insecticide. (Ref. 5.5)

1.1.4 Physical properties (Ref. 5.3-5.5)

CAS #	141-66-2
IMIS #	0902
Molecular weight:	237.21
Molecular formula:	$C_8H_{16}NO_5P$
Boiling point:	400 °C
Vapor pressure:	no information found
Appearance:	brown liquid (commercial grade)
Solubility:	miscible with water and many organic solvents (i.e., acetone, alcohol, xylene, and isobutanol)
Synonyms:	Bidirl, Bidrin, C 709, Carbicron, Diapadrin, Ektafos, ENT 244842, SD 3562

Chemical name: dimethyl cis-2-dimethyl-carbamoyl-1-methylvinyl phosphate

Structure:



1.2 Limit defining parameters

The detection limit of the analytical procedure is 0.13 ng per injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise. This detection limit takes into account a split ratio of 13.4 to 1 used on the capillary GC.

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 are 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. (Figure 1)

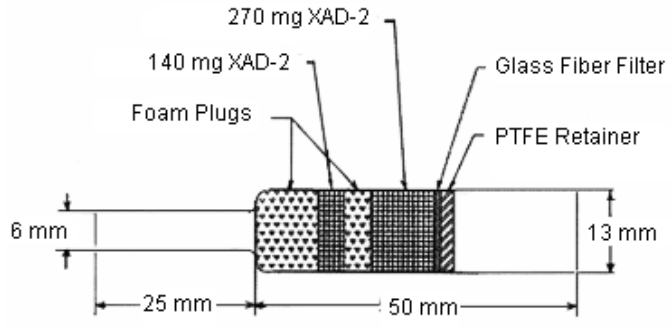


Figure 1 OVS-2 tube

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 do not draw air through it.

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

2.4 Desorption efficiency

A 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 six, 4-mL vials. These vials were then sealed with PTFE-lined septa.

Five of these vials were each liquid spiked with 27 µL of a 4.37 mg/mL solution of dicrophotos in toluene by injecting through the septum onto the glass fiber filter. After replacing the punctured septums, these vials were allowed to equilibrate overnight in a closed drawer at room temperature. They were then desorbed with 2.0 mL of toluene containing triphenyl phosphate (TPP) as an internal standard and analyzed as in Section 3.5.

Table 2.4
Desorption Study

tube #	µg spiked	µg recovered	% recovered
1	118.0	109.5	92.8
2	118.0	107.6	91.2
3	118.0	106.1	89.9
4	118.0	103.8	88.0
5	118.0	102.9	87.2
6	0.00	0.00	blank

average recovery = 89.8%

2.5 Retention efficiency

Six OVS-2 tubes were each liquid spiked with 27 µL of a 4.37 mg/mL solution of dicrotophos in toluene 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, 480 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 3.5. No dicrotophos was found on the backup sections of these tubes.

Table 2.5
Retention Efficiency Study

tube #	µg spiked	µg recovered	% recovered
1	118.0	107.9	91.4
2	118.0	106.8	90.5
3	118.0	110.7	93.8
4	118.0	0.00	blank

average recovery = 91.9%

2.6 Sample Storage

The remaining three spiked tubes from Section 2.5 (and a blank tube) were stored for a total of 8 days in a drawer at room temperature. They were then desorbed and analyzed as in Section 3.5. No dicrotophos was found in the backup sections of these tubes.

Table 2.6
Storage Study

tube #	µg spiked	µg recovered	% recovered
1	118.0	111.9	94.8
2	118.0	104.0	88.1
3	118.0	106.7	90.4
4	118.0	0.00	blank

average recovery = 91.1%

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 dicrotophos. 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 capillary 5890A GC, equipped with both an FPD operating in the phosphorus mode and a Hewlett-Packard 7673A automatic sampler was used in this evaluation.

3.1.2 A GC column capable of separating dicrotophos from any interference. A 45-m × 0.2-mm i.d. (0.25-µm d_f SE-54) capillary column was used in this evaluation and is available from Supelco, Inc., Bellefonte, PA.

3.1.3 An electronic integrator or other suitable means of measuring detector response. A Hewlett-Packard 3392A Integrator and a Hewlett-Packard 3357 data system were used in this evaluation.

3.1.4 Vials, 2-mL and 4-mL glass with capped PTFE-lined septa.

3.2 Reagents

3.2.1 Hydrogen, air, and nitrogen, GC grade.

3.2.2 Toluene, Pesticide grade.

3.2.3 Dicrotophos. A 95% pure standard from EPA was used in this evaluation.

3.2.4 Triphenyl phosphate (TPP), practical grade from J.T. Baker. If an internal standard method is used, the desorbing solution is prepared by adding the internal standard to the toluene. A 40 µg/mL solution of TPP was used as the internal standard in this evaluation.

3.3 Standard preparation

Prepare stock standards by adding either toluene or desorbing solution (if an internal standard is used) to preweighed amounts of dicrotophos. Prepare working range standards by diluting stock solutions with either toluene or desorbing solution (if an internal standard is used). 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 vial. Place the first foam plug and the 140-mg backup section in a separate 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 either toluene or the desorbing solution (if an internal standard is used) to each 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.

3.4.4 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 Analytical conditions (These conditions were developed for a series of organophosphorus pesticides, which was run in several groups. (See Figure 2)

GC Conditions

GC column: 45-m × 0.2-mm i.d. (0.25 µm d_f SE-54) capillary

Carrier gas:	hydrogen
Flow rate:	2.05 mL/min at 220 °C
Split ratio:	13.4 to 1 at 220 °C
Retention time:	4.40 min

Injector conditions

Temperature:	250 °C
Volume:	1 µL

Oven temperature program

Initial temperature:	220 °C
Initial time:	5 min
Rate:	15 °C/min
Final temperature:	260 °C
Final time:	15 min

FPD conditions

Hydrogen flow rate:	75 mL/min
Airflow rate:	100 mL/min
Auxiliary gas:	nitrogen
Flow rate:	28 mL/min
Temperature:	250 °C

3.5.2 Chromatogram

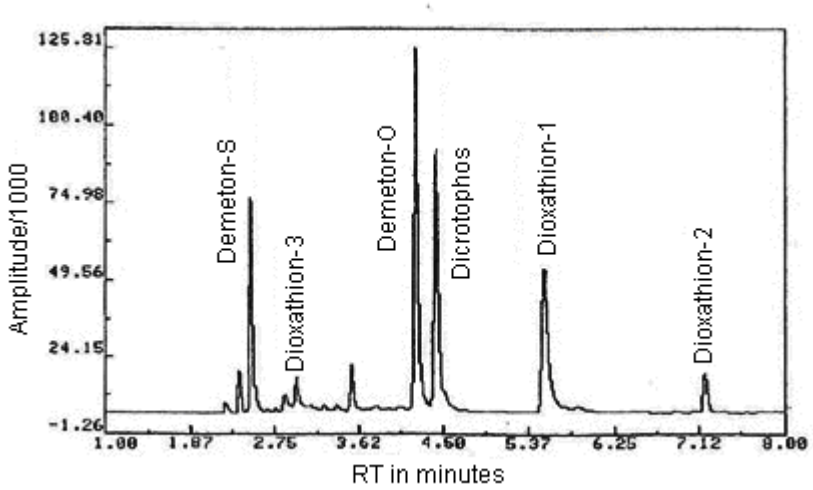


Figure 2 Chromatogram of Dicrotophos.
(This chromatogram also contains other pesticides.)

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 GC column 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.

3.7.2 Determine the concentration of dicrotophos in each sample from the calibration curve. If dicrotophos 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:

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

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, gloves, and a lab coat at all times in laboratory areas.

4 Recommendations for Further Study

This method should be fully validated.

5 References

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

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 Windholz, H., Ed.; "Merck Index," 10th ed.; Merck and Co.: Rahway, NJ, 1983; p 449.

5.4 "Documentation of the Threshold Limit Values and Biological Exposure Indices," 5th ed.; American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1986; p 193.

5.5 "Farm Chemicals Handbook"; Meister Publishing Co.: Willoughby, OH, 1986; p C82.