Method number:	PV2063
Target Concentration:	1.0 mg/m^3 with a skin notation (Arbitrary). There is no OSHA permissible exposure level (PEL) or ACGIH threshold limit value (TLV) for cypermethrin.
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 desorbing solution (see Section 3.2) and analyzed by gas chromatography (GC) using an electron capture detector (ECD).
Recommended air volume and sampling rate:	60 minutes at 1.0 L/min (60 L)
Detection limit of the overall procedure:	0.014 mg/m^3 (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.
Special Requirement:	Samples should be refrigerated.

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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 cypermethrin. It follows the procedure developed for pyrethrum (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)

Besides being absorbed following inhalation or ingestion, cypermethrin is readily adsorbed 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.

Cypermethrin has an acute oral LD_{50}, of 70 mg/Kg and acute dermal LD_{50} of 500 mg/Kg for rats (Ref. 5.4).

Due to these factors an arbitrary target concentration of 1.0 mg/m^3 with a skin notation, was chosen for cypermethrin.

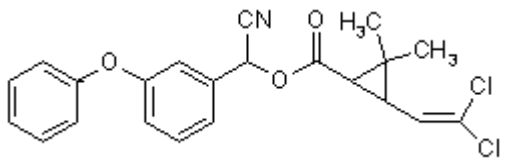
1.1.3 Potential workplace exposure

Cypermethrin is an insecticide/pesticide used to control insects on ornamental plants, vegetables, fruits, farm crops, and on pets. It can also be used for termite control. No data is available on the extent of work place exposure (Ref. 5.3).

1.1.4 Physical properties (Ref. 5-3, 5.4 and 5.5)

CAS number:	52315-07-8
IMIS number:	C628
Molecular weight:	416.3
Molecular formula:	$C_{22}H_{19}CL_2NO_3$
Melting point:	60 to 80 °C at 101.3 kPa (760 mmHg)
Solubility:	insoluble in water, soluble in methanol, acetone, xylene, methylene chloride
Synonyms:	cypermethrin
Chemical name:	3-(2,2-Dichloroethenyl)-2,2,-di-methylcyclopropanecarboxylic acid cyano (3-phenoxyphenyl) methyl ester
Trade names:	Cypercopal, Cyperkill, Cyperma
Appearance:	colorless crystals (pure isomer)

Structure:



1.2 Limit defining parameters

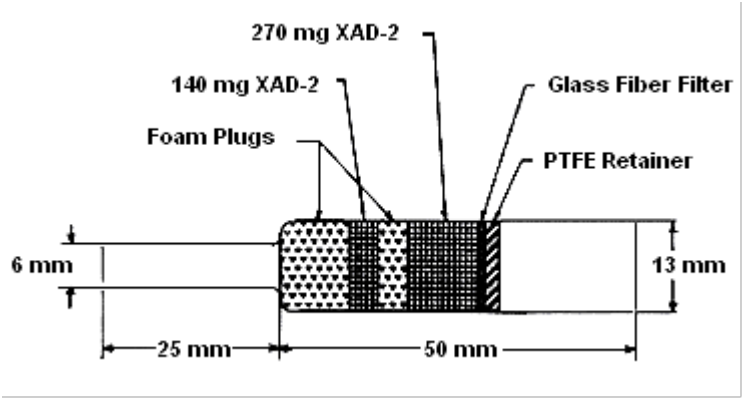
The detection limit of the analytical procedure, including an 11:1 split ratio, is 0.012 ng per injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise.

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 ±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 XAD-2 adsorbent. 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 (i.e., SKC, Supelco).



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 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 eighteen 4-mL vials. They were divided into three groups of six vials each. These groups were liquid spiked respectively with 22, 12, and 2 µL of

2.65 mg/mL solution of cypermethrin in toluene by spiking the glass fiber filter. These amounts represent 1.0×, 0.5×, and 0.1× the target concentration. They were then sealed with PTFE-lined septa and allowed to equilibrate overnight in a drawer at room temperature. The vials, along with a blank vial, were desorbed with 3.0 mL of the desorbing solution, and analyzed as in Section 3. The average desorption efficiency was 97.03%. The results are listed in Table 2.4.

Table 2.4
Desorption Efficiency

sample #	µg spiked	µg found	% recovered
D1	60.95	58.44	95.88
D2	60.95	60.72	99.62
D3	60.95	60.99	100.06
D4	60.95	56.97	93.47
D5	60.95	59.37	97.47
D6	60.95	61.05	100.16
Average of 1× TC = 97.70%			
D7	31.8	32.97	103.67
D8	31.8	30.78	96.79
D9	31.8	29.43	92.54
D10	31.8	30.57	96.13
D11	31.8	31.56	99.24
D12	31.8	30.15	94.81
Average of 0.5× TC = 97.19%			
D13	5.3	5.16	97.35
D14	5.3	5.58	105.28
D15	5.3	4.98	93.96
D16	5.3	4.95	93.39
D17	5.3	5.16	97.35
D18	5.3	4.77	90.00
Average of 0.1× TC = 96.22%			

2.5 Retention efficiency

Six OVS-2 tubes were each liquid Spiked with 22 µL (1× TC) of 2.65 mg/mL solution of cypermethrin in toluene by spiking the glass fiber filter. These were allowed to equilibrate overnight in a drawer at room temperature and then 60 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 3.0 mL of desorbing solution, and analyzed as in Section 3. No analyte was observed in backup sections. The results are listed in Table 2.5.

Table 2.5
Retention Efficiency

sample #	µg spiked	µg found	% recovered
R1	60.95	58.23	95.53
R2	60.95	56.70	93.02
R3	60.95	58.95	96.71
R4	60.95	60.30	98.93
R5	60.95	57.54	94.40
R6	60.95	57.54	94.40
Average = 95.54%			

2.6 Sample storage

Twelve OVS-2 tubes were each liquid spiked with 22 µL (1× TC) of a 2.65 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 60 L of humid air (80% relative humidity) were drawn through each tube at 1.0 L/min. The twelve tubes were divided into two groups of six tubes each. The first group was stored in a drawer at ambient temperature, the second group was stored in a freezer (- 5 °C). After fifteen days, they were extracted and analyzed as in Section 3. No analyte was observed in backup sections. The results are given in Tables 2.6.1 and 2.6.2.

Table 2.6.1
Ambient Storage

days stored	µg spiked	µg found	% recovered
15	60.95	49.92	81.90
15	60.95	50.25	82.24
15	60.95	47.04	77.17
15	60.95	42.12	69.10
15	60.95	54.36	89.18
15	60.95	46.50	76.29

Average = 78.31%

Table 2.6.2
Freezer Storage

days stored	µg spiked	µg found	% recovered
15	60.95	54.51	89.43
15	60.95	53.85	88.35
15	60.95	60.51	99.27
15	60.95	54.81	89.92
15	60.95	57.15	93.76
15	60.95	60.84	99.81

Average = 93.42%

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 cypermethrin. 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 ECD. A Hewlett-Packard 5890A GC (capillary) equipped with both an ECD and a Hewlett-Packard 7673A Autosampler was used in this evaluation.

3.1.2 A GC column capable of separating cypermethrin from any interference. A 45-m x 0.32-mm i.d., (0.25 µm d_f SE-30) capillary column was used in this evaluation.

3.1.3 An electronic integrator or some other suitable means to measure detector response. A 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 Vials, 2-mL and 4-mL with PTFE-lined caps.

3.1.6 Mechanical shaker.

3.2 Reagents

3.2.1 Cypermethrin. A 99% pure standard obtained from EPA was used in this evaluation.

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

3.2.3 p-Chlorobiphenyl. The p-chlorobiphenyl was purchased from ICN.

3.2.4 Desorbing solution. If an internal standard (ISTD) is used, the desorbing solution is prepared by adding 8 µL of p-chlorobiphenyl to 100 mL of toluene. Otherwise, toluene alone can be used.

3.3 Standard preparation

Prepare stock standards by adding desorbing solution to preweighed amounts of cypermethrin. Prepare working range standards by diluting stock solutions with 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 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 after it has been cleaned by surfactant or solvent washing.

3.4.2 Add 3.0 mL of desorbIng solution 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 appropriate GC vials. 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: 45-m × 0.32-mm i.d., (0.25 µm d_f SE-30)

Temperature:
Injector temperature: 250 °C
Detector temperature: 300 °C
Column temperature: 230 °C

Head pressure: 12 psi

FPD conditions:
hydrogen flow rate: 2 mL/min
Injection volume: 1 µL

Split ratio: 11:1

Retention time: There are four distinctive peaks of Cypermethrin (Retention time window 9.9 to 10.4 minutes)

3.5.2 Chromatogram

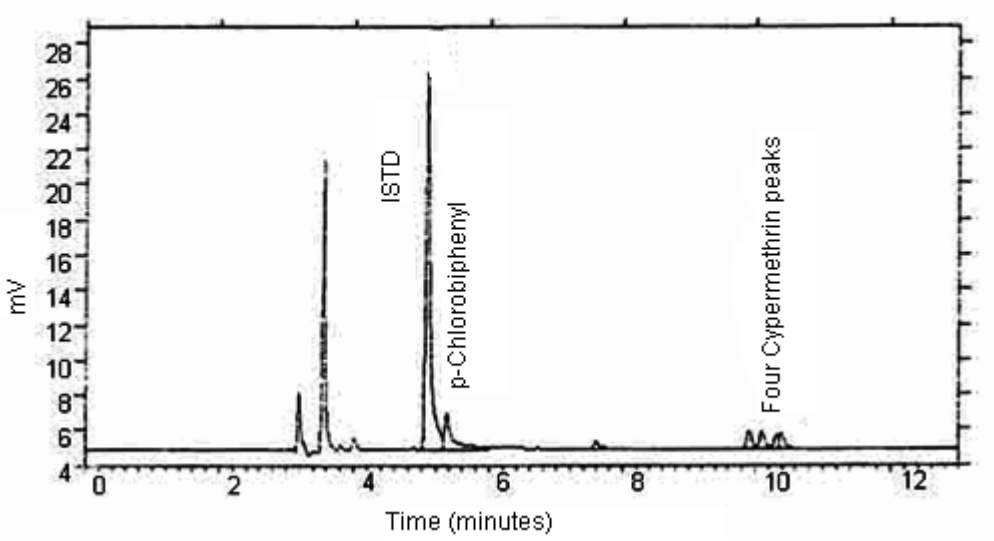


Figure 2. Chromatogram of cypermethrin.

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

3.6 Interferences (analytical)

3.6.1 Any collected compound which produces an ECD response and has a similar retention time as cypermethrin 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 chromatography (HPLC) and confirmation by mass spectrometry are additional means of identification.

3.7 Calculations

3.7.1 A calibration curve may be constructed by plotting the concentration of analyte (ug/mL) versus detector response of the cypermethrin standards. Cypermethrin has 8 possible isomers. The standard used has 4 distinctive peaks. Therefore, peak summation is advised for calculation. Bracket the samples with prepared analytical standards over a range of concentrations.

3.7.2 Determine the concentration of cypermethrin in both sections of each sample and blank from the calibration curve. If cypermethrin 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.

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

$$(ppm)(MW) = (mg/m^3)(24.46)$$

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

Where:

24.46 = molar volume (liters/mole) at 101.3 kPa (760 mmHg) and 25 °C
416.3 = molecular weight (g/mole) of cypermethrin

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and air exposure to cypermethrin.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses, gloves and a lab coat while working in the laboratory.

4 Recommendation for Further Study

This method should be fully validated.

5 References

5.1 Burright, D.; Methods #70 "PYRETHRUM"; OSHA Analytical Laboratory, Salt Lake City, UT, published, 1988.

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

5.3 Cypermethrin material safety data sheet, OCCUPATIONAL HEALTH SERVICES.

5.4 "Farm Chemicals Handbook"; Meister Publishing Co.: Willoughby, OH, 1990; PP C99-100.

5.5 Windholz, H., Budavari, S., Blumetti, RF., and Otterbeint Lr., The Merck Index, 11th ed., Merck & CO., Inc., Rahway, N.J., 1983; p 434.