PIPERONYL BUTOXIDE

Method no.	PV2110
Target concentration:	10 mg/m³ (Arbitrary). There is no OSHA permissible exposure level (PEL) or ACGIH threshold limit value (TLV) for piperonyl butoxide.
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 methanol and analyzed by high performance liquid chromatography (HPLC) using an ultraviolet (UV) detector.
Recommended air volume and sampling rate:	30 minutes at 1.0 L/min (30 Liters)
Detection limit of the overall procedure:	0.08 mg/m³ (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:	Ship promptly and refrigerate sample upon receiving in the lab.

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Yogi Shah

Organic Service Branch II
OSHA Salt Lake Technical Center
Salt Lake City UT

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 piperonyl butoxide. It follows the sampling 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)

Piperonyl butoxide is an "insecticide synergist". It appears in the "Toxic Substance Control Act's" initial inventory.

Some of the oldest naturally occurring insecticides are the pyrethrins. These botanical insecticides and their synthetic analogs, the pyrethroids, decompose in the environment. In order to increase their effective lifetime, synergist like piperonyl butoxide is added.

Piperonyl butoxide is commonly used in spray formulation as a synergist. Even though it is relatively nontoxic, its extensive use has generated interest among industrial hygienist and regulatory officials. It has an Oral LD_{50} >7500 mg/kg for rat (Ref.5.3).

Due to these factors, an arbitrary target concentration of 10 mg/m³ was chosen for piperonyl butoxide.

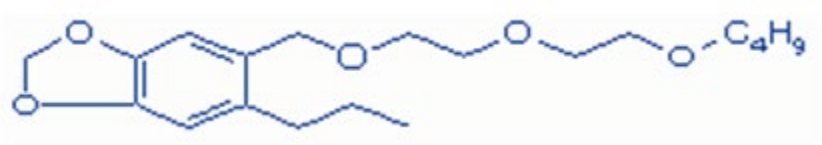
1.1.3 Potential workplace exposure

No data is available on the extent of work place exposure (Ref. 5.3).

1.1.4 Physical properties (Ref. 5.2, 5.3)

CAS number:	51-03-6
IMIS number:	P209
Molecular weight:	338.43
Molecular formula:	$C_{19}H_{30}O_5$
Solubility:	Soluble in methanol, ethanol, benzene, freons, and oils
Synonyms:	Piperonyl butoxide, Butacide
Chemical name:	Butyl carbitol 6-propyl piperonyl ether
Appearance:	Light brown liquid

Structure:



1.2 Limit defining parameters

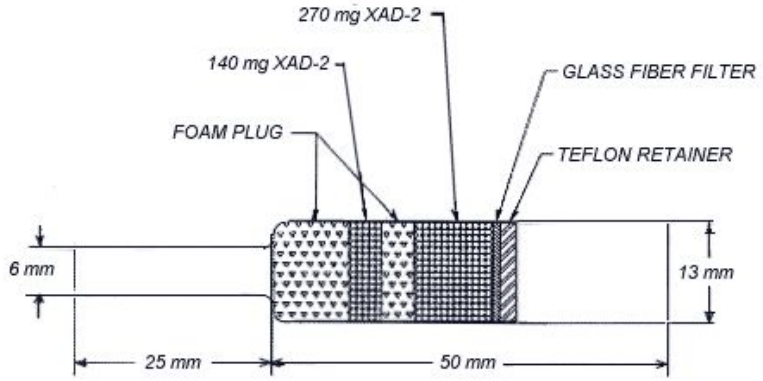
The detection limit of the analytical procedure is 0.08 ng per injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise.

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 from SKC and 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 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 twelve 4-mL vials. They were divided into three groups of four vials each. These groups were liquid spiked respectively with 10, 5, and 1 μL of a 29.7 mg/mL solution of piperonyl butoxide in methanol by spiking the glass fiber filter. These amounts represent 1.0x, 0.5x, and 0.lx the target concentration (TC). 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 methanol, and analyzed as in Section 3. The overall average desorption efficiency was 93.9%. The results are listed in Table 2.4.

Table 2.4
Desorption Efficiency

Sample #	amount spiked (μg)	amount found (μg)	% recovered
D1	297.0	281.5	94.8
D2	297.0	290.7	97.9
D3	297.0	281.2	94.7
D4	297.0	288.5	97.1
			Av. of 1x TC = 96.1%
D5	148.5	142.9	96.2
D6	148.5	137.0	92.3
D7	148.5	141.1	95.0
D8	148.5	138.5	93.3
			Av. Of .5x TC = 94.2%
D9	29.7	26.9	90.7
D10	29.7	26.6	89.4
D11	29.7	29.0	97.7
D12	29.7	26.0	87.5
			Av. of .1x TC = 91.3%

2.5 Retention efficiency

Four OVS-2 tubes were each liquid spiked with 10 μL 1x TC of a 29.7 mg/mL solution of piperonyl butoxide in methanol by spiking the glass fiber filter. These were allowed to equilibrate overnight in a drawer at room temperature and then 30 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 methanol, 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	297.0	270.5	91.1
R2	297.0	274.3	92.4
R3	297.0	265.0	89.2
R4	297.0	282.2	95.0
			average = 91.9%

2.6 Sample storage

Eight OVS-2 tubes were each liquid spiked with 10 µL 1x TC of a 29.7 mg/mL solution of piperonyl butoxide in methanol by spiking the glass fiber filter. These tubes were allowed to equilibrate overnight in a drawer at room temperature and then 30 L of humid air (~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 (-50 °C). After fifteen days, they were extracted and analyzed as in section 3. No analyte was observed in 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
15	297.0	257.3	86.6
15	297.0	249.8	84.1
15	297.0	262.5	88.4
15	297.0	236.7	79.7
			average = 84.7%

Table 2.6.2
Freezer Storage

days stored	amount spiked (μg)	amount found (μg)	% recovered
15	297.0	280.0	94.3
15	297.0	258.6	87.1
15	297.0	270.1	90.9
15	297.0	269.0	90.6
			average = 90.7%

2.7 Recommended air volume and sampling rate

2.7.1 The recommended air volume is 30 L.

2.7.2 The recommended flow rate is 1.0 L/min.

2.8 Interferences (sampling)

It is not known if any compound will interfere with the collection of piperonyl butoxide. 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 high performance liquid chromatograph equipped with an ABI 785 variable wavelength UV detector and Waters 717 autosampler was used in this evaluation.

3.1.2 An HPLC column capable of separating piperonyl butoxide from any interference. A 25-cm x 4.6-mm i.d. (5-µm Supelco LC-DB-18) 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, 4-mL, with PTFE-lined caps.

3.1.6 Mechanical shaker.

3.2 Reagents

3.2.1 Piperonyl butoxide. A 99% pure standard from EPA was used in this evaluation.

3.2.2 Methanol. The methanol used in this evaluation was purchased from Burdick and Jackson.

3.2.3 Acetonitrile. The ACN used in this evaluation was purchased from Burdick and Jackson.

3.2.4 Water. HPLC grade water was obtained from Millipore Milli-O water purification system.

3.3 Standard preparation

Prepare stock standards by adding methanol to preweighed amounts of piperonyl butoxide. Prepare working range standards by diluting stock solutions with methanol. 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 methanol to each vial and seal with a PTFE-lined cap.

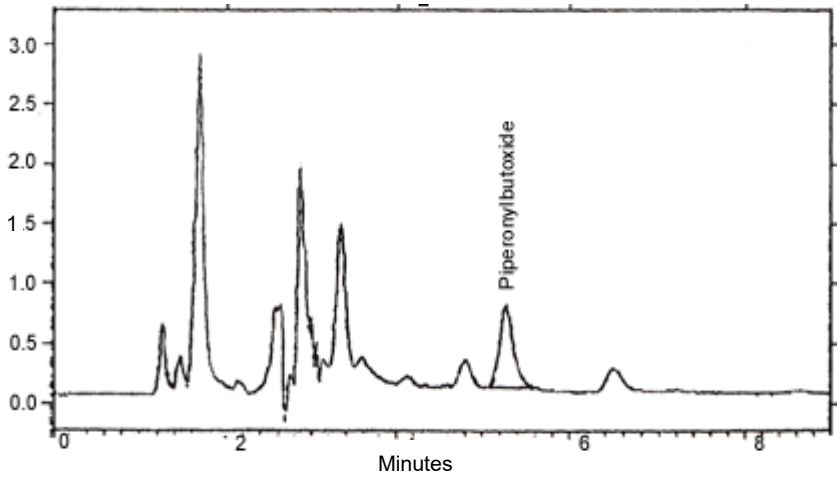
3.4.3 Shake the vials on a mechanical shaker for half an hour.

3.5 Analysis

3.5.1 Instrument conditions

Column:	25-cm × 4.6-mm id, (5-µm Supelco LC-DB-18)
Mobile phase:	ACN/Water (75%/25%)
Flow rate:	1 mL/min
Injection volume:	10 µL
Detector wavelength:	230 nm
Retention time:	6.00 min for Piperonyl butoxide.

3.5.2 Chromatogram of piperonyl butoxide at detection level.



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 absorbs at 230 nm and has a similar retention time as piperonyl butoxide is a potential interference.

3.6.2 HPLC 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 HPLC column and confirmation by mass spectrometry are additional means of identification.

3.7 Calculations

3.7.1 A calibration curve may be constructed by plotting concentration of analyte per mL versus detector response. Bracket the samples with prepared analytical standards over a range of concentrations.

3.7.2 Determine the μg/mL of piperonyl butoxide in both sections of each sample and blank from the calibration curve. If piperonyl butoxide 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.

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

$$ppm = \frac{(mg/m^3)(24.46)}{(338.43)}$$

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and air exposure to piperonyl butoxide.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses in laboratory.

4 Recommendation for further Study

This method should be fully validated.

5 References

5.1 "OSHA Analytical Methods Manual", U.S. Department of Labor Occupational Safety and Health Administration, OSHA Salt Lake Technical Center, Salt Lake City, UT, Method 70, American Conference of Governmental Hygienists (ACGIH) Cincinnati, OH 1985 ISBN 0-936712-66-X.

5.2 "Farm Chemicals Handbook"; Meister Publishing CO.: Willoughby, OH, 1992; p C265.

5.3 Windholz, M.; Budavari, S.; Blumetti, RF.; and Otterbein, E.; The Merck Index, 11th ed., Merck & CO., Inc., Rahway, N.J., 1983; p 1187.