Method number:	PV2037
Target Concentration:	1 mg/m^3, OSHA permissible exposure level (PEL).
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:	240 minutes at 1.0 L/min (240 L)
Detection limit of the overall procedure	35 µg/m^3, (based on the recommended air volume and the analytical detection limit):
Status of method:	Partially Validated method. This method has been partially evaluated and is presented for information and trial use only.

May 1990 (first draft) Duane Lee

Carcinogen/Pesticide Branch
OSHA Salt Lake technical Center
Salt Lake City UT 84115-1802

1 General Discussion

1.1 Background

1.1.1 History of procedure

This evaluation was undertaken because OSHA recently adopted the sulprofos TLV as a PEL. The OVS-2 sampling tube was tested as an effective sampling device for sulprofos. This method follows the procedure developed for 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 toxicity of sulprofos is dependent on the species tested. The oral LD_{50} in rats is 100-300 mg/kg and in mice is 1600-1800 mg/kg. Rat inhalation studies at 14 mg/m^3 have shown a significant depression of cholinesterase in the blood, while inhalation studies at 6 mg/m^3 were without effects. (Ref. 5.5)

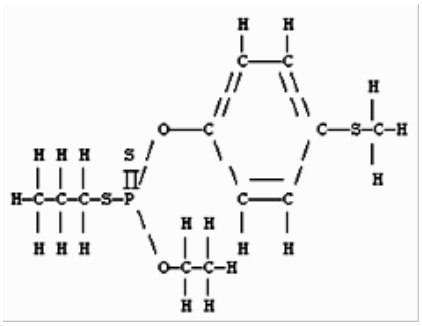
1.1.3 Potential workplace exposure

Sulprofos is used as a selective insecticide. There was no information available on the number of workers exposed to sulprofos.

1.1.4 Physical properties (Ref. 5.2 to 5.5)

CAS number:	35400-43-2
IMIS number:	S129
Molecular weight:	322.43
Molecular formula:	$C_{12}H_{19}O_2PS_3$
Density:	1.2 at 20 °C
Boiling point:	125 °C at 1 kPa (0.01 mbar)
Solubility:	soluble in organic solvents; low solubility in water
Chemical name:	O-ethyl O-[4-(methylthio)phenyl] S-propyl phosphorodithioate
Synonyms:	Bay-ntn-9306; Bolstar; O-Ethyl O-(4-(methylmercapto)phenyl)-S-n-propylphosphorothionothiolate; O-Ethyl O-(4-(methylthio)-phenyl)-phosphorodithioic acid S-propyl ester; Helothion; Ntn 9306
Description:	tan colored liquid with a typical sulfide odor

Structure:



1.2 Limit defining parameters

The detection limit of the analytical procedure, including a 28:1 split ratio, is 0.3 ng per injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise. (Figure 1.)

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., packed with two sections of cleaned XAD-2 adsorbent and a 13-mm diameter glass fiber filter. The sampling section and backup section contain 270 and 140 mg respectively. The backup section is retained by two foam plugs and the sampling section is between a foam plug and the glass fiber filter. The glass fiber filter is held next to the sampling section by a polytetrafluoroethylene (PTFE) retainer. (Figure 2.)

2.2 Reagents

No sampling reagents are required.

2.3 Sampling technique

2.3.1 Immediately before sampling, remove the plastic caps from the OVS-2 tube.

2.3.2 Attach the small end of the tube to the sampling pump with flexible tubing.

2.3.3 Attach the tube vertically in the employee's breathing zone in such a manner that it does not impede work performance.

2.3.4 After sampling for the appropriate time, remove the tube and seal it with plastic caps.

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

2.3.6 Record the air volume for each sample, and list any possible interference.

2.3.7 Submit at least one blank for each set of samples. Handle the blank in the same manner as the samples, except no air is drawn through it.

2.3.8 Submit bulk samples for analysis in a separate container. Do not ship with air samples.

2.4 Desorption efficiency (glass fiber filter and XAD-2 adsorbent)

Six vials each containing a 13-mm glass fiber filter and 270-mg of XAD-2 adsorbent were each liquid spiked on the glass fiber filter with 23 µL of a 10.648 mg/mL sulprofos standard and allowed to dry overnight in a drawer at ambient temperature. These samples were each desorbed with 2.0 mL of toluene, shaken for 30 min and analyzed as in Section 3. The results are listed in Table 2.4.

Table 2.4
Desorption Efficiency

sample #	µg spiked	µg found	% recovered
1	244.9	240.2	98.1
2	244.9	230.4	94.1
3	244.9	254.0	103.7
4	244.9	209.3	85.5
5	244.9	240.7	98.3
6	244.9	225.1	91.9

average = 95.3%

2.5 Retention efficiency

Eighteen OVS-2 tubes were each liquid spiked with 23 µL of a 10.648 mg/mL sulprofos standard on the glass fiber filter. These were allowed to dry overnight and then 240 L of humid air (~81% relative humidity) were drawn through each tube at 1 L/min. Six of the tubes were each desorbed with 2.0 mL of toluene, shaken for 30 min and then analyzed as in Section 3. The results are listed in Table 2.5. The remaining samples were stored, 6 in a drawer at ambient temperature and 6 in a freezer.

Table 2.5
Retention Efficiency

sample #	µg spiked	µg found	% recovered
1	244.9	259.1	105.8
2	244.9	210.6	86.0
3	244.9	208.9	85.3
4	244.9	227.6	92.9
5	244.9	253.1	103.3
6	244.9	232.5	94.9

average = 94.7%

2.6 Sample storage

After 7 days of storage, 6 tubes, 3 from the ambient storage group and 3 from the freezer storage group, were each desorbed with 2.0 mL of toluene, shaken for 30 min and then analyzed as in Section 3. The remaining tubes were desorbed and analyzed after 9 days of storage. The results are given in Table 2.6.1 and Table 2.6.2.

Table 2.6.1
Ambient Storage

sample #	µg spiked	µg found	% recovered
7	244.9	221.0	90.2
7	244.9	243.7	99.5
7	244.9	239.7	97.9
9	244.9	221.7	90.5
9	244.9	246.6	100.7
9	244.9	283.1	115.6

average for 7 days = 95.7%
average for 9 days = 102.3%

Table 2.6.2
Freezer Storage

sample #	µg spiked	µg found	% recovered
7	244.9	230.5	94.1
7	244.9	257.9	105.3
7	244.9	214.8	87.7
9	244.9	227.2	92.8
9	244.9	252.3	103.0
9	244.9	239.2	97.9

average for 7 days = 95.7%
average for 9 days = 97.9%

2.7 Recommended air volume and sampling rate

2.7.1 The recommended air volume is 240 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 sulprofos. Any suspected interferences should be reported to the laboratory.

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 balance capable of weighing to the nearest tenth of a milligram. A Mettler HL52 balance was used in this evaluation.

3.1.2 A mechanical shaker.

3.1.3 A GC equipped with an FPD using a sulfur filter. A Hewlett-Packard (HP) 5890 equipped with an autosampler was used in this evaluation.

3.1.4 A GC column capable of separating sulprofos from any interference. A 30-m × 0.32-mm i.d. (1.0 µm d_f DB-5) capillary column was used in this evaluation.

3.1.5 An electronic integrator, or some other suitable means for measuring detector response. The Waters 860 Laboratory Data System was used in this evaluation.

3.1.6 Volumetric flasks and pipettes.

3.1.7 Vials, 2-mL and 4-mL.

3.2 Reagents

3.2.1 Toluene, reagent grade.

3.2.2 Sulprofos, reagent grade. A standard obtained from EPA (EPA # 6350, 95.5% purity) was used in this evaluation.

3.3 Standard preparation

Prepare sulprofos stock standards by weighing 10 to 15 mg of sulprofos. Transfer the sulprofos to separate 10-mL volumetric flasks, and add toluene to the mark. Make working range standards of 4.2 to 266 µg/mL by diluting the stock standards with toluene. Store stock and diluted 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 section in a separate 4-mL 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 toluene to each vial and seal with a PTFE-lined cap.

3.4.3 Shake the vials for 30 minutes on a mechanical shaker.

3.4.4 If necessary, transfer the samples to 2-mL vials for use on an HP autosampler.

3.5 Analysis

3.5.1 Instrument conditions

Column: 30-m × 0.32-mm i.d., (1.0 µm d_f DB-5)

Instrument Temperatures

Injector temperature: 250 °C
Column temperature: 220 °C
Detector temperature: 225 °C

Gas flows:

Column: 1 mL/min hydrogen
FPD make up: 42 mL/min nitrogen

Injection volume: 2 µL

Split ratio: 28:1
Retention time: 7.2 min

3.5.2 Chromatogram (Figure 3.)

3.6 Interferences (analytical)

3.6.1 Any collected compound having a similar retention time to that of the analyte 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 or detector, high performance liquid chromatography (HPLC) and confirmation by mass spectrometry are additional means of identification.

3.7 Calculations

3.7.1 Construct a calibration curve (Figure 4.) by plotting detector response versus concentration (µg/mL) of sulprofos.

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

3.7.3 Blank correct each section by subtracting the µg/mL found in each blank section from the µg/mL found in each corresponding sample section and then add the values together.

3.7.4 Determine the air concentration by using the following formula.

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

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and air exposure to sulprofos.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times.

4 Recommendation for Further Study

4.1 This method should be fully validated.

4.2 A GC having an FPD with a phosphorus filter may yield better sensitivity.

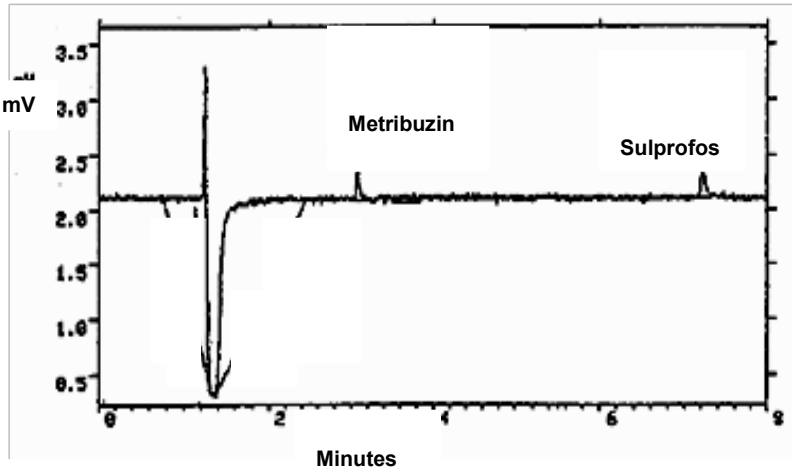


Figure 1. Detection Limit Chromatogram of
Sulprofos with another Compound

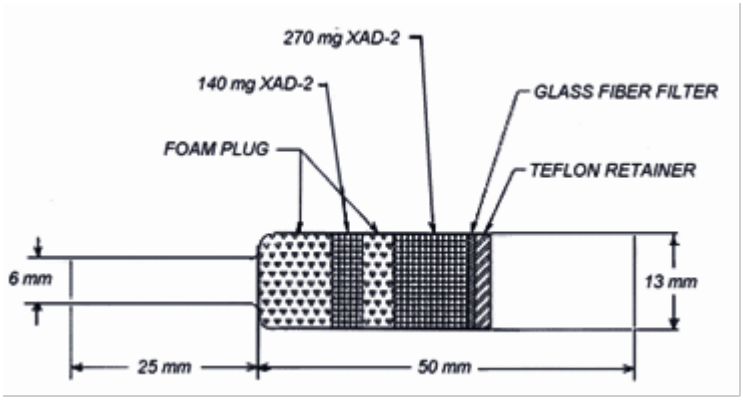


Figure 2.
OVS-2 Sampling Tube

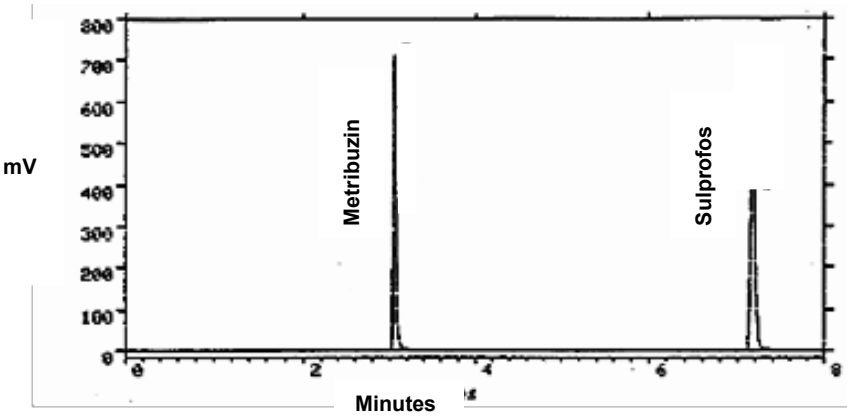


Figure 3.
Chromatogram of Sulprofos with another Compound

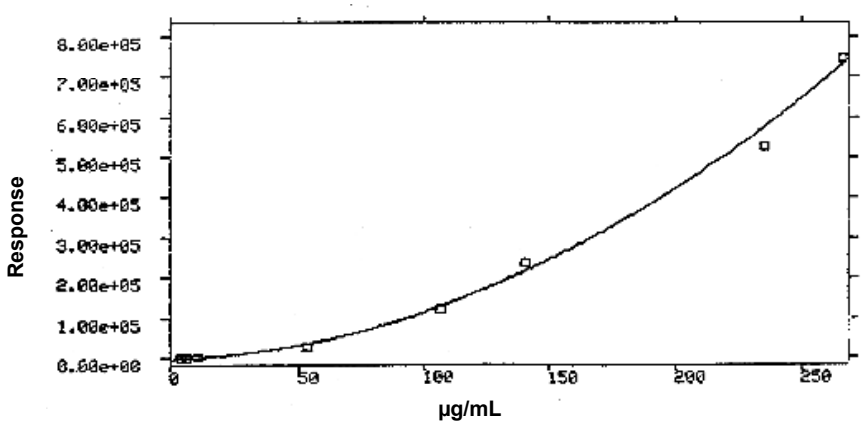


Figure 4.
Calibration Curve

5 References

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

5.2 Registry of Toxic Effects of Chemical Substances 1985-86 Edition; DHHS (NIOSH) Publication No. 87-114, U.S. Department of Health and Human Services: Cincinnati, OH, 1987; p 3415.

5.3 Farm Chemicals Handbook; Berg, Gordon L. Ed.; Meister: Willoughby, Ohio, 1989; p C45.

5.4 Merck Index, 10th ed.; Windholz, Martha ED.; Merck: Rahway, N.J., 1983; p 1292.

5.5 Documentation of Threshold Limit Values and Biological Exposures Indices; American Conference of Governmental Industrial Hygienists Inc., Fifth Edition 1986, p 547.