ENDOSULFAN

Method no.	PV2023
Target Concentration:	0.1 mg/m^3 (TLV TWA)
Procedure:	Samples are collected by drawing known volumes of air through OSHA versatile sampler tubes (OVS-2) containing a glass fiber filter and two sections of XAD-2 adsorbent. Samples are desorbed with toluene 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 (60L)
Detection limit of the overall procedure (based on the recommended air volume):	3.4 μg/m^3
Status of method:	Partially validated method. This method has been only partially evaluated and is presented for information and trial use.

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1. General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA Analytical Laboratory received a set of samples requesting the analysis of endosulfan from glass fiber filters. Retention and storage studies on glass fiber filters yielded poor recoveries of endosulfan. Therefore, this report describes the preliminary validation of a sampling and analytical method using OVS-2 tubes.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy).

Technical endosulfan consists of about four parts of α-cis isomer, and one part of ß-trans isomer. The α-cis isomer, which is somewhat more insecticidal, is slowly converted to the more stable ß-trans form at high temperatures and both isomers are oxidized slowly in air and biological systems and rapidly by peroxides or permanganates to endosulfan sulfate (Ref. 5.2). Endosulfan has an acute LD_{50} to the rat of 30 mg/kg in alcohol suspension, 70 mg/kg in aqueous suspension, and 110 mg/kg in oil (Ref. 5.1). For fish, the LC_{50} value is 0.001-0.003 ppm (Ref. 5.2).

There are reports of workers becoming ill from inhalation of dust from endosulfan. Symptoms of slight nausea, confusion, excitement, flushing and dry mouth were experienced (Ref. 5.3). In addition, endosulfan is a central nervous system stimulant for which no specific antidote is available (Ref. 5.1).

Accordingly, a TLV of 0.1 mg/m^3, as a time-weighted average, is recommended for endosulfan (Ref. 5.3).

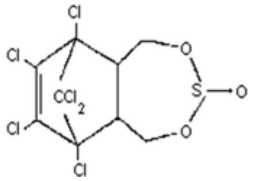
1.1.3 Potential workplace exposure

No estimate of worker exposure to endosulfan could be found. Endosulfan is a broad-spectrum insecticide for control of vegetable, fruit, field crop, and ornamental pests (Ref. 5.1).

1.1.4 Physical properties (Refs. 5.1 and 5.3)

CAS #:	115-29-7
Molecular weight:	406.95
Molecular formula:	$C_9H_6Cl_6O_3S$
Specific gravity:	1.735 at 20 ^oC
Melting point:	70 -100 ^oC
Solubility:	Insoluble in water; soluble in xylene, kerosene, chloroform, acetone, and alcohol; decomposes in the presence of acids and alkalies to form sulfur dioxide.
Chemical name:	6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,3,4-benzodioxathiepin-3-oxide
Synonyms:	Thiodan, Benzoepin, Cyclodan, Beosit, Endocel, Chlorthiepin, Crisulfan, Endosan, Endosol, Hildan, Insectophene, Malix, Thifor, Thimul, Thiofor, Thionex, Tiovel.
Description:	Technical endosulfan is a tan, semi-waxy solid that is a mixture of two isomers with an odor of hexachlorocyclopentadiene and may have a slight sulfur dioxide odor.

Structure:



1.2 Limit defining parameters

The detection limit of the analytical procedure is 13.5 pg per injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise.

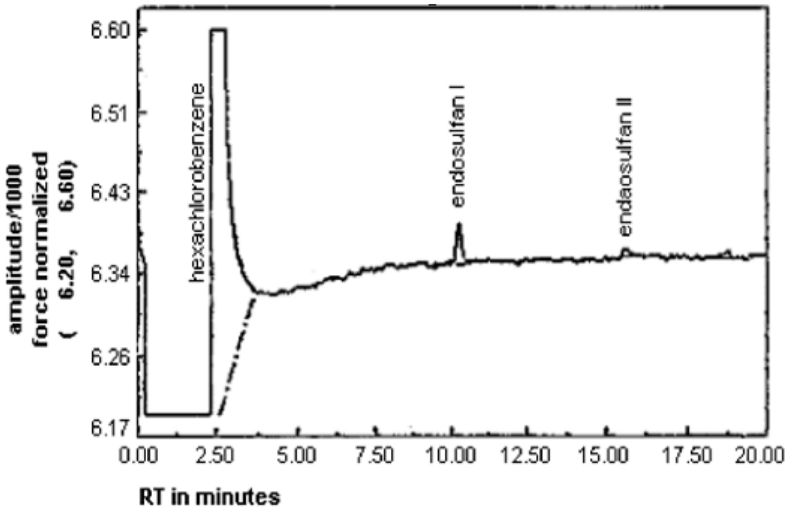


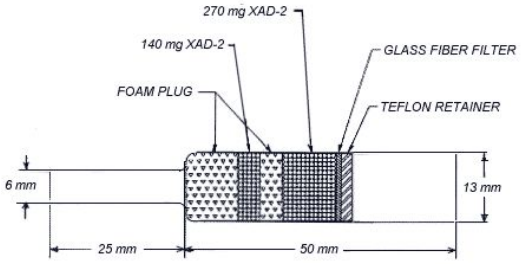
Figure 1. chromatogram of endosulfan I & II at the detection limit

2. Sampling procedure

2.1 Apparatus

2.1.1 Samples are 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 Samples are collected with OVS-2 tubes, which are specially made 13-mm o.d. glass tubes that are tapered to 6-mm o.d., packed with 140-mg backup section and a 270-mg sampling section of cleaned XAD-2 and a 13-mm glass fiber filter. The backup section is retained by two foam plugs and the sampling section is between one foam plug and the glass fiber filter. The glass fiber filter is held next to the sampling section by a polytetrafluoroethylene (PTFE) retainer.



OVS-2 sample tube

2.2 Reagents

None

2.3 Sampling technique

2.3.1 Attach the small end of the 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.

2.3.2 Attach the sampler vertically 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-21seal.

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

2.3.6 Record the air volume (in liters of air) for each sample, and list any possible interference.

2.3.7 Submit bulk samples for analysis in a separate container.

2.4 Desorption efficiency

Six OVS-2 tubes were each liquid spiked with 15 μL of a 422 μg/mL endosulfan standard. The tubes were stored in a drawer overnight at room temperature. The next day the samples were analyzed using the following procedure.

2.4.1 Transfer the glass fiber filter and large section of the adsorbent of each sample to a 4-mL vial. Place the separating foam plug and the small section of adsorbent of each sample into a separate 4-mL vial.

2.4.2 Pipette 3.0 mL desorbing solvent, (hexachlorobenzene (2 μg/mL) in toluene) with a PTFE-lined septum.

2.4.3 Place vials on a rotator for 60 minutes and then analyze by transferring 1 mL desorbed sample to a 2-mL sample vial for analysis in GC. The results are listed in table 2.4.

table 2.4
desorption efficiency

sample #	amount spiked, μg	amount found, μg	% recovered
1	6.33	5.40	85.3
2	6.33	5.19	82.0
3	6.33	5.47	86.4
4	6.33	5.16	81.5
5	6.33	5.30	83.7
6	6.33	5.36	84.7
		average	83.9

2.5 Retention efficiency

Five OVS-2 tubes were liquid spiked with 15 μL of a 422 μg/mL standard and humid air (~80% relative humidity) was drawn through each tube at 1 L/min for 60 minutes. The tubes were stored in a drawer, overnight at room temperature. The next day the tubes were analyzed. The results are listed in table 2.5.

table 2.5
retention efficiency

sample #	amount spiked, μg	amount found, μg	% recovered
1	6.33	5.68	89.7
2	6.33	5.85	92.4
3	6.33	5.65	89.3
4	6.33	5.59	88.3
5	6.33	5.36	84.7
		average	88.9

2.6 Sample storage

Twelve tubes were liquid spiked with 15 μL of a 422 μg/mL standard and humid air (~80% relative humidity) was drawn through each tube at 1 L/min for 60 minutes. Six of the samples were stored at ambient temperature in a drawer, and six were stored in a refrigerator. After four days of storage, three samples from each group were desorbed with 3 mL of desorbing solvent by rotating for 60 min and then analyzed. The remaining samples were desorbed and analyzed after seven days of storage. The results are given in the tables below.

table 2.6.1
ambient storage

days stored	amount spiked, μg	amount found, μg	% recovered
4	6.33	6.08	96.0
4	6.33	5.72	90.4
4	6.33	5.77	91.2
7	6.33	5.99	94.6
7	6.33	5.74	90.7
7	6.33	5.41	85.5
		average day 4	92.5
		average day 7	90.3

table 2.6.2
refrigerated storage

days stored	amount spiked, μg	amount found, μg	% recovered
4	6.33	6.08	96.0
4	6.33	5.85	92.4
4	6.33	5.48	86.8
7	6.33	5.67	89.6
7	6.33	5.77	91.2
7	6.33	5.69	89.9
		average day 4	91.7
		average day 7	90.2

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

It is not known if any compounds will interfere with the collection of endosulfan.

2.9 Safety precautions

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 Mechanical rotator.

3.1.3 A gas chromatograph (GC) equipped with an electron capture detector (ECD). A Hewlett Packard 5890 (GC/ECD) was used in this evaluation.

3.1.4 A GC column capable of separating endosulfan from any interference. A 10-m x 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 method for measuring detector response. The Hewlett-Packard 3357 Laboratory Data System was used in this evaluation.

3.1.6 Volumetric flasks and pipettes.

3.1.7 4-mL glass vials with PTFE-lined septum.

3.1.8 2-mL glass vials suitable for use on GC autosamplers.

3.2 Reagents

3.2.1 Toluene high purity Burdick and Jackson.

3.2.2 Endosulfan, EPA 3180, 97.6% purity.

3.2.3 Hexachlorobenzene (internal standard), reagent grade.

3.2.4 Desorbing solvent, hexachlorobenzene (2 μg/mL) in toluene.

3.3 Standard preparation

Prepare stock standards by weighing 10 to 14 mg of endosulfan into 25-mL volumetric flasks and dilute to volume with desorbing solvent. Make working range standards by pipette dilutions

of the stock standards with the desorbing solvent. Store stock and dilute standards in a freezer.

3.4 Sample preparation

3.4.1 Transfer the glass fiber filter and large section of the adsorbent of each sample to a 4-mL glass vial. Place the separating foam plug and small section of adsorbent of each sample in a separate 4-mL glass vial.

3.4.2 Pipette 3.0 mL of desorbing solvent into each vial and seal with a PTFE-lined septum.

3.4.3 Rotate the vials for 60 minutes.

3.5 Analysis

3.5.1 Instrument conditions

Column:	10-m x 0.32-mm i.d., (1.0 μm d_f DB-5)
Temperatures:	
injector temperature:	235 °C
column temperature:	170 °C
detector temperature:	300 °C
Gas flows:	
column:	8.6 mL/min hydrogen
make up:	42 mL/min nitrogen
Injector volume:	1.0 μL
split ratio:	5:1
Retention time:	10.3 min endosulfan I
	15.6 min endosulfan II

3.5.2 Chromatogram

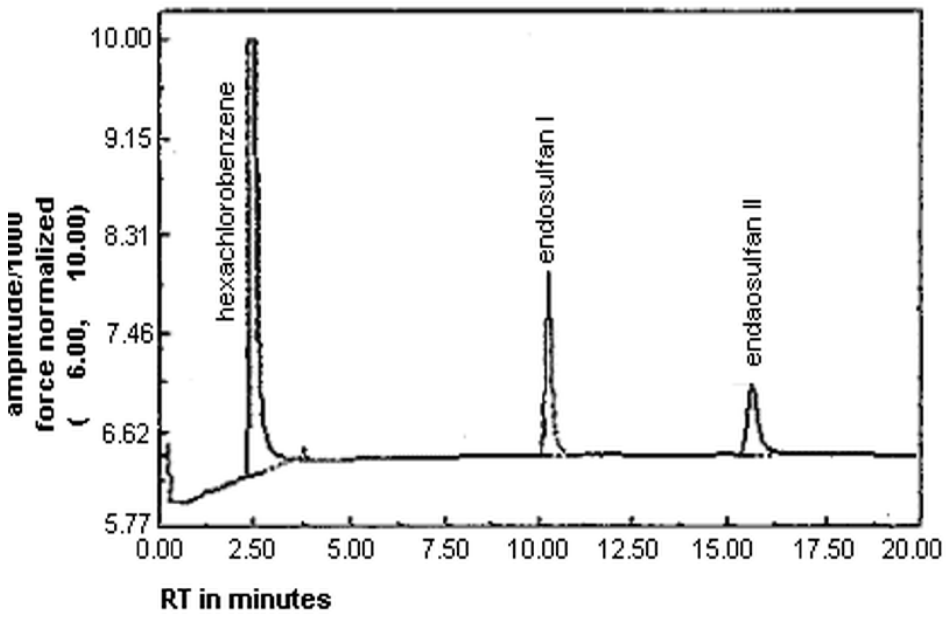


Figure 2. chromatogram of endosulfan I & II

3.6 Interferences

3.6.1 Any collected compound having a similar retention time as endosulfan, the internal standard, and responds to an ECD is interference.

3.6.2 GC conditions may be varied to circumvent interference.

3.6.3 Retention time alone is not proof of chemical identity. Analysis by an alternate GC column and confirmation by GC/mass spectrometry are additional means of identification.

3.7 Calculations

3.7.1 A calibration curve is constructed by plotting detector response versus standard concentration. The detector response is the value calculated from an internal standard method that sums the areas of the endosulfan I and endosulfan II peaks.

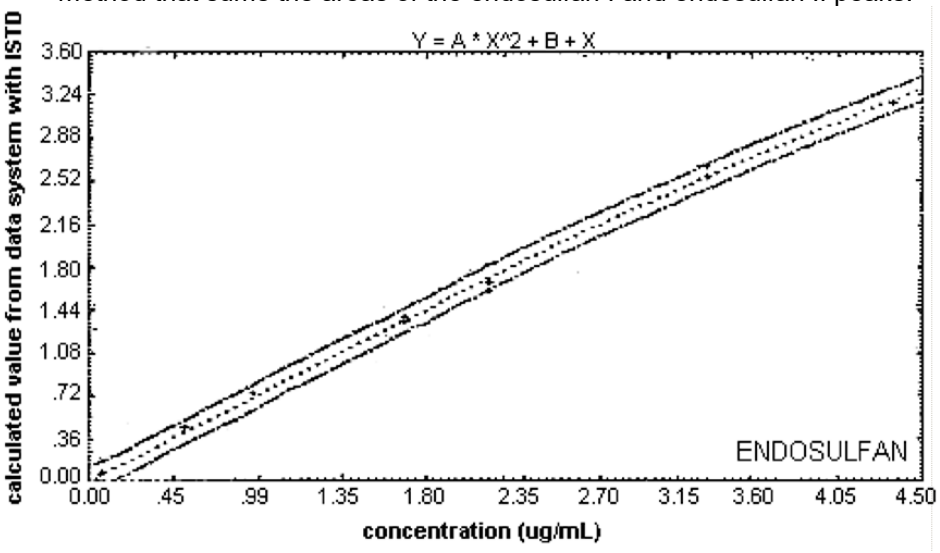


Figure 3. calibration curve

3.7.2 The concentration of endosulfan in a sample is determined from the calibration curve.

3.7.3 The air concentration is then determined by the following formula.

$$\frac{(\mu g / mL) \times (Extraction\ Vol, mL)}{(Air\ Vol, L) \times (Desorption\ Efficiency)} = mg/m^3$$

3.8 Safety precautions

3.8.1 Avoid skin contact and air exposure to endosulfan.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times.

4. Recommendations for further study

The method should be fully validated.

5. References

5.1 *Farm Chemicals Handbook;* Meister Publishing Willoughly, Ohio, 1986, p C97.

5.2 *Kirk-Othmer Encyclopedia of Chemical Technology;* John Wiley & Sons: New York, 1981, Volume 13, PP 435-7.

5.3 *Documentation of Threshold Limit Values and Biological Exposure Indices;* American Conference of Governmental Industrial Hygienists Inc., Fifth Edition, 1986, p 230.