



Methoxychlor

Method number: PV2038

Target Concentration: 15 mg/m³ 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 acetonitrile 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: 4.3 µg/m³ (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.

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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 methoxychlor and other pesticides. The samples had been collected on OVS-2 tubes. This report describes the analytical method developed for methoxychlor.

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

The oral LD₅₀ of methoxychlor is 6000 mg/kg for rats. Animal studies have been done and the data did not provide evidence of being carcinogenic. The ACGIH has a threshold limit value (TLV) of 10 mg/kg because of the low toxicity of methoxychlor. This level will be adopted by OSHA. (Ref. 5.1 and 5.2)

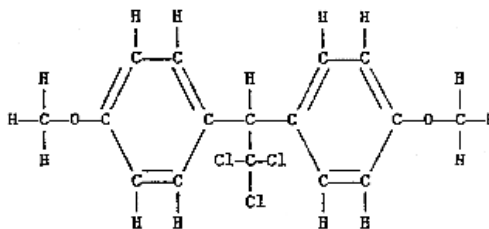
1.1.3 Potential workplace exposure

Methoxychlor is used as an insecticide. In the United States, a total of 2.5 million kg of methoxychlor was produced in 1975. The previous year 1.5 million kg of methoxychlor were used. (Ref. 5.2) No information could be found on the number of workers exposed to methoxychlor.

1.1.4 Physical properties (Ref. 5.1 to 5.4)

CAS number: 72-43-5
IMIS number: 1646
Molecular weight: 345.65
Molecular formula: C₁₆H₁₅Cl₃O₂
Melting point: 89 °C
Solubility: soluble in benzene, ether, dimethyl sulfoxide, ethanol, acetone, aromatic solvents, chlorinated solvents, paraffinic solvents, and petroleum oils; in water 0.1 mg/L
Chemical name: 2,2-bis (p-methoxyphenyl)-1,1,1-trichloroethane;
Synonyms: 1,1'-(2,2,2-trichloroethylidene)- bis[4-methoxybenzene]; 1,1,1-trichloro-2,2-bis(p-methoxyphenyl) ethane; Marlate; Chemform; DMDT; methoxy-DDT
Description: white crystalline solid

Structure:



1.2 Limit defining parameters

The detection limit of the analytical procedure, including a 15:1 split ratio, is 0.006 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 personal sampling pump that can be calibrated to within $\pm 5\%$ 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 a 140-mg backup section, a 270-mg sampling section of cleaned XAD-2 adsorbent, and a 13-mm diameter 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. (Figure 1.)

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 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 258.85 μg of methoxychlor and allowed to dry for 2 hours. These samples were each desorbed with 3.0 mL of acetonitrile, 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	258.85	232.16	89.7
2	258.85	224.37	86.7
3	258.85	228.11	88.1
4	258.85	225.25	87.0
5	258.85	221.64	85.6
6	258.85	227.86	88.0

average = 87.5%

2.5 Retention efficiency

Eighteen OVS-2 tubes were each liquid spiked with 258.85 µg of methoxychlor on the glass fiber filter. These were allowed to dry for 2 hours and then 240 L of humid air (~80% relative humidity) were drawn through each tube at 1 L/min. Six of the tubes were each desorbed with 3.0 mL of acetonitrile, 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	258.85	242.92	93.8
2	258.85	236.03	91.2
3	258.85	231.45	89.4
4	258.85	217.13	83.9
5	258.85	223.86	86.5
6	258.85	233.46	90.2

average = 89.2%

2.6 Sample storage

After 4 days of storage, 6 tubes, 3 from the ambient storage group and 3 from the freezer storage group, were each desorbed with 3.0 mL of acetonitrile, shaken for 30 min and then analyzed as in Section 3. The remaining tubes were desorbed and analyzed after 7 days of storage. The results are given in Tables 2.6.1. and 2.6.2.

Table 2.6.1
Ambient Storage

sample #	µg spiked	µg found	% recovered
4	258.85	229.31	88.6
4	258.85	223.93	86.5
4	258.85	246.38	95.2
7	258.85	212.65	82.2
7	258.85	234.35	90.5
7	258.85	238.09	92.0

average after 4 days = 90.1%

average after 7 days = 88.3%

Table 2.6.2
Freezer Storage

sample #	µg spiked	µg found	% recovered
4	258.85	228.24	88.2
4	258.85	242.49	93.7
4	258.85	248.22	95.9
7	258.85	206.63	79.8
7	258.85	219.09	84.6
7	258.85	240.29	92.8

average after 4 days = 92.6%
average after 7 days = 85.7%

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 methoxychlor. 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 ECD. A Hewlett Packard (HP) 5890 equipped with an autosampler was used in this evaluation.

3.1.4 A GC column capable of separating methoxychlor from any interference. A 15-m × 0.32-mm i.d., (1.0 µm d_r 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 Hewlett-Packard 3357 Laboratory Data System was used in this evaluation.

3.1.6 Volumetric flasks and pipets.

3.1.7 Vials, 2.mL and 4-mL.

3.2 Reagents

3.2.1 Acetonitrile, reagent grade.

3.2.2 Methoxychlor, reagent grade. A standard obtained from EPA (EPA #4541, 99.1% purity) was used in this evaluation.

3.3 Standard preparation

Prepare methoxychlor stock standards by weighing 10 to 15 mg of methoxychlor. Transfer the methoxychlor to separate 10-mL volumetric flasks, and add acetonitrile to the mark. Make working range standards of 0.5 to 150 µg/mL by pipette dilutions of the stock standards with acetonitrile. 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 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 3.0 mL of acetonitrile 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 Transfer, if necessary, the samples to 2-mL vials for use on an HP autosampler.

3.5 Analysis

3.5.1 Instrument conditions

Column: 15-m × 0.32-mm i.d., (1.0 µm DB-5)

Instrument

Injector temperature: 275 °C

Column temperature: 220 °C

Detector temperature: 300 °C

Gas flows:

Column: 4 mL/min hydrogen

ECD make up: 42 mL/min nitrogen

Injection volume: 1 µL

Split ratio: 15:1

Retention time: 13.8 min

3.5.2 Chromatogram (Figure 2.)

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, 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 3.) by plotting detector response versus concentration ($\mu\text{g}/\text{mL}$) of methoxychlor.

3.7.2 Determine the $\mu\text{g}/\text{mL}$ of methoxychlor in both sections of each sample and blank from the calibration curve.

3.7.3 Blank correct each section by subtracting the $\mu\text{g}/\text{mL}$ found in the blank section from the $\mu\text{g}/\text{mL}$ found in the sample section. Calculate the concentration in each section then add the sections together.

3.7.4 Determine the air concentration by using the following formula.

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

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and air exposure to methoxychlor.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times.

4 Recommendation for further study

This method should be fully validated.

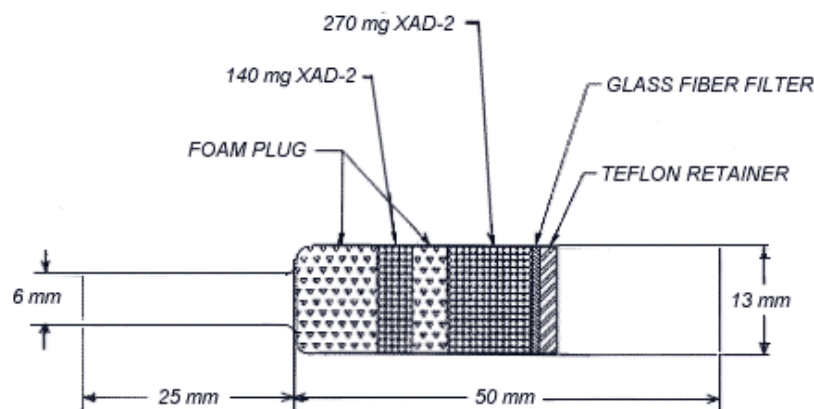


Figure 1.
OVS-2 Sampling Tube

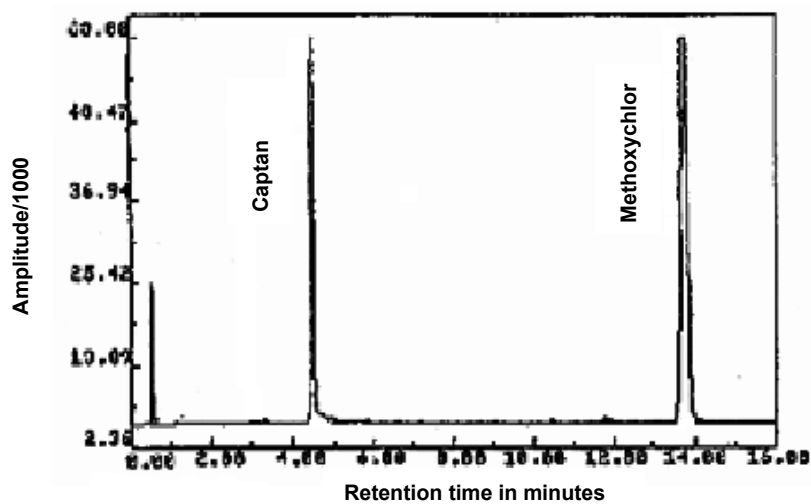


Figure 2.
Chromatogram of Methoxychlor

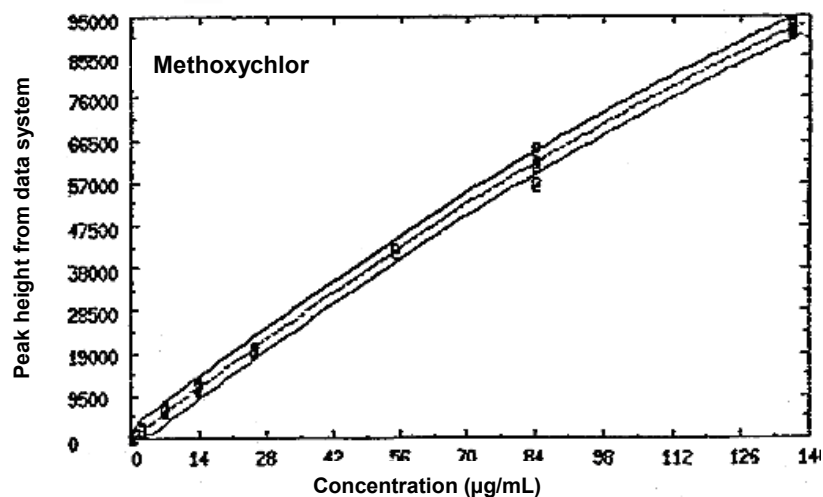


Figure 3.
Calibration Curve

5 References

- 5.1 IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans; International Agency for Research on Cancer: Lyon, 1979; Vol. 20, pp 259-281.
- 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 364.
- 5.3 Farm Chemicals Handbook; Berg, Gordon L. Ed.; Meister: Willoughby, Ohio, 1986; p C154.
- 5.4 Merck Index, 10th ed.; Windholz, Martha ED.; Merck: Rahway, N.J., 1983; p 861.