Methoxychlor

Analyte:	Methoxychlor	Method No.:	S371
Matrix:	Air	Range:	7.7-31 mg/cu m in a 100-L sample
OSHA Standard:	15 mg/cu m	Precision ($\overline{CV}_T$):	0.054
Procedure:	Filter collection, iso-octane extraction, GC, electrolytic conductivity detection	Validation Date:	12/23/77

1. Synopsis

1.1 A known volume of air is drawn through a glass fiber filter to collect particulate matter containing methoxychlor.

1.2 Methoxychlor is extracted from the filter with iso-octane, and the sample is analyzed by gas chromatography using ECD.

2. Working Range Sensitivity, and Detection Limit

2.1 This method was validated over the range of 7.7-31 mg/cu m at an atmospheric temperature of 23°C and atmospheric pressure of 761 mm Hg, using a 100-liter sample.

2.2 The upper limit of the range of the method depends on the capacity of the glass fiber filter. If higher concentrations than those tested are to be sampled, smaller volumes should be used.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as methoxychlor at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.3 Technical formulations usually contain 6-12% of the o,p' isomer of methoxychlor. Gas chromatographic conditions should be adjusted so the isomers are separated.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 7.7-31 mg/cu m was 0.054 for 18 samples collected from test atmospheres. This value corresponds to a 0.81 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.

4.2 On the average, the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 0.3% higher than the "true" concentrations for 18 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries, collection efficiency of the filter, and storage stability were good and would not contribute to a bias in a determined concentration. Storage stability studies on samples collected from a test atmosphere at a concentration of 15.36 mg/cu m indicate that collected samples are stable for at least 7 days. The mean of samples analyzed immediately versus the mean of samples analyzed after 7 days of collection compare within 5%.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

5.2 The analytical method is selective for halogenated compounds.

6. Apparatus

6.1 Filter Unit: The filter unit consists of a 37-mm diameter glass fiber filter (Gelman Type A/E or equivalent) and a polystyrene 37-mm two-piece cassette filter holder. The filter is held in the two-piece filter holder supported by a backup pad. The filter must be free of organic binders. Filter holders made of Tenite should not be used.

6.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined within 5% at the recommended flow rate. Each personal sampling pump must be calibrated with a representative filter cassette in the line to minimize errors associated with uncertainties in the volume sampled.

6.3 Manometer.

6.4 Thermometer.

6.5 Scintillation vials: 20-mL, with Teflon-lined caps, or equivalent.

6.6 Gas chromatograph equipped with an electrolytic conductivity detector.

6.7 Column (5.5-m long x 4-mm I.D. glass) packed with 5% SE-30 on Chromosorb W.

6.8 An electronic integrator or some other suitable method for measuring peak areas.

6.9 Tweezers.

6.10 Microliter syringes: 25-microliter.

6.11 Volumetric flasks: Convenient sizes for preparing standard solutions.

6.12 Pipets: Convenient sizes for preparing standard solutions, and 15-mL pipets for measuring the extraction medium.

7. Reagents

Whenever possible, reagents should be ACS reagent grade or better.

7.1 Methoxychlor.

7.2 Iso-octane.

7.3 Helium, purified.

7.4 Hydrogen, prepurified.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the scintillation vials should be detergent washed and thoroughly rinsed with tap water and distilled water, and dried.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter in the two-piece filter cassette holder and close firmly. The filter is supported by a backup pad.

8.2.2 Remove the cassette plugs and attach the cassette to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

8.2.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.2.4 A sample size of 100 liters is recommended. Sample at a flow rate of 1.5 liter/minute. The flow rate should be known with an accuracy of 5%.

8.2.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading of greater than 2 mg of dust per sample or by the presence of oil mists or other liquids in the air, the rotameter should be observed frequently, and sampling should be terminated at any evidence of a problem.

8.2.6 Terminate sampling at the predetermined time and record ambient temperature and pressure, sample flow rate, and collection time. If pressure reading is not available, record the elevation.

8.2.7 Cap each end of the filter cassette firmly.

8.2.8 Record the sample identity and all relevant sampling data.

8.2.9 The filter cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.2.10 With each batch of ten samples, submit one filter from the same lot of filters used for sample collection. This filter must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this filter as a blank.

8.2.11 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the collected samples.

8.3 Analysis of Samples

8.3.1 Each sample is analyzed separately.

8.3.2 Remove the glass fiber filter from the cassette filter holder and place it in a clean scintillation vial. Care must be taken to handle the filter with clean tweezers.

8.3.3 Pipet 15 mL of iso-octane into each vial. Swirl the contents in each vial occasionally for a period of 15 minutes.

8.3.4 Appropriate filter blanks must be analyzed at the same time as the samples.

8.3.5 GC Conditions. The typical operating conditions for the gas chromatograph are:

80 mL/minute helium carrier gas flow
80 mL/minute hydrogen flow through pyrolysis tube of the detector
225°C column temperature
250°C injector temperature
250°C transfer block temperature
820°C furnace temperature

The retention time of the p,p' isomer of methoxychlor is 6.0 minutes. The o,p' isomer will elute before the p,p' isomer.

8.3.6 Injection. The first step in the analysis is to inject the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, a solvent flush injection technique should be used. A 25-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe, the needle is removed from the solvent, and the plunger is pulled back about 1.0 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 15-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and before injection, the plunger is pulled back 2.0 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

Since a 15-microliter aliquot is likely to cause malfunction of the electrolytic conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.3.5), it was found that 3.0 minutes was adequate to elute the solvent.

8.3.7 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

9. Calibration and Standardization

A series of standards varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg methoxychlor/15 mL versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the electrolytic conductivity response.

9.1 Prepare several stock standard solutions of methoxychlor in iso-octane.

9.2 From the above stock solutions, appropriate aliquots are withdrawn and dilutions are made in iso-octane. Prepare at least 5 working standards to cover the range of 0.15-4.5 mg/15 mL. This range is based on a 100-liter sample.

9.3 Prepare a standard calibration curve by plotting concentration of methoxychlor in mg/15 mL versus peak area.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/15 mL of iso-octane and the volume of sample injected is identical to the volume of the standards injected.

10.2 A correction for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample filter

mg blank = mg found in blank filter

10.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.4 The concentration of methoxychlor in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.2)} \times 1000 \text{ (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.3)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Methoxychlor, prepared under NIOSH Contract No. 210-76-0123.