

Dichlorvos

Measurements Research Branch

Analytical Method

Analyte: Dichlorvos
(2,2-Dichloroethenyl-
dimethyl phosphate) Method No.: P&CAM 295
Range: 0.38 - 1.71 mg/cu m

Matrix: Air Precision: (\overline{CV}_T): 0.054

Procedure: Adsorption on XAD-2, desorption with toluene,
GC/FPD Classification: E (Proposed)

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1. Synopsis

A known volume of air is drawn through a tube containing XAD-2 to trap the organic vapors present. The sampling tube consists of a front adsorbing section and a backup section.

The XAD-2 in each tube is transferred to respective vials and the dichlorvos is desorbed with toluene. An aliquot of this sample solution is injected into a gas chromatograph equipped with a flame photometric detector and phosphorus filter.

- 1.3 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Working Range, Sensitivity and Detection Limit

- 2.1 This method was tested over the range of 0.382-1.707 mg/cu m at an atmospheric temperature of 24.0°C, and an atmospheric pressure of 758.1 mm Hg using a 120-liter sample volume. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

The upper limit of the range of the method is dependent on the absorptive capacity of the XAD-2 resin. This capacity varies with the concentrations of dichlorvos and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 100 mg XAD-2) reaches 5% of the concentration in the test gas mixture. When an atmosphere at 90% relative humidity containing an average of

1.73 mg/cu m of dichlorvos was sampled at 1.092 liter per minute, no breakthrough was observed after 240 minutes (capacity = 26.3 liters or 0.24 mg). The sample size recommended is less than two-thirds the 5% breakthrough capacity to minimize the probability of overloading the sampling tube.

The detection limit for dichlorvos was found to be 0.2 µg/sample.

3. Interferences

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

It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 0.382-1.707 mg/cu m was 0.0535. This value corresponds to a 0.0535 mg/cu m standard deviation at the 1 mg/cu m level. Statistical information and details of the experimental test procedures can be found in References 11.1 and 11.2.

The accuracy of this method has not been determined. The desorption efficiency was determined to be 0.922 for a collector loading of 0.063 mg. In storage stability studies, the mean of generated samples analyzed after seven days was 94.5% of the mean of samples analyzed immediately after collection. Experiments performed in these studies are described in Reference 11.2

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The collected samples are analyzed by means of a quick, instrumental method.

One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of dichlorvos found on the backup XAD-2 section exceeds 25% of that found on the front section, the probability of sample loss exists.

The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and may cause the volume to be imprecise because the pump is usually calibrated for one tube only.

5.4 The accuracy of the analytical method is unknown.

6. Apparatus

Sampling Equipment. The sampling unit for the sorbent collection method consists of the following components:

6.1.1 Sampling Pump. A calibrated personal sampling pump suitable for sampling at 1.0 liter per minute for 120 minutes. The pump must be accurate to within $\pm 5\%$ at the recommended flow rate.

6.1.2 Sampling Tubes. Wash the glass tubes with acetone prior to packing with the sorbent. Allow them to air-dry. (This will prevent the XAD-2 resin from adhering to the walls of the tube.) The sampling tube consists of a glass tube, flame-sealed at both ends, 10-cm long with an 8-mm O.D., and 6-mm I.D., packed with two sections of 20/50 mesh XAD-2. The XAD-2 used must be prewashed with toluene, and air-dried. The two sections include a front adsorbing section containing 100 mg of XAD-2 and a backup section containing 30 mg. The two sections are separated by a portion of silylated glass wool. A plug of silylated glass wool is placed at each end of the sorbent tube. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1.0 liter per minute.

6.2 Gas chromatograph with a flame photometric detector and phosphorus filter.

Column, 6-ft x 1/4-in glass, packed with 1.5% OV-101 stationary phase on 100/120 mesh Supelcoport.

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

Microliter syringes, 10- and 100- μ L and other convenient sizes for making standards and for taking sample aliquots.

Pipettes, 2-mL, delivery type.

Volumetric flasks, 10-mL or other convenient sizes for making standard solutions.

Sample vials, 4-mL, screw cap, with Teflon cover.

7. Reagents

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

Dichlorvos.

Toluene.

- 7.3 Tributyl phosphate - 98%+ or other suitable internal standard. The appropriate solution of the internal standard is prepared in toluene.

Pre-cleaned Resin. XAD-2 resin (20/50 mesh) can be obtained from Rohm and Haas Company. XAD-2 resin is purified by charging an amount into a Soxhlet extractor. Twenty-four hour extractions are then performed successively with water, methanol, and methylene chloride. Resin has been prepared in this manner using charges of about 700 grams of resin and 1.5 liters of each solvent. The resin is dried in a fluidized bed using nitrogen gas at room temperature from a liquid nitrogen cylinder. The drying process is terminated when essentially no solvent is detected in the effluent. A final quality control check is performed by desorbing a portion of the resin and analyzing the resulting solution by gas chromatography. Residual solvent should be less than 1000 ppm in concentration. Finally, several washings with toluene are recommended to reduce possible interferences to a minimum when the sorbent is desorbed with this solvent. This can be done in a beaker of the appropriate volume. The resin is then air-dried in a hood.

- 7.5 Helium, purified.

- 7.6 Hydrogen, prepurified.

Air, filtered, compressed.

8. Procedure

Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative resin tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

Collection and Shipping of Samples

- 8.3.1 Immediately before sampling, the ends of the tubes should be broken so as to provide openings approximately one-half of the internal diameter of the tubes (3-mm).

- 8.3.2 The section containing 30 mg of XAD-2 is used as a backup and should be positioned nearest the sampling pump. The XAD-2 tube should be maintained in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.
- 8.3.3 Air being sampled should not be passed through any hose or tubing before entering the front section of the XAD-2 tube.
- A sample size of 120 liters is recommended. Sample at a known flow rate between 0.5 and 1 liter per minute. Set the flow rate as accurately as possible using the manufacturer's directions. Record the necessary information to determine flow rate and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.
- 8.3.5 The XAD-2 tubes should be labeled properly and capped with the supplied plastic caps immediately after sampling.
- 8.3.6 One XAD-2 tube should be handled in the same manner as the tubes (break, seal, and transport), except for the taking of an air sample. This set of tubes should be labeled as a blank. Submit one blank for every ten samples.
- 8.3.7 At least two unused XAD-2 tubes should accompany the samples. These tubes are used in desorption efficiency studies in conjunction with these samples because desorption efficiency may vary from one batch of XAD-2 to another.
- 8.3.8 Capped XAD-2 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

Preparation of Samples. In preparation for analysis, each tube is scored with a file and broken open. The glass wool is removed and discarded. The XAD-2 in each tube is transferred to a 5-mL Teflon-lined screw-cap sample vial. Each tube is analyzed separately.

- 8.4.2 Desorption of Sample. Prior to analysis, 2.0 mL of toluene is pipetted into each sample vial. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally

during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 2.0 mL of toluene containing a known amount of internal standard.

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

1. 35 mL/min (60 psig) helium carrier gas flow
2. 50 mL/min (25 psig) hydrogen gas flow to detector
3. 200 mL/min (60 psig) air flow to detector
4. 235°C injector temperature
5. 220°C flame photometric detector
6. 150°C column temperature

A retention time of approximately 75 seconds is to be expected for the analyte using these conditions and the column recommended in Section 6.3. The internal standard elutes in approximately six minutes.

8.4.4 Injection of Sample. A 1- μ L aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of Area. The signal of the sample peak is measured by an electronic integrator or some other suitable form of measurement such as peak height, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of XAD-2 to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for a particular batch of resin used for sample collection and over the concentration range of interest.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the amount of dichlorvos found in the samples.

The analytical samples are prepared as follows: XAD-2 resin, equivalent to the amount in the front section (100 mg), is measured into a 4-mL screw-cap vial. This resin must be from the same batch used in obtaining the samples. A known amount of a solution of dichlorvos in toluene (spiking solution) is injected directly into the resin by means of a microliter syringe. Adjust the concentration of the spiking solution such that no more than a 10- μ L aliquot is used to prepare the analytical samples

Six analytical samples at each of the three concentration levels (0.5, 1, and 2X the OSHA standard) are prepared by adding an amount of dichlorvos equivalent to a 120-liter sample at the selected level. A stock solution containing 30.0 milligrams of dichlorvos per milliliter of toluene is prepared. Aliquots (2.0, 4.0 and 8.0 μ L) of the solution are added to the XAD-2 resin vials to produce 0.5, 1 and 2X the OSHA standard level. The analytical samples are allowed to stand overnight to assure complete adsorption of the analyte onto the resin. A parallel blank vial is treated in the same manner except that no sample is added to it.

- 8.5.3 Desorption and Analysis. Desorption and analysis experiments are done on the analytical samples as described in Section 8.4. Calibration standards are prepared by adding the appropriate volume of spiking solution to 2.0 mL of toluene with the same syringe used in the preparation of the samples. Standards should be prepared and analyzed at the same time the sample analysis is done.

If the internal standard method is used, prepare calibration standards by using 2.0 mL of toluene containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the vial divided by the weight in mg added to the vial, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered} - \text{Resin Blank (mg)}}{\text{Weight (mg) added}}$$

The desorption efficiency may be dependent on the amount of dichlorvos collected on the resin. Plot the desorption efficiency versus weight of dichlorvos. This curve is used in Section 10.3 to correct for adsorption losses.

9. Calibration and Standardization

A series of standards varying in concentration over the range corresponding to 120-liter collections at 0.1-3 times the OSHA standard

is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. This is done in order to minimize variations in FPD response. It is convenient to express concentration of standards in terms of mg per 2.0 mL since the samples are desorbed in 2.0 mL of toluene. A calibration curve is established by plotting peak area versus concentration in mg per 2.0 mL.

- 9.1 Prepare a stock standard solution containing about 30 mg/mL of dichlorvos in toluene.
- 9.2 From the above stock solution, appropriate aliquots are added to 2.0 mL of toluene. Prepare at least five standards to cover the range of 0.012-0.360 milligrams/sample. The range is based on a 120-liter air sample.
- 9.3 For the internal standard method, use toluene containing a predetermined amount of an internal standard such as tributyl phosphate. The internal standard concentration used for these studies was equivalent to the analyte concentration for a standard solution representing a 120-liter collection at 2X the OSHA standard. However, the area of the tributyl phosphate peak at this level was approximately 70% of the area of the dichlorvos due to differences in detector response to the two compounds. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in mg per 2.0 mL.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg per 2.0 mL and the volume of sample injected is identical to the volume of the standards injected.
- 10.2 Corrections for the sample blank (Section 8.3.6) must be made for each sample:

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

where

$$\text{mg sample} = \text{mg found in sample vial}$$

$$\text{mg blank} = \text{mg found in blank vial}$$

A similar procedure is followed for the backup sections.

- 10.3 Add the weights found in the front and backup sections to determine the total weight of the sample.

- 10.4 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the front section of the tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

- 10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

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

where:

f = sampling flow rate

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)

- 10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m which is numerically equal to µg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{220.93} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

220.93 = molecular weight of dichlorvos
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

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

Backup Data Report No. 295 for Dichlorvos, prepared under NIOSH Contract No. 210-76-0123,

Philip L. Levins
Richard H. Smith
Doris Wilson
ARTHUR D. LITTLE, INC.
NIOSH Contract No. 210-76-0123