Analyte:	Heptachlor	Method No.:	S287
Matrix:	Air	Range:	0.23-1 mg/cu m
OSHA Standard:	0.5 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.066
Procedure:	Adsorption on Chromosorb 102, desorption with toluene, GC/EC	Validation Date:	1/19/78

1. Synopsis

A known volume of air is drawn through a glass tube containing Chromosorb 102 to trap heptachlor vapor.

Heptachlor is desorbed from the Chromosorb 102 with toluene, and the sample is analyzed by gas chromatography using an electron capture detector.

2. Working Range, Sensitivity, and Detection Limit

This method was validated over the range of 0.23-1 mg/cu m at an atmospheric temperature of 25°C and atmospheric pressure of 762 mm Hg, using a 60-liter sample. 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 depends on the adsorptive capacity of the Chromosorb 102. This capacity may vary with the concentrations of heptachlor and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 100 mg of Chromosorb 102) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 240 minutes at an average sampling rate of 0.954 liter/minute and relative humidity of 81% and temperature of 26°C. The breakthrough test was conducted at a concentration of 1.57 mg/cu m.

2.3 Under the instrumental conditions used in the validation study, a sensitivity of 180 mv sec/ng heptachlor was obtained.

2.4 The detection limit of the method is estimated to be at least 0.10 microgram heptachlor per sample.

3. Interferences

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

Any compound that has the same retention time as heptachlor 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.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.23-1 mg/cu m was 0.066. This value corresponds to a 0.03 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.

In validation experiments, this method was found to be capable of coming within $\pm$25% of the "true value" on the average 95% of the time over the validation range. The concentrations obtained at 0.5, 1, and 2 times the OSHA environmental limit averaged 4.8% lower than the dynamically generated test concentrations (n=16). The desorption efficiency was determined to be 0.995 for a collector loading of 13.45 micrograms. In storage stability studies, the mean of samples analyzed after 7 days were within 6.7% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The sample is 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 sorbent will hold before overloading. When the amount of heptachlor found on the backup section exceeds 25% of that found on the front section, the probability of sample loss exists.

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

6. Apparatus

Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate. Each personal sampling pump must be calibrated with a representative Chromosorb 102 tube in the line to minimize errors associated with uncertainties in the volume sampled.

Chromosorb 102 Tubes. The sampling tube consists of a glass tube with both ends unsealed, 7-cm long with a 8-mm O.D. and a 6-mm I.D., packed with two sections of 20/40 mesh Chromosorb 102*. Before use the Chromosorb 102 must be extracted with 1:1 methanol/acetone solution in a Soxhlet extractor for two hours and then dried at 115°C for one hour in a vacuum oven. The two sections include a front adsorbing section containing 100 mg of Chromosorb 102 and a backup section containing 50 mg. A plug of silylated glass wool is placed at the ends of the tube and between the two sections of Chromosorb 102. The pressure drop across the tube must be less than 1 inch of mercury at a flow rate of 1.0 liter/minute.

Immediately prior to packing, the empty glass tubes should be rinsed with acetone and dried to eliminate the problem of Chromosorb 102 adhering to the walls of the glass tubes. The tubes are capped with plastic caps at each end.

6.3 Gas chromatograph equipped with a Ni 63 electron capture detector and linearizer.

Column (6-ft long x 1/4-in O.D. glass) packed with 80/100 mesh 5% SE-30 on Chromosorb W, DMCS.

An electronic integrator or some other suitable method of determining peak areas.

Microliter Syringes: 10-microliter.

Pipets: 10-mL and other convenient sizes for preparing standards.

Volumetric Flasks: Convenient sizes for preparing standard solutions.

Scintillation Vials: 20-mL with Teflon-lined screw caps or equivalent.

6.10 Stopwatch.

6.11 Manometer.

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* Chromosorb 102 is a porous polymer manufactured by Johns-Manville Company.

7. Reagents

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

7.1 Toluene.

Heptachlor.

Acetone.

Methanol.

Heptachlor Stock Solution for Determination of Desorption Efficiencies (7.5 mg/mL). Weigh out 750 mg of heptachlor and dilute to 100 mL with toluene.

Heptachlor Stock Standard Solution for Preparation of Standard Calibration Curve. Weigh out approximately 50 mg of heptachlor and dilute to 100 mL with toluene.

7.7 95% Argon/5% methane mixture, purified.

8. Procedure

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

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, remove the caps from the ends of the Chromosorb 102 tubes. All tubes must be packed with Chromosorb 102 from the same manufacturer's lot.

8.2.2 The section containing 50 mg of Chromosorb 102 is used as a backup and should be positioned nearest the sampling pump. The tube should be placed in a vertical direction during sampling to minimize channeling through the Chromosorb 102.

8.2.3 Air being sampled should not be passed through any hose or tubing before entering the Chromosorb 102 tube.

8.2.4 Set the flow rate as accurately as possible using the manufacturer's directions. A sample size of 60 liters is recommended. Sample at a flow rate between 0.01 and 1.0 liter/minute. Do not sample at a flow rate less than 0.01 liter/minute. Record sampling time, flow rate, and type of sampling pump used.

8.2.5 The temperature, pressure and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.2.6 The Chromosorb 102 tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.2.7 With each batch or partial batch of ten samples, submit one tube from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label these tubes as the blanks.

8.2.8 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. Postal regulations and DOT procedures should be followed when mailing heptachlor samples.

8.2.9 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the Chromosorb 102 tubes. A minimum of 18 extra Chromosorb 102 tubes should be provided for desorption efficiency determinations.

8.3 Analysis of Samples

8.3.1 Desorption of Heptachlor. Remove the plastic caps from both ends of the Chromosorb 102 tube. Transfer the front glass wool plug and the front Chromosorb 102 section to a sample vial. Pipet 5.0 mL of toluene into the vial and cap. The backup Chromosorb 102 section should be handled in a similar manner, transferring the sorbent and two glass wool plugs to a separate sample vial. The two samples are analyzed separately.

Shake the sample vigorously. Desorption is complete in 15 minutes. Analyses should be completed within one day after the heptachlor is desorbed.

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

100 mL/min carrier gas
20 mL/min purge } (40 psig) argon/methane
240°C injector manifold temperature
340°C detector manifold temperature
200°C column temperature

Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Two microliters of solvent are drawn into the

syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 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 5-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 prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0-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.

A retention time of approximately 8 minutes is to be expected for heptachlor under the above conditions and using the column recommended in Section 6.4.

8.3.5 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.

8.4 Determination of Desorption Efficiency

8.4.1 The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of Chromosorb 102 to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of Chromosorb 102.

8.4.2 Chromosorb 102 sample tubes, prepared as described in Section 6.2, are used to determine desorption efficiency. The Chromosorb 102 must be from the same batch as that used in obtaining the samples. A known amount of a toluene solution of heptachlor containing 7.5 mg/mL (Section 7.5) is injected directly into the Chromosorb 102 with a microliter syringe, and the tube is capped with plastic caps. The amount injected is equivalent to that present in a 60-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the heptachlor onto the Chromosorb 102. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.3.

8.4.3 Standards are prepared by adding the appropriate volume of spiking solution to 5.0 mL of toluene with the same syringe used in preparation of the samples. Standards should be prepared and analyzed at the same time the sample analysis is done.

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

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

The desorption efficiency may be dependent on the amount of heptachlor collected on the Chromosorb 102. Plot the desorption efficiency versus weight of heptachlor found. This curve is used in Section 10.4 to correct for adsorption losses.

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 micrograms/5.0 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 electron capture detector response.

From the stock standard solution of heptachlor in toluene (Section 7.6), appropriate aliquots are withdrawn and dilutions are made in toluene. Prepare at least 5 working standards to cover the range of 3.0-90 micrograms/5 mL. This range is based on a 60-liter sample.

Analyze the standards as described in Section 8.3.

Prepare a standard calibration curve by plotting concentration of heptachlor in micrograms/5 mL versus peak area.

10. Calculations

10.1 Read the weight, in micrograms, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on micrograms/5.0 mL and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in front section of sample tube
μg blank = μg found in blank tube

A similar procedure is followed for the backup section.

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

10.4 Read the desorption efficiency from the curve (see Section 8.4.4) for the amount found in the sample tube. Divide the total weight by this desorption efficiency to obtain the corrected μg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 For personal sampling pumps with rotameters only, the following 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 (liters/min)
t = sampling time (min)
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 heptachlor in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.4)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	=	pressure (mm Hg) of air sampled
T	=	temperature (°C) of air sampled
24.45	=	molar volume (liters/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight (g/mole) of heptachlor
760	=	standard pressure (mm Hg)
298	=	standard temperature (°K)

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 No. S287 for Heptachlor, prepared under NIOSH Contract No. 210-76-0123.