Analyte:	Dieldrin	Method No.: S283
Matrix:	Air	Range: 0.12-0.59 mg/cu m
OSHA Standard:	0.25 mg/cu m - skin	Precision ($\overline{CV}_T$): 0.086
Procedure:	Filter collection, iso-octane extraction, GC	Validation Date: 3/26/76

1. Principle of the Method

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

1.2 The filter is transferred to a screw cap bottle within one hour after sampling and stored for analysis.

1.3 The analyte is extracted from the filter with iso-octane. An aliquot of the extract is analyzed by gas chromatography.

1.4 The area of the resulting peak is determined and compared with the areas for standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.122-0.587 mg/cu m at an atmospheric temperature and pressure of 22°C and 759 mm Hg, using a 170-liter sample. The probable useful range of this method is 0.25-0.75 mg/cu m for 170-liter samples.

2.2 The upper limit of the range of the method is dependent on the capacity of the glass fiber filter. If higher concentrations than those tested are to be sampled, smaller sample 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 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method may be an interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.122-0.587 mg/cu m was 0.086. This value corresponds to a standard deviation of 0.02 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 A collection efficiency of 1.00 was determined for the collection medium, thus, no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. There was also no significant bias in the sampling and analytical method, so no analytical method recovery corrections were made. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

6. Apparatus

6.1 The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and a polystyrene 37-mm two-piece cassette filter holder. Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% (Reference 11.1) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Manometer

6.1.4 Thermometer

6.1.5 Stopwatch

6.2 Glass fiber filter, similar to Gelman Type AE with a 37-mm diameter. The filter must be free of organic binders. The filter is held in the two-piece filter holder supported by a backup pad. The glass fiber filter should be at least 99.7% efficient against particles as small as 0.3 micron.

6.3 Screw cap bottles. Within 1 hour after sample has been collected, the filter is transferred to a clean screw cap bottle (a 45-mm tissue sample holder is satisfactory) for shipping. The bottle caps should be lined with Teflon for proper seal.

6.4 Gas chromatograph equipped with an electrolytic conductivity detector (Tracor or equivalent). The system includes an in-line vent between the exhaust end of the GC column and the reduction furnace, a quartz furnace operated in the reductive mode, an electrolytic conductivity cell, and a conductivity bridge.

6.5 Column (4-ft long X 1/8-in O.D. glass) packed with 5% SE-30 on 80/100 mesh, acid washed DMCS Chromosorb W.

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

6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions, and 25-microliter for making GC injections.

6.8 Volumetric flasks: Convenient sizes for preparing standard solutions.

6.9 Pipets of convenient sizes.

6.10 Tweezers.

7. Reagents

7.1 Dieldrin, reagent grade.

7.2 Iso-octane, nanograde.

7.3 Benzene, reagent grade.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

8. Procedure

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

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

8.3 Collection and Shipping of Samples.

8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly. The filter is held in place by a backup pad.

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

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

8.3.4 A sample size of 180 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm$5%.

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

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

8.3.7 The glass fiber filter should be removed from the cassette filter holder within 1 hour of sampling and placed in a clean screw cap bottle. Care must be taken to handle the filter only with clean tweezers.

8.3.8 Carefully record the sample identity and all relevant sampling data.

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

8.3.10 The screw cap bottles in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Each sample is analyzed separately.

8.4.2 Pipet 15 ml of iso-octane into each screw cap bottle.

8.4.3 Swirl the contents in each bottle occasionally for one hour.

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

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

1. 160 ml/min nitrogen carrier gas flow
2. 140 ml/min hydrogen gas flow to furnace
3. 770°C furnace temperature
4. 225°C transfer temperature
5. 260°C vent temperature
6. 190°C column temperature

8.4.6 Injection. The first step in the analysis is the injection of an aliquot 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 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 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 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 prior to injection, the plunger is pulled back 1.0 microliter 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. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column, but before it enters a reduction furnace. Since a 15-microliter aliquot is likely to cause malfunction of the 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 8.4.5), it was found that 20 seconds was adequate to elute the solvent. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/15 ml iso-octane, because samples are extracted in this amount of iso-octane. A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Crystalline dieldrin is weighed and made up to volume in a volumetric flask. Stock solutions are prepared in 1:5 mixtures by volume of benzene/iso-octane. These solutions will keep indefinitely if the flask is well stoppered. Dilute standards are prepared by diluting measured volumes of stock solutions to known volumes with iso-octane. Curves are established by plotting concentration in mg/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the electrolytic conductivity detector response.

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.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in sample filter
mg blank = mg found in blank filter

10.3 The concentration of the analyte in the air sample can be expressed in mg/cu m.

$$mg/cu\ m = \frac{mg\ (Section\ 10.2) \times 1000\ (liter/cu\ m)}{Air\ Volume\ Sampled\ (liter)}$$

11. Reference

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.