Analysis method for Pesticides by GC

APPARATUS AND MATERIALS:

1) Gas chromatograph: An analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and recorder/integrator or data system.
2) GC columns: This method describes procedures for both single-column and dual-column analyses. The single-column approach involves one analysis to determine that a compound is present, followed by a second analysis to confirm the identity of the compound
3) Column rinsing kit
4) Volumetric flasks, 10-mL and 25-mL, for preparation of standards.

REAGENTS: Reagent grade or pesticide grade chemicals shall be used in all tests. N-hexane, diethyl ether, Methylene chloride, Acetone, Ethyl acetate, and Isooctane (2,2,4-trimethylpentane) and must be exchanged to n-hexane or isooctane prior to analysis. Organic-free reagent water

Stock standard solutions (1000 mg/L) - May be prepared from pure standard materials or can be purchased as certified solutions.

Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

BHC, Dieldrin, and some other standards may not be adequately soluble in isooctane. A small amount of acetone or toluene should be used to dissolve these compounds during the preparation of the stock standard solutions.

Composite stock standard - May be prepared from individual stock solutions.

For composite stock standards containing less than 25 components, take exactly 1 mL of each individual stock solution at a concentration of 1000 mg/L, add solvent, and mix the solutions in a 25-mL volumetric flask. For example, for a composite containing 20 individual standards, the resulting concentration of each component in the mixture, after the volume is adjusted to 25 mL, will be 1 mg/25 mL. This composite solution can be further diluted to obtain the desired concentrations.

For composite stock standards containing more than 25 components, use volumetric flasks of the appropriate volume (e.g., 50 mL, 100 mL), and follow the procedure described above.

Calibration standards should be prepared at a minimum of five different concentrations by dilution of the composite stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

Although all single component analytes can be resolved on a new 35 percent phenyl methyl silicone column, two calibration mixtures should be prepared for the single component analytes of this method. This procedure is established to minimize potential resolution and quantitation problems on confirmation columns or on older 35 percent phenyl methyl silicone) columns and to allow determination of Endrin and DDT breakdown for method QC.

Separate calibration standards are required for each multi-component target analyte (e.g., Toxaphene and Chlordane). Analysts should evaluate the specific Toxaphene standard carefully. Some Toxaphene components, particularly the more heavily chlorinated components, are subject to dechlorination reactions. As a result, standards from different vendors may exhibit marked differences which could lead to possible false negative results or to large differences in quantitative results.

PROCEDURE

Sample extraction

Choose the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride using a separatory funnel or a continuous liquid-liquid extractor or other appropriate technique. Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using one of the Soxhlet extraction, pressurized fluid extraction, Ultrasonic extraction or other appropriate technique.

Hexane-acetone (1:1) may be more effective as an extraction solvent for organochlorine pesticides in some environmental and waste matrices than is methylene chloride-acetone (1:1). Relative to the methylene chloride-acetone mixture, use of hexane-acetone generally reduces the amount of interferences that are extracted and improves signal-to-noise.

Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Each sample type must be spiked with the compounds of interest to determine the percent recovery and the limit of detection for that sample.

Extract cleanup

Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before

analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. General guidance for sample extract cleanup is provided

GC conditions

This method allows the analyst to choose between a single-column or a dual-column configuration in the injector port. Either wide- or narrow-bore columns may be used. Identifications based on retention times from a single-column must be confirmed on a second column or with an alternative qualitative technique.

Single-column analysis

This capillary GC/ECD method allows the analyst the option of using 0.25-0.32 mm capillary columns (narrow-bore) or 0.53 mm capillary columns (wide-bore). Performance data are provided for both options. Figures 1-6 provide example chromatograms.

The use of narrow-bore (#0.32 mm) columns is recommended when the analyst requires greater chromatographic resolution. Use of narrow-bore columns is suitable for relatively clean samples or for extracts that have been prepared with one or more of the clean-up options referenced in the method. Wide-bore columns (0.53 mm) are suitable for more complex environmental and waste matrices.

Table 1 lists average retention times and method detection limits (MDLs) for the target analytes in water and soil matrices, using wide-bore capillary columns. Table 2 lists the GC operating conditions for the single-column method of analysis.

Dual-column analysis

The dual-column/dual-detector approach involves the use of two 30 m x 0.53 mm ID fused-silica open-tubular columns of different polarities, thus, different selectivities towards the target analytes. The columns are connected to an injection tee and separate electron capture detectors.

Retention times for the organochlorine analytes on dual-columns are in Table 6. The GC operating conditions for the compounds in Table 6 are given in Table

Multi-component mixtures of Toxaphene and Strobane were analyzed separately (Figures 5 and 6) using the GC operating conditions found in Table 7.

Figure 6 is a sample chromatogram for a mixture of organochlorine pesticides. The retention times of the individual components detected in these mixtures are given in Tables 6 and 7.

Gas chromatographic analysis of sample extracts

The same GC operating conditions used for the initial calibration must be employed for samples analyses.

Verify calibration each 12-hour shift by injecting calibration verification standards prior to conducting any sample analyses. Analysts should alternate the use of high and low concentration mixtures of single-component analytes and multi-component analytes for calibration verification. A calibration standard must also be injected at intervals of not less than once every twenty samples (after every 10 samples is recommended to minimize the number of samples requiring re-injection when QC limits are exceeded) and at the end of the analysis sequence.

The calibration factor for each analyte should not exceed a ± 15 percent difference from the mean calibration factor calculated for the initial calibration

TABLE 1

GAS CHROMATOGRAPHIC RETENTION TIMES FOR THE ORGANOCHLORINE PESTICIDES

USING WIDE-BORE CAPILLARY COLUMNS SINGLE-COLUMN METHOD OF ANALYSIS

Compound	Retention Time(min)
Aldrin	11.84
α-BHC	8.14
β-BHC	9.86
δ-BHC	11.2
Y-BHC (Lindane)	9.52
α-Chlordane	15.24
γ-Chlordane	14.63
4,4'-DDD	18.43
4,4'-DDE	16.34
4,4'-DDT	19.48
Dieldrin	16.41
Endosulfan I	15.25

GC OPERATING CONDITIONS FOR ORGANOCHLORINE COMPOUNDS
SINGLE-COLUMN ANALYSIS USING NARROW-BORE COLUMNS

Column 1 - 30 m x 0.25 or 0.32 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1 µm film thickness.

Carrier gas	Helium
Carrier gas pressure	16 psi
Injector temperature	225EC
Detector temperature	300EC
Initial temperature	100EC, hold 2 minutes
Temperature program	100EC to 160EC at 15EC/min, followed by 160EC to 270EC at 5EC/min