METHOD 8081A

ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8081 is used to determine the concentrations of various organochlorine pesticides in extracts from solid and liquid matrices, using fused-silica, open-tubular, capillary columns with electron capture detectors (ECD). When compared to the packed columns, these columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis. The compounds listed below may be determined by either a single- or dual-column analysis system.

Compound	CAS Registry No.
Aldrin	309-00-2
α-BHC	319-84-6
β-BHC	319-85-7
γ-BHC (Lindane)	58-89-9
δ-BHC	319-86-8
Chlorobenzilate	510-15-6
α-Chlordane	5103-71-9
γ-Chlordane	5103-74-2
Chlordane - not otherwise specified	57-74-9
DBCP	96-12-8
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Diallate	2303-16-4
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorocyclopentadiene	77-47-4
Isodrin	465-73-6
Methoxychlor	72-43-5
Toxaphene	8001-35-2

1.2 This revision of Method 8081 no longer includes the PCBs as Aroclors in the list of target analytes. The analysis of PCBs should be undertaken using Method 8082, which includes specific cleanup and quantitation procedures designed for PCB analysis. This change was made to obtain PCB data of better quality and to eliminate the complications inherent in a combined organochlorine pesticide and PCB method. Therefore, if the presence of PCBs is expected, use Method 8082 for

PCB analyses, and this method (8081) for the organochlorine pesticides. If there is no information of the likely presence of PCBs, either employ a PCB-specific screening procedure such as an immunoassay (e.g., Method 4020), or split the sample extract *prior to* any cleanup steps, and process part of the extract for organochlorine pesticide analysis and the other portion for PCB analysis using Method 8082.

1.3 The analyst must select columns, detectors and calibration procedures most appropriate for the specific analytes of interest in a study. Matrix-specific performance data must be established and the stability of the analytical system and instrument calibration must be established for each analytical matrix (e.g., hexane solutions from sample extractions, diluted oil samples, etc.).

1.4 Although performance data are presented for many of the target analytes, it is unlikely that all of them could be determined in a single analysis. The chemical and chromatographic behaviors of many of these chemicals can result in co-elution of some target analytes. Several cleanup/fractionation schemes are provided in this method and in Method 3600.

1.5 Several multi-component mixtures (i.e., Chlordane and Toxaphene) are listed as target analytes. When samples contain more than one multi-component analyte, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of multi-component analytes that have been subjected to environmental degradation or degradation by treatment technologies. These result in "weathered" multi-component mixtures that may have significant differences in peak patterns than those of standards.

1.6 Compound identification based on single-column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS Method 8270 is also recommended as a confirmation technique, if sensitivity permits (Sec. 8.0).

1.7 This method includes a dual-column option. The option allows a hardware configuration of two analytical columns joined to a single injection port. The option allows one injection to be used for dual-column analysis. Analysts are cautioned that the dual-column option may not be appropriate when the instrument is subject to mechanical stress, many samples are to be run in a short period, or when contaminated samples are analyzed.

1.8 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.9 Extracts suitable for analysis by this method may also be analyzed for organophosphorus pesticides (Method 8141). Some extracts may also be suitable for triazine herbicide analysis, if low recoveries (normally samples taken for triazine analysis must be preserved) are not a problem.

1.10 The following compounds may also be determined using this method:

Compound	CAS Registry No.
Alachlor	15972-60-8
Captafol	2425-06-1
Chloroneb	2675-77-6

Compound	CAS Registry No.
Chloropropylate	99516-95-7
Chlorothalonil	1897-45-6
DCPA	1861-32-1
Dichlone	117-80-6
Dicofol	115-32-2
Etridiazole	2593-15-9
Halowax-1000	58718-66-4
Halowax-1001	58718-67-5
Halowax-1013	12616-35-2
Halowax-1014	12616-36-3
Halowax-1051	2234-13-1
Halowax-1099	39450-05-0
Mirex	2385-85-5
Nitrofen	1836-75-5
PCNB	82-68-8
Permethrin	51877-74-8
Perthane	72-56-0
Propachlor	1918-16-7
Strobane	8001-50-1
trans-Nonachlor	39765-80-5
Trifluralin	1582-09-8

1.11 Kepone extracted from samples or standards exposed to water or methanol may produce peaks with broad tails that elute later than the standard by up to 1 minute. This shift is presumably the result of the formation of a hemi-acetal from the ketone functionality. As a result, Method 8081 is not recommended for determining Kepone. Method 8270 may be more appropriate for the analysis of Kepone.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

2.2 Liquid samples are extracted at neutral pH with methylene chloride using either Method 3510 (separatory funnel), Method 3520 (continuous liquid-liquid extractor), or other appropriate technique.

2.3 Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Method 3540 (Soxhlet), Method 3541 (automated Soxhlet), Method 3545 (pressurized fluid extraction), Method 3550 (ultrasonic extraction), or other appropriate technique.

2.4 A variety of cleanup steps may be applied to the extract, depending on the nature of the matrix interferences and the target analytes. Suggested cleanups include alumina (Method 3610), Florisil (Method 3620), silica gel (Method 3630), gel permeation chromatography (Method 3640), and sulfur (Method 3660).

2.5 After cleanup, the extract is analyzed by injecting a 1-µL sample into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector (GC/ECD) or an electrolytic conductivity detector (GC/ELCD).

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Sec. 3.0, in particular), 3600, and 8000, for a discussion of interferences.

3.2 Sources of interference in this method can be grouped into three broad categories.

3.2.1 Contaminated solvents, reagents, or sample processing hardware.

3.2.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

3.2.3 Compounds extracted from the sample matrix to which the detector will respond.

3.2.4 Interferences co-extracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

3.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations.

3.3.1 These materials may be removed prior to analysis using Method 3640 (Gel Permeation Cleanup) or Method 3630 (Silica Gel Cleanup).

3.3.2 Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations.

3.3.3 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled.

3.3.4 Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination. Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

3.4 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware and dry it in an oven at 130°C for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.

3.5 The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur contamination should be expected with sediment samples. Method 3660 is suggested for removal of sulfur. Since the recovery of Endrin aldehyde (using the TBA procedure) is drastically reduced, this compound must be determined prior to sulfur cleanup.

3.6 Waxes, lipids, and other high molecular weight materials can be removed by Method 3640 (gel-permeation cleanup).

3.7 Other halogenated pesticides or industrial chemicals may interfere with the analysis of pesticides. Certain co-eluting organophosphorus pesticides are eliminated by Method 3640 (gel permeation cleanup - pesticide option). Co-eluting chlorophenols may be eliminated by using Method 3630 (silica gel), Method 3620 (florisil), or Method 3610 (alumina). Polychlorinated biphenyls (PCBs) also may interfere with the analysis of the organochlorine pesticides. The problem may be most severe for the analysis of multicomponent analytes such as Chlordane, Toxaphene, and Strobane. If PCBs are known or expected to occur in samples, the analyst should consult Methods 3620 and 3630 for techniques that may be used to separate the pesticides from the PCBs.

3.8 Co-elution among the many target analytes in this method can cause interference problems. The following target analytes may coelute on the GC columns listed, when using the single-column analysis scheme:

DB 608	Trifluralin/Diallate isomers PCNP/Dichlone/Isodrin
DB 1701	Captafol/Mirex Methoxychlor/Endosulfan sulfate

3.9 The following compounds may coelute using the dual-column analysis scheme. In general, the DB-5 column resolves fewer compounds that the DB-1701.

DB-5	Permethrin/Heptachlor epoxide Endosulfan I/α-Chlordane Perthane/Endrin Endosulfan II/Chloropropylate/Chlorobenzilate 4,4'-DDT/Endosulfan sulfate Methoxychlor/Dicofol
DB-1701	Chlorothalonil/β-BHC δ-BHC/DCPA/Permethrin α-Chlordane/*trans*-Nonachlor

Nitrofen, Dichlone, Carbophenothion, Dichloran exhibit extensive peak tailing on both columns. Simazine and Atrazine give poor responses on the ECD detector. Triazine compounds should be analyzed using Method 8141 (NPD option).

4.0 APPARATUS AND MATERIALS

4.1 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.

4.2 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 (Sec. 8.4 describes how GC/MS

confirmation techniques may be employed). The single-column approach may employ either narrow-bore (≤0.32 mm ID) columns or wide-bore (0.53 mm ID) columns. The dual-column approach involves a single injection that is split between two columns that are mounted in a single gas chromatograph. The dual-column approach employs only wide-bore (0.53 mm ID) columns.

The columns listed in this section were the columns used to develop the method performance data. The mention of these columns in this method is not intended to exclude the use of other columns that may be developed. Laboratories may use other capillary columns provided that they document method performance data (e.g., chromatographic resolution, analyte breakdown, and MDLs) that equals or exceeds the performance described in this method, or as appropriate for the intended application.

4.2.1 Narrow-bore columns for single-column analysis (use both columns to confirm compound identifications unless another confirmation technique such as GC/MS is employed).

4.2.1.1 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.

4.2.1.2 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent), 2.5 µm coating thickness, 1 µm film thickness.

4.2.1.3 Narrow bore columns should be installed in split/splitless (Grob-type) injectors.

4.2.2 Wide-bore columns for single-column analysis (use two of the three columns listed to confirm compound identifications unless another confirmation technique such as GC/MS is employed).

4.2.2.1 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

4.2.2.2 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

4.2.2.3 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 95 percent dimethyl - 5 percent diphenyl polysiloxane (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

4.2.2.4 Wide-bore columns should be installed in 1/4 inch injectors, with deactivated liners designed specifically for use with these columns.

4.2.3 Wide-bore columns for dual-column analysis (choose one of the two pairs of columns listed below).

4.2.3.1 Column pair 1

30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Column pair 1 is mounted in a press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog No. 705-0733) or a Y-shaped fused-silica connector (Restek, Catalog No. 20405), or equivalent.

4.2.3.2 Column pair 2

30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 0.83 µm film thickness.

30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Column pair 2 is mounted in an 8 in. deactivated glass injection tee (Supelco, Catalog No. 2-3665M), or equivalent.

4.3 Column rinsing kit: Bonded-phase column rinse kit (J&W Scientific, Catalog No. 430-3000), or equivalent.

4.4 Volumetric flasks, 10-mL and 25-mL, for preparation of standards.

5.0 REAGENTS

5.1 Reagent grade or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4°C in polytetrafluoroethylene (PTFE)-sealed containers in the dark. When a lot of standards is prepared, it is recommended that aliquots of that lot be stored in individual small vials. All stock standard solutions must be replaced after one year or sooner if routine QC tests (Sec. 8.0) indicate a problem. All other standard solutions must be replaced after six months or sooner if routine QC (Sec. 8.0) indicates a problem.

5.2 Solvents used in the extraction and cleanup procedures (appropriate 3500 and 3600 series methods) include 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.

Therefore, n-hexane and isooctane will be required in this procedure. Acetone or toluene may be required for the preparation of some standard solutions (see Sec. 5.4.2). All solvents should be pesticide quality or equivalent, and each lot of solvent should be determined to be phthalate free.

5.3 Organic-free reagent water - All references to water in this method refer to organic-free reagent water as defined in Chapter One.

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

5.4.1 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.

5.4.2 β-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.

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

5.5.1 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.

5.5.2 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.

5.6 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.

5.6.1 Although all single component analytes can be resolved on a new 35 percent phenyl methyl silicone column (e.g., DB-608), 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 (e.g. DB-608) columns and to allow determination of Endrin and DDT breakdown for method QC (Sec. 8.0).

5.6.2 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.

5.7 Internal standard (optional)

5.7.1 Pentachloronitrobenzene is suggested as an internal standard for the single-column analysis, when it is not considered to be a target analyte. 1-bromo-2-nitrobenzene may also be used. Prepare a solution of 5000 mg/L (5000 ng/µL) of pentachloronitrobenzene or 1-bromo-2-nitrobenzene. Spike 10 µL of this solution into each 1 mL sample extract.

5.7.2 1-bromo-2-nitrobenzene is suggested as an internal standard for the dual-column analysis. Prepare a solution of 5000 mg/L (5000 ng/µL) of 1-bromo-2-nitrobenzene. Spike 10 µL of this solution into each 1 mL of sample extract.

5.8 Surrogate standards

The performance of the method should be monitored using surrogate compounds. Surrogate standards are added to all samples, method blanks, matrix spikes, and calibration standards. The following compounds are recommended as possible surrogates.

5.8.1 Decachlorobiphenyl and tetrachloro-m-xylene have been found to be a useful pair of surrogates for both the single-column and dual-column configurations. Method 3500, Sec. 5.0, describes the procedures for preparing these surrogates.

5.8.2 4-Chloro-3-nitrobenzotrifluoride may also be useful as a surrogate if the chromatographic conditions of the dual-column configuration cannot be adjusted to preclude co-elution of a target analyte with either of the surrogates in Sec. 5.8.1. However, this compound elutes early in the chromatographic run and may be subject to other interference problems. A recommended concentration for this surrogate is 500 ng/µL. Use a spiking volume of 100 µL for a 1-L aqueous sample.

5.8.3 Store surrogate spiking solutions at 4°C in PTFE-sealed containers in the dark.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Four, Organic Analytes, Sec. 4.0, for sample collection and preservation instructions.

6.2 Extracts must be stored under refrigeration in the dark and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Sample extraction

Refer to Chapter Two and Method 3500 for guidance in choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520), 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 (Method 3540 or 3541), pressurized fluid extraction (Method 3545), ultrasonic extraction (Method 3550), or other appropriate technique.

NOTE: 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 (see Chapter One). See Method 8000 for guidance on demonstration of initial method proficiency as well as guidance on matrix spikes for routine sample analysis.

7.2 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 in this section and in Method 3600.

7.2.1 If a sample is of biological origin, or contains high molecular weight materials, the use of Method 3640 (GPC cleanup - pesticide option) is recommended. Frequently, one of the adsorption chromatographic cleanups (alumina, silica gel, or florisil) may also be required following the GPC cleanup.

7.2.2 Method 3610 (alumina) may be used to remove phthalate esters.

7.2.3 Method 3620 (florisil) may be used to separate organochlorine pesticides from aliphatic compounds, aromatics, and nitrogen-containing compounds.

7.2.4 Method 3630 (silica gel) may be used to separate single component organochlorine pesticides from some interferants.

7.2.5 Elemental sulfur, which may be present in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur should be removed by the technique described in Method 3660.

7.3 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.

7.3.1 Single-column analysis

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

7.3.1.1 The use of narrow-bore ($\leq$0.32 mm ID) 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 ID) are suitable for more complex environmental and waste matrices.

7.3.1.2 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 average retention times and method detection limits (MDLs) for the target analytes in water and soil matrices, using narrow-bore capillary columns. The MDLs for the components of a specific sample are dependent upon the nature of interferences in the sample matrix and may differ from those listed in Tables 1 and 2. Table 3 lists the Estimated Quantitation Limits (EQLs) for other matrices.

7.3.1.3 Table 4 lists the GC operating conditions for the single-column method of analysis.

7.3.2 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.

7.3.2.1 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 7.

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

7.3.2.3 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.

7.3.2.4 Operating conditions for a more heavily loaded DB-5/DB-1701 pair are given in Table 8. This column pair was used for the detection of multi-component organochlorine compounds.

7.3.2.5 Operating conditions for a DB-5/DB-1701 column pair with thinner films, a different type of splitter, and a slower temperature programming rate are provided in Table 7. These conditions gave better peak shapes for Nitrofen and Dicofol. Table 6 lists the retention times for the compounds detected on this column pair.

7.4 Calibration

7.4.1 Prepare calibration standards using the procedures in Sec. 5.0. Refer to Method 8000 (Sec. 7.0) for proper calibration techniques for both initial calibration and calibration verification. The procedure for either internal or external calibration may be used. In most cases, external standard calibration is used with Method 8081 because of the sensitivity of the electron capture detector and the probability of the internal standard being affected by interferences. Because several of the pesticides may co-elute on any single-column, analysts should use two calibration mixtures (see Sec. 3.8). The specific mixture should be selected to minimize the problem of peak overlap.

NOTE: Because of the sensitivity of the electron capture detector, the injection port and column should always be cleaned prior to performing the initial calibration.

7.4.1.1 Unless otherwise necessary for a specific project, the analysis of the multi-component analytes employs a single-point calibration. A single calibration standard near the mid-point of the expected calibration range of each multi-component analyte is included with the initial calibration of the single component analytes for pattern recognition, so that the analyst is familiar with the patterns and retention times on each column.

7.4.1.2 For calibration verification (each 12-hour shift) all target analytes required in the project plan must be injected.

7.4.2 Establish the GC operating conditions appropriate for the configuration (single-column or dual column, Sec. 7.3) using Tables 4, 5, 7, or 8 as guidance. Optimize the instrumental conditions for resolution of the target analytes and sensitivity. An initial oven temperature $\leq$140 -150°C is required to resolve the four BHC isomers. A final temperature of 240 - 270°C is required to elute decachlorobiphenyl. Use of injector pressure programming will improve the chromatography of late eluting peaks.

NOTE: Once established, the same operating conditions must be used for both calibrations and sample analyses.

7.4.3 A 2 µL injection volume of each calibration standard is recommended. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest.

7.4.4 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day or more. Therefore, the GC column should be primed (or deactivated) by injecting a pesticide standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning the initial calibration or calibration verification.

CAUTION: Several analytes, including Aldrin, may be observed in the injection just following this system priming. Always run an acceptable blank prior to running any standards or samples.

7.4.5 Calibration factors

When external standard calibration is employed, calculate the calibration factor for each analyte at each concentration, the mean calibration factor, and the relative standard deviation (RSD) of the calibration factors, using the formulae below. If internal standard calibration is employed, refer to Method 8000 for the calculation of response factors.

7.4.5.1 Calculate the calibration factor for each analyte at each concentration as:

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

7.4.5.2 Calculate the mean calibration factor for each analyte as:

$$\text{mean CF} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

where n is the number of standards analyzed.

7.4.5.3 Calculate the standard deviation (SD) and the RSD of the calibration factors for each analyte as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{CF}} \times 100$$

If the RSD for each analyte is $\leq$ 20%, then the response of the instrument is considered linear and the mean calibration factor can be used to quantitate sample results. If the RSD is greater than 20%, then linearity through the origin cannot be assumed. The analyst must use a calibration curve or a non-linear calibration model (e.g., a polynomial equation) for quantitation. See Method 8000 for information on non-linear calibrations.

7.4.6 Retention time windows

Absolute retention times are used for compound identification. Retention time windows are crucial to the identification of target compounds, and should be established by one of the approaches described in Method 8000.

7.4.6.1 Before establishing the retention time windows, make sure the gas chromatographic system is operating within optimum conditions.

7.4.6.2 The widths of the retention time windows are defined as described in Method 8000. However, the experience of the analyst should weigh heavily in the interpretation of the chromatograms.

7.5 Gas chromatographic analysis of sample extracts

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

7.5.2 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. See Sec. 8.4.4 for additional guidance on the frequency of the standard injections.

7.5.2.1 The calibration factor for each analyte should not exceed a ± 15 percent difference from the mean calibration factor calculated for the initial calibration. If a non-

linear calibration model or a linear model not through the origin has been employed for the initial calibration, consult Sec. 7 of Method 8000 for the specifics of calibration verification.

$$\% \text{ Difference} = \frac{CF - \overline{CF_v}}{\overline{CF}} \times 100$$

7.5.2.2 If this criterion is exceeded for any analyte, use the approach described in Sec. 7 of Method 8000 to calculate the average percent difference across all analytes. If the average of the responses for all analytes is within ±15%, then the calibration has been verified. However, the conditions in Sec. 7 of Method 8000 also apply, e.g., the average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project, and the data user must be provided with the calibration verification data or a list of those analytes that exceeded the ±15% limit.

7.5.2.3 If the calibration does not meet the ±15% limit (either on the basis of each compound or the average across all compounds), check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ±15%, then a new initial calibration must be prepared. The effects of a failing calibration verification standard on sample results are discussed in Sec. 7.5.7.

7.5.3 Compare the retention time of each analyte in the calibration standard with the absolute retention time windows established in Sec. 7.4.6. As described in Method 8000, the center of the absolute retention time window for each analyte is its retention time in the mid-concentration standard analyzed during the initial calibration. Each analyte in each standard must fall within its respective retention time window. If not, the gas chromatographic system must either be adjusted so that a second analysis of the standard does result in all analytes falling within their retention time windows, or a new initial calibration must be performed and new retention time windows established.

7.5.4 Inject a 2-µL aliquot of the concentrated sample extract. Record the volume injected to the nearest 0.05 µL and the resulting peak size in area units.

7.5.5 Tentative identification of an analyte occurs when a peak from a sample extract falls within the absolute retention time window. Each tentative identification must be confirmed using either a second GC column of dissimilar stationary phase or using another technique such as GC/MS (see Sec. 7.7).

When results are confirmed using a second GC column of dissimilar stationary phase, the analyst should check the agreement between the quantitative results on both columns once the identification has been confirmed. See Sec. 7 of Method 8000 for a discussion of such a comparison. Unless otherwise specified in an approved project plan, the higher result should be reported, as this is a conservative approach relative to protection of the environment. If the relative percent difference of the results exceeds 40%, consult Method 8000 for steps that may be taken to address the discrepancy.

7.5.6 When using the external calibration procedure (Method 8000), determine the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes, as follows. Proper quantitation requires the appropriate selection of a baseline from which the peak area or height can be determined.

7.5.6.1 For aqueous samples

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(V_t)(D)}{(\overline{CF})(V_i)(V_s)}$$

where:

A_x = Area (or height) of the peak for the analyte in the sample.

V_t = Total volume of the concentrated extract (µL).

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

$\overline{CF}$ = Mean calibration factor from the initial calibration (area/ng).

V_i = Volume of the extract injected (µL). The injection volume for samples and calibration standards must be the same. For purge-and-trap analysis, V_i is not applicable and therefore is set at 1.

V_s = Volume of the aqueous sample extracted in mL. If units of liters are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.

7.5.6.2 For non-aqueous samples

$$\text{Concentration } (\mu g/kg) = \frac{(A_x)(V_t)(D)}{(\overline{CF})(V_i)(W_s)}$$

where A_x, V_t, D, $\overline{CF}$, and V_i are the same as for aqueous samples, and

W_s = Weight of sample extracted (g). The wet weight or dry weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.

7.5.6.3 See Method 8000 for the equation used for internal standard quantitation.

7.5.6.4 If the responses exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.5.6.5 If partially overlapping or coeluting peaks are found, change GC columns or try GC/MS quantitation (see Sec. 8.0 and Method 8270).

7.5.7 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hour analytical shift), or calibration standards interspersed within the samples.

Although analysis of a single mid-concentration standard (standard mixture or multi-component analyte) will satisfy the minimum requirements, analysts are urged to use different calibration verification standards during organochlorine pesticide analyses. Also, multi-level standards (mixtures or multi-component analytes) are highly recommended to ensure that the detector response remains stable for all the analytes over the calibration range.

The results from these bracketing standards must meet the calibration verification criteria in Sec. 7.5.2. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be evaluated to prevent mis-quantitations and possible false negative results, and re-injection of the sample extracts may be required. More frequent analyses of standards will minimize the number of sample extracts that would have to be reinjected if the QC limits are violated for the standard analysis.

However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >15%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, as the verification standard has demonstrated that the analyte would have been detected were it present. In contrast, if an analyte above the QC limits was detected in a sample extract, then re-injection is necessary to ensure accurate quantitation. If an analyte was not detected in the sample and the standard response is more than 15% below the initial calibration response, then re-injection is necessary to ensure that the detector response has not deteriorated to the point that the analyte would not have been detected even though it was present (i.e., a false negative result).

7.5.8 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. It is *recommended* that standards be analyzed after every 10 samples (*required* after every 20 samples and at the end of a set) to minimize the number of samples that must be re-injected when the standards fail the QC limits. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

7.5.9 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.

7.5.10 Validation of GC system qualitative performance

7.5.10.1 Use the calibration standards analyzed during the sequence to evaluate retention time stability. The retention time windows are established using the absolute retention time of each analyte as described in Method 8000.

7.5.10.2 Each subsequent injection of a standard during the 12-hour analytical shift (i.e., those standards injected every 20 samples, or more frequently) must be checked against the retention time windows. If any of these subsequent standards fall outside their absolute retention time windows, the GC system is out of control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

7.5.11 Identification of mixtures (i.e. Chlordane and Toxaphene) is based on the characteristic "fingerprint" retention time and shape of the indicator peak(s); and quantitation is based on the area under the characteristic peaks as compared to the area under the corresponding calibration peak(s) of the same retention time and shape generated using either internal or external calibration procedures.

7.5.12 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector is warranted. Rerun the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to Method 3600 for the procedures to be followed in sample cleanup.

7.6 Quantitation of multi-component analytes - Multi-component analytes present problems in measurement. Suggestions are offered in the following sections for handing Toxaphene, Strobane, Chlordane, BHC, and DDT.

7.6.1 Toxaphene and Strobane - Toxaphene is manufactured by the chlorination of camphenes, whereas Strobane results from the chlorination of a mixture of camphenes and pinenes. Quantitation of Toxaphene or Strobane is difficult, but reasonable accuracy can be obtained. To calculate Toxaphene from GC/ECD results:

7.6.1.1. Adjust the sample size so that the major Toxaphene peaks are 10-70% of full-scale deflection (FSD).

7.6.1.2 Inject a Toxaphene standard that is estimated to be within ± 10 ng of the sample amount.

7.6.1.3 Quantitate Toxaphene using the total area of the Toxaphene pattern or using 4 to 6 major peaks.

7.6.1.3.1 While Toxaphene contains a large number of compounds that will produce well resolved peaks in a GC/ECD chromatogram, it also contains many other components that are not chromatographically resolved. This unresolved complex mixture results in the "hump" in the chromatogram that is characteristic of this mixture. Although the resolved peaks are important for the identification of the mixture, the area of the unresolved complex mixture contributes a significant portion of the area of the total response.

7.6.1.3.2 To measure total area, construct the baseline of Toxaphene in the sample chromatogram between the retention times of the first and last eluting Toxaphene components in the standard. In order to use the total area approach, the pattern in the sample chromatogram must be compared to that of the standard to ensure that all of the major components in the standard are present in the sample. Otherwise, the sample concentration may be significantly underestimated.

7.6.1.3.3 Toxaphene may also be quantitated on the basis of 4 to 6 major peaks. A collaborative study of a series of Toxaphene residues evaluated several approaches to quantitation of this compound, including the use of the total area of the peaks in the Toxaphene chromatogram and the use of a subset of 4 to 6 peaks. That study indicated that the use of 4 to 6 peaks provides

results that agree well with the total peak area approach and may avoid difficulties when interferences with Toxaphene peaks are present in the early portion of the chromatogram from compounds such as DDT. Whichever approach is employed should be documented and available to the data user, if necessary.

7.6.1.3.4 When Toxaphene is determined using the 4 to 6 peaks approach, the analyst must take care to evaluate the relative areas of the peaks chosen in the sample and standard chromatograms. It is highly unlikely that the peaks will match exactly, but the analyst should not employ peaks from the sample chromatogram whose relative sizes or areas appear to be disproportionally larger or smaller in the sample compared to the standard.

7.6.1.3.5 The heights or areas of the 4 to 6 peaks should be summed together and used to determine the Toxaphene concentration. Alternatively, use each peak in the standard to calculate a calibration factor for that peak, using the total mass of Toxaphene in the standard. These calibration factors are then used to calculate the concentration of each corresponding peak in the sample chromatogram and the 4 to 6 resulting concentrations are averaged to provide the final result for the sample.

7.6.2 Chlordane - Technical Chlordane is a mixture of at least 11 major components and 30 or more minor components that is used to prepare specific pesticide formulations. The CAS Registry number for Technical Chlordane is properly given as 12789-03-6. *Trans*-Chlordane (or α-Chlordane, CAS RN 5103-71-9) and *cis*-Chlordane (γ-Chlordane, CAS RN 5103-74-2), are the two most prevalent major components of Technical Chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch. Moreover, changes may occur when the technical material is used to prepare specific pesticide formulations. The approach used for evaluating and reporting Chlordane results will often depend on the end use of the results and the analyst's skill in interpreting this multi-component pesticide residue. The following sections discuss three specific options: reporting Technical Chlordane (12789-03-6), reporting Chlordane (not otherwise specified, 57-74-9), and reporting the individual Chlordane components that can be identified under their individual CAS numbers.

7.6.2.1 When the GC pattern of the residue resembles that of Technical Chlordane, the analyst may quantitate Chlordane residues by comparing the total area of the Chlordane chromatogram using three to five major peaks or the total area. If the Heptachlor epoxide peak is relatively small, include it as part of the total Chlordane area for calculation of the residue. If Heptachlor and/or Heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected Chlordane area.

NOTE: Octachloro epoxide, a metabolite of Chlordane, can easily be mistaken for Heptachlor epoxide on a nonpolar GC column.

To measure the total area of the Chlordane chromatogram, inject an amount of a Technical Chlordane standard which will produce a chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms. Construct the baseline of Technical Chlordane in the standard chromatogram between the retention times of the first and last eluting toxaphene components. Use this area and the mass of Technical Chlordane in the standard to calculate a calibration factor.

Construct a similar baseline in the sample chromatogram, measure the area, and use the calibration factor to calculate the concentration in the sample.

7.6.2.2 The GC pattern of a Chlordane residue in a sample may differ considerably from that of the Technical Chlordane standard. In such instances, it may not be practical to relate a sample chromatogram back to the pesticide active ingredient Technical Chlordane. Therefore, depending on the objectives of the analysis, the analyst may choose to report the sum of all the identifiable Chlordane components as "Chlordane (n.o.s.)" under the CAS number 57-74-9.

7.6.2.3 The third option is to quantitate the peaks of α-Chlordane, γ-Chlordane, and Heptachlor separately against the appropriate reference materials, and report these individual components under their respective CAS numbers.

7.6.2.4 To measure the total area of the Chlordane chromatogram, inject an amount of a Technical Chlordane standard which will produce a chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms.

7.6.3 Hexachlorocyclohexane - Hexachlorocyclohexane is also known as BHC, from the former name, benzene hexachloride. Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor. It consists of a mixture of six chemically distinct isomers and one or more heptachlorocyclohexanes and octachlorocyclohexanes. Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. Quantitate each isomer (α, β, γ, and δ) separately against a standard of the respective pure isomer.

7.6.4 DDT - Technical DDT consists primarily of a mixture of 4,4'-DDT (approximately 75%) and 2,4'-DDT (approximately 25%). As DDT weathers, 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, and 2,4'-DDD are formed. Since the 4,4'-isomers of DDT, DDE, and DDD predominate in the environment, these are the isomers normally regulated by EPA. Therefore, sample extracts should be quantitated against standards of the respective pure isomers of 4,4'-DDT, 4,4'-DDE, and 4,4'-DDD.

7.7 GC/MS confirmation may be used in conjunction with either single-column or dual-column analysis if the concentration is sufficient for detection by GC/MS.

7.7.1 Full-scan GC/MS will normally require a concentration of approximately 10 ng/µL in the final extract for each single-component compound. Ion trap or selected ion monitoring will normally require a concentration of approximately 1 ng/µL.

7.7.2 The GC/MS must be calibrated for the specific target pesticides when it is used for quantitative analysis.

7.7.3 GC/MS may not be used for confirmation when concentrations are below 1 ng/µL in the extract.

7.7.4 GC/MS confirmation should be accomplished by analyzing the same extract that is used for GC/ECD analysis and the extract of the associated method blank.

7.7.5 The base/neutral/acid extract and the associated blank may be used for GC/MS confirmation if the surrogates and internal standards do not interfere and if it is demonstrated

that the analyte is stable during acid/base partitioning. However, if the compounds are *not* detected in the base/neutral/acid extract, then GC/MS analysis of the pesticide extract should be performed.

7.7.6 A QC reference sample containing the compound must also be analyzed by GC/MS. The concentration of the QC reference sample must demonstrate that those pesticides identified by GC/ECD can be confirmed by GC/MS.

7.8 Suggested chromatographic system maintenance - When system performance does not meet the established QC requirements, corrective action is required, and may include one or more of the following.

7.8.1 Splitter connections - For dual-columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few centimeters (up to 30 cm) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

7.8.2 GC injector ports can be of critical concern, especially in the analysis of DDT and Endrin. Injectors that are contaminated, chemically active, or too hot can cause the degradation ("breakdown") of the analytes. Endrin and DDT breakdown to Endrin aldehyde, Endrin ketone, DDD, or DDE. When such breakdown is observed, clean and deactivate the injector port, break off at least 30 cm of the column and remount it. Check the injector temperature and lower it to 205°C, if required. Endrin and DDT breakdown are less of a problem when ambient on-column injectors are used.

7.8.3 Metal injector body - Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.8.3.1 Place a beaker beneath the injector port inside the oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene, catching the rinsate in the beaker.

7.8.3.2 Prepare a solution of a deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, rinse the injector body with toluene, methanol, acetone, then hexane. Reassemble the injector and replace the columns.

7.8.4 Column rinsing - The column should be rinsed with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone. Methylene chloride is a good final rinse and in some cases may be the only solvent required. The column should then be filled with methylene chloride and allowed to stand flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation techniques can be found in Method 3500. If an extract cleanup procedure was performed, refer to Method 3600 for the appropriate quality control procedures. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification, and chromatographic analysis of samples.

8.3 Initial Demonstration of Proficiency

8.3.1 Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made.

8.3.2 It is suggested that the quality control (QC) reference sample concentrate (as discussed in Section 8.0 of Methods 8000 and 3500) contain each analyte of interest at 10 mg/L. If this method is to be used for analysis of Chlordane or Toxaphene only, the QC reference sample concentrate should contain the most representative multi-component mixture at a suggested concentration of 50 mg/L in acetone. See Method 8000, Sec. 8.0 for additional information on how to accomplish this demonstration.

8.3.3 Calculate the average recovery and the standard deviation of the recoveries of the analytes in each of the four QC reference samples. Refer to Sec. 8.0 of Method 8000 for procedures for evaluating method performance.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, a matrix spike, a duplicate, a laboratory control sample (LCS), and the addition of surrogates to each field sample and QC sample.

8.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.2 In-house method performance criteria should be developed using the guidance found in Sec. 8.0 of Method 8000 for procedures for evaluating method performance.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same

concentrations as the matrix spike. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 Include a calibration standard after each group of 20 samples (it is *recommended* that a calibration standard be included after every 10 samples to minimize the number of repeat injections) in the analysis sequence as a calibration check. Thus, injections of method blank extracts, matrix spike samples, and other non-standards are counted in the total. Solvent blanks, injected as a check on cross-contamination, need not be counted in the total. The response factors for the calibration should be within ±15% of the initial calibration (see Sec. 7.5.2). When this calibration verifiction standard falls out of this acceptance window, the laboratory should stop analyses and take corrective action.

8.4.5 Whenever quantitation is accomplished using an internal standard, internal standards must be evaluated for acceptance. The measured area of the internal standard must be no more than 50 percent different from the average area calculated during calibration. When the internal standard peak area is outside the limit, all samples that fall outside the QC criteria must be reanalyzed.

8.4.6 DDT and Endrin are easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a standard containing only 4,4'-DDT and Endrin. Presence of 4,4'-DDE, 4,4'-DDD, Endrin ketone or Endrin indicates breakdown. If degradation of either DDT or Endrin exceeds 15%, take corrective action before proceeding with calibration.

8.4.6.1 Calculate percent breakdown as follows:

$$\%\ \text{breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD + DDE)}}{\text{sum of all peak areas (DDT + DDE + DDD)}} \times 100$$

$$\%\ \text{breakdown of Endrin} = \frac{\text{sum of degradation peak areas (aldehyde + ketone)}}{\text{sum of all peak areas (Endrin + aldehyde + ketone)}} \times 100$$

8.4.6.2 The breakdown of DDT and Endrin should be measured before samples are analyzed and at the beginning of each 12-hour shift. Injector maintenance and recalibration should be completed if the breakdown is greater than 15% for either compound (Sec. 7.8.2).

8.4.7 Whenever silica gel (Method 3630) or Florisil (Method 3620) cleanups are used, the analyst must demonstrate that the fractionation scheme is reproducible. Batch to batch variation in the composition of the silica gel or Florisil or overloading the column may cause a change in the distribution patterns of the organochlorine pesticides. When compounds are found in two fractions, add the concentrations found in the fractions, and correct for any additional dilution.

8.4.8 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries: The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method

8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined in Chapter One. A laboratory should develop its own matrix-specific MDLs using the guidance found in Chapter One.

9.2 The chromatographic separations in this method have been tested in a single laboratory by using clean hexane and liquid and solid waste extracts that were spiked with the test compounds at three concentrations. Single-operator precision, overall precision, and method accuracy were found to be related to the concentration of the compound and the type of matrix.

9.3 This method has been applied in a variety of commercial laboratories for environmental and waste matrices. Performance data were obtained for a limited number of target analytes spiked into sewage sludge and dichloroethene stillbottoms at high concentrations. These data are provided in Tables 9 and 10.

9.4 The accuracy and precision obtainable with this method depend on the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used.

9.5 Tables 9 and 10 contain precision and recovery data generated for sewage sludge and dichloroethane stillbottoms. Table 11 contains recovery data for a clay soil, taken from Reference 10. The spiking concentration was for the clay soil was 500 µg/kg. The spiking solution was mixed into the soil and then immediately transferred to the extraction device and immersed in the extraction solvent. The spiked sample was then extracted by Method 3541 (Automated Soxhlet). The data represent a single determination. Analysis was by capillary column gas chromatography/electron capture detector following Method 8081 for the organochlorine pesticides.

10.0 REFERENCES

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TABLE 1

GAS CHROMATOGRAPHIC RETENTION TIMES
FOR THE ORGANOCHLORINE PESTICIDES
USING WIDE-BORE CAPILLARY COLUMNS
SINGLE-COLUMN METHOD OF ANALYSIS

Compound	Retention Time (min) DB 608[a]	DB 1701[a]
Aldrin	11.84	12.50
α-BHC	8.14	9.46
β-BHC	9.86	13.58
δ-BHC	11.20	14.39
γ-BHC (Lindane)	9.52	10.84
α-Chlordane	15.24	16.48
γ-Chlordane	14.63	16.20
4,4'-DDD	18.43	19.56
4,4'-DDE	16.34	16.76
4,4'-DDT	19.48	20.10
Dieldrin	16.41	17.32
Endosulfan I	15.25	15.96
Endosulfan II	18.45	19.72
Endosulfan Sulfate	20.21	22.36
Endrin	17.80	18.06
Endrin aldehyde	19.72	21.18
Heptachlor	10.66	11.56
Heptachlor epoxide	13.97	15.03
Methoxychlor	22.80	22.34
Toxaphene	MR	MR

NA = Data not available.

MR = Multiple response compound.

[a] See Table 4 for GC operating conditions.

TABLE 2

GAS CHROMATOGRAPHIC RETENTION TIMES
FOR THE ORGANOCHLORINE PESTICIDES
USING NARROW-BORE CAPILLARY COLUMNS
SINGLE-COLUMN METHOD OF ANALYSIS

Compound	Retention Time (min) DB 608[a]	DB 5[a]
Aldrin	14.51	14.70
α-BHC	11.43	10.94
β-BHC	12.59	11.51
δ-BHC	13.69	12.20
γ-BHC (Lindane)	12.46	11.71
α-Chlordane	NA	NA
γ-Chlordane	17.34	17.02
4,4'-DDD	21.67	20.11
4,4'-DDE	19.09	18.30
4,4'-DDT	23.13	21.84
Dieldrin	19.67	18.74
Endosulfan I	18.27	17.62
Endosulfan II	22.17	20.11
Endosulfan sulfate	24.45	21.84
Endrin	21.37	19.73
Endrin aldehyde	23.78	20.85
Heptachlor	13.41	13.59
Heptachlor epoxide	16.62	16.05
Methoxychlor	28.65	24.43
Toxaphene	MR	MR

NA = Data not available.

MR = Multiple response compound.

[a] See Table 4 for GC operating conditions.

TABLE 3

FACTORS FOR DETERMINATION OF ESTIMATED QUANTITATION LIMITS[a] (EQLs)
FOR VARIOUS MATRICES

Matrix	Factor
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a] Laboratories may estimate the quantitation limits of the target analytes in environmental and waste media by generating MDLs in organic-free reagent water and using the following equation (see Sec. 5.0 of Chapter One for information on generating MDL data):

EQL = [MDL in water] times [factor in this table]

For nonaqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. EQLs determined using these factors are provided as guidance and may not always be achievable.

TABLE 4

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	225°C
Detector temperature	300°C
Initial temperature	100°C, hold 2 minutes
Temperature program	100°C to 160°C at 15°C/min, followed by 160°C to 270°C at 5°C/min
Final temperature	270°C

Column 2 - 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent), 25 µm coating thickness, 1 µm film thickness.

Carrier gas	Nitrogen
Carrier gas pressure	20 psi
Injector temperature	225°C
Detector temperature	300°C
Initial temperature	160°C, hold 2 minutes
Temperature program	160°C to 290°C at 5°C/min
Final temperature	290°C, hold 1 min

TABLE 5

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

Column 1 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

Column 2 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Both Column 1 and Column 2 use the same GC operating conditions.

Carrier gas	Helium
Carrier gas flow rate	5-7 mL/minute
Makeup gas	argon/methane (P-5 or P-10) or nitrogen
Makeup gas flow rate	30 mL/min
Injector temperature	250°C
Detector temperature	290°C
Initial temperature	150°C, hold 0.5 minute
Temperature program	150°C to 270°C at 5°C/min
Final temperature	270°C, hold 10 min

Column 3 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

Carrier gas	Helium
Carrier gas flow rate	6 mL/minute
Makeup gas	argon/methane (P-5 or P-10) or nitrogen
Makeup gas flow rate	30 mL/min
Injector temperature	205°C
Detector temperature	290°C
Initial temperature	140°C, hold 2 min
Temperature program	140°C to 240°C at 10°C/min, hold 5 minutes at 240°C, 240°C to 265°C at 5°C/min
Final temperature	265°C, hold 18 min

TABLE 6

RETENTION TIMES OF THE ORGANOCHLORINE PESTICIDES[a]
DUAL-COLUMN METHOD OF ANALYSIS

Compound	DB-5 RT (min)	DB-1701 RT (min)
DBCP	2.14	2.84
Hexachlorocyclopentadiene	4.49	4.88
Etridiazole	6.38	8.42
Chloroneb	7.46	10.60
Hexachlorobenzene	12.79	14.58
Diallate	12.35	15.07
Propachlor	9.96	15.43
Trifluralin	11.87	16.26
α-BHC	12.35	17.42
PCNB	14.47	18.20
γ-BHC	14.14	20.00
Heptachlor	18.34	21.16
Aldrin	20.37	22.78
Alachlor	18.58	24.18
Chlorothalonil	15.81	24.42
Alachlor	18.58	24.18
β-BHC	13.80	25.04
Isodrin	22.08	25.29
DCPA	21.38	26.11
δ-BHC	15.49	26.37
Heptachlor epoxide	22.83	27.31
Endosulfan-I	25.00	28.88
γ-Chlordane	24.29	29.32
α-Chlordane	25.25	29.82
trans-Nonachlor	25.58	30.01
4,4'-DDE	26.80	30.40
Dieldrin	26.60	31.20
Perthane	28.45	32.18
Endrin	27.86	32.44
Chloropropylate	28.92	34.14
Chlorobenzilate	28.92	34.42
Nitrofen	27.86	34.42
4,4'-DDD	29.32	35.32
Endosulfan II	28.45	35.51
4,4'-DDT	31.62	36.30
Endrin aldehyde	29.63	38.08
Mirex	37.15	38.79
Endosulfan sulfate	31.62	40.05
Methoxychlor	35.33	40.31
Captafol	32.65	41.42

(continued)

TABLE 6 (continued)

RETENTION TIMES OF THE ORGANOCHLORINE PESTICIDES[a]
DUAL-COLUMN METHOD OF ANALYSIS

Compound	DB-5 RT (min)	DB-1701 RT (min)
Endrin ketone	33.79	42.26
Permethrin	41.50	45.81
Kepone	31.10	[b]
Dicofol	35.33	[b]
Dichlone	15.17	[b]
α,α´-Dibromo-m-xylene	9.17	11.51
2-Bromobiphenyl	8.54	12.49

[a] See Table 7 for GC operating conditions.

[b] Not detected at 2 ng per injection.

TABLE 7

GC OPERATING CONDITIONS FOR ORGANOCHLORINE PESTICIDES
FOR DUAL-COLUMN METHOD OF ANALYSIS
LOW TEMPERATURE, THIN FILM

Column 1:	DB-1701 or equivalent 30 m x 0.53 mm ID 1.0 µm film thickness
Column 2:	DB-5 or equivalent 30 m x 0.53 mm ID 0.83 µm film thickness
Carrier gas	Helium
Carrier gas flow rate	6 mL/minute
Makeup gas	Nitrogen
Makeup gas flow rate	20 mL/min
Injector temperature	250°C
Detector temperature	320°C
Initial temperature	140°C, hold 2 minutes
Temperature program	140°C to 270°C at 2.8°C/min
Final temperature	270°C, hold 1 minute

TABLE 8

GC OPERATING CONDITIONS FOR ORGANOCHLORINE PESTICIDES
FOR THE DUAL COLUMN METHOD OF ANALYSIS
HIGH TEMPERATURE, THICK FILM

Column 1:	DB-1701 (J&W) or equivalent 30 m x 0.53 mm ID 1.0 µm
Column 2:	DB-5 (J&W) or equivalent 30 m x 0.53 mm ID 1.5 µm
Carrier gas:	Helium
Carrier gas flowrate:	6 mL/minute
Makeup gas:	Nitrogen
Makeup gas flowrate:	20 (mL/min)
Injector temperature:	250°C
Detector temperature:	320°C
Initial temperature:	150°C, hold 0.5 min
Temperature program:	150°C to 190°C at 12°C/min, hold 2 min 190°C to 275°C at 4°C/min
Final temperature	275°C, hold 10 min

TABLE 9

ANALYTE RECOVERY FROM SEWAGE SLUDGE

Compound	Ultrasonic Extraction %Recovery	Ultrasonic Extraction %RSD	Soxhlet %Recovery	Soxhlet %RSD
Hexachloroethane	80	7	79	1
2-Chloronapthalene	50	56	67	8
4-Bromodiphenyl ether	118	4	nd	nd
α-BHC	88	25	265	18
γ-BHC	55	9	155	29
Heptachlor	60	13	469	294
Aldrin	92	33	875	734
β-BHC	351	71	150	260
δ-BHC	51	11	57	2
Heptachlor epoxide	54	11	70	3
Endosulfan I	52	11	70	4
γ-Chlordane	50	9	65	1
α-Chlordane	49	8	66	0
DDE	52	11	74	1
Dieldrin	89	19	327	7
Endrin	56	10	92	15
Endosulfan II	52	10	88	11
DDT	57	10	95	17
Endrin aldehyde	45	6	42	10
DDD	57	11	99	8
Tetrachloro-m-xylene	71	19	82	1
Decachlorobiphenyl	26	23	28	48

Concentration spiked in the sample: 500-1000 ng/g, three replicates analyses.

Soxhlet extraction by Method 3540 with methylene chloride.

Ultrasonic extraction by Method 3550 with methylene chloride/acetone (1:1).

Cleanup by Method 3640.

GC column: DB-608, 30 m x 0.53 mm ID.

TABLE 10

ANALYTE RECOVERY FROM DICHLOROETHANE STILLBOTTOMS

Compound	Ultrasonic Extraction %Recovery	Ultrasonic Extraction %RSD	Soxhlet %Recovery	Soxhlet %RSD
Hexachloroethane	70	2	50	30
2-Chloronapthalene	59	3	35	35
4-Bromodiphenyl ether	159	14	128	137
α-BHC	55	7	47	25
β-BHC	43	6	30	30
Heptachlor	48	6	55	18
Aldrin	48	5	200	258
β-BHC	51	7	75	42
δ-BHC	43	4	119	129
Heptachlor epoxide	47	6	66	34
Endosulfan I	47	4	41	18
γ-Chlordane	48	5	47	13
α-Chlordane	45	5	37	21
DDE	45	4	70	40
Dieldrin	45	5	58	24
Endrin	50	6	41	23
Endosulfan II	49	5	46	17
DDT	49	4	40	29
Endrin aldehyde	40	4	29	20
DDD	48	5	35	21
Tetrachloro-m-xylene	49	2	176	211
Decachlorobiphenyl	17	29	104	93

Concentration spiked in the sample: 500-1000 ng/g, three replicates analyses.

Soxhlet extraction by Method 3540 with methylene chloride.

Ultrasonic extraction by Method 3550 with methylene chloride/acetone (1:1).

Cleanup by Method 3640.

GC column: DB-608, 30 m x 0.53 mm ID.

TABLE 11

SINGLE LABORATORY ACCURACY DATA FOR THE EXTRACTION OF ORGANOCHLORINE PESTICIDES FROM SPIKED CLAY SOIL BY METHOD 3541 (AUTOMATED SOXHLET)[a]

Compound Name	% Recovery DB-5	DB-1701
α-BHC	89	94
β-BHC	86	ND
Heptachlor	94	95
Aldrin	ND	92
Heptachlor epoxide	97	97
trans-Chlordane	94	95
Endosulfan I	92	92
Dieldrin	ND	113
Endrin	111	104
Endosulfan II	104	104
4,4'-DDT	ND	ND
Mirex	108	102

[a] The operating conditions for the automated Soxhlet were:

Immersion time 45 min; extraction time 45 min; 10 g sample size; extraction solvent, 1:1 acetone/hexane. No equilibration time following spiking.

ND = Not able to determine because of interference.

All compounds were spiked at 500 µg/kg.

Data taken from Reference 10.

TABLE 12

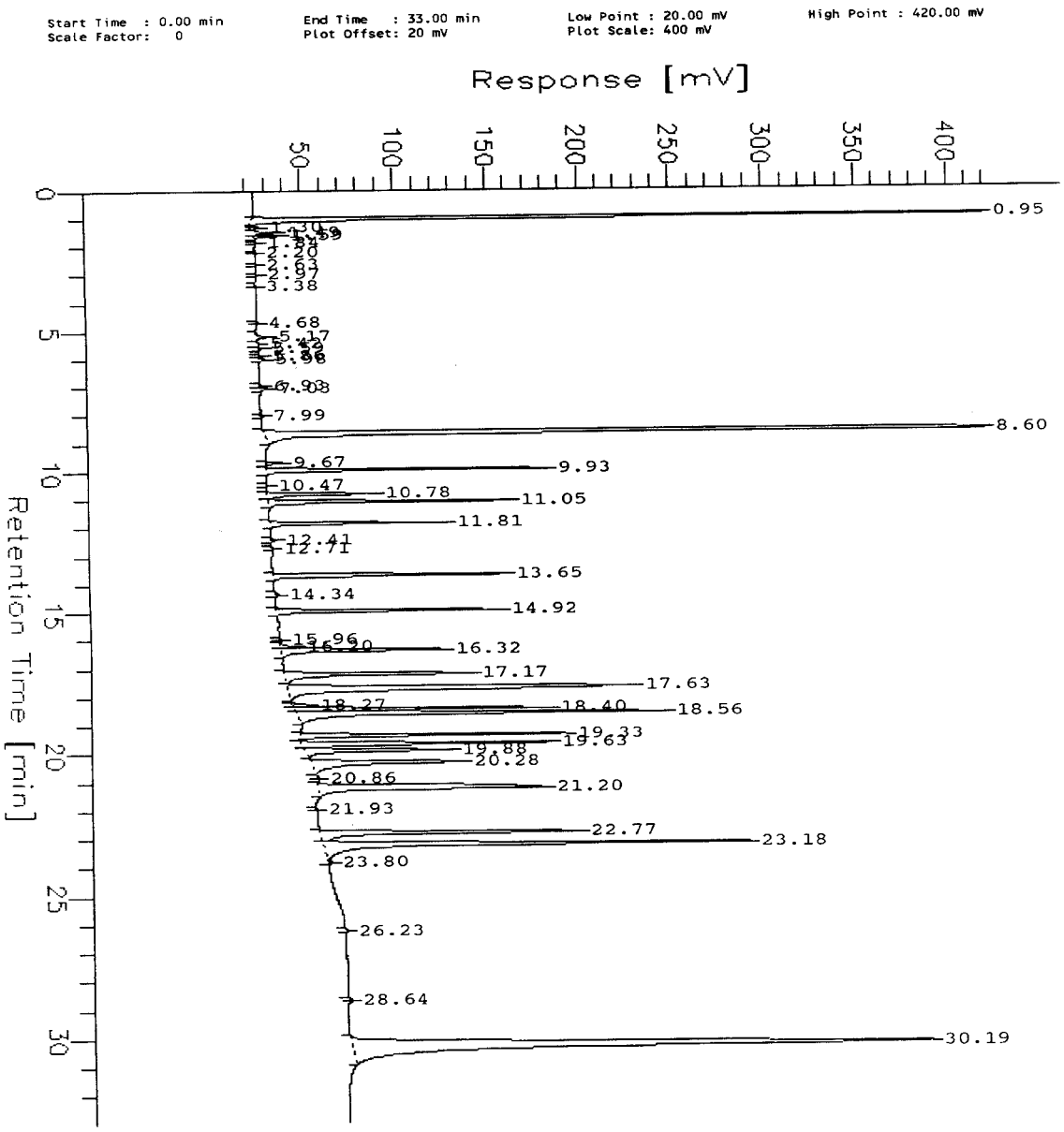
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR SOLID PHASE EXTRACTION BY METHOD 3535[1]

Compound	Bias (%)				Precision (%)				MDL (µg/L)	
	Ground water (low)	Ground water (high)	Waste water (low)	Waste water (high)	Ground water (low)	Ground water (high)	Waste water (low)	Waste water (high)	Ground water	Waste water
Aldrin	37.3	93.5	79.3	94.0	23.7	5.5	6.7	3.4	1.4	0.83
β-BHC	89.2	107.8	79.7	82.3	6.5	2.5	1.6	4.2	0.91	0.20
δ-BHC	106.2	86.0	88.9	83.4	5.6	2.4	2.5	4.2	0.93	0.35
α-Chlordane	75.4	112.3	78.9	89.5	12.8	2.7	4.7	2.4	1.5	0.58
γ-Chlordane	70.7	98.9	79.9	93.9	15.8	2.7	4.6	2.9	1.8	0.58
Dieldrin	83.4	96.1	81.2	93.3	7.1	2.3	3.8	3.6	0.9	0.49
Endosulfan I	79.6	99.1	79.6	87.9	10.6	2.3	4.1	3.8	1.3	0.51
Endosulfan II	94.5	101.6	82.7	93.5	5.8	2.8	4.2	4.1	0.9	0.54
Endrin	88.3	98.4	85.1	89.6	6.2	2.3	3.1	2.9	1.7	0.82
Endrin Aldehyde	87.5	99.9	69.0	80.2	6.0	4.0	3.3	5.9	0.8	0.36
Heptachlor	43.1	95.4	71.8	78.6	19.2	3.9	5.0	2.8	1.3	0.56
Heptachlor Epoxide	76.4	97.6	75.3	83.4	12.1	2.4	2.9	3.3	1.5	0.34
Lindane	81.3	115.2	82.1	85.3	11.1	3.2	2.4	3.1	1.4	0.32
p,p'-DDE	80.3	96.0	85.1	97.9	8.3	2.5	4.4	2.4	1.0	0.59
p,p'-DDT	86.6	105.4	105	111	4.4	2.7	4.3	4.7	0.6	0.71
p,p'-TDE (DDD)	90.5	101.1	74.9	79.6	4.8	2.4	4.6	2.9	1.4	0.85

[1]All results determined from seven replicates of each sample type. Two spiking levels were used. "Low" samples were spiked at 5-10 µg/L for each analyte, while "high" samples were spiked at 250 - 500 µg/L. MDL values were determined from the "low" samples without further consideration of the spiking level.

FIGURE 1

GAS CHROMATOGRAM OF THE MIXED ORGANOCHLORINE PESTICIDE STANDARD

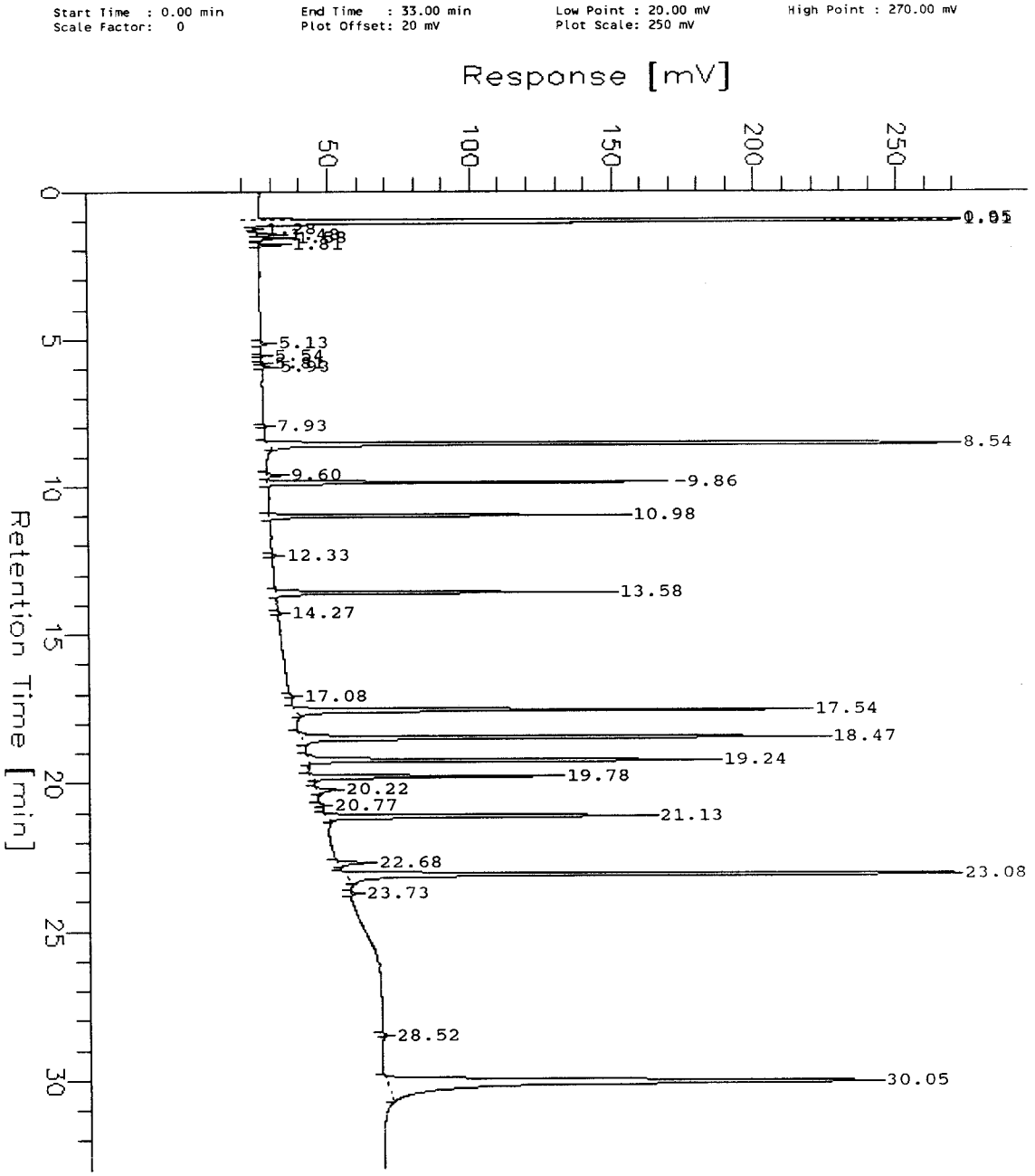


Column: 30 m x 0.25 mm ID, DB-5

Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 2

GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX A

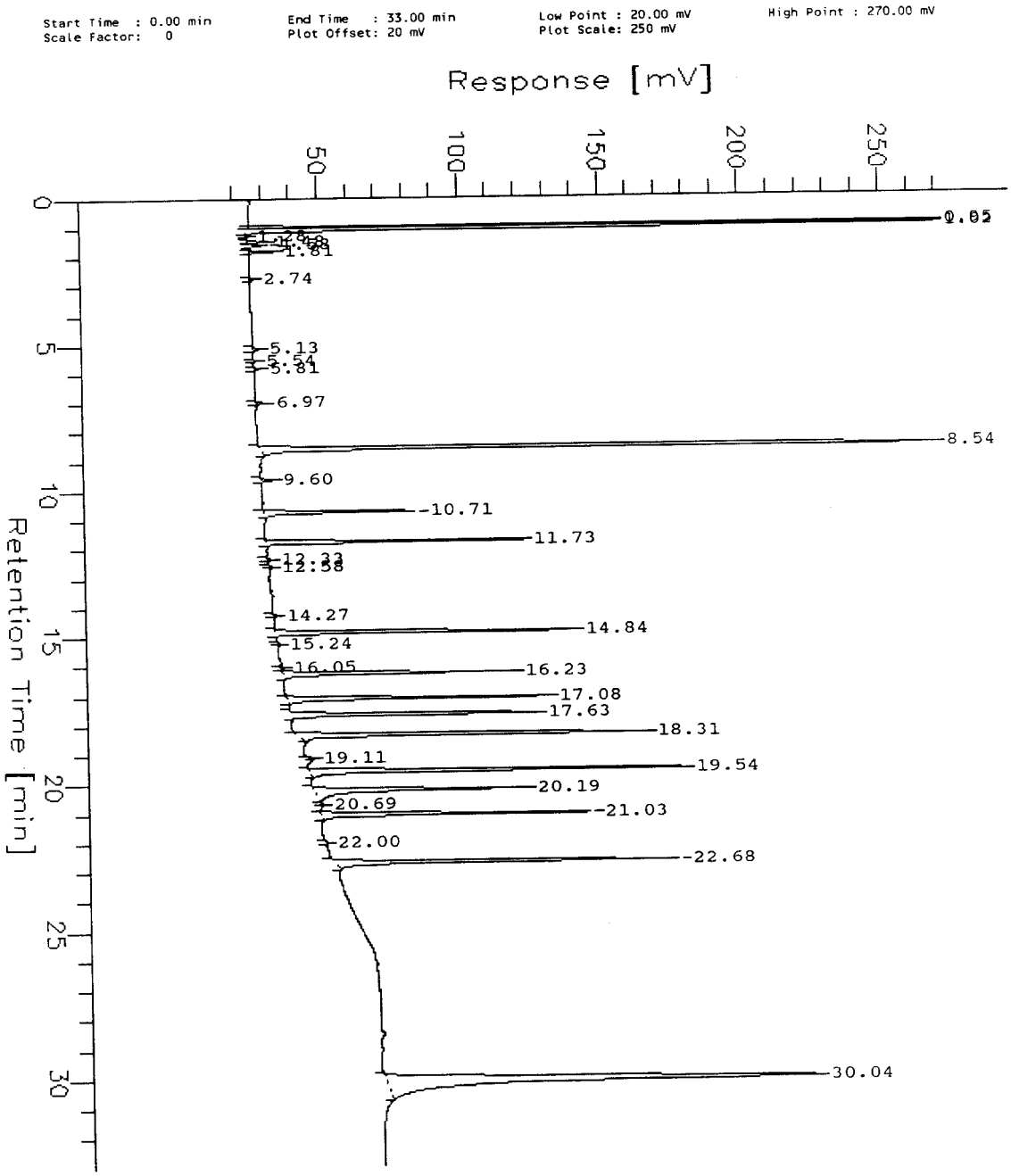


Column: 30 m x 0.25 mm ID, DB-5

Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 3

GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX B

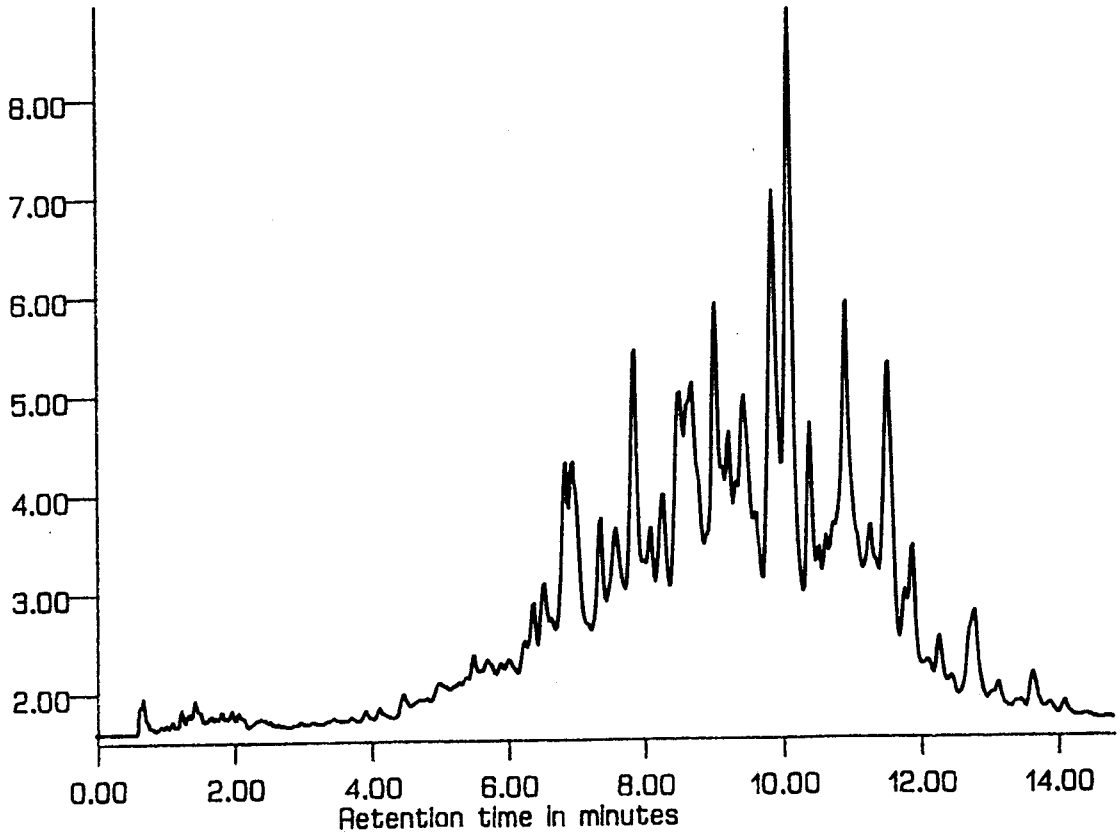


Column: 30 m x 0.25 mm ID, DB-5

Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 4

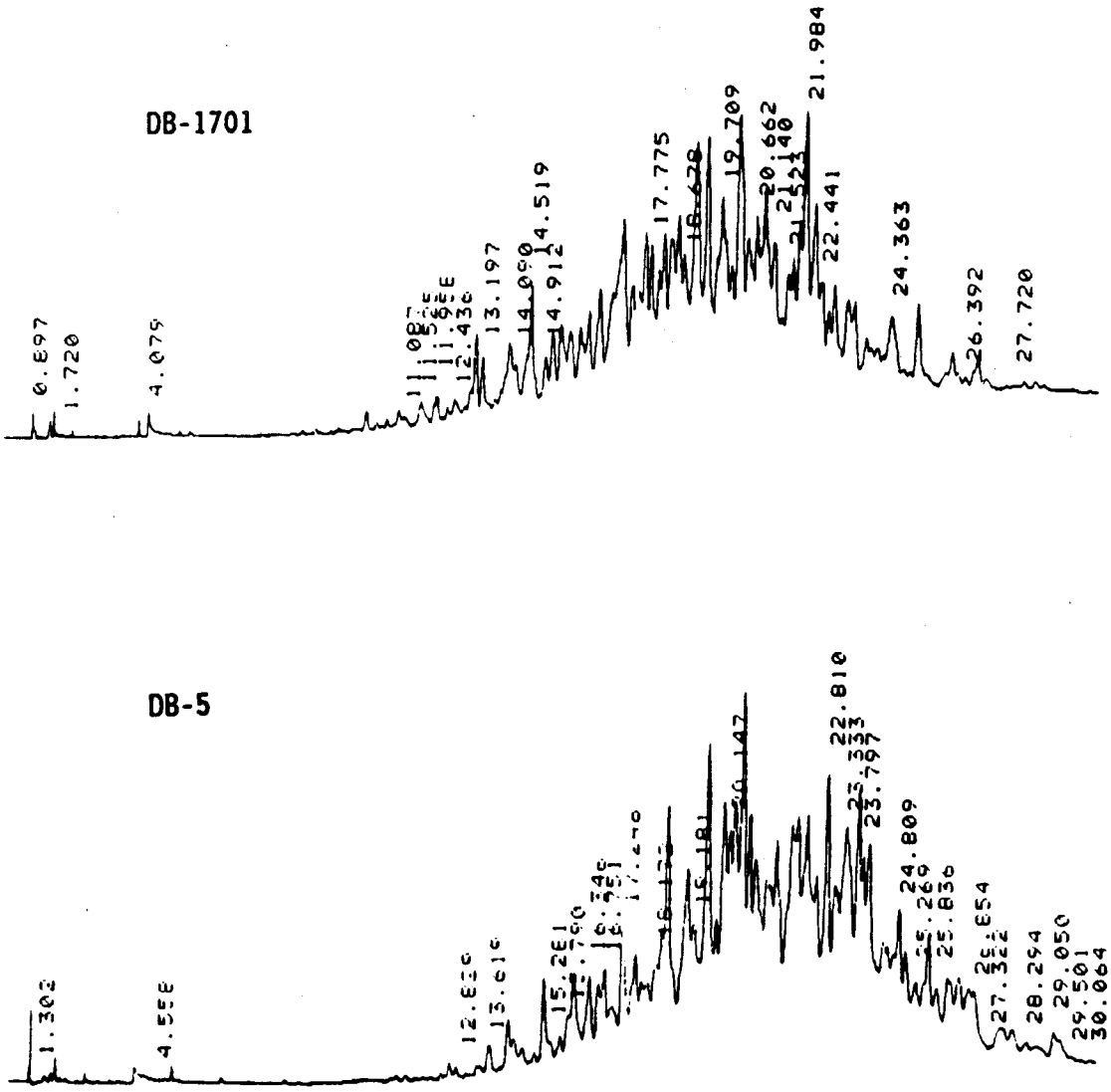
GAS CHROMATOGRAM OF TOXAPHENE



Toxaphene analyzed on an SPB-608 fused-silica open-tubular column. The GC operating conditions were as follows: 30 m x 0.53 mm ID SPB-608. Temperature program: 200°C (2 min hold) to 290°C at 6°C/min.

FIGURE 5

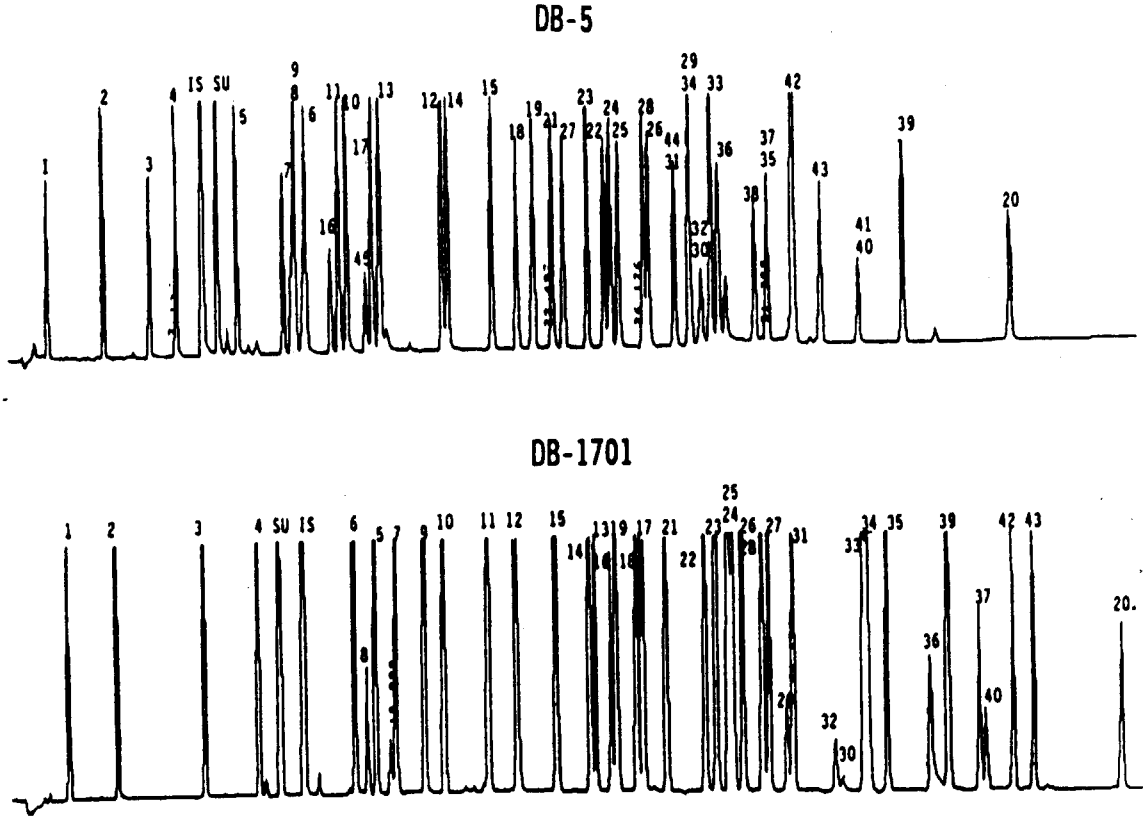
GAS CHROMATOGRAM OF STROBANE



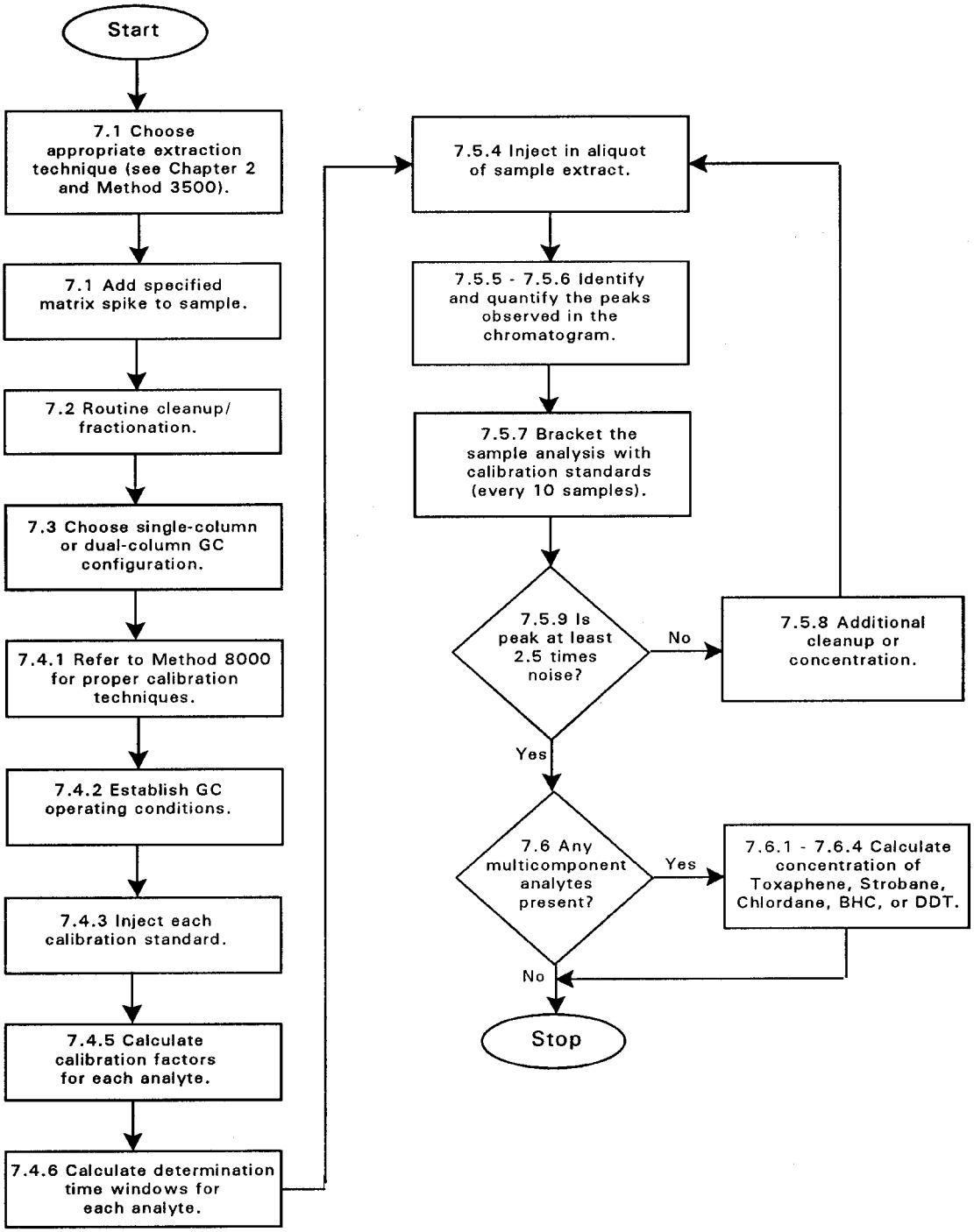
Strobane analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

FIGURE 6

GAS CHROMATOGRAM OF ORGANOCHLORINE PESTICIDES



Organochlorine pesticides analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (0.83-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to an 8 in. injection tee (Supelco Inc.). Temperature program: 140°C (2 min hold) to 270°C (1 min hold) at 2.8°C/min.


Start
7.1 Choose appropriate extraction technique (see Chapter 2 and Method 3500).
7.1 Add specified matrix spike to sample.
7.2 Routine cleanup/ fractionation.
7.3 Choose single-column or dual-column GC configuration.
7.4.1 Refer to Method 8000 for proper calibration techniques.
7.4.2 Establish GC operating conditions.
7.4.3 Inject each calibration standard.
7.4.5 Calculate calibration factors for each analyte.
7.4.6 Calculate determination time windows for each analyte.
7.5.4 Inject in aliquot of sample extract.
7.5.5 - 7.5.6 Identify and quantify the peaks observed in the chromatogram.
7.5.7 Bracket the sample analysis with calibration standards (every 10 samples).
7.5.9 Is peak at least 2.5 times noise?
No
7.5.8 Additional cleanup or concentration.
Yes
7.6 Any multicomponent analytes present?
Yes
7.6.1 - 7.6.4 Calculate concentration of Toxaphene, Strobane, Chlordane, BHC, or DDT.
No
Stop