ORGANOPHOSPHORUS COMPOUNDS BY GAS CHROMATOGRAPHY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the gas chromatographic (GC) determination of organophosphorus (OP) compounds. The compounds listed in the table below have been determined by GC using capillary columns equipped with a flame photometric detector (FPD) or a nitrogen-phosphorus detector (NPD). Triazine herbicides have also been determined with this method when the NPD is used. Although performance data are presented for each of the listed chemicals, it is unlikely that all of them could be determined in a single analysis. This limitation exists because the chemical and chromatographic behavior of many of these chemicals can result in coelution. The analyst must select columns, detectors, and calibration procedures for the specific analytes of interest. Any listed chemical is a potential method interference when it is not a target analyte.

Analyte	CAS Registry No.[1]
Organophosphorus Pesticides	
Aspon[b]	3244-90-4
Azinphos-ethyl[a]	2642-71-9
Azinphos-methyl	86-50-0
Bolstar (Sulprofos)	35400-43-2
Carbophenothion[a]	786-19-6
Chlorfenvinphos[a]	470-90-6
Chlorpyrifos	2921-88-2
Chlorpyrifos methyl[a]	5598-13-0
Coumaphos	56-72-4
Crotoxyphos[a]	7700-17-6
Demeton-O[c]	8065-48-3
Demeton-S[c]	8065-48-3
Diazinon	333-41-5
Dichlorofenthion[a]	97-17-6

Analyte	CAS Registry No.[1]
Dichlorvos (DDVP)	62-73-7
Dicrotophos[a]	141-66-2
Dimethoate	60-51-5
Dioxathion[a,c]	78-34-2
Disulfoton	298-04-4
EPN	2104-64-5
Ethion[a]	563-12-2
Ethoprop	13194-48-4
Famphur[a]	52-85-7
Fenitrothion[a]	122-14-5
Fensulfothion	115-90-2
Fenthion	55-38-9
Fonophos[a]	944-22-9
Leptophos[a,d]	21609-90-5
Malathion	121-75-5
Merphos[c]	150-50-5
Mevinphos[e]	7786-34-7
Monocrotophos	6923-22-4
Naled	300-76-5
Parathion, ethyl	56-38-2
Parathion, methyl	298-00-0
Phorate	298-02-2
Phosmet[a]	732-11-6
Phosphamidon[a]	13171-21-6
Ronnel	299-84-3
Stirophos (Tetrachlorvinphos, Gardona)	22248-79-9
Sulfotepp	3689-24-5
Tetraethyl pyrophosphate (TEPP)[d]	107-49-3
Terbufos[a]	13071-79-9
Thionazin[a,b] (Zinophos)	297-97-2
Tokuthion[b] (Prothiofos)	34643-46-4
Trichlorfon[a]	52-68-6
Trichloronate[b]	327-98-0
Industrial Chemicals	
Hexamethyl phosphoramide[a] (HMPA)	680-31-9
Tri-*o*-cresyl phosphate[a,d] (TOCP)	78-30-8

Analyte	CAS Registry No.[1]
Triazine Herbicides (NPD only)	
Atrazine[a]	1912-24-9
Simazine[a]	122-34-9
Carbamates and Related Compounds	
Bendiocarb	22781-23-3
Butylate	2008-41-5
EPTC	759-94-4
Methiocarb	2032-65-7
Molinate	2212-67-1
Pebulate	1114-71-2
o-Phenylenediamine	95-54-5
Propham	122-42-9
Prosulfocarb	52888-80-9
Triallate	2303-17-5

[1]Chemical Abstract Service Registry Number
[a] This analyte has been evaluated using a 30-m column only (see Sec. 1.5).
[b] Production discontinued in the U.S., standard not readily available.
[c] Standards may have multiple components because of oxidation.
[d] Compound is extremely toxic or neurotoxic.
[e] Adjacent major/minor peaks can be observed due to *cis* and *trans* isomers.

1.2 This method includes a dual-column option that describes a hardware configuration in which two GC columns are connected to a single injection port and to two separate detectors. The option allows one injection to be used for dual-column simultaneous analysis.

1.3 Two detectors, either FPD or NPD, can be used for the listed organophosphorus chemicals. The FPD works by measuring the emission of phosphorus- or sulfur-containing species. Detector performance is optimized by selecting the proper optical filter and adjusting the hydrogen and air flows to the flame. The NPD is a flame ionization detector equipped with a rubidium ceramic flame tip which enhances the response of phosphorus- and nitrogen-containing analytes. The FPD is more sensitive and more selective, but is a less common detector in environmental laboratories.

1.4 The use of a 15-m column system has not been fully validated for the determination of all of the compounds listed in Sec. 1.1. The analyst must demonstrate chromatographic resolution of the analytes of interest and performance appropriate for the intended application prior to reporting data for the following analytes, or any additional analytes:

Azinphos-ethyl	Phosphamidon	Dioxathion
Ethion	Chlorfenvinphos	Leptophos
Carbophenothion	HMPA	TOCP
Famphur	Terbufos	Phosmet

1.5 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 (see Sec. 9.0 of this method). GC/AED may also be used as a confirmation technique, if sensitivity permits (see Method 8085).

1.6 EPA notes that there are limited published data on the efficiency of ultrasonic extraction with regard to organophosphorus pesticides at low part-per-billion (ppb) concentrations and below. As a result, use of this method for these compounds in particular should be supported by performance data such as those discussed in Method 3500.

1.7 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.8 Use of this method is restricted to use by, or under the supervision of, personnel appropriately experienced and trained in the use of capillary gas chromatography and in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method provides gas chromatographic conditions for the determination of part- per-billion concentrations of organophosphorus compounds. Prior to the use of this method, a measured volume or weight of liquid or solid sample is extracted using the appropriate matrix-specific sample extraction technique.

2.1.1 Aqueous samples may be extracted at neutral pH with methylene chloride using either Method 3510 (separatory funnel), Method 3520 (continuous liquid-liquid extraction), Method 3535 (solid-phase extraction), or other appropriate technique.

2.1.2 Solid samples may be extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Method 3540 (Soxhlet extraction), Method 3541 (automated Soxhlet extraction), Method 3545 (pressurized fluid extraction), Method 3546 (microwave extraction), Method 3550 (ultrasonic extraction), or other appropriate technique.

2.2 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), or other appropriate technique.

2.3 After cleanup, the extract is analyzed by injecting a measured aliquot into a gas chromatograph equipped with either a narrow-bore or wide-bore fused-silica capillary column, and either a flame photometric detector (FPD) or a nitrogen-phosphorus detector (NPD).

2.4 Organophosphorus esters and thioesters can hydrolyze under both acid and base conditions. Therefore, sample preparation procedures employing acid and base partitioning procedures are not appropriate for extracts to be analyzed by this method.

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware. Also refer to Methods 3500, 3600, and 8000, and Sec. 1.1 of this method for further information about interferences.

4.2 The use of Florisil® cleanup (Method 3620) for some of the compounds in this method was demonstrated to yield recoveries less than 85 percent and is therefore not recommended for all compounds. Refer to Method 3620 for example recoveries of organophosphorus compounds. Use of an FPD often eliminates the need for sample cleanup. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each analyte is not less than 85 percent.

4.3 The use of gel permeation cleanup (GPC) (Method 3640) for extract cleanup has been demonstrated to yield recoveries of less than 85 percent for many method analytes because the analytes elute before bis(2-ethylhexyl) phthalate. Therefore Method 3640 is not recommended for use with this method, unless analytes of interest are listed in Method 3640 or are demonstrated to give greater than 85 percent recovery.

4.4 Use of a flame photometric detector in the phosphorus mode will minimize interferences from materials that do not contain phosphorus or sulfur. Elemental sulfur will interfere with the determination of certain organophosphorus compounds by flame photometric gas chromatography. If Method 3660 is used for sulfur cleanup, only the tetrabutylammonium (TBA)-sulfite option should be employed, since copper may destroy OP pesticides. The stability of each analyte must be tested to ensure that the recovery from the TBA-sulfite sulfur cleanup step is not less than 85 percent.

4.5 A halogen-specific detector (i.e., electrolytic conductivity or microcoulometry) is very selective for the halogen-containing compounds and may be used for the determination of Chlorpyrifos, Ronnel, Coumaphos, Tokuthion, Trichloronate, Dichlorvos, EPN, Naled, and

Stirophos only. Many of the OP pesticides may also be detected by the electron capture detector (ECD), however, the ECD is not as specific as the NPD or FPD. The ECD should only be used when previous analyses have demonstrated that interferences will not adversely effect quantitation, and that the detector sensitivity is sufficient to meet project requirements.

4.6 Certain analytes will coelute, particularly on 15-m columns (Table 1). If coelution is observed, analysts should (1) select a second column of different polarity for confirmation, (2) use 30-m x 0.53-mm columns, or (3) use 0.25- or 0.32-mm ID columns. See Figures 1 through 4 for combinations of compounds that do not coelute on 15-m columns.

4.7 The following pairs coeluted on the DB-5/DB-210 30-m column pair:

GC Column	Coeluting pair
DB-5	Terbufos/tri-*o*-cresyl phosphate
	Naled/Simazine/Atrazine
	Dichlorofenthion/Demeton-O
	Trichloronate/Aspon
	Bolstar/Stirophos/Carbophenothion
	Phosphamidon/Crotoxyphos
	Fensulfothion/EPN
DB-210	Terbufos/tri-*o*-cresyl phosphate
	Dichlorofenthion/Phosphamidon
	Chlorpyrifos, methyl/Parathion, methyl
	Chlorpyrifos/Parathion, ethyl
	Aspon/Fenthion
	Demeton-O/Dimethoate
	Leptophos/Azinphos-methyl
	EPN/Phosmet
	Famphur/Carbophenothion

See Table 2 for examples of the retention times of these compounds on 30-m columns.

4.8 Analytical difficulties encountered for target analytes

4.8.1 Tetraethyl pyrophosphate (TEPP) is an unstable diphosphate which is readily hydrolyzed in water and is thermally labile (decomposes at 170 EC). Care must be taken to minimize loss during GC analysis and during sample preparation. Identification of bad standard lots is difficult since the electron impact (EI) mass spectrum of TEPP is nearly identical to its major breakdown product, triethyl phosphate.

4.8.2 The water solubility of dichlorvos (DDVP) is 10 g/L at 20 EC, and recovery is poor from aqueous solution.

4.8.3 Naled is converted to dichlorvos (DDVP) on column by debromination. This reaction may also occur during sample preparation. The extent of debromination will depend on the nature of the matrix being analyzed. The analyst must consider the potential for debromination when naled is to be determined.

4.8.4 Trichlorfon rearranges and is dehydrochlorinated in acidic, neutral, or basic media to form dichlorvos (DDVP) and hydrochloric acid. If this method is to be used for the determination of organophosphates in the presence of trichlorfon, the analyst should be aware of the possibility of its rearrangement to dichlorvos and the possibility of misidentification.

4.8.5 Demeton (systox) is a mixture of two compounds; O,O-diethyl O-[2-(ethylthio)ethyl]phosphorothioate (demeton-O) and O,O-diethyl S-[2-(ethylthio)ethyl]phosphorothioate (demeton-S). Two peaks are observed in all the chromatograms corresponding to these two isomers. It is recommended that the early eluting compound (demeton-S) be used for quantitation.

4.8.6 Dioxathion is a single-component pesticide. However, several extra peaks are observed in the chromatograms of standards. These peaks appear to be the result of spontaneous oxygen-sulfur isomerization. Because of this, dioxathion is not included in composite standard mixtures.

4.8.7 Merphos (tributyl phosphorotrithioite) is a single-component pesticide that is readily oxidized to its phosphorotrithioate (merphos oxone). Chromatographic analysis of Merphos almost always results in two peaks (unoxidized merphos elutes first). As the relative amounts of oxidation of the sample and the standard are probably different, quantitation based on the sum of both peaks may be most appropriate.

4.8.8 Retention times of some analytes, particularly monocrotophos, may increase with increasing concentrations in the injector. Analysts should check for retention time shifts in highly-contaminated samples.

4.8.9 Many analytes will degrade on reactive sites in the chromatographic system. Analysts must ensure that injectors and splitters are free from contamination and are silanized. Columns should be installed and maintained properly.

4.8.10 The performance of chromatographic systems will degrade with time. Column resolution, analyte breakdown, and baselines may be improved by column washing (see Sec. 11.0). Oxidation of columns is not reversible.

4.9 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing reagent blanks (see Sec. 9.0).

4.10 NP detector interferences -- Triazine herbicides, such as atrazine and simazine, and other nitrogen-containing compounds may interfere.

5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Gas chromatograph

An analytical system equipped with a gas chromatograph suitable for on-column or split/splitless injection, and all necessary accessories, including syringes, analytical columns, gases, suitable detector(s), and a recording device. The analyst should select the detector for the specific measurement application, either the flame photometric detector or the nitrogen-phosphorus detector. A data system for measuring peak areas and dual display of chromatograms is highly recommended.

6.2 GC columns

This method employs capillary columns (0.53-mm, 0.32-mm, or 0.25-mm ID and 15-m or 30-m length, depending on the needed resolution). Columns of 0.53-mm ID are recommended for most environmental and waste analysis applications. Dual-column, single-injector analysis needs columns of equal length and bore. See Sec. 4.0 and Figures 1 through 4 for guidance on selecting the proper length and diameter for columns.

The four columns listed in this section were the columns used in developing the method. The listing of these columns in this method is not intended to exclude the use of other columns that are available or that may be developed. Laboratories may use these columns or other capillary columns, provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

6.2.1 Column 1 -- 15-m or 30-m x 0.53-mm wide-bore capillary column, 1.0-µm film thickness, chemically bonded with 50% trifluoropropyl polysiloxane, 50% methyl polysiloxane (DB-210), or equivalent.

6.2.2 Column 2 -- 15-m or 30-m x 0.53-mm wide-bore capillary column, 0.83-µm film thickness, chemically bonded with 35% phenyl methyl polysiloxane (DB-608, SPB-608, RTx-35, or equivalent).

6.2.3 Column 3 -- 15-m or 30-m x 0.53-mm wide-bore capillary column, 1.0-µm film thickness, chemically bonded with 5% phenyl polysiloxane, 95% methyl polysiloxane (DB-5, SPB-5, RTx-50, or equivalent).

6.2.4 Column 4 -- 15- or 30-m x 0.53-mm ID wide-bore capillary column, chemically bonded with methyl polysiloxane (DB-1, SPB-1, or equivalent), 1.0-µm or 1.5-µm film thickness.

6.2.5 Column rinsing kit (optional) -- Bonded-phase column rinse kit (J&W Scientific, catalog no. 430-3000, or equivalent).

6.3 Splitter -- If a dual-column, single-injector configuration is used, the open tubular columns should be connected to one of the following splitters, or an equivalent device:

6.3.1 Splitter 1 -- J&W Scientific press-fit Y-shaped glass 3-way union splitter.

6.3.2 Splitter 2 -- Supelco 8-in glass injection tee, deactivated.

6.3.3 Splitter 3 -- Restek Y-shaped fused-silica connector.

6.4 Injectors

6.4.1 Packed column, 1/4-in injector ports equipped with hourglass liners are recommended for the 0.53-mm columns. These injector ports can be fitted with splitters (see Sec. 6.3) for dual-column analysis.

6.4.2 Split/splitless capillary injectors operated in the split mode are necessary for 0.25-mm and 0.32-mm columns.

6.5 Detectors

6.5.1 A flame photometric detector (FPD) operated in the phosphorus-specific mode is recommended.

6.5.2 A nitrogen-phosphorus detector (NPD) operated in the phosphorus-specific mode is less selective but can detect triazine herbicides.

6.5.3 Halogen-specific detectors (electrolytic conductivity or microcoulometry) may be used only for a limited number of halogenated or sulfur-containing analytes (see Sec. 4.5).

6.5.4 Electron-capture detectors may be used for a limited number of analytes (see Sec. 4.5).

6.6 Data system

6.6.1 A data system capable of presenting chromatograms, retention times, and peak integration data is strongly recommended.

6.6.2 Use of a data system that allows storage of raw chromatographic data is strongly recommended.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade or pesticide-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the 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. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 Extraction solvents

Samples should be extracted using a solvent system that gives optimum, reproducible recovery of the analytes of interest from the sample matrix, at the concentrations of interest. The choice of extraction solvent will depend on the analytes of interest and no single solvent is universally applicable to all analyte groups. Whatever solvent system is employed, including those specifically listed in this method, the analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Each new sample type must be spiked with the compounds of interest to determine the percent recovery. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

All solvents should be pesticide grade in quality or equivalent. Solvents may be degassed prior to use.

7.2.1 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$

7.2.2 Hexane, C_6H_{14}

7.2.3 Acetone, CH_3COCH_3

7.2.4 Tetrahydrofuran (THF), C_4H_8O -- For triazine standards only.

7.2.5 Methyl *tert*-butyl-ether (MTBE), CH_3O-*t*-C_4H_9 -- For triazine standards only.

7.3 Standard solutions

The following sections describe the preparation of stock, intermediate, and working standards for the compounds of interest. This discussion is provided as an example, and other approaches and concentrations of the target compounds may be used, as appropriate for the intended application. See Method 8000 for additional information on the preparation of calibration standards.

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

7.4.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compounds. Dissolve the compounds in suitable mixtures of acetone and 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 may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.4.2 Both simazine and atrazine have low solubilities in hexane. If standards of these compounds are necessary, atrazine should be dissolved in MTBE, and simazine should be dissolved in acetone/MTBE/THF (1:3:1).

7.4.3 Composite stock standard -- This standard may be prepared from individual stock solutions. The analyst must demonstrate that the individual analytes and common oxidation products are resolved by the chromatographic system. For composite stock standards containing less than 25 components, take exactly 1 mL of each individual stock solution at 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 40 mg/L. This composite solution can be further diluted to obtain the desired concentrations. Composite stock standards containing more than 25 components are not recommended.

7.4.4 Store the standard solutions (stock, composite, calibration, internal, and surrogate) at #6 EC in PTFE-sealed containers in the dark. All standard solutions should be replaced after two months, or sooner if routine QC (see Sec. 9.0) indicates a problem. Standards for easily hydrolyzed chemicals including TEPP, methyl parathion, and merphos should be checked at least every 30 days.

7.4.5 It is recommended that the individual lots of standards be subdivided and stored in small vials. Individual vials should be used as working standards to minimize the potential for contamination or hydrolysis of the entire lot.

7.5 Calibration standards should be prepared at a minimum of five concentrations by dilution of the composite stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in field samples and should bracket the linear range of the detector. Organophosphorus calibration standards should be replaced after one or two months, or sooner if comparison with check samples or historical data indicates that there is a problem. Laboratories may wish to prepare separate calibration solutions for the easily hydrolyzed standards identified above. See Method 8000 for additional information on the preparation of calibration standards.

7.6 Internal standards

Internal standards should only be used on well-characterized samples by analysts experienced in the technique. Use of internal standards is complicated by coelution of some OP pesticides and by the differences in detector response to dissimilar chemicals. If internal standards are to be used, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences.

7.6.1 FPD response for organophosphorus compounds is enhanced by the presence of sulfur atoms bonded to the phosphorus atom. It has not been established that a thiophosphate can be used as an internal standard for an OP with a different number of sulfur atoms (e.g., phosphorothioates [P=S] as an internal standard for phosphates [PO_4]) or phosphorodithioates [$P=S_2$]).

7.6.2 When 15-m columns are used, it may be difficult to fully resolve internal standards from target analytes and interferences. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences.

7.6.3 1-Bromo-2-nitrobenzene has been used as an NPD internal standard for a 30-m column pair. Prepare a solution of 1000 mg/L of 1-bromo-2-nitrobenzene. For spiking, dilute this solution to 5 mg/L. Use a spiking volume of 10 µL/mL of extract. The spiking concentration of the internal standards should be kept constant for all samples and calibration standards. Since its FPD response is small, 1-bromo-2-nitrobenzene is not an appropriate internal standard for that detector. No FPD internal standard is suggested.

7.7 Surrogate standards

The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system, and the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and blank with one or two surrogates (e.g., using organophosphorus compounds not expected to be present in the sample). If multiple analytes are to be measured, two surrogates (an early and a late eluter) are recommended. Deuterated analogs of analytes are not appropriate surrogates for GC/FPD or GC/NPD analysis.

7.7.1 If surrogates are to be used, the analyst must select one or more compounds that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate and document that the measurement of a surrogate is not affected by method or matrix interferences. General guidance on the selection and use of surrogates is provided in Method 3500 and Method 8000.

7.7.2 Tributyl phosphate and triphenyl phosphate are recommended as surrogates for either FPD and NPD analyses. A volume of 1.0 mL of a 1-µg/L spiking solution (containing 1 ng of surrogate) is added to each sample. If there is a coelution problem with either of these compounds, 4-chloro-3-nitrobenzo-trifluoride has also been used as a surrogate for NPD analysis. Other surrogate compounds and other spiking solution concentrations and/or volumes may be employed, provided that the analyst can demonstrate and document performance appropriate for the data quality needs of the particular application.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes."

8.2 Many organophosphorus compounds degrade rapidly in environmental samples. Organophosphorus esters hydrolyze under acidic or basic conditions. Therefore, the preservation of aqueous samples at pH=2 is NOT appropriate for most samples. Even with storage at #6 EC and using mercuric chloride as a preservative, most organophosphorus pesticides in groundwater samples collected for a national pesticide survey degraded within a 14-day period (see Reference 12).

8.3 Adjust aqueous samples to a pH of 5 to 8 using sodium hydroxide or sulfuric acid solution as soon as possible after sample collection. Record the volume used. Aqueous samples and solid samples should be chilled to 4 EC upon collection and shipped and stored at #6 EC until extraction.

8.4 Begin extraction of either aqueous or solid samples within 7 days of collection.

8.5 Store extracts at #6 EC and perform analyses within 40 days of extraction.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for specific determinative method QC procedures. Refer to Method 3500 or 5000 for QC procedures to ensure the proper operation of the various sample preparation techniques. If an extract cleanup procedure is performed, refer to Method 3600 for the appropriate QC procedures. Any more specific QC procedures provided in this method will supersede those noted in Methods 8000, 5000, 3500, or 3600.

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

9.4 Initial demonstration of proficiency

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. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish a demonstration of proficiency.

9.4.1 It is suggested that the quality control (QC) reference sample concentrate (as discussed in Methods 8000 and 3500) contain each analyte of interest at 10 mg/L. See Method 8000 for additional information on how to accomplish this demonstration.

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

9.5 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate, if possible, before processing the samples. The blanks should be carried through all

stages of sample preparation and analysis. When new reagents or chemicals are received, the laboratory should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

9.6 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, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample when surrogates are used. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.6.1 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, laboratories may use a 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. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.6.2 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 appropriate. When the results of the matrix spike analysis indicate 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. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.6.3 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance found in Method 8000.

9.7 Surrogate recoveries

If surrogates are used, the laboratory should evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000 for information on evaluating surrogate data and developing and updating surrogate limits. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in an approved project plan.

9.8 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.

10.0 CALIBRATION AND STANDARDIZATION

See Sec. 11.4 for information on calibration and standardization.

11.0 PROCEDURE

11.1 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), a continuous liquid-liquid extractor (Method 3520), solid-phase extraction (Method 3535), or other appropriate technique or solvent. Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using one of the Soxhlet extraction methods (Method 3540 or 3541), pressurized fluid extraction (Method 3545), microwave extraction (Method 3546), ultrasonic extraction (Method 3550), or other appropriate technique or solvents.

EPA notes that the efficiency of the applicable extraction techniques with regard to organophosphorus pesticides at low part-per-billion (ppb) concentrations and below in solid sample matrices is questionable for some compounds. As a result, use of any extraction method for these compounds in particular should be supported by performance data such as those discussed in Method 3500 and that are appropriate for the intended application.

The choice of extraction solvent and procedure will depend on the analytes of interest. No single solvent or extraction procedure is universally applicable to all analyte groups and sample matrices. The analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest, for any solvent system and extraction procedure employed, *including* those specifically listed in this method. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Each new sample type must be spiked with the compounds of interest to determine the percent recovery. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

Organophosphorus esters can hydrolyze under acidic or basic conditions. Therefore, extraction and cleanup procedures that use solutions below pH 4 or above pH 8 are not appropriate for this method.

11.2 Extract cleanup and solvent exchange

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.

11.2.1 If cleanup is necessary, the sample extracts may be cleaned up using Florisil® column cleanup (Method 3620) and sulfur cleanup (Method 3660, TBA-sulfite option), which may have particular application for organophosphorus pesticides.

11.2.2 If sulfur cleanup by Method 3660 is necessary, do not use the copper technique, as the target analytes may be degraded in the presence of copper.

11.2.3 Gel permeation cleanup (GPC, Method 3640) should only be employed if all the target organophosphorus pesticides of interest are listed as analytes of Method 3640, or if the laboratory has demonstrated a recovery of greater than 85 percent for target organophosphorus pesticides at a concentration not greater than 5 times the levels of interest (e.g., the regulatory limit). Laboratories must retain data demonstrating acceptable recovery.

11.2.4 Prior to gas chromatographic analysis, the extract solvent may be exchanged to hexane. The analyst must ensure quantitative transfer of the extract concentrate. Single-laboratory data indicate that samples should not be transferred with 100-percent hexane during sample workup, as the more polar organophosphorus compounds may be lost. Transfer of organophosphorus esters is best accomplished using methylene chloride or a hexane/acetone solvent mixture.

11.2.5 Methylene chloride may be used as an injection solvent with both the FPD and the NPD.

NOTE: Follow manufacturer's instructions as to suitability of using methylene chloride with any specific detector.

11.3 Gas chromatographic conditions

This method allows the analyst to choose between a single-column or a dual-column configuration in the injector port. The columns listed in this section were the columns used to develop the method performance data. Listing these columns in this method is not intended to exclude the use of other columns that are available or that may be developed. Wide-bore or narrow-bore columns may be used with either option. Laboratories may use either the columns listed in this method or other capillary columns or columns of other dimensions, provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

Four different 0.53-mm ID capillary columns are suggested for the determination of organophosphates by this method. Column 1 (DB-210, or equivalent) and Column 2 (SPB-608, or equivalent) of 30-m lengths are recommended if a large number of organophosphorus analytes are to be determined. If superior chromatographic resolution is *not* needed, 15-m columns may be appropriate.

11.3.1 Suggested operating conditions for 15-m columns are listed in Table 6. Suggested operating conditions for 30-m columns are listed in Table 7.

11.3.2 Example retention times for analytes on each set of columns are presented in Tables 1 and 2. These data were developed using the operating conditions in Tables 6 and 7 and are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

11.3.3 Establish the GC operating conditions appropriate for the column employed, using Tables 6 and 7 as guidance. Optimize the instrumental conditions for resolution of the target analytes and sensitivity.

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

11.4 Calibration

Prepare calibration standards using the procedures in Sec. 7.0. Refer to Method 8000 for proper calibration techniques for both initial calibration and calibration verification. Use Tables 6 and 7 as guidance in establishing the proper operating parameters for the columns being employed in the analyses.

Method 8000 recommends checking the calibration by comparing the calculated amount of each standard to the expected amount of the standard, and calculating the difference between the values (%D). When the calculated %D exceeds the recommended value for one or more analytes, analyses may proceed and the results for analytes generated using a failed calibration may be used for screening purposes.

11.4.1 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. Under most circumstances, the calibration factors for the standard should be within ±20% of those from the initial calibration. When this calibration verification standard falls out of this acceptance window, the laboratory should stop analyses and take corrective action. See Method 8000 for information on other options for calibration and calibration verification.

11.4.2 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% 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.

11.5 Gas chromatographic analysis

Method 8000 provides instructions on the analysis sequence, appropriate dilutions, and establishing daily retention time windows and identification criteria.

11.5.1 Automated 1-µL injections are recommended. Manual injections of no more than 2 µL may be used if the analyst demonstrates quantitation precision of ±10% relative standard deviation. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest.

The solvent flush technique may be used if the amount of solvent is kept at a minimum. If the internal standard calibration technique is used, add 10 µL of internal standard to each 1 mL of sample, prior to injection. Example chromatograms of the target organophosphorus compounds are shown in Figures 1 through 4.

11.5.2 Figures 5 and 6 show chromatograms with and without simazine, atrazine, and carbophenothion on 30-m columns.

11.6 Record the sample volume injected to the nearest 0.05 µL and the resulting peak sizes (in area units or peak heights). Using either the internal or external calibration procedure (see Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Method 8000 for calculations.

11.6.1 If peak detection and identification are prevented by the presence of interferences, the use of an FPD or further sample cleanup is necessary. Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to establish elution patterns and to determine recovery of target compounds.

11.6.2 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off-scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

11.6.3 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 extract is warranted.

11.6.4 If partially overlapping or coeluting peaks are found, change columns or try a GC/MS technique. Refer to Sec. 9.0 of this method and refer to Method 8270.

11.7 Suggested chromatograph maintenance

Corrective measures may involve any one or more of the following remedial actions. Refer to Method 8000 for general information on the maintenance of capillary columns and injectors.

11.7.1 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. Reattach the columns after cleanly cutting off at least 30 cm instead from the injection port side of the column using a capillary cutting tool or scribe. The accumulation of high boiling residues can change split ratios between dual columns and thereby change calibration factors.

11.7.2 Columns will be damaged permanently and irreversibly by contact with oxygen at elevated temperature. Oxygen can enter the column during a septum change, when oxygen traps are exhausted, through neoprene diaphragms of regulators, and through leaks in the gas manifold. Polar columns including the DB-210 and DB-608 are more prone to oxidation. Oxidized columns will exhibit baselines that rise rapidly during temperature programming.

11.7.3 Peak tailing for all components will be exacerbated by dirty injectors, pre-columns, and glass "Y"s. Cleaning of this equipment (or replacement/clipping, as appropriate) will greatly reduce the peak tailing. Compounds such as Fensulfothion, Naled, Azinphos-methyl, and Dimethoate are very good indicators of system performance.

11.8 Detector maintenance

11.8.1 Older FPDs may be susceptible to stray light in the photomultiplier tube compartment. This stray light will decrease the sensitivity and the linearity of the detector. Analysts can check for leaks by initiating an analysis in a dark room and turning on the lights. A shift in the baseline indicates that light may be leaking into the photomultiplier

tube compartment. Additional shielding should be applied to eliminate light leaks and minimize stray light interference.

11.8.2 The bead of the NPD will become exhausted with time, which will decrease the sensitivity and the selectivity of the detector. The collector may become contaminated which decreases detector sensitivity.

11.8.3 Both types of detectors use a flame to generate a response. Flow rates of air and hydrogen should be optimized to give the most sensitive, linear detector response for target analytes.

11.9 Second Column Confirmation

Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Confirmation is necessary when the sample composition is not well characterized. Confirmatory techniques such as gas chromatography with a dissimilar column or a mass spectrometer should be used. See Method 8000 for information on confirmation of tentative identifications.

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 Method 8000 for a discussion of such a comparison and appropriate data reporting approaches.

When the dual-column approach is employed, the target analytes are identified and confirmed when they meet the identification criteria on both columns.

11.10 GC/MS confirmation

11.10.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Follow the GC/MS operating specifications described in Method 8270. 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. See Table 8.

11.10.2 The GC/MS must be calibrated for the specific target pesticides when it is used for quantitative analysis. If GC/MS is used only for confirmation of the identification of the target analytes, then the analyst must demonstrate that those pesticides identified by other GC detectors can be confirmed by GC/MS. This demonstration may be accomplished by analyzing a single-point standard containing the analytes of interest at or below the concentrations reported in the GC analysis.

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

11.10.4 Where available, chemical ionization mass spectra may be employed to aid in the qualitative identification process because of the extensive fragmentation of organophosphorus pesticides during electron impact MS processes.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 See Sec. 11.0 and Method 8000 for information on data analysis and calculations.

12.2 Results need to be reported in units commensurate with their intended use and all dilutions need to be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Example retention times are provided for many analytes in Tables 1 and 2. These data are for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

13.3 Recoveries for some method analytes are provided in Tables 3, 4, and 5. All data are taken from Reference 1. These data are provided for guidance purposes only.

13.3 Tables 9 and 10 present data for solid-phase extraction of ground water and waste water samples. Forty four organophosphorus compounds were divided into three sets of analytes. Each set was spiked into seven 250-mL replicate samples of ground water and a waste water at 10 ppb and at 250 ppb. Ground water was obtained from the Stroh Brewery in St. Paul, MN, while the wastewater was obtained from a chemical manufacturing plant. The water samples were extracted using a 47-mm Empore™ Extraction Disk equipped with SDB-RPS, a reversed-phase, sulfonated, poly(styrenedivinylbenzene) copolymer adsorbent. The samples were analyzed using gas chromatography equipped with a nitrogen-phosphorous detector. These data are provided for guidance purposes only.

13.4 Table 11 provides single-laboratory performance data for the pressurized fluid extraction (PFE) of organophosphorus pesticides at two different spiking concentrations in three different soil types. The two spiking concentrations were approximately 250 µg/kg for "low" samples and approximately 2500 µg/kg for "high" samples. Seven replicate extractions were performed for each spiking concentration and soil type using the Dionex Accelerated Solvent Extractor. Three compounds, TEPP, naled, and monocrotophos, were spiked into the samples but not recovered in any of the soil types. The recovery of each compound from each soil type and spiking level was calculated as the percentage of the certified value for each sample. The relative standard deviation of the seven replicate extractions is provided as a measure of the precision. All data are taken from Reference 15. These data are provided for guidance purposes only.

13.5 Tables 12 and 13 present the results of a single-laboratory validation study for the 11 carbamates and related compounds listed in Sec. 1.1. Bulk quantities of a clay soil and the effluent from a publicly-owned treatment works (POTW) were collected and spiked with the carbamates. The spiking levels were based on the Universal Treatment Standards (UTS) for wastewaters and soils. Samples were spiked at approximately 80% of the UTS levels, and spiking levels ranged from 34 to 45 µg/L in the wastewater samples. The soil samples were spiked at 1100 µg/kg. Four replicate aliquots of each matrix were extracted, using continuous liquid-liquid extraction (Method 3520) or Soxhlet extraction (Method 3540) for aqueous and solid samples, respectively. The spiking levels, mean recoveries, and the RSDs of the recoveries are presented in Tables 12 and 13. All data are taken from Reference 16. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC, 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

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17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

EXAMPLE RETENTION TIMES ON 15-m COLUMNS

	Retention Time (min)			
Analyte	DB-5	SPB-608	DB-210	DB-1
TEPP		6.44	5.12	10.66
Dichlorvos (DDVP)	9.63	7.91	12.79	
Mevinphos	14.18	12.88	18.44	
Demeton, -O and -S	18.31	15.90	17.24	
Ethoprop	18.62	16.48	18.67	
Naled		19.01	17.40	19.35
Phorate	19.94	17.52	18.19	
Monocrotophos	20.04	20.11	31.42	
Sulfotepp	20.11	18.02	19.58	
Dimethoate	20.64	20.18	27.96	
Disulfoton	23.71	19.96	20.66	
Diazinon	24.27	20.02	19.68	
Merphos	26.82	21.73	32.44	
Ronnel	29.23	22.98	23.19	
Chlorpyrifos	31.17	26.88	25.18	
Malathion	31.72	28.78	32.58	
Parathion, methyl	31.84	23.71	32.17	
Parathion, ethyl	31.85	27.62	33.39	
Trichloronate	32.19	28.41	29.95	
Tetrachlorovinphos	34.65	32.99	33.68	
Tokuthion (Protothiofos)	34.67	24.58	39.91	
Fensulfothion	35.85	35.20	36.80	
Bolstar (Sulprofos)	36.34	35.08	37.55	
Famphur[b]	36.40	36.93	37.86	
EPN		37.80	36.71	36.74
Azinphos-methyl	38.34	38.04	37.24	
Fenthion	38.83	29.45	28.86	
Coumaphos	39.83	38.87	39.47	

[a] GC operating conditions are shown in Table 6.
[b] This method has not been fully validated for Famphur.
All data are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

TABLE 2

EXAMPLE RETENTION TIMES ON 30-m COLUMNS[a]

	Retention Time (min)			
Analyte	DB-5	DB-210	DB-608	DB-1
Trimethylphosphate	b	2.36		
Dichlorvos (DDVP)	7.45	6.99	6.56	10.43
Hexamethylphosphoramide	b	7.97		
Trichlorfon	11.22	11.63	12.69	
TEPP	b	13.82		
Thionazin	12.32	24.71		
Mevinphos	12.20	10.82	11.85	14.45
Ethoprop	12.57	15.29	18.69	18.52
Diazinon	13.23	18.60	24.03	21.87
Sulfotepp	13.39	16.32	20.04	19.60
Terbufos	13.69	18.23	22.97	
Tri-*o*-cresyl phosphate	13.69	18.23		
Naled	14.18	15.85	18.92	18.78
Phorate	12.27	16.57	20.12	19.65
Fonophos	14.44	18.38		
Disulfoton	14.74	18.84	23.89	21.73
Merphos	14.89	23.22		26.23
Oxidized Merphos	20.25	24.87	35.16	
Dichlorofenthion	15.55	20.09	26.11	
Chlorpyrifos, methyl	15.94	20.45	26.29	
Ronnel	16.30	21.01	27.33	23.67
Chlorpyrifos	17.06	22.22	29.48	24.85
Trichloronate	17.29	22.73	30.44	
Aspon	17.29	21.98		
Fenthion	17.87	22.11	29.14	24.63
Demeton-S	11.10	14.86	21.40	20.18
Demeton-O	15.57	17.21	17.70	
Monocrotophos[c]	19.08	15.98	19.62	19.3
Dimethoate	18.11	17.21	20.59	19.87
Tokuthion	19.29	24.77	33.30	27.63
Malathion	19.83	21.75	28.87	24.57
Parathion, methyl	20.15	20.45	25.98	22.97
Fenithrothion	20.63	21.42		
Chlorfenvinphos	21.07	23.66	32.05	
Parathion, ethyl	21.38	22.22	29.29	24.82
Bolstar	22.09	27.57	38.10	29.53

TABLE 2
(continued)

Analyte	Retention Time (min)			
	DB-5	DB-210	DB-608	DB-1
Stirophos	22.06	24.63	33.40	26.90
Ethion	22.55	27.12	37.61	
Phosphamidon	22.77	20.09	25.88	
Crotoxyphos	22.77	23.85	32.65	
Leptophos	24.62	31.32	44.32	
Fensulfothion	27.54	26.76	36.58	28.58
EPN	27.58	29.99	41.94	31.60
Phosmet	27.89	29.89	41.24	
Azinphos-methyl	28.70	31.25	43.33	32.33
Azinphos-ethyl	29.27	32.36	45.55	
Famphur	29.41	27.79	38.24	
Coumaphos	33.22	33.64	48.02	34.82
Atrazine	13.98	17.63		
Simazine	13.85	17.41		
Carbophenothion	22.14	27.92		
Dioxathion	d	d	22.24	
Trithion methyl			36.62	
Dicrotophos			19.33	
Internal Standard				
1-Bromo-2-nitrobenzene	8.11	9.07		
Surrogates				
Tributyl phosphate			11.1	
Triphenyl phosphate			33.4	
4-Chloro-3-nitrobenzotrifluoride	5.73	5.40		

[a] GC operating conditions are shown in Table 6.

[b] Not detected at 20 ng per injection.

[c] Retention times may shift to longer times with larger amounts injected (shifts of over 30 sec have been observed, see Reference 6).

[d] Shows multiple peaks; therefore, not included in the composite.

All data are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

TABLE 3

EXAMPLE SINGLE-LABORATORY RECOVERY OF 27 ORGANOPHOSPHATES USING SEPARATORY FUNNEL EXTRACTION (METHOD 3510)

	Percent Recovery at Three Spiking Levels		
Analyte	Low	Medium	High
Azinphos methyl	126	143 ± 8	101
Bolstar	134	141 ± 8	101
Chlorpyrifos	7	89 ± 6	86
Coumaphos	103	90 ± 6	96
Demeton	33	67 ± 11	74
Diazinon	136	121 ± 9.5	82
Dichlorvos	80	79 ± 11	72
Dimethoate	NR	47 ± 3	101
Disulfoton	48	92 ± 7	84
EPN	113	125 ± 9	97
Ethoprop	82	90 ± 6	80
Fensulfonthion	84	82 ± 12	96
Fenthion	NR	48 ± 10	89
Malathion	127	92 ± 6	86
Merphos	NR	79	81
Mevinphos	NR	NR	55
Monocrotophos	NR	18 ± 4	NR
Naled	NR	NR	NR
Parathion, ethyl	101	94 ± 5	86
Parathion, methyl	NR	46 ± 4	44
Phorate	94	77 ± 6	73
Ronnel	67	97 ± 5	87
Sulfotep	87	85 ± 4	83
TEPP	96	55 ± 72	63
Tetrachlorvinphos	79	90 ± 7	80
Tokuthion	NR	45 ± 3	90
Trichloroate	NR	35	4

NR = Not recovered

Low and high spiking level results are from a single extraction. Medium level results represent the mean and standard deviation of five replicate extractions.

Low level was approximately 0.3 - 0.5 µg/L, medium level was approximately 1.5 - 2.0 µg/L, and high level was approximately 15 - 20 µg/L. Dichlorvos, monocrotophos, and TEPP were spiked at approximately 10 times higher in each case.

These data are provided for guidance purposes only.

TABLE 4

EXAMPLE SINGLE-LABORATORY RECOVERY OF 27 ORGANOPHOSPHATES USING CONTINUOUS LIQUID-LIQUID EXTRACTION (METHOD 3520)

	Percent Recovery at Three Spiking Levels		
Analyte	Low	Medium	High
Azinphos methyl	NR	129	122
Bolstar	NR	126	128
Chlorpyrifos	13	82 ± 4	88
Coumaphos	94	79 ± 1	89
Demeton	38	23 ± 3	41
Diazinon	NR	128 ± 37	118
Dichlorvos	81	32 ± 1	74
Dimethoate	NR	10 ± 8	102
Disulfoton	94	69 ± 5	81
EPN	NR	104 ± 18	119
Ethoprop	39	76 ± 2	83
Fensulfonthion	90	67 ± 26	90
Fenthion	8	32 ± 2	86
Malathion	105	87 ± 4	86
Merphos	NR	80	79
Mevinphos	NR	87	49
Monocrotophos	NR	30	1
Naled	NR	NR	74
Parathion, ethyl	106	81 ± 1	87
Parathion, methyl	NR	50 ± 30	43
Phorate	84	63 ± 3	74
Ronnel	82	83 ± 7	89
Sulfotep	40	77 ± 1	85
TEPP	39	18 ± 7	70
Tetrachlorvinphos	56	70 ± 14	83
Tokuthion	132	32 ± 14	90
Trichloroate	NR	NR	21

NR = Not recovered

Low and high spiking level results are from a single extraction. Medium level results represent the mean and standard deviation of five replicate extractions.

Low level was approximately 0.3 - 0.5 µg/L, medium level was approximately 1.5 - 2.0 µg/L, and high level was approximately 15 - 20 µg/L. Dichlorvos, monocrotophos, and TEPP were spiked at approximately 10 times higher in each case.

These data are provided for guidance purposes only.

TABLE 5

EXAMPLE SINGLE-LABORATORY RECOVERY OF 27 ORGANOPHOSPHATES USING SOXHLET EXTRACTION (METHOD 3540)

	Percent Recovery at Three Spiking Levels		
Analyte	Low	Medium	High
Azinphos methyl	156	110 ± 6	87
Bolstar	102	103 ± 15	79
Chlorpyrifos	NR	66 ± 17	79
Coumaphos	93	89 ± 11	90
Demeton	169	64 ± 6	75
Diazinon	87	96 ± 3	75
Dichlorvos	84	39 ± 21	71
Dimethoate	NR	48 ± 7	98
Disulfoton	78	78 ± 6	76
EPN	114	93 ± 8	82
Ethoprop	65	70 ± 7	75
Fensulfonthion	72	81 ± 18	111
Fenthion	NR	43 ± 7	89
Malathion	100	81 ± 8	81
Merphos	62	53	60
Mevinphos	NR	71	63
Monocrotophos	NR	NR	NR
Naled	NR	48	NR
Parathion, ethyl	75	80 ± 8	80
Parathion, methyl	NR	41 ± 3	28
Phorate	75	77 ± 6	78
Ronnel	NR	83 ± 12	79
Sulfotep	67	72 ± 8	78
TEPP	36	34 ± 33	63
Tetrachlorvinphos	50	81 ± 7	83
Tokuthion	NR	40 ± 6	89
Trichloroate	56	53	53

NR = Not recovered

Low and high spiking level results are from a single extraction. Medium level results represent the mean and standard deviation of five replicate extractions.

Low level was approximately 30 - 45 µg/kg, medium level was approximately 150 - 230 µg/kg, and high level was approximately 1500 - 2300 µg/L. Dichlorvos, monocrotophos, and TEPP were spiked at approximately 10 times higher in each case.

These data are provided for guidance purposes only.

TABLE 6

SUGGESTED OPERATING CONDITIONS FOR 15-m COLUMNS

Columns 1 and 2 (DB-210 and SPB-608 or their equivalents)	
Carrier gas (He) flow rate	5mL/min
Initial temperature	50 EC, hold for 1 min
Temperature program	50 EC to 140 EC at 5 EC/min, hold for 10 mins, followed by 140 EC to 240 °C at 10 °C/min, hold for 10 min (or a sufficient amount of time for last compound to elute).
Column 3 (DB-5 or equivalent)	
Carrier gas (He) flow rate	5mL/min
Initial temperature	130 EC, hold for 3 min
Temperature program	130 EC, to 180 EC at 5 EC/min, hold for 10 min, followed by 180 EC to 250 EC at 2 EC/min, hold for 15 min (or a sufficient amount of time for last compound to elute).

TABLE 7

SUGGESTED OPERATING CONDITIONS FOR 30-m COLUMNS

Column 1	DB-210 (or equivalent)
	Dimensions: 30-m x 0.53-mm ID
	Film Thickness (µm): 1.0
Column 2	DB-5 (or equivalent)
	Dimensions: 30-m x 0.53-mm ID
	Film Thickness (µm): 1.5
Carrier gas flow rate	6 (mL/min) Helium
Makeup gas flow rate	20 (mL/min) Helium
Temperature program	120 EC (3-min hold) to 270 EC (10-min hold) at 5 EC/min
Injector temperature	250 EC
Detector temperature	300 EC
Injection volume	2 µL
Solvent	Hexane
Type of injector	Flash vaporization
Detector type	Dual NPD
Range	1
Attenuation	64
Type of splitter	Y-shaped or Tee
Data system	Integrator
Hydrogen gas pressure	20 psi
Bead temperature	400 EC
Bias voltage	4

TABLE 8

SUGGESTED QUANTITATION AND CHARACTERISTIC IONS FOR GC/MS ANALYSIS OF SELECTED ORGANOPHOSPHORUS PESTICIDES

Analyte	Quantitation ion	Characteristic ions
Azinphos-methyl	160	77,132
Bolstar (Sulprofos)	156	140,143,113,33
Chlorpyrifos	197	97,199,125.314
Coumaphos	109	97,226,362,21
Demeton-S	88	60,114,170
Diazinon	137	179,152,93,199,304
Dichlorvos (DDVP)	109	79,185,145
Dimethoate	87	93,125,58,143
Disulfoton	88	89,60,61,97,142
EPN	157	169,141,63,185
Ethoprop	158	43,97,41,126
Fensulfothion	293	97,125,141,109,308
Fenthion	278	125,109,93,169
Malathion	173	125,127,93,158
Merphos	209	57,153,41,298
Mevinphos	127	109,67,192
Monocrotophos	127	67,97,192,109
Naled	109	145,147,79
Parathion, ethyl	291	97,109,139,155
Parathion, methyl	109	125,263,79
Phorate	75	121,97,47,260
Ronnel	285	125,287,79,109
Stirophos	109	329,331,79
Sulfotepp	322	97,65,93,121,202
TEPP	99	155,127,81,109
Tokuthion	113	43,162,267,309

These data are provided for guidance purposes only.

TABLE 9

EXAMPLE SINGLE-LABORATORY PERFORMANCE DATA
FOR ORGANOPHOSPHORUS PESTICIDES
IN GROUND WATER USING SOLID-PHASE EXTRACTION (METHOD 3535)

	Ground Water spiked at 250 ppb		Ground Water spiked at 10 ppb	
Analyte	% Recovery	RSD	% Recovery	RSD
Aspon	85.6	11.5	77.7	6.8
Azinphos-methyl	83.0	13.4	109.7	7.0
Azinphos-ethyl	88.3	10.8	92.8	8.1
Bolstar	96.1	4.2	78.2	4.3
Carbophenothion	85.6	11.0	81.7	7.2
Chlorfenvinphos	87.8	10.2	90.1	6.0
Chlorpyrifos	98.8	5.7	77.5	4.2
Chlorpyrifos methyl	82.5	12.0	59.4	7.5
Coumaphos	84.3	8.7	100.8	13.5
Crotoxyphos	86.3	10.5	89.4	5.9
Demeton	93.6	4.5	73.8	5.1
Diazinon	91.7	4.7	70.0	5.0
Dichlorofenthion	85.2	10.9	75.6	6.0
Dichlorvos (DDVP)	88.1	6.7	90.1	7.9
Dicrotophos	88.6	10.8	75.7	5.7
Dimethoate	99.3	1.8	76.7	9.5
Dioxathion	81.6	14.1	92.7	11.0
Disulfoton	93.2	7.6	79.5	6.1
EPN	73.8	10.6	67.9	7.9
Ethion	85.5	10.6	79.2	6.5
Ethoprop	95.6	4.1	81.4	3.7
Famphur	85.2	10.2	75.6	8.3
Fenitrothion	91.2	8.8	85.0	5.0
Fensulfothion	86.2	6.4	97.2	6.0
Fenthion	91.2	5.4	79.5	4.3

TABLE 9
(continued)

	Ground Water spiked at 250 ppb		Ground Water spiked at 10 ppb	
Analyte	% Recovery	RSD	% Recovery	RSD
Fonophos	91.0	8.0	81.6	3.6
Leptophos	81.3	12.2	73.6	8.8
Malathion	79.5	6.9	78.0	8.7
Merphos	113.1	9.3	84.6	4.5
Mevinphos	57.9	6.9	96.8	6.7
Naled	90.1	6.7	88.1	7.9
Parathion, ethyl	76.7	9.6	69.6	8.1
Parathion, methyl	93.9	5.8	83.6	4.7
Phorate	92.3	7.1	70.8	6.7
Phosmet	66.1	17.7	90.3	10.7
Phosphamidon	86.2	11.2	80.6	5.7
Ronnel	94.7	5.2	77.8	4.7
Stirophos	78.6	13.1	106.3	5.9
Sulfotepp	75.3	9.3	68.9	8.6
Terbufos	87.1	10.5	78.0	3.7
Thionazin	95.1	8.0	88.6	3.4
Tokuthion	94.4	4.1	77.8	5.6
Trichlorfon	72.7	13.5	45.6	6.9
Trichloronate	95.3	4.5	75.7	3.9

These data are provided for guidance purposes only.

TABLE 10

EXAMPLE SINGLE-LABORATORY PERFORMANCE DATA
FOR ORGANOPHOSPHORUS PESTICIDES
IN WASTEWATER USING SOLID-PHASE EXTRACTION (METHOD 3535)

	Wastewater spiked at 250 ppb		Wastewater spiked at 10 ppb	
Analyte	% Recovery	RSD	% Recovery	RSD
Aspon	83.7	1.8	76.3	6.7
Azinphos-methyl	102.6	18.0	129.9	12.4
Azinphos-ethyl	79.8	6.8	96.0	6.7
Bolstar	94.4	8.3	84.9	1.4
Carbophenothion	82.4	2.9	82.1	6.7
Chlorfenvinphos	81.7	6.5	88.0	7.2
Chlorpyrifos	91.0	8.3	86.5	1.7
Chlorpyrifos methyl	77.6	2.2	56.7	7.1
Coumaphos	100.2	17.2	111.0	8.5
Crotoxyphos	81.3	5.7	87.5	7.0
Demeton	95.8	5.3	88.5	5.0
Diazinon	91.8	6.5	82.4	3.2
Dichlorfenthion	82.5	1.4	76.2	5.5
Dichlorvos (DDVP)	60.6	11.1	99.7	6.1
Dicrotophos	82.0	1.6	73.4	6.1
Dimethoate	93.5	4.1	115.7	6.7
Dioxathion	84.6	5.6	100.4	9.4
Disulfoton	92.5	5.3	90.4	2.6
EPN	78.1	9.6	80.1	8.6
Ethion	83.5	2.0	78.4	6.4
Ethoprop	96.3	4.7	92.9	3.1
Famphur	85.9	2.5	78.6	7.9
Fenitrothion	83.5	4.8	82.3	5.9
Fensulfothion	101.7	11.4	110.5	6.5
Fenthion	91.7	7.3	88.2	2.7
Fonophos	83.4	2.6	81.3	5.0
Leptophos	81.9	3.3	73.2	7.5
Malathion	94.8	6.7	94.7	5.5
Merphos	94.5	12.7	90.7	1.4
Mevinphos	62.6	11.2	109.0	4.8

TABLE 10
(continued)

	Wastewater spiked at 250 ppb		Wastewater spiked at 10 ppb	
Analyte	% Recovery	RSD	% Recovery	RSD
Naled	60.6	11.1	99.7	6.1
Parathion ethyl	80.2	8.1	83.6	8.6
Parathion methyl	92.9	6.5	93.8	4.4
Phorate	92.4	6.4	85.6	2.4
Phosmet	63.5	8.2	101.3	9.1
Phosphamidon	81.1	3.1	78.0	5.7
Ronnel	91.4	8.4	88.3	2.2
Stirophos	101.4	14.3	126.5	6.5
Sulfotepp	78.7	10.7	87.9	8.8
Terbufos	83.0	1.5	80.1	6.4
Thionazin	85.1	5.8	84.8	4.9
Tokuthion	91.8	8.4	83.6	1.8
Trichlorfon	66.8	4.6	52.2	8.7
Trichloronate	91.3	8.1	84.3	1.6

These data are provided for guidance purposes only.

TABLE 11

EXAMPLE SINGLE-LABORATORY PERFORMANCE DATA
FOR ORGANOPHOSPHORUS PESTICIDES
IN SPIKED SOIL SAMPLES USING PRESSURIZED FLUID EXTRACTION (METHOD 3545)

	Clay				Loam				Sand			
	Low		High		Low		High		Low		High	
Analyte	Rec	RSD	Rec	RSD	Rec	RSD	Rec	RSD	Rec	RSD	Rec	RSD
Dichlorvos	NR		5.6	19.0	10.4	11.4	6.5	22.2	13.9	13.4	9.9	22.2
Mevinphos	66.1	3.8	67.2	4.8	57.3	11.2	63.1	6.5	61.6	14.3	64.7	12.1
Demeton O&S	79.0	3.4	80.2	4.2	73.7	10.0	77.6	6.4	60.0	12.5	77.6	12.7
Ethoprop	83.0	4.7	84.8	4.8	76.1	10.7	77.0	4.9	75.5	12.8	79.0	10.6
Phorate	67.5	3.2	79.4	5.1	63.4	11.8	73.5	5.4	62.9	13.6	76.2	10.8
Sulfotep	66.6	3.7	69.4	4.7	62.6	11.0	66.8	7.3	62.1	13.8	67.7	13.2
Diazinon	80.2	4.7	80.3	4.8	74.4	12.0	75.9	6.0	73.9	14.0	77.4	11.2
Disulfoton	55.9	3.6	93.9	4.7	58.9	11.8	89.4	6.2	52.2	15.3	88.5	12.3
Dimethoate	87.0	5.0	86.7	5.3	70.7	12.1	71.7	18.8	75.0	13.1	80.6	12.5
Ronnel	81.3	3.7	81.1	5.0	73.1	11.1	64.7	6.5	69.0	13.6	73.8	11.6
Chlorpyrifos	99.5	3.1	99.0	5.1	81.7	14.1	87.7	16.8	84.1	13.1	91.6	12.7
Parathion methyl	82.5	3.9	84.5	5.2	74.4	11.5	79.6	5.8	74.9	13.2	80.3	11.3
Parathion ethyl	85.0	3.8	83.5	5.2	77.3	11.9	79.6	6.1	78.0	12.7	80.3	11.5
Fenthion	56.4	3.8	71.4	5.0	44.1	10.8	50.9	6.6	44.3	12.5	51.9	12.6
Tokuthion	96.1	4.7	97.0	5.7	93.2	12.2	93.8	6.1	81.2	12.5	85.4	11.9
Tetrachlorvinphos	72.1	3.3	69.7	5.6	101.4	12.6	64.7	6.5	69.3	11.9	69.6	13.0
Bolstar	89.0	3.4	109.5	6.8	82.2	9.9	89.2	6.2	77.3	11.7	94.2	12.8
Fensulfothion	NR		69.7	4.3	70.4	9.3	52.2	7.1	63.0	9.2	62.0	13.1
EPN	72.6	44.3	76.9	8.0	92.9	10.1	70.4	7.1	68.6	11.2	71.9	11.6
Azinphos-methyl	NR		90.6	5.3	69.7	13.9	70.5	8.7	94.5	12.5	82.5	11.4
Coumaphos	NR		79.6	4.8	62.8	13.4	6.5	10.2	74.8	16.1	72.9	9.2

NR = Not recovered
Rec = Mean recovery, calculated as the percent of the certified spiking value, for 7 replicate extractions
RSD = Relative standard deviation of the results for the 7 replicate extractions

Low spiking level was approximately 250 µg/kg
High spiking level was approximately 2500 µg/kg

Data from Reference 15.

These data are provided for guidance purposes only.

TABLE 12

EXAMPLE SINGLE-LABORATORY PERFORMANCE DATA
FOR CARBAMATES IN WASTEWATER
USING CONTINUOUS LIQUID-LIQUID EXTRACTION (METHOD 3520)

Analyte	Spiking Level (µg/L)	Mean Recovery (%)	RSD (%)
Bendiocarb	45	45.6	22.0
Butylate	34	72.1	5.3
EPTC	34	79.4	6.1
Methiocarb	45	37.8	25.0
Molinate	34	83.8	6.1
Pebulate	34	80.1	6.3
o-Phenylenediamine	45	15.8	20.1
Propham	45	88.3	5.2
Prosulfocarb	34	87.5	4.2
Triallate	34	85.3	4.9
Vernolate	34	80.9	7.6

Four replicate aliquots of a spiked bulk wastewater sample were extracted and analyzed.

Data from Reference 16.

These data are provided for guidance purposes only.

TABLE 13

EXAMPLE SINGLE-LABORATORY PERFORMANCE DATA FOR CARBAMATES IN SOIL SAMPLES USING SOXHLET EXTRACTION (METHOD 3540)

Analyte	Spiking Level (µg/kg)	Mean Recovery (%)	RSD (%)
Bendiocarb	1100	83.2	15.3
Butylate	1100	94.6	1.6
EPTC	1100	103	7.4
Methiocarb	1100	91.1	30.2
Molinate	1100	108	2.8
o-Phenylenediamine	1100	0.0	0.0
Pebulate	1100	105	5.5
Propham	1100	113	3.0
Prosulfocarb	1100	111	3.8
Triallate	1100	113	3.7
Vernolate	1100	107	3.6

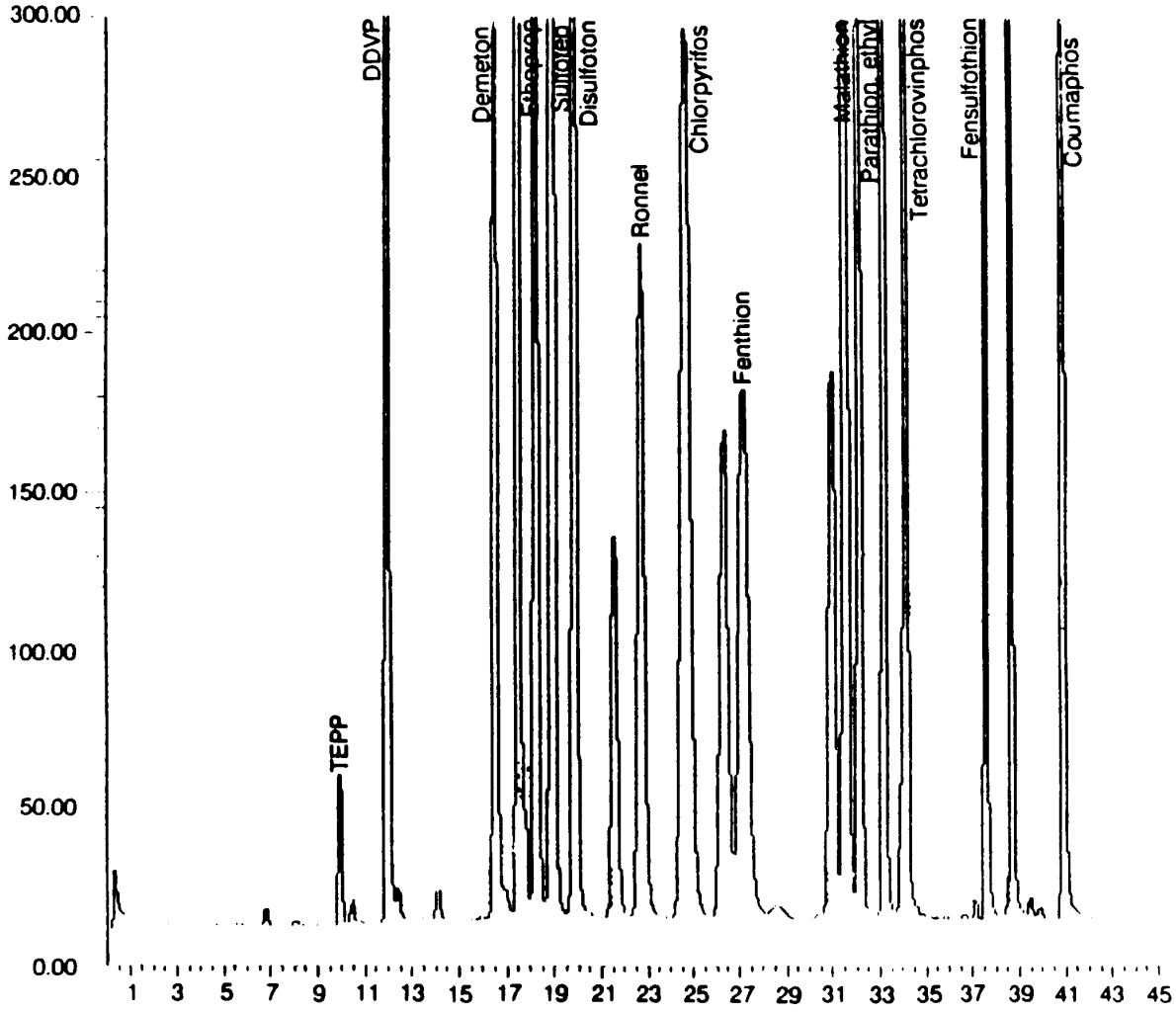
Four replicate aliquots of a spiked bulk clay soil sample were extracted and analyzed.

These data are provided for guidance purposes only.

Data from Reference 16.

FIGURE 1

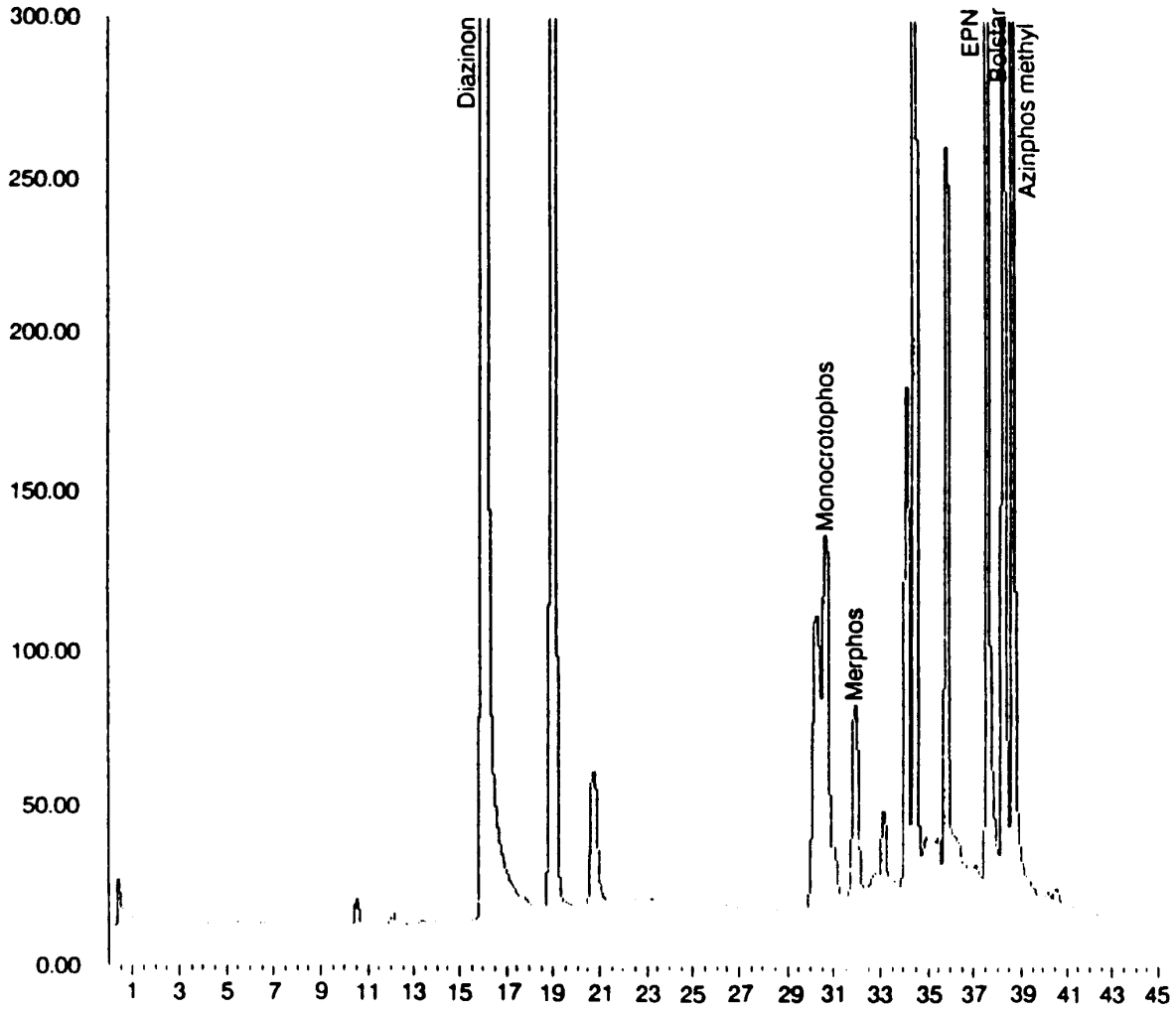
EXAMPLE CHROMATOGRAM OF TARGET ORGANOPHOSPHORUS COMPOUNDS
FROM A 15-m DB-210 COLUMN EQUIPPED WITH FPD DETECTOR



More compounds are shown in Figure 2. See Table 1 for retention times.

FIGURE 2

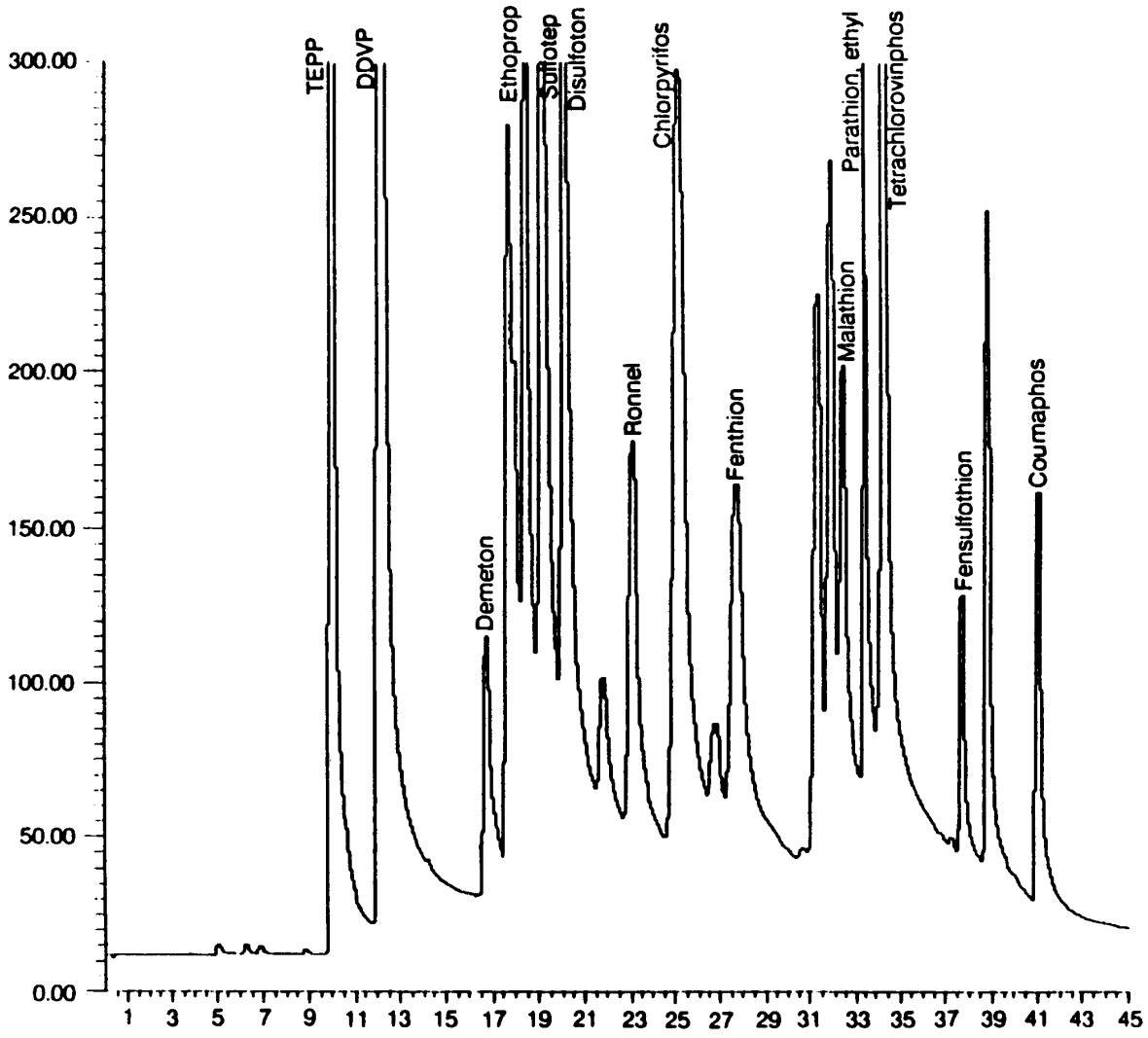
EXAMPLE CHROMATOGRAM OF TARGET ORGANOPHOSPHORUS COMPOUNDS
FROM A 15-m DB-210 COLUMN EQUIPPED WITH FPD DETECTOR



More compounds are shown in Figure 1. See Table 1 for retention times.

FIGURE 3

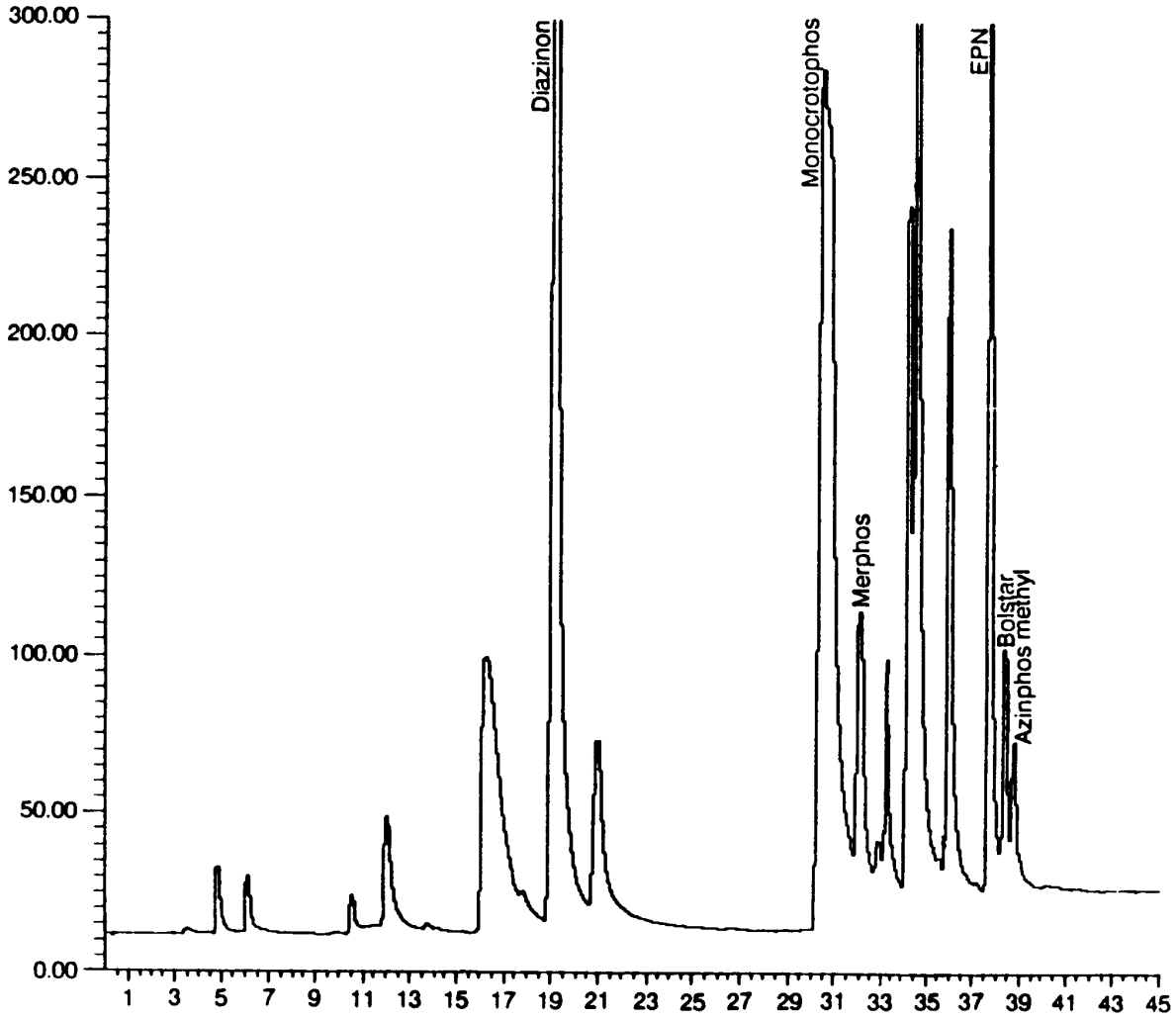
EXAMPLE CHROMATOGRAM OF TARGET ORGANOPHOSPHORUS COMPOUNDS
FROM A 15-m DB-210 COLUMN EQUIPPED WITH NPD DETECTOR



More compounds are shown in Figure 4. See Table 1 for retention times.

FIGURE 4

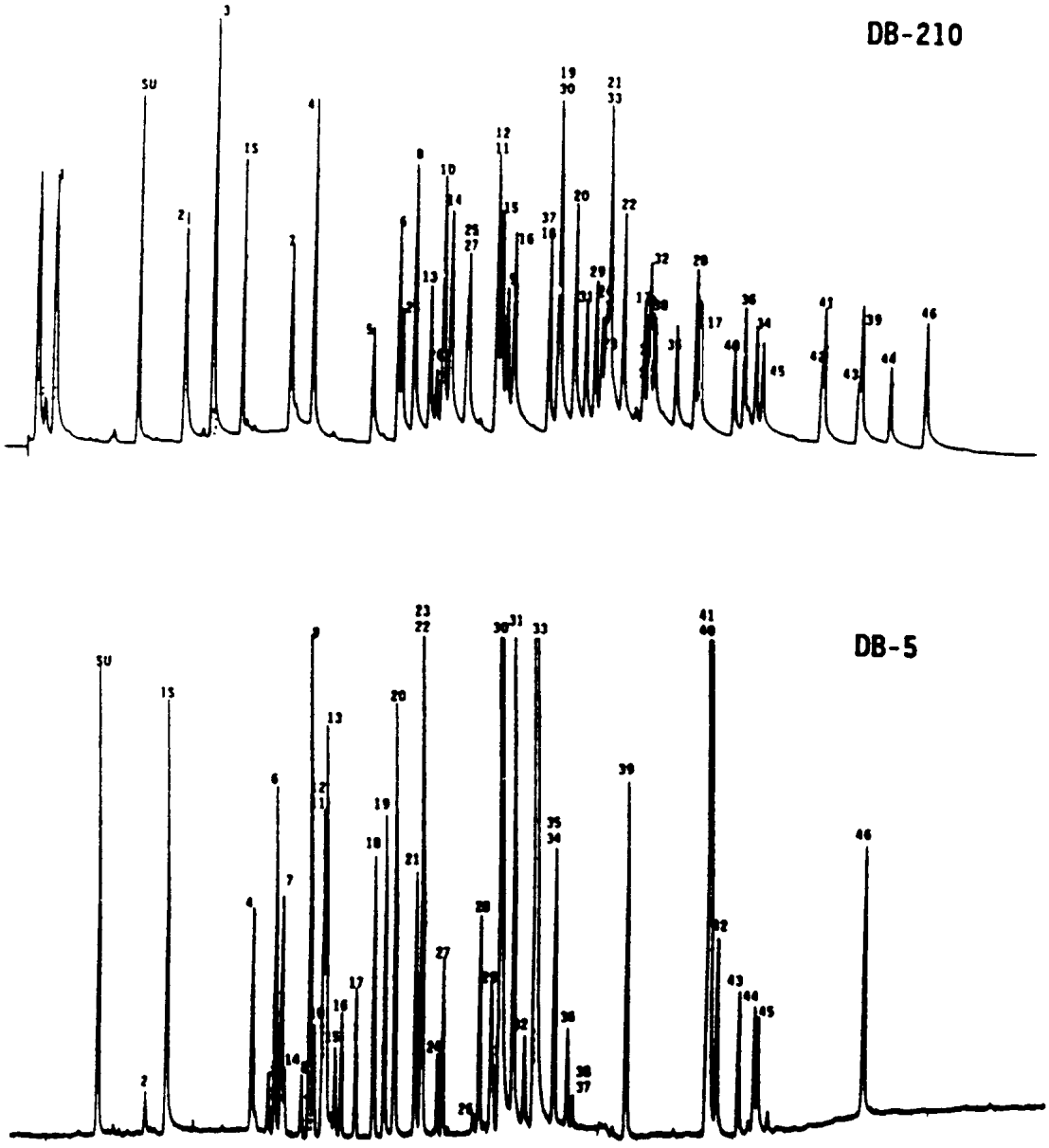
EXAMPLE CHROMATOGRAM OF TARGET ORGANOPHOSPHORUS COMPOUNDS
FROM A 15-m DB-210 COLUMN EQUIPPED WITH NPD DETECTOR



More compounds are shown in Figure 3. See Table 1 for retention times.

FIGURE 5

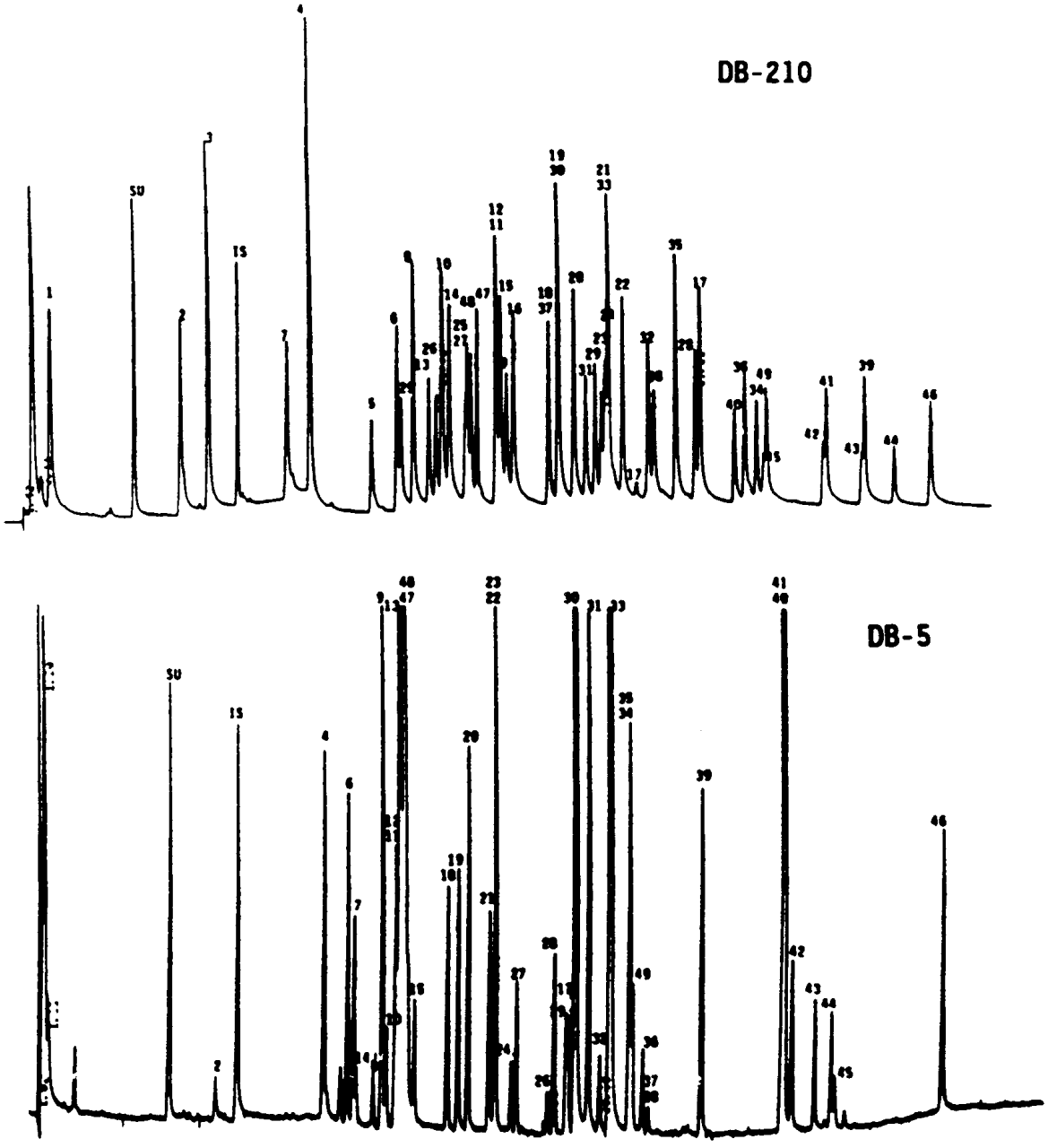
EXAMPLE CHROMATOGRAM OF TARGET ORGANOPHOSPHORUS COMPOUNDS ON A 30-m DB-5/DB-210 COLUMN PAIR EQUIPPED WITH NPD DETECTOR, WITHOUT SIMAZINE, ATRAZINE AND CARBOPHENOTHION



See Table 2 for retention times and for GC operating conditions.

FIGURE 6

EXAMPLE CHROMATOGRAM OF TARGET ORGANOPHOSPHORUS COMPOUNDS
ON A 30-m DB-5/DB-210 COLUMN PAIR EQUIPPED WITH NPD DETECTOR,
WITH SIMAZINE, ATRAZINE AND CARBOPHENOTHION



See Table 2 for retention times and for GC operating conditions.