METHOD 8141B

ORGANOPHOSPHORUS COMPOUNDS BY GAS CHROMATOGRAPHY

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 can be determined by GC using capillary columns with a flame photometric detector (FPD) or a nitrogen-phosphorus detector (NPD). Triazine herbicides can also be 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 results because the chemical and chromatographic behavior of many of these chemicals can result in co-elution. 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.
Organophosphorus Pesticides	
Aspon[b]	3244-90-4
Azinphos-methyl	86-50-0
Azinphos-ethyl[a]	2642-71-9
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
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

Analyte	CAS Registry No.
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)	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
Triazine Herbicides (NPD only)	
Atrazine[a]	1912-24-9
Simazine[a]	122-34-9

Analyte	CAS Registry No.
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

[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 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 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. 8.0). 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, Sec. 2.1, 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 method 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 This method is restricted to use by, or under the supervision of, analysts experienced in the use of capillary gas chromatography and in the interpretation of chromatograms.

2.0 SUMMARY OF METHOD

2.1 Method 8141 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 sample (approximately 1 L for liquids, 2 to 30 g for solids) 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).

2.3 After cleanup, the extract is analyzed by injecting a measured aliquot into a gas chromatograph 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 Method 8141.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000, as well as to Sec. 1.1.

3.2 The use of Florisil Cleanup (Method 3620) for some of the compounds in this method has been demonstrated to yield recoveries less than 85 percent and is therefore not recommended for all compounds. Refer to Table 2 of Method 3620 for 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.

3.3 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 they 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.

3.4 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.

3.5 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..

3.6 Certain analytes will coelute, particularly on 15-m columns (Table 3). 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.

3.7 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 4 for examples of the retention times of these compounds on 30-m columns.

3.8 Analytical difficulties encountered for target analytes

3.8.1 Tetraethyl pyrophosphate (TEPP) is an unstable diphosphate which is readily hydrolyzed in water and is thermally labile (decomposes at 170EC). 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.

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

3.8.3 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.

3.8.4 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.

3.8.5 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.

3.8.6 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.

3.8.7 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.

3.8.8 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.

3.8.9 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.

3.8.10 The performance of chromatographic systems will degrade with time. Column resolution, analyte breakdown, and baselines may be improved by column washing (see Sec. 7). Oxidation of columns is not reversible.

3.9 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 these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing reagent blanks (see Sec. 8.0).

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

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

An analytical system complete with a gas chromatograph suitable for on-column or split/splitless injection, and all required 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.

4.2 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 resolution required). Columns of 0.53-mm ID are recommended for most environmental and waste analysis applications. Dual-column, single-injector analysis requires columns of equal length and bore. See Sec. 3.0 and Figures 1 through 4 for guidance on selecting the proper length and diameter for the column(s).

The four columns listed in this section were the columns used to develop the method performance data presented in Sec. 9. Listing 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 or columns of other dimensions, provided that they document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that meet the data quality needs of the intended application.

4.2.1 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.

4.2.2 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.

4.2.3 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-5), or equivalent.

4.2.4 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.

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

4.3 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:

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

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

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

4.4 Injectors

4.4.1 Packed column, 1/4-in injector ports with hourglass liners are recommended for the 0.53-mm columns. These injector ports can be fitted with splitters (see Sec. 4.3) for dual-column analysis.

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

4.5 Detectors

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

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

4.5.3 Halogen-specific detectors (electrolytic conductivity or microcoulometry) may be used only for a limited number of halogenated or sulfur-containing analytes (see Sec. 3.5).

4.5.4 Electron-capture detectors may be used for a limited number of analytes (see Sec. 3.5).

4.6 Data system

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

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

5.0 REAGENTS

5.1 Solvents - All solvents must be pesticide quality or equivalent.

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

5.1.2 Hexane, C_6H_{14}

5.1.3 Acetone, CH_3COCH_3

5.1.4 Tetrahydrofuran (THF), C_4H_8O - for triazine standards only.

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

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

5.2.1 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 may 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.

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

5.2.3 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.

5.2.4 Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4EC in PTFE-sealed containers in the dark. All standard solutions should be replaced after two months, or sooner if routine QC (see Sec. 8.0) indicates a problem. Standards for easily hydrolyzed chemicals including TEPP, methyl parathion, and merphos should be checked at least every 30 days.

5.2.5 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.

5.3 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.

5.4 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.

5.4.1 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]).

5.4.2 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.

5.4.3 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.

5.5 Surrogates

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., 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/NPD analysis.

5.5.1 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 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 Sec. 5.0 of Method 3500.

5.5.2 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 co-elution 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, as appropriate for the specific application.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to Chapter Four, "Organic Analytes," Sec. 4.0.

6.2 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 4EC 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 Ref. 12).

6.3 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 4EC upon collection and shipped and stored at 4 ± 2EC until extraction.

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

6.5 Store extracts at 4EC and perform analyses 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), a continuous liquid-liquid extractor (Method 3520), solid-phase extraction (Method 3535), 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 methods (Method 3540 or 3541), pressurized fluid extraction (Method 3545), microwave extraction (Method 3546), ultrasonic extraction (Method 3550), or other appropriate technique.

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.

The choice of extraction solvent will depend on the analytes of interest. No single solvent is universally applicable to all analyte groups. The analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest, for any solvent system employed, *including* those specifically listed in this method. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Sec. 8.2 of 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 will 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.

7.2 Extract cleanup and solvent exchange

7.2.1 If required, 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.

7.2.2 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.

7.2.3 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.

7.2.4 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.

7.2.5 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.

7.3 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 may be developed. Wide-bore or narrow-bore columns may be used with either option. Laboratories may use other capillary columns or columns of other dimensions, provided that they document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that meet the data quality needs of 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* required, 15-m columns may be appropriate.

7.3.1 Suggested operating conditions for 15-m columns are listed in Table 8. Suggested operating conditions for 30-m columns are listed in Table 9.

7.3.2 Example retention times for analytes on each set of columns are presented in Tables 3 and 4. These data were developed using the operating conditions in Tables 8 and 9 and are provided for illustrative purposes only.

7.3.3 Establish the GC operating conditions appropriate for the column employed, using Tables 8 and 9 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.

7.4 Calibration

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. Use Tables 8 and 9 as guidance in establishing the proper operating parameters for the columns being employed in the analyses.

7.5 Gas chromatographic analysis

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

7.5.1 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 percent 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.

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

7.6 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.

7.6.1 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.

7.6.2 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.

7.6.3 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.

7.6.4 If partially overlapping or coeluting peaks are found, change columns or try a GC/MS technique. Refer to Sec. 8.0 and Method 8270.

7.7 Suggested chromatograph maintenance

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

7.7.1 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 one foot 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.

7.7.2 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.

7.7.3 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.

7.8 Detector maintenance

7.8.1 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.

7.8.2 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.

7.8.3 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.

7.9 GC/MS confirmation

7.9.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Follow the GC/MS operating requirements 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.

7.9.2 The GC/MS must be calibrated for the specific target pesticides when it is used for <u>quantitative</u> 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.

7.9.3 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.

7.9.4 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.

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 performance 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. 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 and accuracy). At a minimum, this includes the analysis of QC samples including a method blank and a laboratory control sample (LCS) in each analytical batch, the addition of surrogates to each field sample and QC sample, and routine analyses of matrix spike and matrix spike duplicate aliquots.

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 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.

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. Under most circumstances, the calibration factors for the standard should be within ±15% 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.

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 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. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in an approved project plan.

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 MDL is defined in Chapter One. **Estimated MDLs for a short list of the target compounds in water and clean soil are presented in Table 1 and are provided for**

illustrative purposes only. Each laboratory should develop its own matrix-specific MDLs, if necessary, using the guidance found in Chapter One. Estimated quantitation limits (EQLs) may be determined using the factors in Table 2.

9.2 Example retention times are provided for many analytes in Tables 3 and 4. These data are for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

9.3 Recoveries for some method analytes are provided in Tables 5, 6, and 7. All data are taken from Reference 1.

9.4 Tables 11 and 12 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 with SDB-RPS, a reversed-phase, sulfonated, poly(styrenedivinylbenzene) copolymer adsorbent. The samples were analyzed using gas chromatography with a nitrogen-phosphorous detector.

9.5 Table 13 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.

9.6. Tables 14 and 15 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 14 and 15. All data are taken from Reference 16.

10.0 REFERENCES

1. Taylor, V.; Hickey, D.M.; Marsden, P.J. "Single Laboratory Validation of EPA Method 8140," U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, 1987; EPA-600/4-87-009.

2. Pressley, T.A; Longbottom, J.E. "The Determination of Organophosphorus Pesticides in Industrial and Municipal Wastewater: Method 614," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1982; EPA-600/4-82-004.

3. "Analysis of Volatile Hazardous Substances by GC/MS: Pesticide Methods Evaluation," Letter Reports 6, 12A, and 14 to the U.S. Environmental Protection Agency on Contract 68-03-2697, 1982.

4. "Method 622, Organophosphorus Pesticides," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

5. Lopez-Avila, V.; Baldin, E.; Benedicto, J; Milanes, J.; Beckert, W. F. "Application of Open-Tubular Columns to SW-846 GC Methods," final report to the U.S. Environmental Protection Agency on Contract 68-03-3511, Mid-Pacific Environmental Laboratory, Mountain View, CA, 1990.

6. Hatcher, M.D.; Hickey, D.M.; Marsden, P.J.; and Betowski, L.D.; "Development of a GC/MS Module for RCRA Method 8141," final report to the U.S. EPA Environmental Protection Agency on Contract 68-03-1958, S-Cubed, San Diego, CA, 1988.

7. Chau, A.S.Y.; Afghan, B.K. *Analysis of Pesticides in Water*; "Chlorine and Phosphorus-Containing Pesticides," CRC Press, Boca Raton, FL, 1982, Vol. 2, pp 91-113, 238.

8. Hild, J.; Schulte, E; Thier, H.P. "Separation of Organophosphorus Pesticides and Their Metabolites on Glass-Capillary Columns," *Chromatographia*, 1978, 11-17.

9. Luke, M.A.; Froberg, J.E.; Doose, G.M.; Masumoto, H.T. "Improved Multiresidue Gas Chromatographic Determination of Organophosphorus, Organonitrogen, and Organohalogen Pesticides in Produce, Using Flame Photometric and Electrolytic Conductivity Detectors," *J. Assoc. Off. Anal. Chem.* 1981, 1187, 64.

10. Sherma, J.; Berzoa, M. "Analysis of Pesticide Residues in Human and Environmental Samples," U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/8-80-038.

11. Desmarchelier, J.M.; Wustner, D.A.; Fukuto, T.R. "Mass Spectra of Organophosphorus Esters and Their Alteration Products," *Residue Reviews* , 1974, pp 63, 77.

12. Munch, D.J. and Frebis, C.P., "Analyte Stability Studies Conducted during the National Pesticide Survey," *ES & T*, 1992, vol 26, 921-925.

13. T.L. Jones, "Organophosphorus Pesticide Standards: Stability Study," EMSL-LV Research Report, EPA 600/X-92/040, April, 1992

14. Kotronarou, A., et al., "Decomposition of Parathion in Aqueous Solution by Ultrasonic Irradiation," *ES&T*, 1992, Vol. 26, 1460-1462.

15. Richter, B, Ezzell, J., and Felix D, "Single Laboratory Method Validation Report - Extraction of Organophosphorus Pesticides, Herbicides and Polychlorinated Biphenyls using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC/NPD and GC/ECD," Dionex, Salt Lake City, UT, Document 101124, December 2, 1994.

16. "Carbamates Method Evaluation Report," report for EPA Contract 68-W6-0068, Science Applications International Corporation, Dunn Loring, VA 22027, August 25, 1998.

TABLE 1

EXAMPLE METHOD DETECTION LIMITS IN A WATER AND A SOIL MATRIX USING 15-m COLUMNS AND A FLAME PHOTOMETRIC DETECTOR

	Method Detection Limit	
Compound	Reagent Water[a] (µg/L)	Soil[b] (µg/kg)
Azinphos-methyl	0.10	5.0
Bolstar (Sulprofos)	0.07	3.5
Chlorpyrifos	0.07	5.0
Coumaphos	0.20	10.0
Demeton, -O, -S	0.12	6.0
Diazinon	0.20	10.0
Dichlorvos (DDVP)	0.80	40.0
Dimethoate	0.26	13.0
Disulfoton	0.07	3.5
EPN	0.04	2.0
Ethoprop	0.20	10.0
Fensulfothion	0.08	4.0
Fenthion	0.08	5.0
Malathion	0.11	5.5
Merphos	0.20	10.0
Mevinphos	0.50	25.0
Naled	0.50	25.0
Parathion, ethyl	0.06	3.0
Parathion, methyl	0.12	6.0
Phorate	0.04	2.0
Ronnel	0.07	3.5
Sulfotepp	0.07	3.5
TEPP[c]	0.80	40.0
Tetrachlorovinphos	0.80	40.0
Tokuthion (Protothiofos)[c]	0.07	5.5
Trichloronate[c]	0.80	40.0

[a] Samples extracted using Method 3510, separatory funnel liquid-liquid extraction.
[b] Samples extracted using Method 3540, Soxhlet extraction.
[c] Purity of these standards not established by the EPA Pesticides and Industrial Chemicals Repository, Research Triangle Park, NC.

MDLs are provided for illustrative purposes only.

TABLE 2

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

Matrix	Factor
Ground water (Methods 3510 or 3520)	10[b]
Low-concentration soil by Soxhlet and no cleanup	10[c]
Non-water miscible waste (Method 3580)	1000[c]

[a] EQL = [Method detection limit (see Table 1)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix dependent. The EQLs calculated using this approach are for illustrative purposes only. Even using an MDL generated within a specific laboratory (as opposed to those from Table 1), the resulting EQL is simply an estimate of the quantitative capabilities of the method.

[b] Multiply this factor times the reagent water MDL in Table 1.

[c] Multiply this factor times the soil MDL in Table 1.

TABLE 3

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 8.
[b] Method 8141 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 4

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	

TABLE 4
(continued)

Analyte	Retention Time (min) DB-5	DB-210	DB-608	DB-1
Parathion, ethyl	21.38	22.22	29.29	24.82
Bolstar	22.09	27.57	38.10	29.53
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 8.

[b] Not detected at 20 ng per injection.

[c] Retention times may shift to longer times with larger amounts injected (shifts of over 30 seconds 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 5

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.

TABLE 6

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.

TABLE 7

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.

TABLE 8

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	50EC, hold for 1 minute
Temperature program	50EC to 140EC at 5EC/min, hold for 10 minutes, followed by 140EC to 240°C at 10°C/min, hold for 10 minutes (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	130EC, hold for 3 minutes
Temperature program	130°C, to 180°C at 5°C/min, hold for 10 minutes, followed by 180°C to 250°C at 2°C/min, hold for 15 minutes (or a sufficient amount of time for last compound to elute).

TABLE 9

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	120EC (3-min hold) to 270EC (10-min hold) at 5EC/min
Injector temperature	250EC
Detector temperature	300EC
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	400EC
Bias voltage	4

TABLE 10

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

TABLE 11

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	MDL[a]
Aspon	85.6	11.5	77.7	6.8	1.7
Azinphos-methyl	83.0	13.4	109.7	7.0	2.4
Azinphos-ethyl	88.3	10.8	92.8	8.1	2.4
Bolstar	96.1	4.2	78.2	4.3	1.1
Carbophenothion	85.6	11.0	81.7	7.2	1.9
Chlorfenvinphos	87.8	10.2	90.1	6.0	1.7
Chlorpyrifos	98.8	5.7	77.5	4.2	1.0
Chlorpyrifos methyl	82.5	12.0	59.4	7.5	1.4
Coumaphos	84.3	8.7	100.8	13.5	4.3
Crotoxyphos	86.3	10.5	89.4	5.9	1.7
Demeton	93.6	4.5	73.8	5.1	1.2
Diazinon	91.7	4.7	70.0	5.0	1.1
Dichlorofenthion	85.2	10.9	75.6	6.0	1.4
Dichlorvos (DDVP)	88.1	6.7	90.1	7.9	2.2
Dicrotophos	88.6	10.8	75.7	5.7	1.3
Dimethoate	99.3	1.8	76.7	9.5	2.3
Dioxathion	81.6	14.1	92.7	11.0	3.2
Disulfoton	93.2	7.6	79.5	6.1	1.5
EPN	73.8	10.6	67.9	7.9	1.7
Ethion	85.5	10.6	79.2	6.5	1.6
Ethoprop	95.6	4.1	81.4	3.7	0.9
Famphur	85.2	10.2	75.6	8.3	2.0
Fenitrothion	91.2	8.8	85.0	5.0	1.3

TABLE 11
(continued)

Analyte	Ground Water spiked at 250 ppb		Ground Water spiked at 10 ppb		
	% Recovery	RSD	% Recovery	RSD	MDL[a]
Fensulfothion	86.2	6.4	97.2	6.0	1.8
Fenthion	91.2	5.4	79.5	4.3	1.7
Fonophos	91.0	8.0	81.6	3.6	0.9
Leptophos	81.3	12.2	73.6	8.8	2.0
Malathion	79.5	6.9	78.0	8.7	2.1
Merphos	113.1	9.3	84.6	4.5	1.2
Mevinphos	57.9	6.9	96.8	6.7	2.0
Naled	90.1	6.7	88.1	7.9	2.2
Parathion, ethyl	76.7	9.6	69.6	8.1	1.8
Parathion, methyl	93.9	5.8	83.6	4.7	1.2
Phorate	92.3	7.1	70.8	6.7	1.5
Phosmet	66.1	17.7	90.3	10.7	3.0
Phosphamidon	86.2	11.2	80.6	5.7	1.4
Ronnel	94.7	5.2	77.8	4.7	1.2
Stirophos	78.6	13.1	106.3	5.9	2.0
Sulfotepp	75.3	9.3	68.9	8.6	1.9
Terbufos	87.1	10.5	78.0	3.7	0.9
Thionazin	95.1	8.0	88.6	3.4	1.0
Tokuthion	94.4	4.1	77.8	5.6	1.4
Trichlorfon	72.7	13.5	45.6	6.9	1.0
Trichloronate	95.3	4.5	75.7	3.9	0.9

[a] All MDLs are in µg/L, are highly matrix dependant, and are provided for illustrative purposes only.

TABLE 12

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	MDL[a]
Aspon	83.7	1.8	76.3	6.7	1.6
Azinphos-methyl	102.6	18.0	129.9	12.4	5.1
Azinphos-ethyl	79.8	6.8	96.0	6.7	2.0
Bolstar	94.4	8.3	84.9	1.4	0.4
Carbophenothion	82.4	2.9	82.1	6.7	1.7
Chlorfenvinphos	81.7	6.5	88.0	7.2	2.0
Chlorpyrifos	91.0	8.3	86.5	1.7	0.5
Chlorpyrifos methyl	77.6	2.2	56.7	7.1	1.3
Coumaphos	100.2	17.2	111.0	8.5	3.0
Crotoxyphos	81.3	5.7	87.5	7.0	1.9
Demeton	95.8	5.3	88.5	5.0	1.4
Diazinon	91.8	6.5	82.4	3.2	0.8
Dichlorfenthion	82.5	1.4	76.2	5.5	1.3
Dichlorvos (DDVP)	60.6	11.1	99.7	6.1	1.9
Dicrotophos	82.0	1.6	73.4	6.1	1.4
Dimethoate	93.5	4.1	115.7	6.7	2.4
Dioxathion	84.6	5.6	100.4	9.4	3.0
Disulfoton	92.5	5.3	90.4	2.6	0.7
EPN	78.1	9.6	80.1	8.6	2.2
Ethion	83.5	2.0	78.4	6.4	1.6
Ethoprop	96.3	4.7	92.9	3.1	0.9
Famphur	85.9	2.5	78.6	7.9	1.9
Fenitrothion	83.5	4.8	82.3	5.9	1.5
Fensulfothion	101.7	11.4	110.5	6.5	2.3
Fenthion	91.7	7.3	88.2	2.7	0.7
Fonophos	83.4	2.6	81.3	5.0	1.3
Leptophos	81.9	3.3	73.2	7.5	1.7
Malathion	94.8	6.7	94.7	5.5	1.6
Merphos	94.5	12.7	90.7	1.4	0.4

TABLE 12
(continued)

Analyte	Wastewater spiked at 250 ppb		Wastewater spiked at 10 ppb		MDL[a]
	% Recovery	RSD	% Recovery	RSD	
Mevinphos	62.6	11.2	109.0	4.8	1.6
Naled	60.6	11.1	99.7	6.1	1.9
Parathion ethyl	80.2	8.1	83.6	8.6	2.3
Parathion methyl	92.9	6.5	93.8	4.4	1.3
Phorate	92.4	6.4	85.6	2.4	0.6
Phosmet	63.5	8.2	101.3	9.1	2.9
Phosphamidon	81.1	3.1	78.0	5.7	1.4
Ronnel	91.4	8.4	88.3	2.2	0.6
Stirophos	101.4	14.3	126.5	6.5	2.6
Sulfotepp	78.7	10.7	87.9	8.8	2.4
Terbufos	83.0	1.5	80.1	6.4	1.6
Thionazin	85.1	5.8	84.8	4.9	1.3
Tokuthion	91.8	8.4	83.6	1.8	0.5
Trichlorfon	66.8	4.6	52.2	8.7	1.4
Trichloronate	91.3	8.1	84.3	1.6	0.4

[a] All MDLs are in µg/L, are highly matrix dependant, and are provided for illustrative purposes only.

TABLE 13

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.

TABLE 14

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.

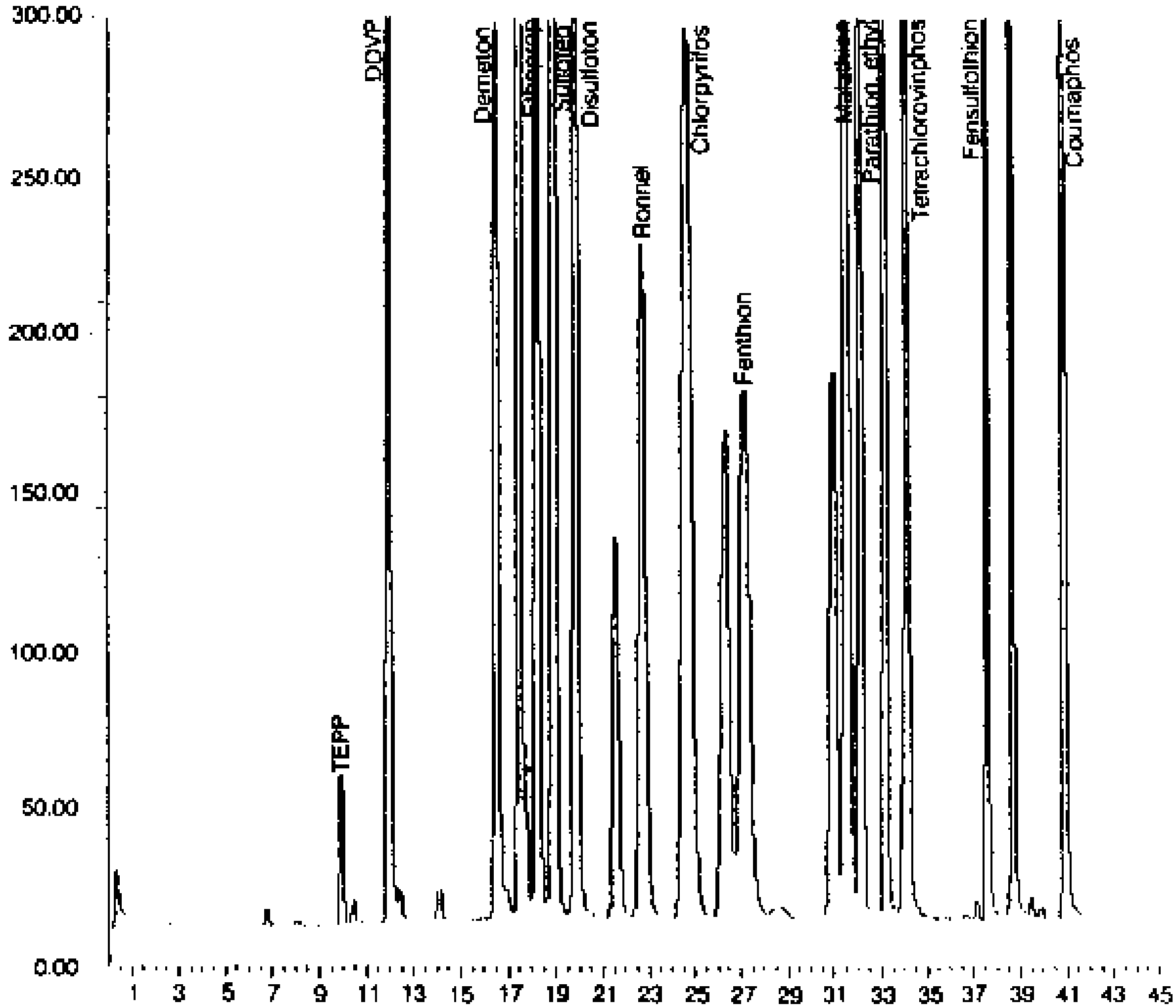
TABLE 15

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

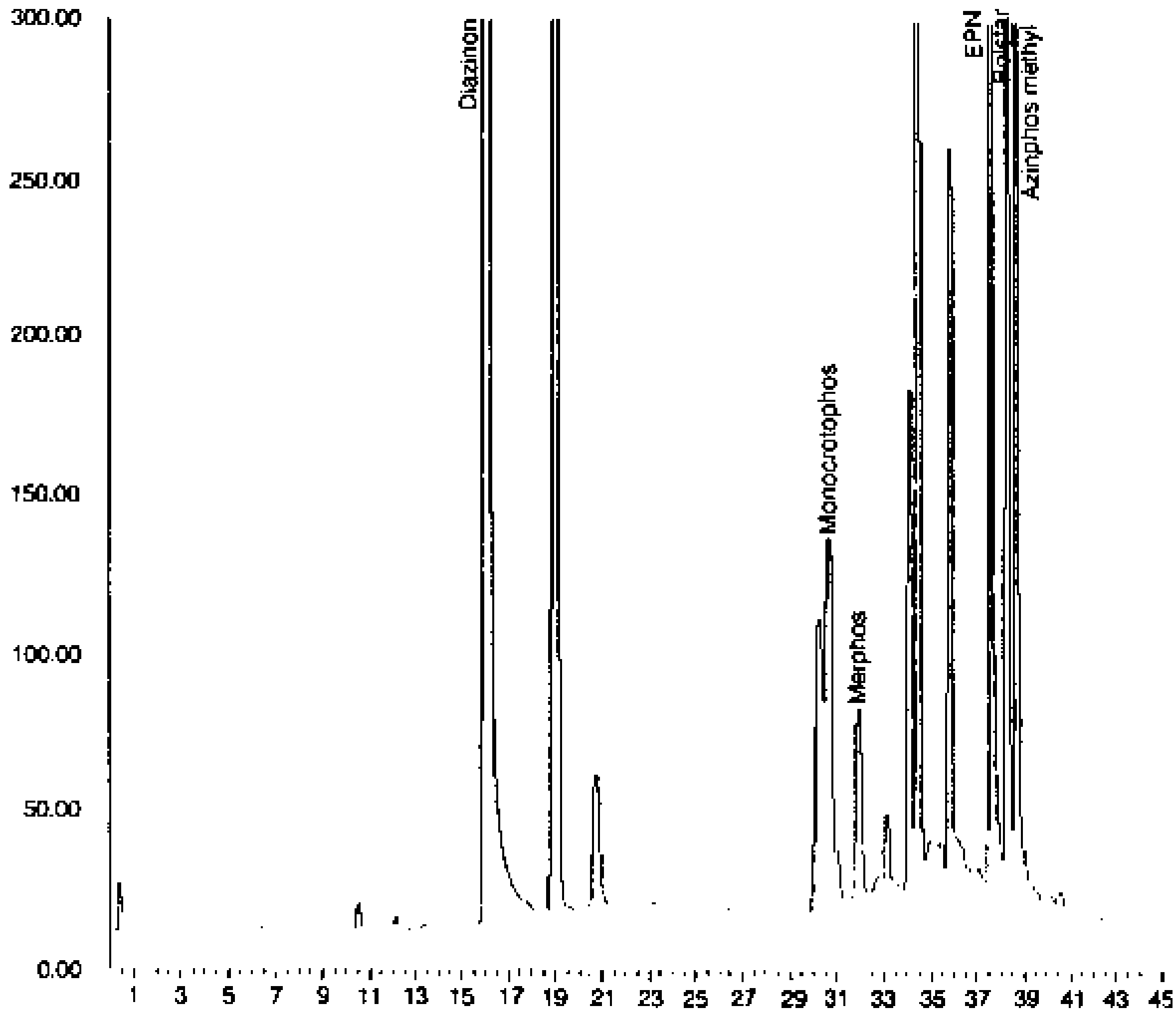
Four replicate aliquots of a spiked bulk clay soil sample were extracted and analyzed.

Data from Reference 16.



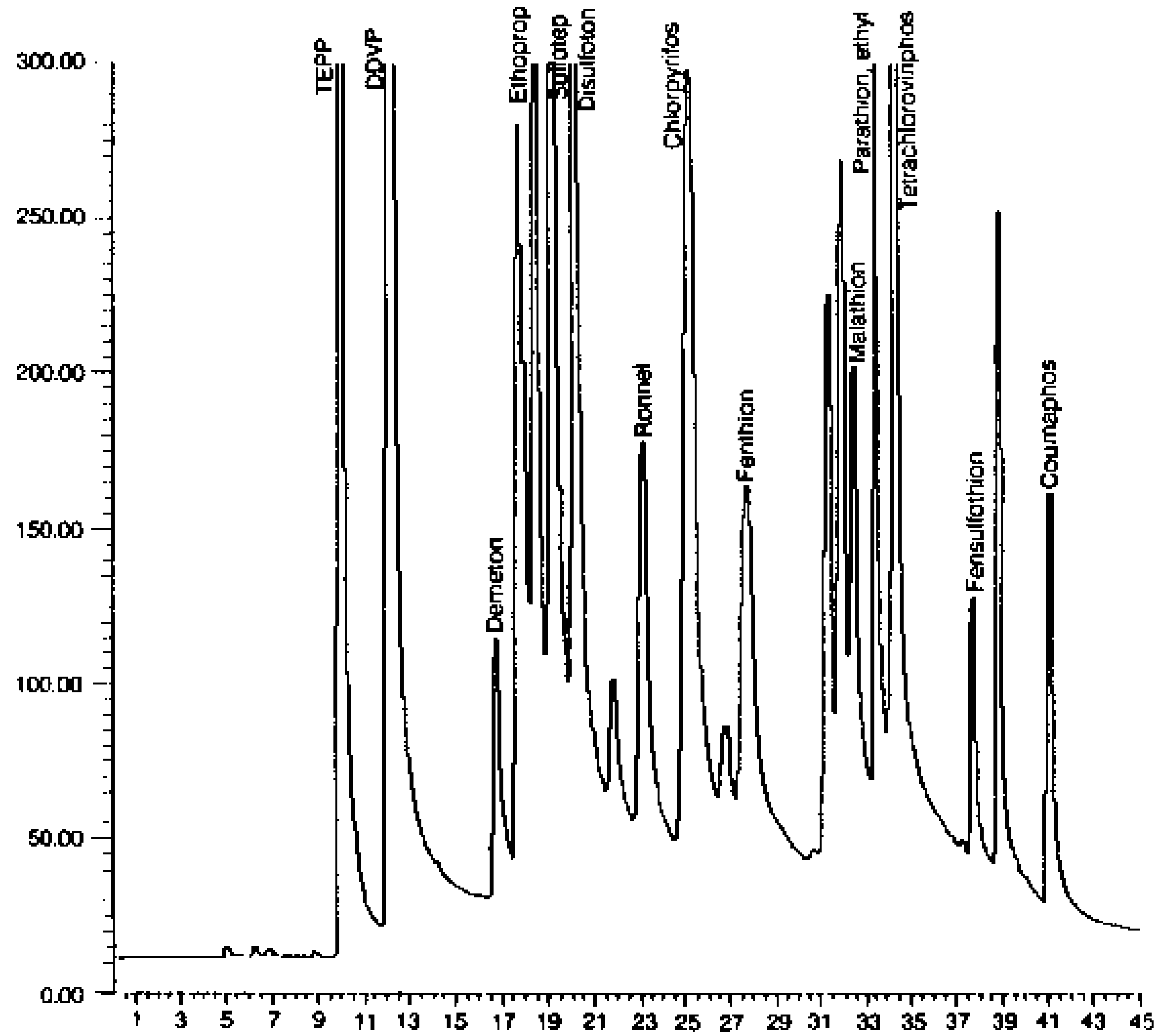
Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with FPD detector. More compounds are shown in Figure 2. See Table 3 for retention times.

FIGURE 2



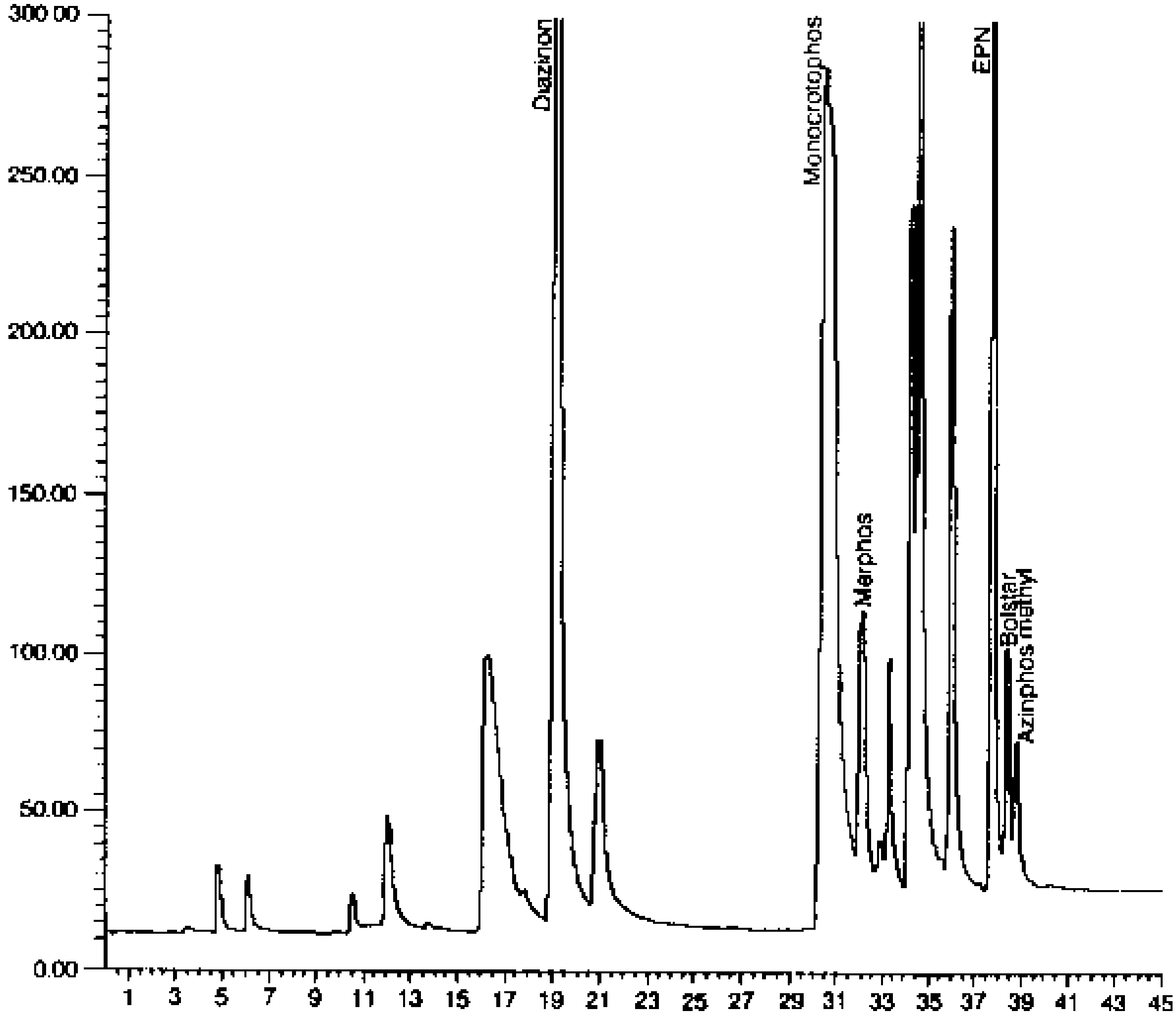
Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with FPD detector. More compounds are shown in Figure 1. See Table 3 for retention times.

FIGURE 3



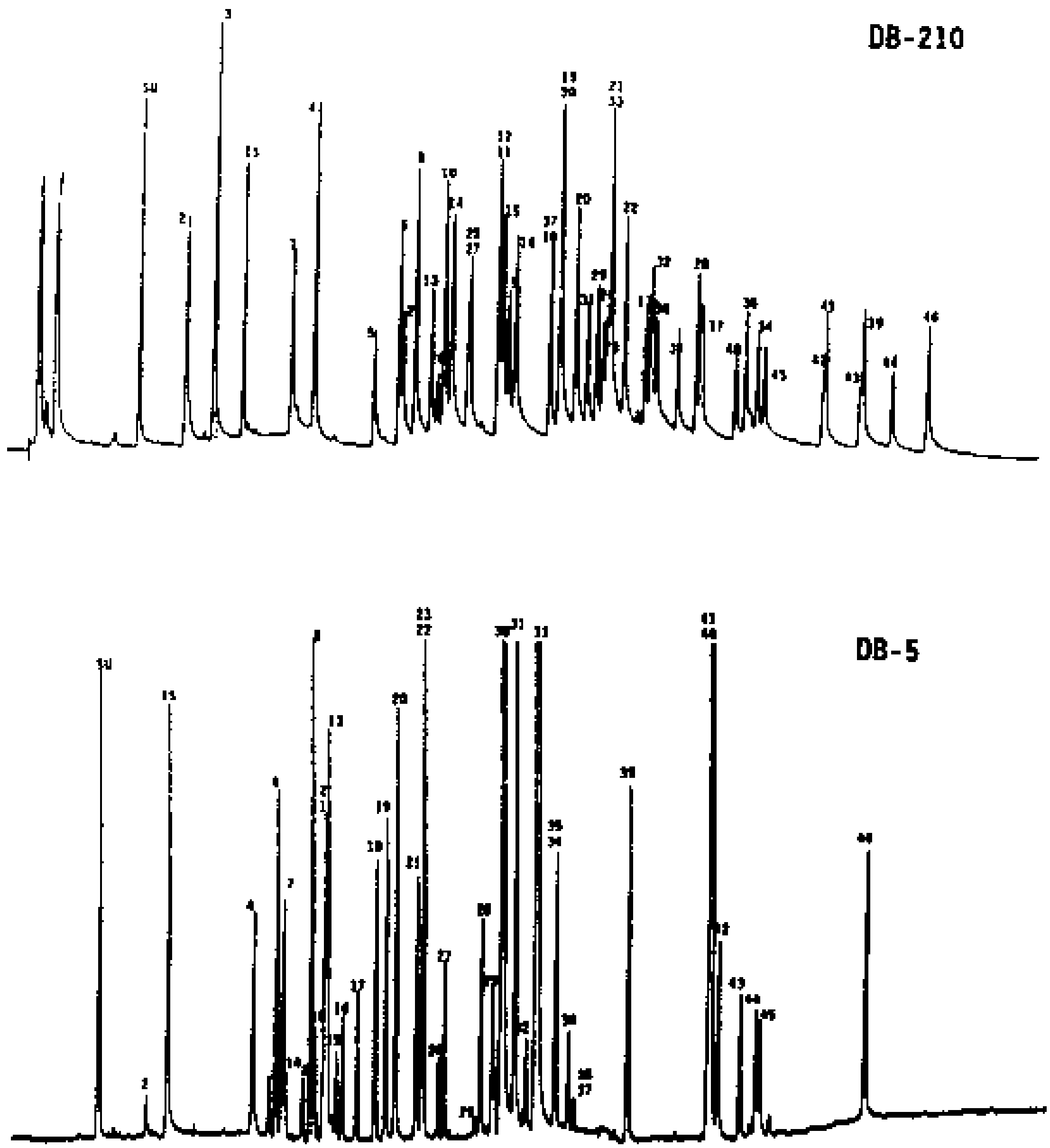
Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with NPD detector. More compounds are shown in Figure 4. See Table 3 for retention times.

FIGURE 4



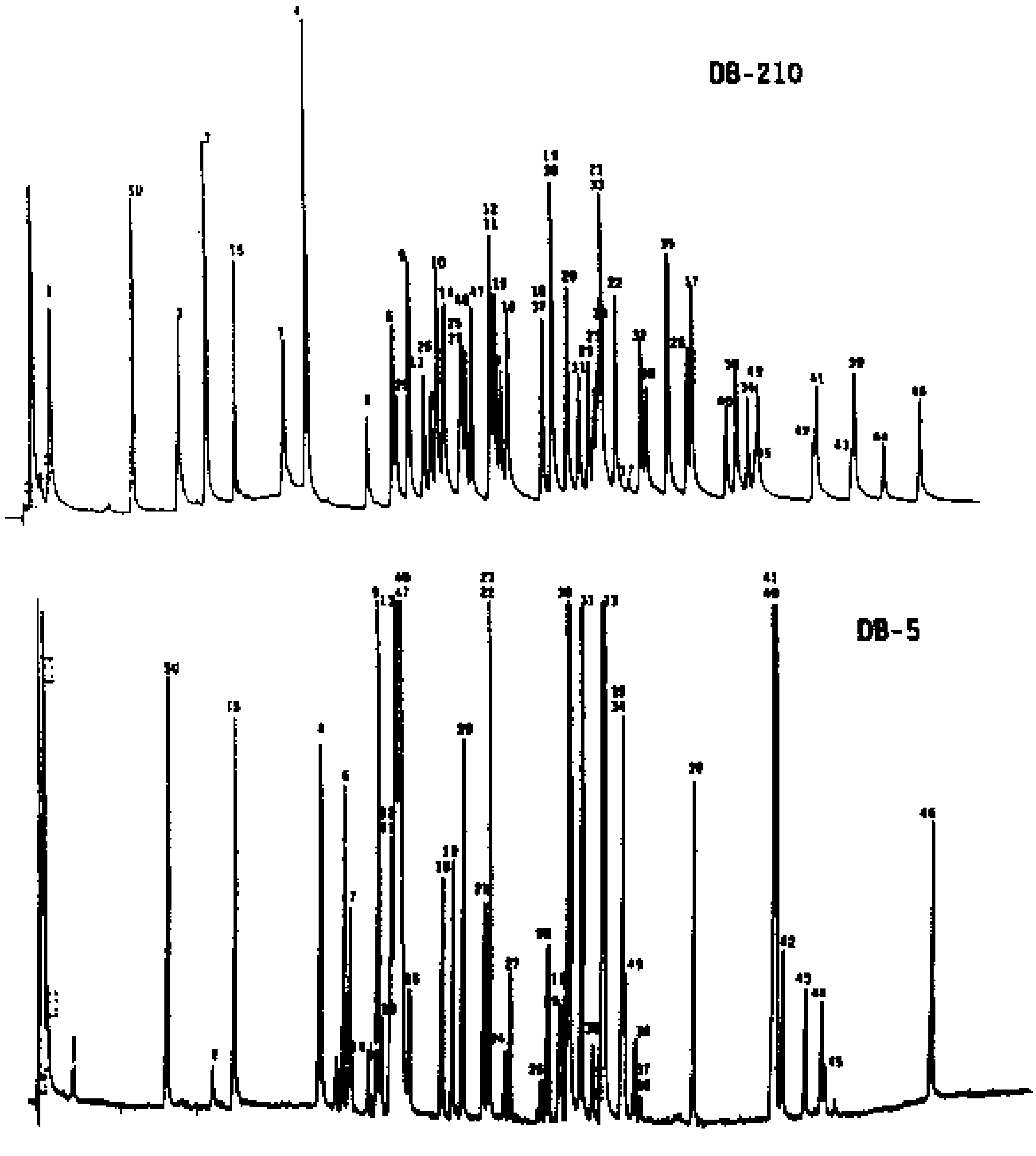
Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with NPD detector. More compounds are shown in Figure 3. See Table 3 for retention times.

FIGURE 5



Chromatogram of target organophosphorus compounds on a 30-m DB-5/DB-210 column pair with NPD detector, without simazine, atrazine and carbophenothion. See Table 4 for retention times and for GC operating conditions.

FIGURE 6



Chromatogram of target organophosphorus compounds on a 30-m DB-5/DB-210 column pair with NPD detector, with simazine, atrazine and carbophenothion. See Table 4 for retention times and for GC operating conditions.

ORGANOPHOSPHORUS COMPOUNDS BY GAS CHROMATOGRAPHY