ORGANOPHOSPHORUS COMPOUNDS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8141 is a capillary gas chromatographic (GC) method used to determine the concentration of organophosphorus (OP) compounds. The fused-silica, open-tubular columns specified in this method offer improved resolution, better selectivity, increased sensitivity, and faster analysis than packed columns. 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 in a study. Any listed chemical is a potential method interference when it is not a target analyte.

Compound Name	CAS Registry No.
OP 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
Fenitrothion[a]	122-14-5
Fensulfothion	115-90-2

Compound Name	CAS Registry No.
Fonophos[a]	944-22-9
Fenthion	55-38-9
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 (Tetrachlorovinphos)	22248-79-9
Sulfotepp	3689-24-5
TEPP[d]	21646-99-1
Terbufos[a]	13071-79-9
Thionazin[a,b] (Zinophos)	297-97-2
Tokuthion[b] (Protothiofos)	34643-46-4
Trichlorfon[a]	52-68-6
Trichloronate[b]	327-98-0
Industrial Chemicals	
Hexamethylphosphoramide[a] (HMPA)	680-31-9
Tri-o-cresylphosphate[a,d] (TOCP)	78-30-8
Triazine Herbicides (NPD only)	
Atrazine[a]	1912-24-9
Simazine[a]	122-34-9

a This analyte has been evaluated using a 30-m column only.
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/trans isomers.

1.2 A dual-column/dual-detector approach may be used for the analysis of relatively clean extracts. Two 15- or 30-m x 0.53-mm ID fused-silica, open-tubular columns of different polarities are connected to an injection tee and each is connected to a detector. Analysts are cautioned regarding the use of a dual column configuration when their instrument is subject to mechanical stress,

when many samples are analyzed over a short time, or when extracts of contaminated samples are analyzed.

1.3 Two detectors can be used for the listed OP 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 Table 1 lists method detection limits (MDLs) for the target analytes, using 15-m columns and FPD, for water and soil matrices. Table 2 lists the estimated quantitation limits (EQLs) for other matrices. MDLs and EQLs using 30-m columns will be very similar to those obtained from 15-m columns.

1.5 The use of a 15-m column system has not been fully validated for the determination of the following compounds. The analyst must demonstrate chromatographic resolution of all analytes, recoveries of greater than 70 percent, with precision of no more than 15 percent RSD, before data generated on the 15-m column system can be reported for these, or any additional, analytes:

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

1.6 When Method 8141 is used to analyze unfamiliar samples, compound identifications should be supported by confirmatory analysis. Sec. 8.0 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.7 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 detection of ppb concentrations of organophosphorus compounds. Prior to the use of this method, appropriate sample preparation techniques must be used. Water samples are extracted at a neutral pH with methylene chloride by using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Soxhlet extraction (Method 3540) or automated Soxhlet extraction (Method 3541) using methylene chloride/acetone (1:1) are used for solid samples. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. A gas chromatograph with a flame photometric or nitrogen-phosphorus detector is used for this multiresidue procedure.

2.2 Organophosphorus esters and thioesters can hydrolyze under both acid and base conditions. Samples prepared using acid and base partitioning procedures are not suitable for analysis by Method 8141.

2.3 Ultrasonic Extraction (Method 3550) is not an appropriate sample preparation method for Method 8141 and should not be used because of the potential for destruction of target analytes during the ultrasonic extraction process.

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 sample cleanup has been demonstrated to yield recoveries of less than 85 percent for many method analytes because they elute before bis-(2-ethylhexyl) phthalate. Method 3640 is therefore 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 and mercury 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 regulatory limits.

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:

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 retention times of these compounds on 30-m columns.

3.8 Analytical difficulties encountered for target analytes include:

3.8.1 Tetraethyl pyrophosphate (TEPP) is an unstable diphosphate which is readily hydrolyzed in water and is thermally labile (TEPP decomposes at 170°C). 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 20°C, 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 workup. 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 rearrangement to Dichlorvos to prevent 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 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 Performance of chromatographic systems will degrade with time. Column resolution, analyte breakdown and baselines may be improved by column washing (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 (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.

4.1.1 Capillary Columns (0.53-mm, 0.32-mm, or 0.25-mm ID x 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).

4.1.1.1 Column 1 - 15- 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.

4.1.1.2 Column 2 - 15- 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.

4.1.1.3 Column 3 - 15- 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.

4.1.1.4 Column 4 - 15- or 30-m x 0.53-mm ID fused-silica open-tubular column, chemically bonded with methyl polysiloxane (DB-1, SPB-1, or equivalent), 1.0-µm or 1.5-µm film thickness.

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

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

4.1.2.1 Splitter 1 - J&W Scientific press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog no. 705-0733).

4.1.2.2 Splitter 2 - Supelco 8-in glass injection tee, deactivated (Supelco, Catalog no. 2-3665M).

4.1.2.3 Splitter 3 - Restek Y-shaped fused-silica connector (Restek, Catalog no. 20405).

4.1.3 Injectors:

4.1.3.1 Packed column, 1/4-in injector port with hourglass liner are recommended for 0.53-mm column. These injector ports can be fitted with splitters (Sec. 4.0) for dual-column analysis.

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

4.1.4 Detectors:

4.1.4.1 Flame Photometric Detector (FPD) operated in the phosphorus-specific mode is recommended.

4.1.4.2 Nitrogen-Phosphorus Detector (NPD) operated in the phosphorus-specific mode is less selective but can detect triazine herbicides.

4.1.4.3 Halogen-Specific Detectors (electrolytic conductivity or microcoulometry) may be used only for a limited number of halogenated or sulfur-containing analytes (Sec. 3.0).

4.1.4.4 Electron-capture detectors may be used for a limited number of analytes (Sec. 3.0).

4.1.5 Data system:

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

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

5.0 REAGENTS

5.1 Solvents

5.1.1 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$ - Pesticide quality or equivalent.

5.1.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.1.3 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.1.4 Tetrahydrofuran (THF), C_4H_8O - Pesticide quality or equivalent (for triazine standards only).

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

5.2 Stock standard solutions (1000 mg/L): Can 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 can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Both Simazine and Atrazine have low solubilities in hexane. If Simazine and Atrazine standards 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 can 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 4°C in Teflon-sealed containers in the dark. All standard solutions should be replaced after two months, or sooner if routine QC (Sec. 8.0) indicates a problem. Standards for easily hydrolyzed chemicals including TEPP, Methyl Parathion, and Merphos should be checked every 30 days.

5.2.5 It is recommended that 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 real 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 standard: Internal standards should only be used on well-characterized samples by analysts experienced in the technique. Use of internal standards is complicated by co-elution of some OP pesticides and by the differences in detector response to dissimilar chemicals.

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 numbers of sulfur atoms (e.g., phosphorothioates [P=S] as an internal standard for phosphates [PO_4]) or phosphorodithioates [$P=S_2$]).

5.4.2 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.

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

5.4.4 The following NPD internal standard has been used for a 30-m column pair. Make 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 Surrogate standard spiking solutions - 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 gas chromatographic/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 used as FPD and NPD surrogates. A volume of 1.0 mL of a 1-µg/L spiking solution (1 ng of surrogate) is added to each water sample and each soil/sediment sample. If there is a co-elution problem, 4-chloro-3-nitrobenzo-trifluoride has also been used as an NPD-only surrogate.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Extracts are to be refrigerated at 4°C and analyzed within 40 days of extraction. See Sec. 5.2.4 for storage of standards.

6.3 Organophosphorus esters will hydrolyze under acidic or basic conditions. Adjust 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.

6.4 Even with storage at 4°C and use of mercuric chloride as a preservative, most OPs in groundwater samples collected for the national pesticide survey degraded within a 14-day period. Begin sample extraction within 7 days of collection.

7.0 PROCEDURE

7.1 Extraction and cleanup:

7.1.1 Refer to Chapter Two and Method 8140 for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3541 with methylene chloride/acetone (1:1 v/v) or hexane/acetone (1:1 v/v) as the extraction solvent. Method 3550 is an inappropriate extraction technique for the target analytes of this method (See Sec. 2.3).

7.1.2 Extraction and cleanup procedures that use solutions below pH 4 or above pH 8 are not appropriate for this method.

7.1.3 If required, the samples may be cleaned up using the Methods presented in Chapter Four, Sec. 2. Florisil Column Cleanup (Method 3620) and Sulfur Cleanup (Method 3660, TBA-sulfite option) may have particular application for OPs. Gel Permeation Cleanup (Method 3640) should not generally be used for OP pesticides.

7.1.3.1 If sulfur cleanup by Method 3660 is required, do not use mercury or copper.

7.1.3.2 GPC may only be employed if all target OP pesticides are listed as analytes of Method 3640, or if the laboratory has demonstrated a recovery of greater than 85 percent for target OPs at a concentration not greater than 5 times the regulatory action level. Laboratories must retain data demonstrating acceptable recovery.

7.1.4 Prior to gas chromatographic analysis, the extraction 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.

7.1.5 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.

7.2 Gas chromatographic conditions:

7.2.1 Four 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 length are recommended if a large number of organophosphorus analytes are to be determined. If superior chromatographic resolution is not required, 15-m lengths columns may be appropriate. Operating conditions for 15-m columns

are listed in Table 5. Operating conditions for 30-m columns are listed in Table 6.

7.2.2 Retention times for analytes on each set of columns are presented in Tables 3 and 4.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 5 and Table 6 for establishing the proper operating parameters for the set of columns being employed in the analyses.

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

7.4.1 Automatic injections of 1 µL are recommended. Hand injections of no more than 2 µL may be used if the analyst demonstrates quantitation precision of ≤ 10 percent relative standard deviation. 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 mL of sample prior to injection. Chromatograms of the target organophosphorus compounds are shown in Figures 1 through 4.

7.4.2 Figures 5 and 6 show chromatograms with and without Simazine, Atrazine, and Carbophenothion on 30-m columns.

7.5 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 (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 calculation equations.

7.5.1 If peak detection and identification is prevented by the presence of interferences, the use of an FPD or further sample cleanup is required. 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. The absence of interference from reagents must be demonstrated by routine processing of reagent blanks through the chosen cleanup procedure. Refer to Sec. 3.0 for interferences.

7.5.2 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.

7.5.3 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.

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

7.6 Suggested chromatograph maintenance: Corrective measures may require any one or more of the following remedial actions.

7.6.1 Refer to Method 8000 for general information on the maintenance of capillary columns and injectors.

7.6.2 Splitter connections: For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector (J&W Scientific, Restek, or equivalent), 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.

7.6.3 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.

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

7.7 Detector maintenance:

7.7.1 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.

7.7.2 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 decreased detector sensitivity.

7.7.3 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.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Include a mid-level check standard after each group of 10 samples in the analysis sequence. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000.

8.3 GC/MS confirmation

8.3.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Follow the GC/MS operating requirements specified in Method 8270.

8.3.2 When available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

8.3.3 To confirm an identification of a compound, the background-corrected mass spectrum of the compound must be obtained from the sample extract and must be compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. At least 25 ng of material should be injected into the GC/MS. The following criteria must be met for qualitative confirmation:

8.3.3.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

8.3.3.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

8.3.3.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

8.3.3.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the

reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

8.3.3.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

8.3.3.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

8.3.3.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of nontarget analytes. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within $\pm$ 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

8.3.4 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.

8.3.5 Should the MS procedure fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional sample cleanup.

9.0 METHOD PERFORMANCE

9.1 Estimated MDLs and associated chromatographic conditions for water and clean soil (uncontaminated with synthetic organics) are listed in Table 1. As detection limits will vary with the particular matrix to be analyzed, guidance for determining EQLs is given in Table 2. Recoveries for several method analytes are provided in Tables 5, 6, and 7.

10.0 REFERENCES

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TABLE 1
METHOD DETECTION LIMITS IN A WATER AND A SOIL
MATRIX USING 15-m COLUMNS AND A FLAME PHOTOMETRIC DETECTOR

Compound	Reagent Water (3510)[a] (µg/L)	Soil (3540)[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] Sample extracted using Method 3510, Separatory Funnel Liquid-Liquid Extraction.

[b] Sample 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.

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 to be determined herein are for guidance and may not always be achievable.

[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.
RETENTION TIMES FOR METHOD 8141A ANALYTES
EMPLOYING 15-m COLUMNS

	Capillary Column		
Compound	DB-5	SPB-608	DB-210
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
Monochrotophos	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*	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

*Method 8141A has not been fully validated for Famphur.

Initial temperature	130°C	50°C	50°C
Initial time	3 minutes	1 minute	1 minute
Program 1 rate	5°C/min	5°C/min	5°C/min
Program 1 final temp.	180°C	140°C	140°C
Program 1 hold	10 minutes	10 minutes	10 minutes
Program 2 rate	2°C/min	10°C/min	10°C/min
Program 2 final temp.	250°C	240°C	240°C
Program 2 hold	15 minutes	10 minutes	10 minutes

TABLE 4.
RETENTION TIMES FOR METHOD 8141A ANALYTES
EMPLOYING 30-m COLUMNS[a]

Compound	RT (min) 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
Stirophos	22.06	24.63	33.40	26.90
Ethion	22.55	27.12	37.61	

(continued)

TABLE 4. (Continued)

Compound	RT (min) DB-5	DB-210	DB-608	DB-1
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-Cl-3-nitrobenzotrifluoride	5.73	5.40		

[a] The GC operating conditions were as follows:

DB-5 and DB-210 - 30-m x 0.53-mm ID column, DB-5 (1.50-μm film thickness) and DB-210 (1.0-μm film thickness). Both connected to a press-fit Y-shaped inlet splitter. Temperature program: 120°C (3-min hold) to 270°C (10-min hold) at 5°C/min; injector temperature 250°C; detector temperature 300°C; bead temperature 400°C; bias voltage 4.0; hydrogen gas pressure 20 psi; helium carrier gas 6 mL/min; helium makeup gas 20 mL/min.

DB-608 - 30-m x 0.53-mm ID column, DB-608 (1.50-μm film thickness) installed in an 0.25-in packed-column inlet. Temperature program: 110°C (0.5-min hold) to 250°C (4-min hold) at 3°C/min; injector temperature 250°C; helium carrier gas 5 mL/min; flame photometric detector.

DB-1 30-m x 0.32-mm ID column, DB-1 (0.25-μm film thickness) split/splitless with head pressure of 10 psi, split valve closure at 45 sec, injector temp. 250°C, 50°C (1-min hold) to 280°C (2-min hold) at 6°C/min, mass spectrometer full scan 35-550 amu.

[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, Hatcher et. al.)
[d] Shows multiple peaks; therefore, not included in the composite.

TABLE 5.
PERCENT RECOVERY OF 27 ORGANOPHOSPHATES BY SEPARATORY FUNNEL EXTRACTION

Compound	Percent Recovery		
	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	94

NR = Not recovered.

TABLE 6
PERCENT RECOVERY OF 27 ORGANOPHOSPHATES BY CONTINUOUS LIQUID-LIQUID EXTRACTION

Compound	Percent Recovery		
	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
Famphur	--	63 + 15	--
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.

TABLE 7.
PERCENT RECOVERY OF 27 ORGANOPHOSPHATES BY SOXHLET EXTRACTION

Compound	Percent Recovery		
	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.

TABLE 8.

SUGGESTED OPERATING CONDITIONS FOR 15-m COLUMNS

Columns 1 and 2 (DB-210 and SPB-608 or their equivalent)	
Carrier gas (He) flow rate =	5 mL/min
Initial temperature =	50°C, hold for 1 minute
Temperature program =	50°C to 140°C at 5°C/min, hold for 10 minutes, followed by 140°C 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 =	5 mL/min
Initial temperature =	130°C, 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:

Type: DB-210
Dimensions: 30-m x 0.53-mm ID
Film Thickness (µm): 1.0

Column 2:

Type: DB-5
Dimensions: 30-m x 0.53-mm ID
Film Thickness (µm): 1.5

Carrier gas flowrate (mL/min): 6 (Helium)

Makeup gas flowrate (mL/min): 20 (Helium)

Temperature program: 120°C (3-min hold) to 270°C (10-min hold) at 5°C/min

Injector temperature: 250°C

Detector temperature: 300°C

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°C

Bias voltage: 4

TABLE 10
QUANTITATION AND CHARACTERISTIC IONS FOR OP PESTICIDES

Compound Name	Quantitation ions	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, ethy	1291	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

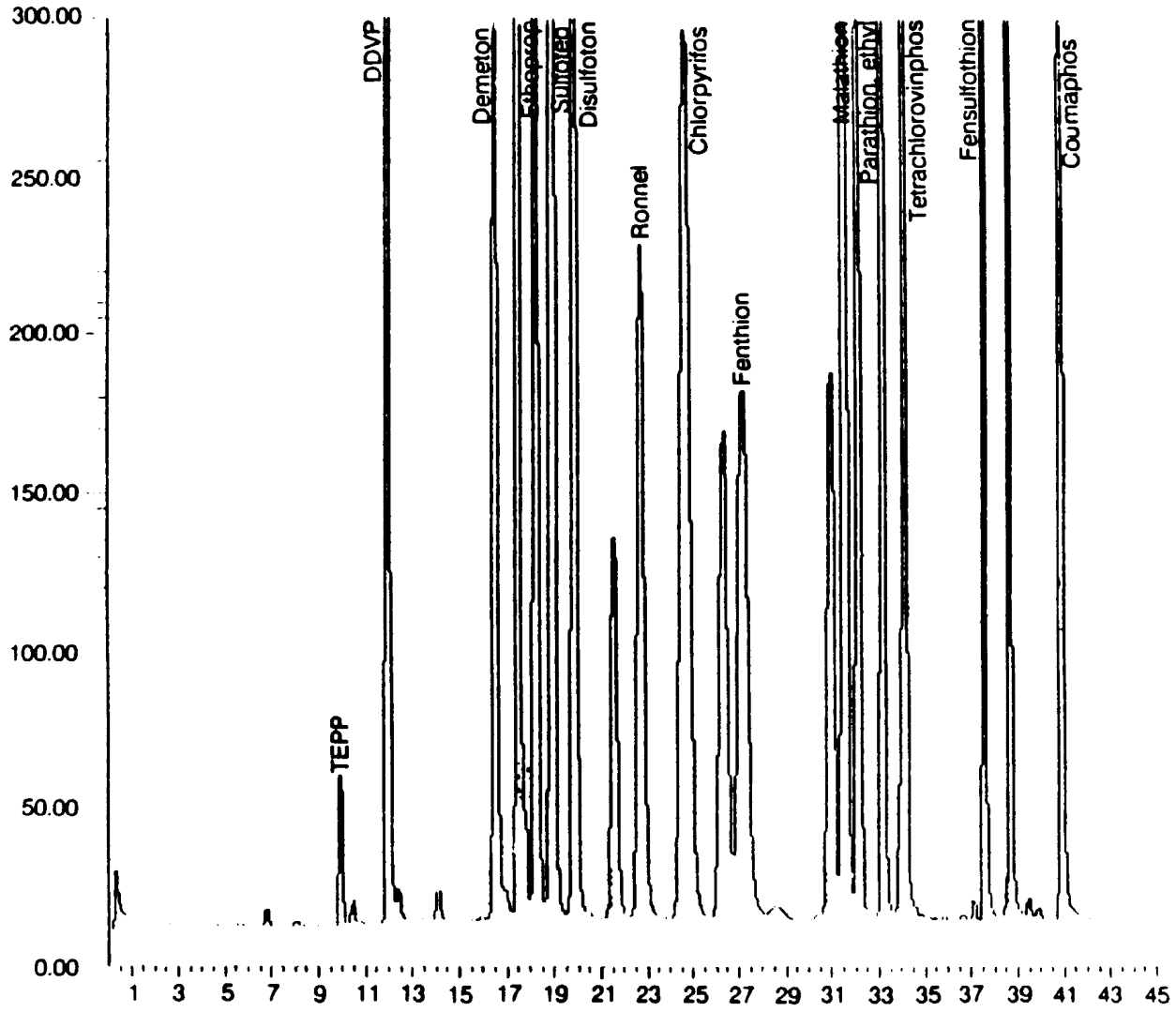


Figure 1. Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with FPD detector. More compounds are shown in Figure 2. See Table 3 for retention times.

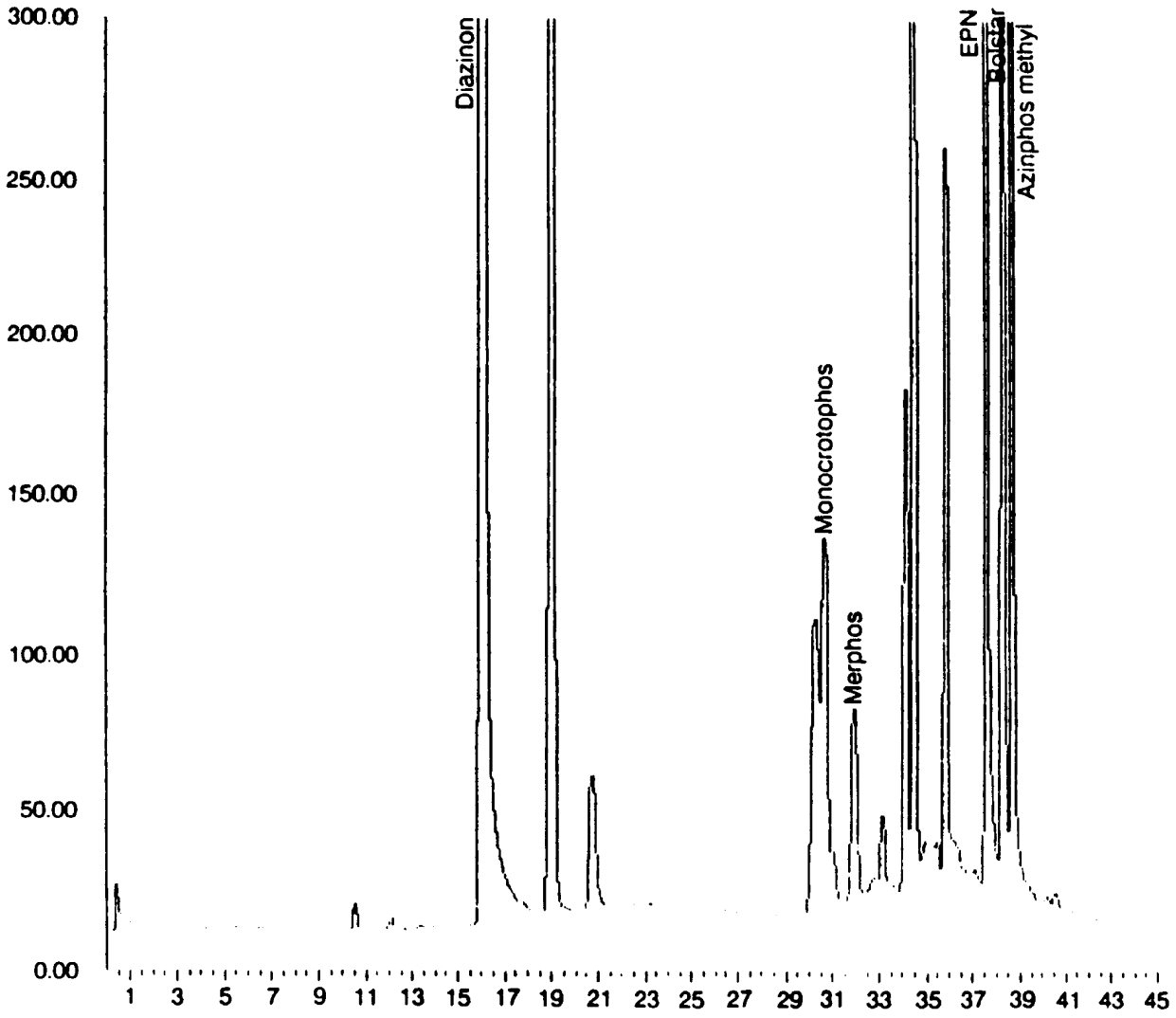


Figure 2. Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with FPD detector. More compounds are shown in Figure 1. See Table 3 for retention times.

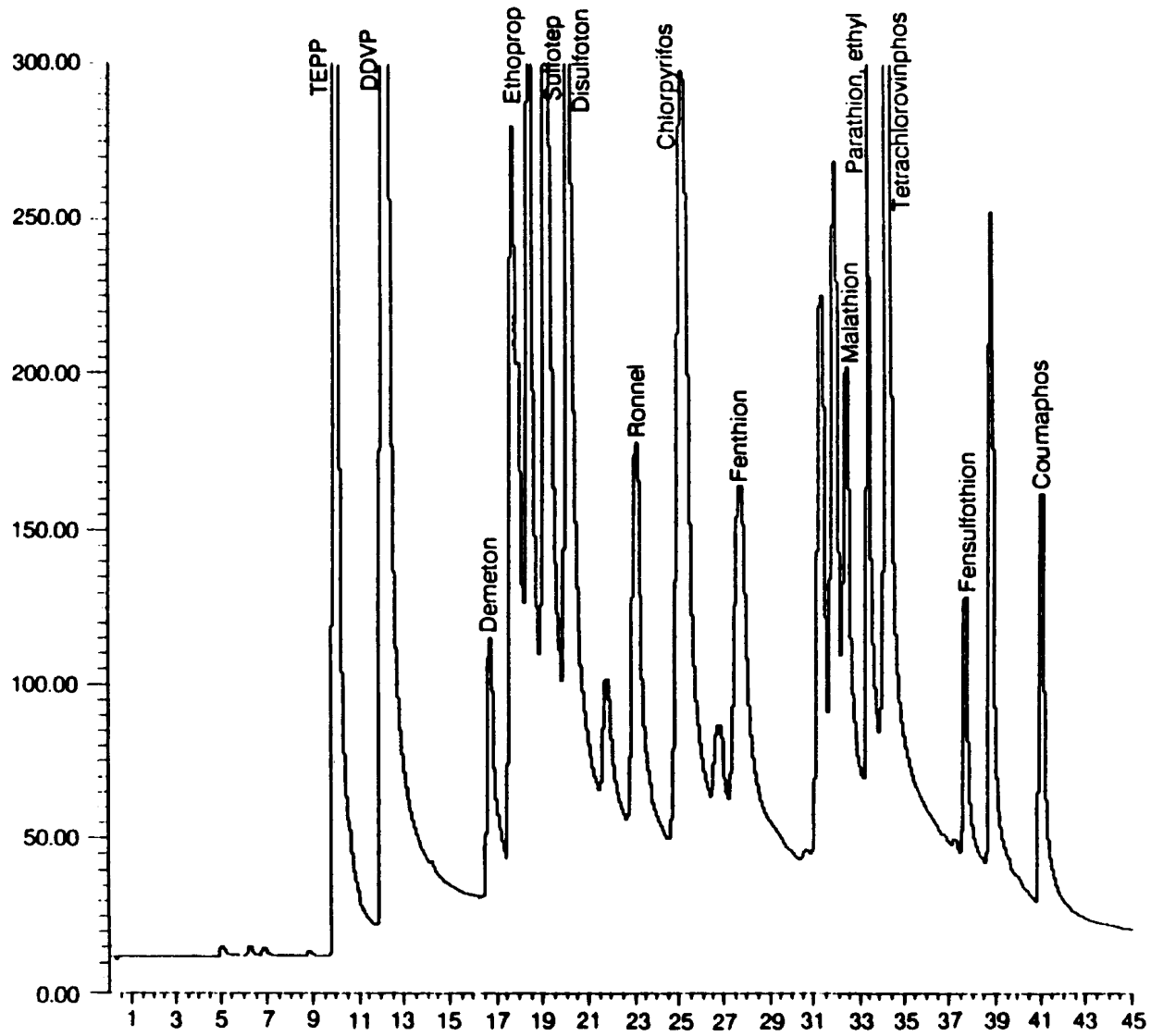


Figure 3. Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with NPD detector. More compounds are shown in Figure 4. See Table 3 for retention times.

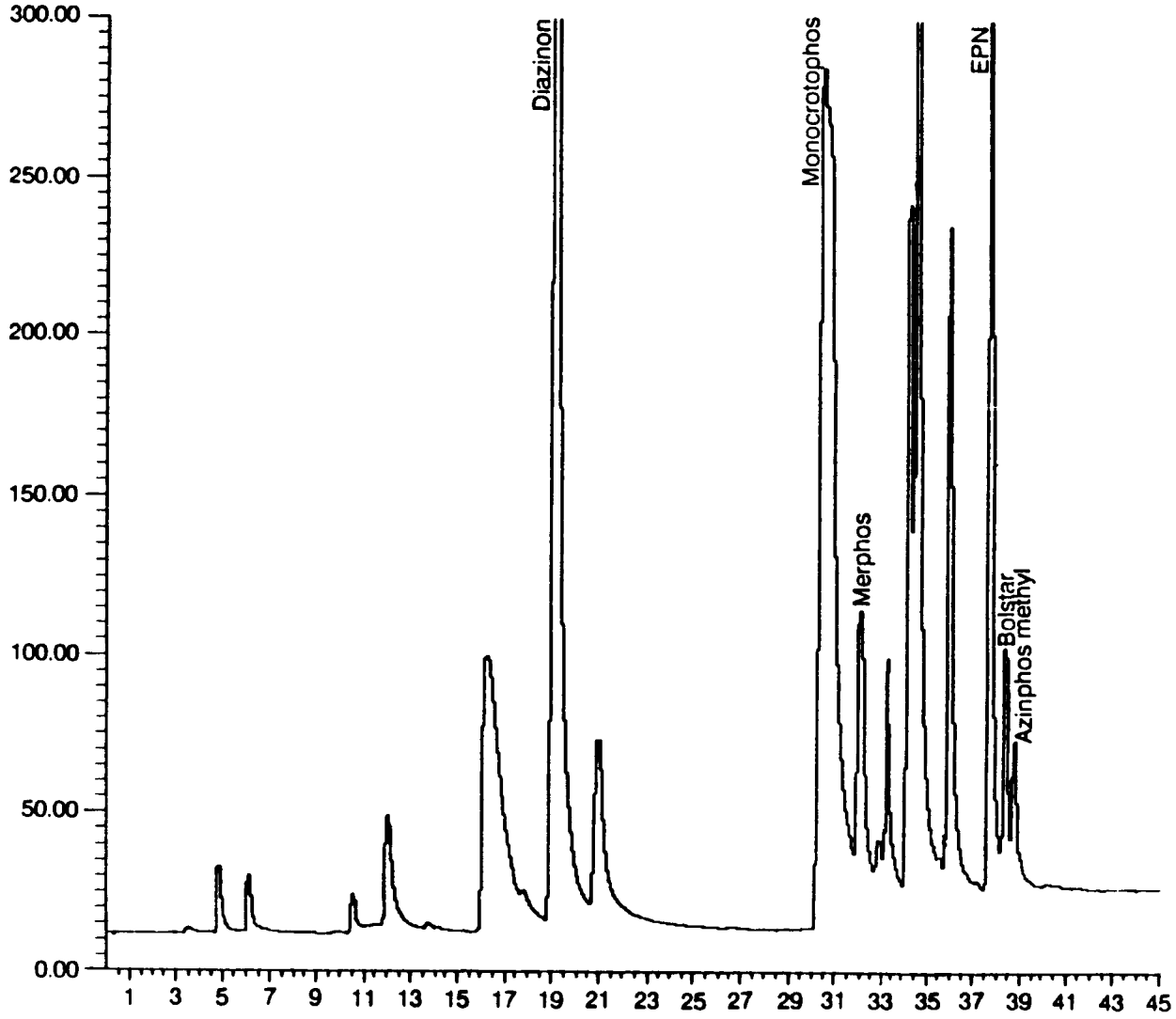


Figure 4. Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with NPD detector. More compounds are shown in Figure 3. See Table 3 for retention times.

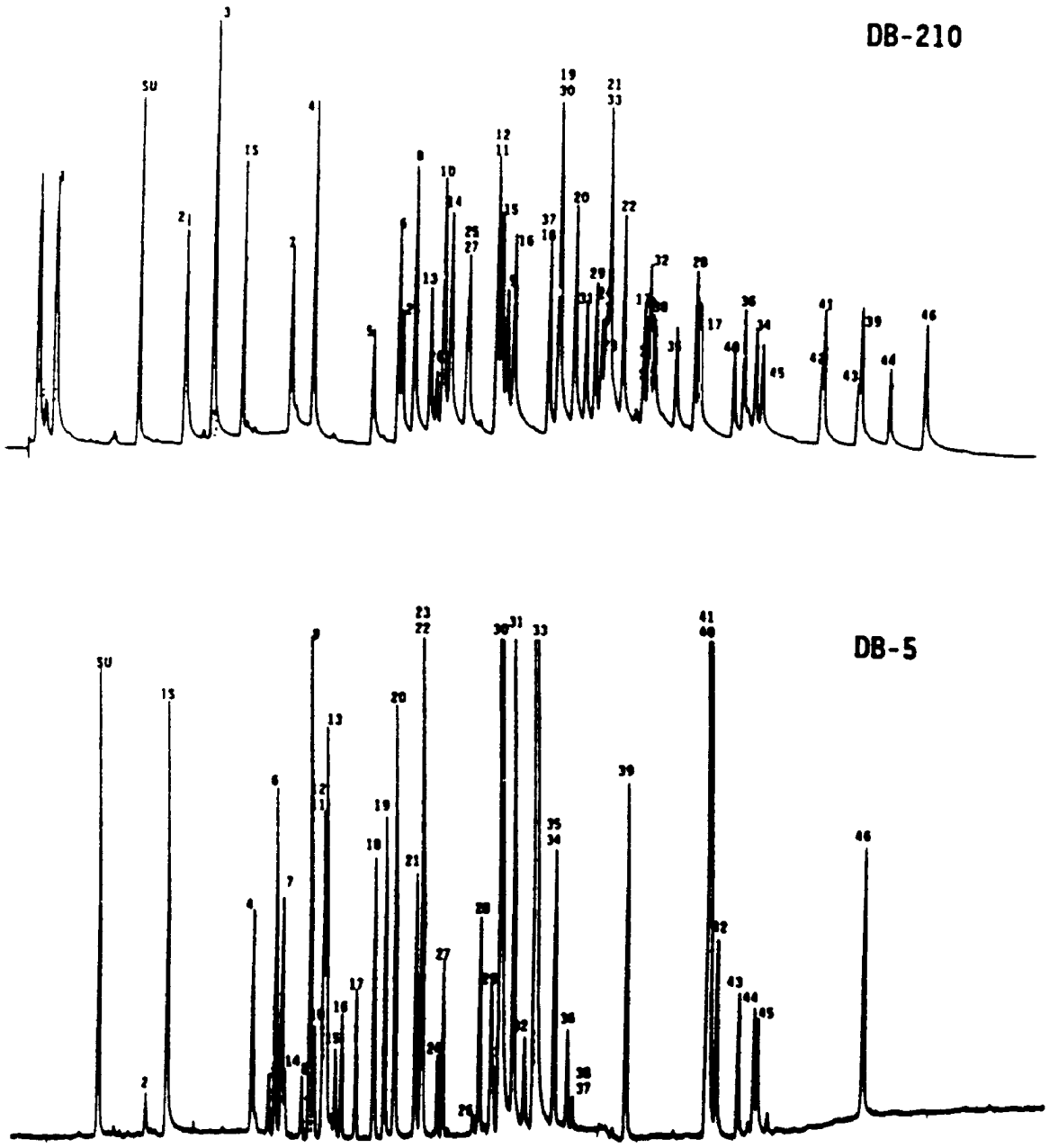


Figure 5. Chromatogram of target organophosphorus compounds on a 30-m DB-5/DB-210 column pair with NPD detector, without Simazine, Atrazine and Carbophenothion. See Table 4 for retention times and for GC operating conditions.

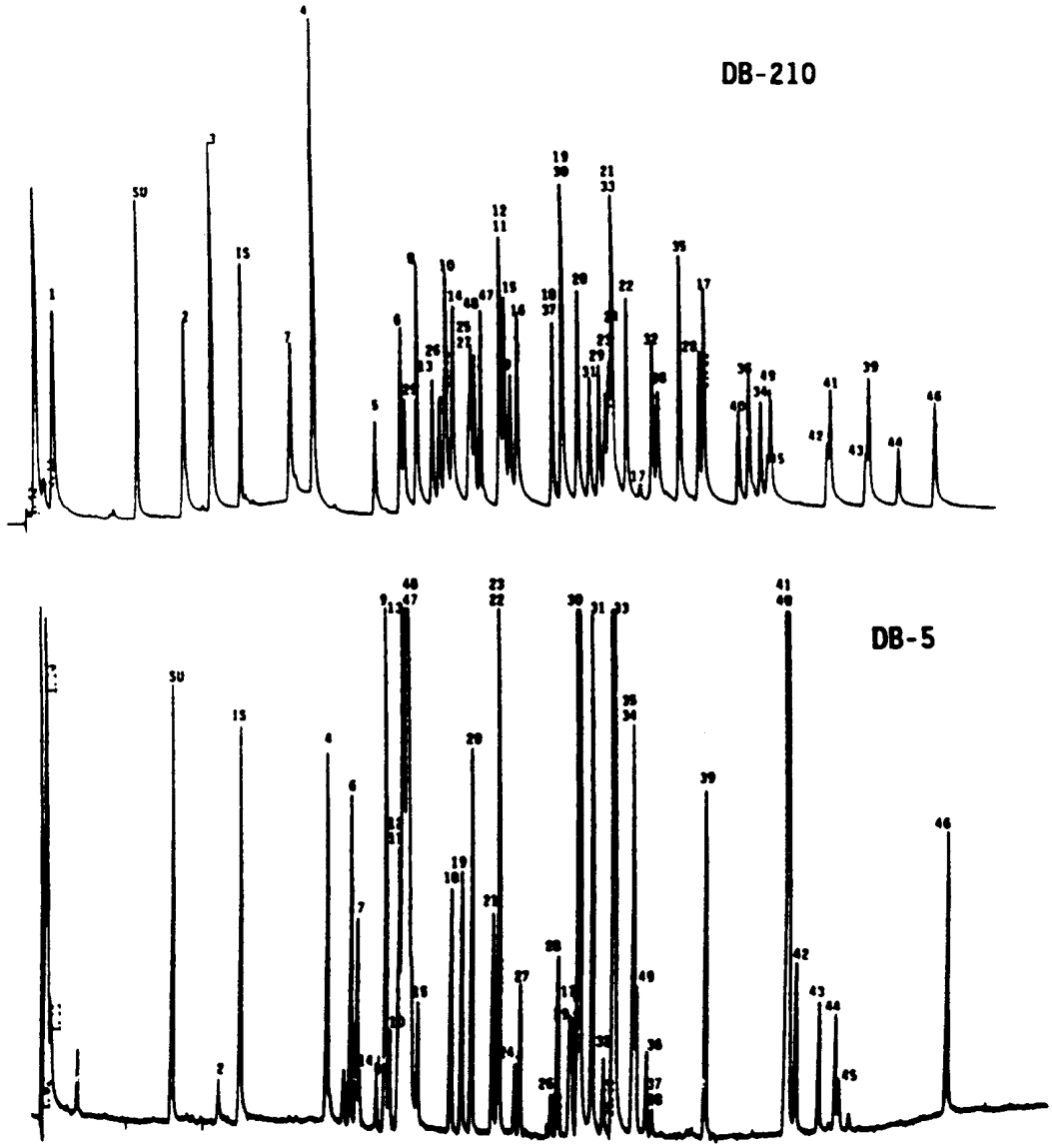
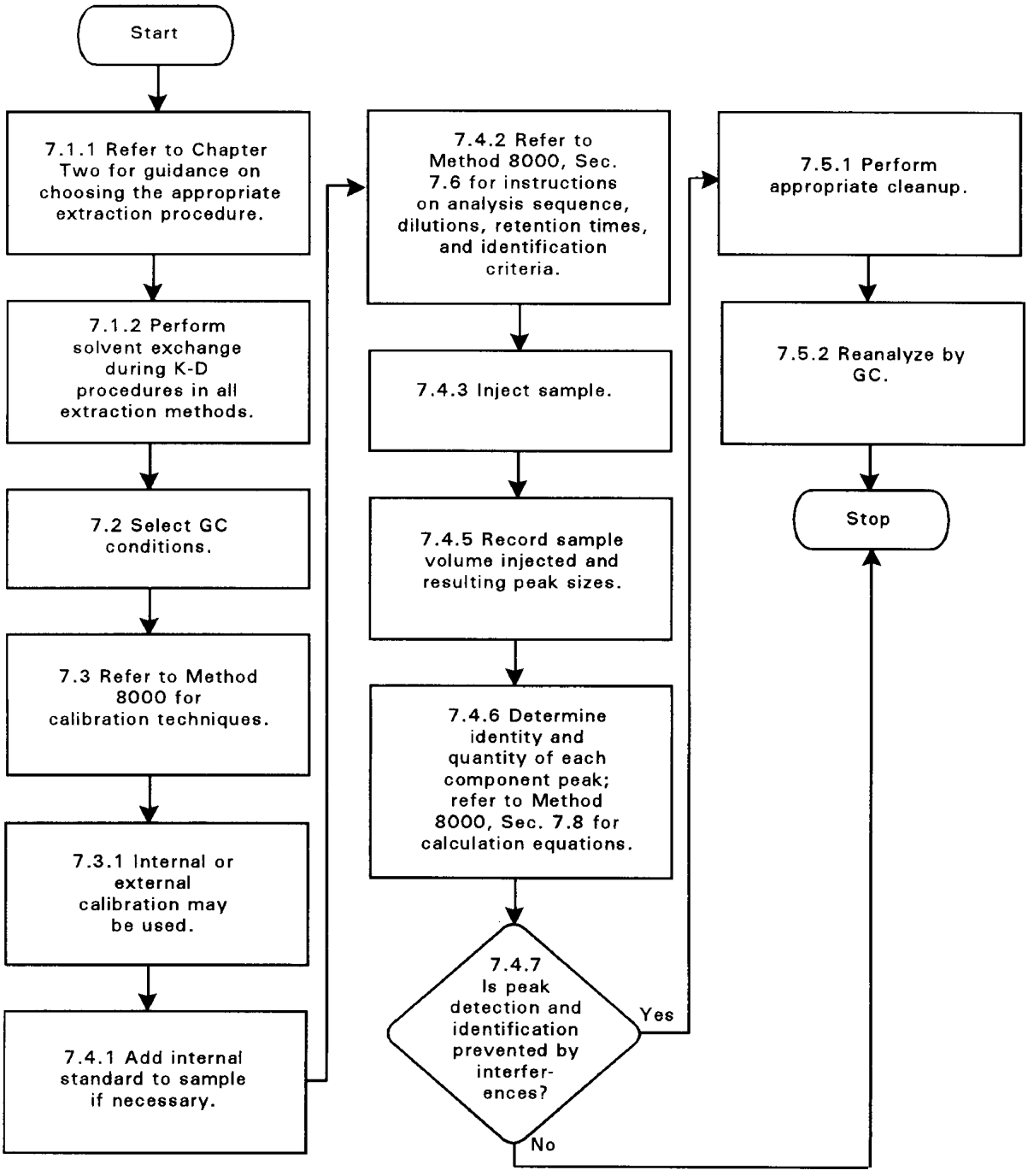


Figure 6. Chromatogram of target organophosphorus compounds on a 30-m DB-5/DB-210 column pair with NPD detector, with Simazine, Atrazine and Carbophenothion. See Table 4 for retention times and for GC operating conditions.


Start
7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure.
7.1.2 Perform solvent exchange during K-D procedures in all extraction methods.
7.2 Select GC conditions.
7.3 Refer to Method 8000 for calibration techniques.
7.3.1 Internal or external calibration may be used.
7.4.1 Add internal standard to sample if necessary.
7.4.2 Refer to Method 8000, Sec. 7.6 for instructions on analysis sequence, dilutions, retention times, and identification criteria.
7.4.3 Inject sample.
7.4.5 Record sample volume injected and resulting peak sizes.
7.4.6 Determine identity and quantity of each component peak; refer to Method 8000, Sec. 7.8 for calculation equations.
7.4.7 Is peak detection and identification prevented by interfer-ences?
Yes
No
7.5.1 Perform appropriate cleanup.
7.5.2 Reanalyze by GC.
Stop