Method 614.1: The Determination of Organophosphorus Pesticides in Municipal and Industrial Wastewater

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1.   SCOPE AND APPLICATION

1.1   This method covers the determination of certain organophosphorus pesticides in municipal and industrial wastewater. The following parameters may be determined by this method.

Parameter	STORET No.	CAS No.
Dioxathion		78-34-2
EPN		2104-64-5
Ethion	39398	563-12-2
Terbufos		13071-79-9

1.2   The estimated detection limit (EDL) for each parameter is listed in Table 1. The EDL was calculated from the minimum detectable response of the nitrogen/phosphorus detector equal to 5 times the gas chromatographic (GC) background noise assuming a 1.0-mL final extract volume of a 1-L reagent water sample and an injection of 5 μL. The EDL for a specific wastewater may be different depending on the nature of interferences in the sample matrix.

1.3   This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges. When this method is used to analyze unfamiliar samples for any or all of the compounds listed above, compound identifications should be supported by at least one additional qualitative technique.   Section 13 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative confirmation of compound identifications.

1.4   This method is restricted to use by or under the supervision of analysts experienced in the operation of gas chromatographs and in the interpretation of chromatograms.

2.   SUMMARY OF METHOD

2.1   Organophosphorus pesticides are removed from the sample matrix by extraction with 15% methylene chloride in hexane. The extract is dried, exchanged into hexane, and analyzed by gas chromatography. Column chromatography is used as necessary to eliminate interferences which may be encountered. Measurement of the pesticides is accomplished with a nitrogen/phosphorus-specific detector.

2.2   Confirmatory analysis by GC/MS is recommended when a new or undefined sample type is being analyzed if the concentration is adequate for such determination.

3. INTERFERENCES

3.1   Solvent, reagents, glassware, and other sample-processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 9.1.

      3.1.1   The use of high-purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

      3.1.2   Glassware must be scrupulously cleaned.[1] Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water and reagent water. It should then be drained dry and heated in a muffle furnace at 400°C for 15 to 30 minutes. Solvent rinses with acetone and pesticide-quality hexane may be substituted for the heating. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store the glassware inverted or capped with aluminum foil.

3.2   Interferences coextracted from the samples will vary considerably from source to source, depending on the diversity of the industrial complex or municipality being sampled. While general cleanup procedures are provided as part of this method, unique samples may require additional cleanup approaches to achieve the detection limits listed in Table 1.

4. SAFETY

4.1   The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[2-4] for the information of the analyst.

5. APPARATUS AND EQUIPMENT

5.1   Sample containers: Narrow-mouth glass bottles, 1-L or 1-quart volume, equipped with polytetrafluoroethylene (PTFE)-lined screw-caps. Wide-mouth glass bottles, 1-quart volume, equipped with PTFE-lined screw-caps may also be used. Prior to use, wash bottles and cap liners with detergent and rinse with tap and distilled water. Allow the bottles and cap liners to air dry, then muffle at 400°C for 1 hour. After cooling, rinse the cap liners with hexane, seal the bottles, and store in a dust-free environment.

5.1.1 Automatic sampler (optional): Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow-proportional composites.

5.2   Kuderna-Danish (K-D) glassware.

5.2.1 Synder column: Three-ball macro (Kontes K-503000-0121 or equivalent) and two-ball micro (Kontes K-569001-0219 or equivalent).

5.2.2 Concentrator tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent) with ground-glass stopper.

5.2.3 Evaporative flask: 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.3   Gas chromatography system.

5.3.1 The gas chromatograph must be equipped with a glass-lined injection port compatible with the detector to be used. A data system is recommended for measuring peak areas.

5.3.1.1 Column 1: 180 cm long by 2 mm ID, glass, packed with 3% OV-225 on Supelcoport (100/120 mesh) or equivalent.

5.3.1.2 Column 2:   120 cm long by 2 mm ID, Pyrex[R] glass, packed with 1.5% OV-17/1.95 % QF-1 on Gas Chrom Q, 80/100 mesh or equivalent.

5.3.1.3 Column 1 was used to develop the accuracy and precision statements in Section 12. Guidelines for the use of alternative column packings are provided in Section 10.3.1.

5.3.1.4 Detector: nitrogen/phosphorus. This detector has proven effective in the analysis of wastewaters for the parameters listed in the scope and was used to develop the method performance statements in Section 12. Guidelines for the use of alternative detectors are provided in Section 10.3.1.

5.4   Chromatographic column: 300 mm long by 10 mm ID Chromaflex, equipped with coarse-fitted bottom plate and PTFE stopcock. (Kontes K-420540-0213 or equivalent).

5.5   Drying column: Approximately 400 mm long by 20 mm ID borosilicate glass, equipped with coarse-fitted bottom plate.

5.6 Miscellaneous.

    5.6.1 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g.

    5.6.2 Separatory funnel: 2-L, equipped with PTFE stopcock.

    5.6.3 Water bath: Heated with concentric ring cover, capable of temperature control ($\pm 2°C$). The bath should be used in a hood.

    5.6.4 Standard solution storage containers: 15-mL bottles with PTFE-lined screw-caps.

    5.6.5 Boiling chips: Approximately 10/40 mesh. Heat to 400°C for 30 minutes or perform a Soxhlet extraction with methylene chloride.

6. REAGENTS AND CONSUMABLE MATERIALS

6.1 Reagents.

    6.1.1 Acetone, hexane, and methylene chloride: Demonstrated to be free of analytes.

    6.1.2 Silica gel: Woelm 70-230 mesh. Activate approximately 100 g of silica gel at 200°C for 6 hours in a tared 500-mL Erlenmeyer flask with ground-glass stopper. Allow to cool to room temperature, reweigh, and determine the weight of activated silica gel. Deactivate by adding 3% by weight of distilled water. Restopper the flask, and shake on a wrist-action shaker for at least one hour. Allow to equilibrate for 3 or more hours at room temperature.

    6.1.3 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

    6.1.4 Sodium hydroxide (NaOH) solution (10N): Dissolve 40 g NaOH in reagent water and dilute to 100 mL.

    6.1.5 Sodium sulfate: Granular, anhydrous. Condition by heating at 400°C for 4 hours in a shallow tray.

    6.1.6 Sulfuric acid (H_2SO_4) solution (1+1): Add measured volume of concentrated H_2SO_4 to equal volume of reagent water.

6.2 Standard stock solutions (1.00 µg/µL): These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures.

    6.2.1 Prepare standard stock solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in hexane and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the standard stock.

6.2.2   Store standard stock solutions at 4°C in 15-mL bottles equipped with PTFE-lined screw-caps. Standard stock solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.2.3   Standard stock solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.   SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1   Collect all samples in duplicate. Grab samples must be collected in glass containers. Conventional sampling practices[5] should be followed, except that the bottle must not be prewashed with sample before collection.

7.2   The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

7.3   Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0 to 8.0 with sodium hydroxide or sulfuric acid.

7.4   All samples must be extracted within 7 days and completely analyzed within 40 days of extraction.[6]

8.   CALIBRATION AND STANDARDIZATION

8.1   Calibration.

8.1.1   A set of at least three calibration solutions containing the method analytes is needed. One calibration solution should contain each analyte at a concentration approaching but greater than the estimated detection limit (Table 1) for that compound; the other two solutions should contain analytes at concentrations that bracket the range expected in samples. For example, if the detection limit for a particular analyte is 0.2 µg/L, and a sample expected to contain approximately 5 µg/L is analyzed, solutions of standards should be prepared at concentrations of 0.3 µg/L, 5 µg/L, and 10 µg/L for the particular analyte.

8.1.2   To prepare a calibration solution, add an appropriate volume of a standard stock solution to a volumetric flask and dilute to volume with hexane.

8.1.3   Starting with the standard of lowest concentration, analyze each calibration standard according to Section 10.3.2 and tabulate peak height or area responses versus the mass of analyte injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (<10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

8.1.4 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve.

9. QUALITY CONTROL

9.1 Monitoring for interferences: Analyze a laboratory reagent blank each time a set of samples is extracted. A laboratory reagent blank is a 1-L aliquot of reagent water. If the reagent blank contains a reportable level of any analyte, immediately check the entire analytical system to locate and correct for possible interferences and repeat the test.

9.2 Assessing accuracy.

9.2.1 After every 10 samples, and preferably in the middle of each day, analyze a laboratory control standard. Calibration standards may not be used for accuracy assessments and the laboratory control standard may not be used for calibration of the analytical system.

9.2.1.1 Laboratory control standard concentrate: From stock standards prepared as described in Section 6.2, prepare a laboratory control standard concentrate that contains each analyte of interest at a concentration of 2 µg/mL in acetone or other suitable solvent.[7]

9.2.1.2 Laboratory control standard: Using a pipette, add 1.00 mL of the laboratory control standard concentrate to a 1-L aliquot of reagent water.

9.2.1.3 Analyze the laboratory control standard as described in Section 10. For each analyte in the laboratory control standard, calculate the percent recovery (P_i) with the equation:

Equation 1

$$P_i = \frac{100 S_i}{T_i}$$

where
S_i = *Analytical results from the laboratory control standard, in µg/L*
T_i = *Known concentration of the spike, in µg/L*

9.2.2 At least annually, the laboratory should participate in formal performance evaluation studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared.

9.3 Assessing precision.

9.3.1 Precision assessments for this method are based upon the analysis of field duplicates (Section 7.1). Analyze both sample bottles for at least 10% of all samples. To the extent practical, the samples for duplication should contain reportable levels of most of the analytes.

9.3.2 For each analyte in each duplicate pair, calculate the relative range[7] (RR_i) with the equation:

Equation 2

$$RR_i = \frac{100R_i}{X_i}$$

where

R_i = *Absolute difference between the duplicate measurements X_1 and X_2, in µg/L*

X_i = *Average concentration found* $\left(\dfrac{X_1 + X_2}{2} \right)$, *in µg/L*

9.3.3 Individual relative range measurements are pooled to determine average relative range or to develop an expression of relative range as a function of concentration.

10. PROCEDURE

10.1 Sample extraction.

10.1.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5 to 9 with sodium hydroxide or sulfuric acid.

10.1.2 Add 60 mL of 15% methylene chloride/hexane to the sample bottle and shake for 30 seconds to rinse the walls. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends on the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the extract in a 250-mL Erlenmeyer flask.

10.1.3 Add an additional 60-mL volume of 15% methylene chloride/hexane to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

10.1.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing about 10 cm of anhydrous sodium sulfate, and collect it in a 500-mL K-D flask equipped with a 10-mL concentrator tube. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.1.5 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 to 85°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in steam. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for this operation. If the extract requires cleanup, proceed to Section 10.2 (cleanup and separation). If cleanup has been performed or if the extract does not require cleanup, proceed with Section 10.1.6.

10.1.6 Add a clean boiling chip to the concentrator tube. Attach a two-ball micro-Snyder column. Prewet the micro-Snyder column by adding about 0.5 mL of hexane to the top. Place this micro K-D apparatus on a steaming-water bath (80 to 85°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation, the balls will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small volume of hexane. Adjust the final volume to 1.0 mL or to a volume suitable for cleanup or gas chromatography, and stopper the concentrator tube; store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to PTFE-sealed screw-cap bottles. Proceed with gas chromatographic analysis.

10.1.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

10.2 Cleanup and separation.

10.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedures recommended in this method have been used for the analysis of various clean waters and municipal effluents. The silica gel procedure allows for a select fractionation of the compounds and will eliminate non-polar materials. The single-operator precision and accuracy data in Table 2 were gathered using the recommended cleanup procedures. 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 compound of interest is no less than that recorded in Table 2.

10.2.2 Prepare silica gel columns using a glass column 200 mm long by 10 mm ID. Rinse column with hexane. Add approximately 50 mL of hexane to the empty column. Add 3.5 grams of 3% deactivated silica gel. Pack by rotating slowly to release air bubbles. Top with 1.5 cm of Na_2SO_4. Drain hexane to the top of Na_2SO_4 layer.

10.2.3 Just prior to exposure of the sodium sulfate layer to the air, transfer the sample extract onto the column using an additional 2 mL of hexane to complete the transfer.

10.2.4 Just prior to exposure of the sodium sulfate layer to the air, add 30 mL of 6% methylene chloride/hexane and continue the elution of the column, collecting the eluate in a 500-mL K-D flask equipped with a 10-mL concentration tube. Elution of the column should be at a rate of about 2 mL per minute. Add 50 mL of hexane to the flask and concentrate the collected fraction by the standard technique prescribed in Sections 10.1.5 and 10.1.6.

10.2.5 Continue the elution of the column according to the scheme outlined in Table 3. The elution of the compounds may vary with different sample matrices.

10.2.6 Analyze the fractions by gas chromatography.

10.3 Gas chromatographic analysis.

10.3.1 Recommended columns and detector for the gas chromatography system are described in Section 5.3.1. Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are estimated retention times and detection limits that can be achieved by this method. Examples of the separations achieved are shown in Figures 1 and 2. Other packed columns, chromatographic conditions, or detectors may be used if data quality comparable to Table 2 are achieved. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and data quality comparable to Table 2 are achieved.

10.3.2 Inject 2 to 5 µL of the sample extract using the solvent-flush technique.[8] Record the volume injected to the nearest 0.05 µL, the total extract volume, and the resulting peak size in area or peak height units.

10.3.3 The width of the retention-time window used to make identifications should be based upon measurements of actual retention-time variations of standards over the course of the day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

10.3.4 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

10.3.5 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

11. CALCULATIONS

11.1 Determine the concentration (C) of individual compounds in the sample in micrograms per liter with the equation:

Equation 3

$$C = \frac{(A)\ (V_t)}{(V_i)\ (V_s)}$$

where

A = Amount of material injected, in ng
V_i *= Volume of extract injected, in µL*
V_t *= Volume of total extract, in µL*
V_s *= Volume of water extracted, in mL*

11.2 Report the results for the unknown samples in microgram per liter. Round off the results to the nearest 0.1 µg/L or two significant figures.

12. METHOD PERFORMANCE

12.1 Estimated detection limits (EDL) and associated chromatographic conditions are listed in Table 1.[9] The detection limits were calculated from the minimum detectable response of the N/P detector equal to 5 times the GC background noise, assuming a 1.0 mL final extract volume of a 1-L sample and a GC injection of 5 µL.

12.2 Single laboratory accuracy and precision studies were conducted by ESE,[6] using spiked relevant industrial wastewater samples. The results of these studies are presented in Table 2.

13. GC/MS CONFIRMATION

13.1 It is recommended that GC/MS techniques be judiciously employed to support qualitative identifications made with this method. The mass spectrometer should be capable of scanning the mass range from 35 amu to a mass 50 amu above the molecular weight of the compounds of interest. The instrument must be capable of scanning the mass range at a rate to produce at least 5 scans per peak, but not to exceed 7 scans per peak utilizing a 70 V (nominal) electron energy in the electron impact ionization mode. A GC-to-MS interface constructed of all-glass or glass-lined materials is recommended.

A computer system should be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program.

13.2   Gas chromatographic columns and conditions should be selected for optimum separation and performance. The conditions selected must be compatible with standard GC/MS operating practices. Chromatographic tailing factors of less than 5.0 must be achieved. The calculation of tailing factors is illustrated in Method 625.[10]

13.3   At the beginning of each day that confirmatory analyses are to be performed, the GC/MS system must be checked to see that all DFTPP performance criteria are achieved.[11]

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

    13.4.1   The molecular ion and other ions that are present above 10% relative abundance in the mass spectrum of the standard must be present in the mass spectrum of the sample with agreement to ±10%. For example, if the relative abundance of an ion is 30% in the mass spectrum of the standard, the allowable limits for the relative abundance of that ion in the mass spectrum for the sample would be 20 to 40%.

    13.4.2   The retention-time of the compound in the sample must be within 6 seconds of the same compound in the standard solution.

    13.4.3   Compounds that have similar mass spectra can be explicitly identified by GC/MS only on the basis of retention-time data.

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

13.6   Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These may include the use of alternative packed or capillary GC columns or additional cleanup.

References

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Table 1.   Gas Chromatography of Organophosphorus Pesticides

| | Retention Time (min) | | Detection Limit (µg/L) |
Parameter	Column 1	Column 2	
Terbufos	1.41	1.9	.004
Dioxathion	2.3	2.3	.01
Ethion	8.3	6.4	0.1
EPN	13.3	8.3	0.2

Column 1: 180 cm long by 2 mm ID, glass, packed with 3% OV-225 on 100/120 Supelcoport; nitrogen carrier gas at a flow rate of 50 mL/min. Column temperature is 200°C for 2 minutes, then programmed at 5°/min. to 240°C and held for 5 minutes.

Column 2: 120 cm long by 2 mm ID, Pyrex[R] glass, packed with 1.5% OC-17/1.95% QF-1 on 80/100 mesh Gas Chrom Q or equivalent; nitrogen carrier gas at a flow rate of 30 mL/min. Column temperature is 180°C for 2 minutes, then programmed at 8°/min. to 250°C and held for 4 minutes.

Table 2.   Single-Laboratory Accuracy and Precision

Parameter	Matrix Type*	Spike Range (µg/L)	Number of Replicates	Average Percent Recovery	Standard Deviation (%)
Dioxathion	1	1,978.0	7	94.3	19.9
	1	19.8	7	99.0	27.5
EPN	1	1,293.0	7	96.1	6.1
Ethion	1	1,788.0	7	89.2	4.5
Terbufos	1	15.1	7	101.0	12.4
	1	1,508.0	7	95.0	3.4

*1 = Combined industrial wastewaters

Table 3.   Silica Gel Cleanup of Organophosphorus Pesticides

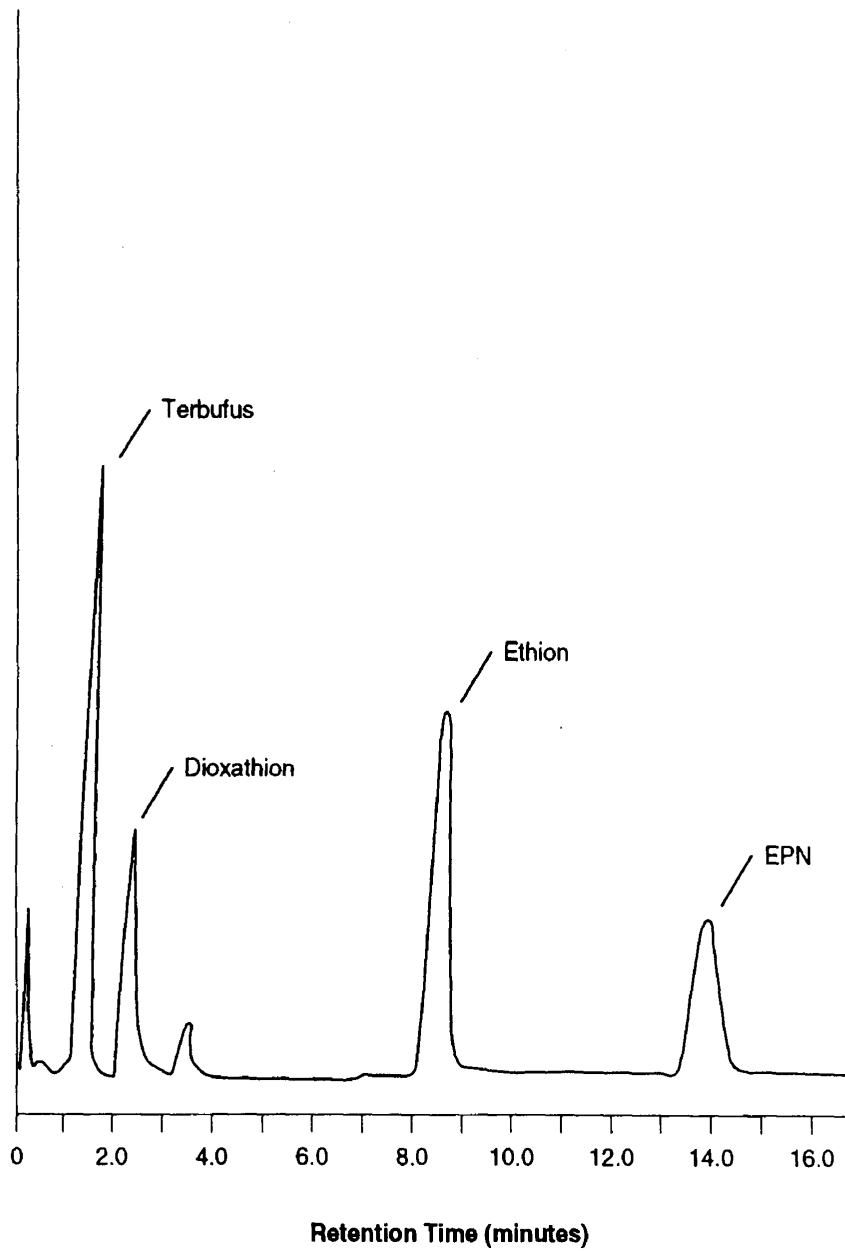| Silica Gel Fraction*	Percent Recoveries			
	Terbufos	Dioxathion	Ethion	EPN
1	0	0	0.8	0
2	0	0	1.9	0
3	93.0	35.1	94.9	46.4
4	0	52.7	3.0	56.0
Total Percent Recoveries	93.0	87.8	101	102

*Fraction 1 = 30 mL 6% $MeCl_2$ in hexane
 Fraction 2 = 30 mL 15% $MeCl_2$ in hexane
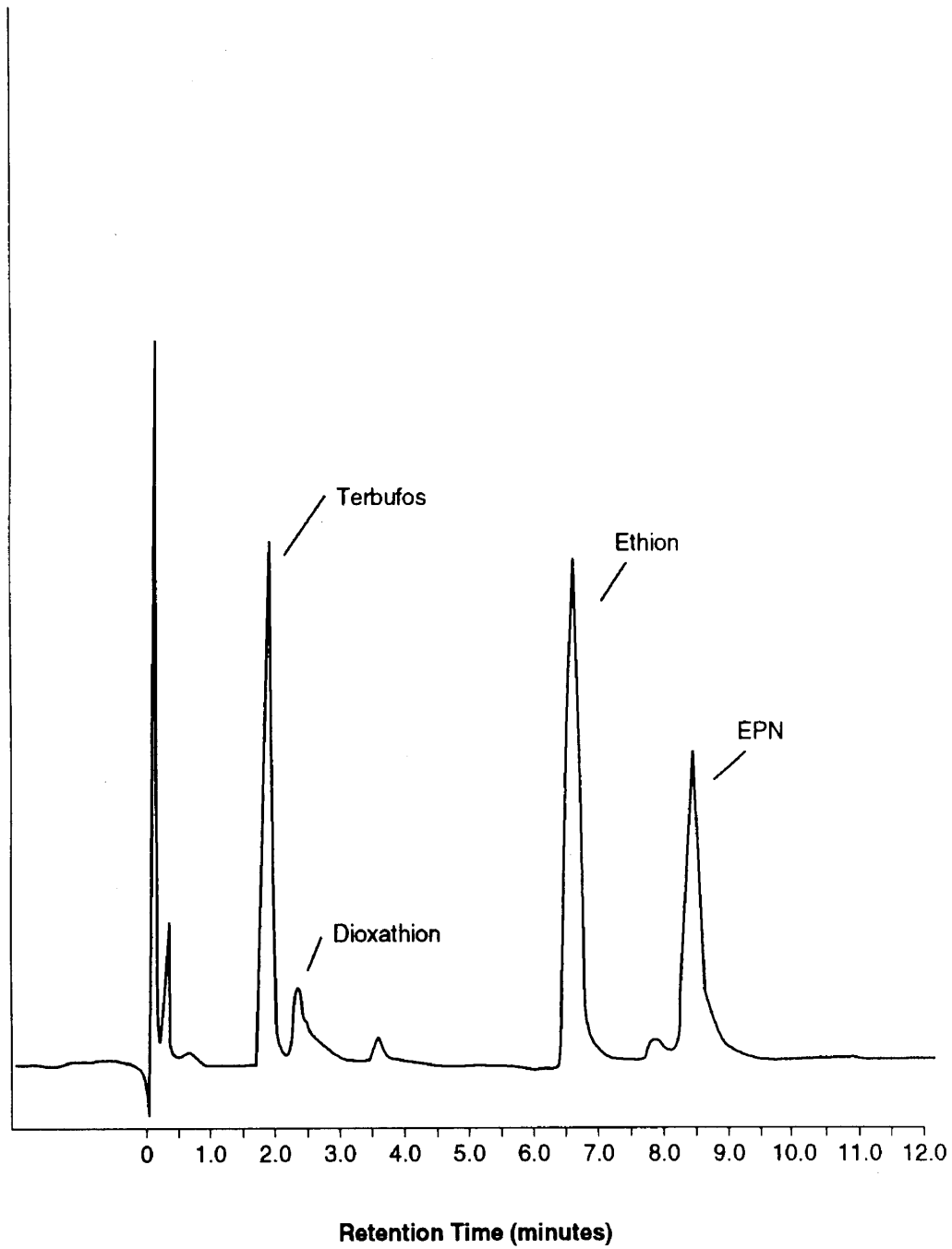 Fraction 3 = 30 mL 50% $MeCl_2$ in hexane
 Fraction 4 = 30 mL 100% $MeCl_2$

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Figure 1.   Gas Chromatogram of Organophosphorous Pesticides (Column 1)

Retention Time (minutes)

A52-002-38A

Figure 2.   Gas Chromatogram of Organophosphorous Pesticides (Column 2)