METHOD 608.2: ANALYSIS OF CERTAIN ORGANOCHLORINE PESTICIDES IN WASTEWATER BY GAS CHROMATOGRAPHY

1. SCOPE AND APPLICATION

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

Parameter	STORET No.	CAS No.
Chlorothalonil		1897-45-6
DCPA	39770	1861-32-1
Dichloran		99-30-9
Methoxychlor	39480	72-43-5
Permethrin		52645-53-1

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 electron capture detector equal to 5 times the detector background noise assuming a 10.0 mL final extract volume of a 1 L reagent water sample and a gas chromatographic (GC) injection volume 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 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 Organochlorine pesticides are removed from the sample matrix by extraction with methylene chloride. 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 an electron capture detector.

2.2 Confirmatory analysis by gas chromatography/mass spectrometry is recommended (Section 13) 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 muffle furnace 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 co-extracted 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-liter 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 the glass bottles at 400°C for 1 hour. After cooling, rinse the cap liners with hexane, seal the bottles with aluminium foil, 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).

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 1.5 percent OV-17/1.95 percent OV-210 on Chromosorb W-HP (100/120 mesh) or equivalent.

5.3.1.2 Column 2—180 cm long x 2 mm ID, glass, packed with 4-percent SE-30/6-percent SP-2401 on Supelcoport (100/120 mesh) or equivalent. Guidelines for the use of alternate column packings are provided in Section 10.3.1.

5.3.1.3 Detector—Electron capture. 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 alternate detectors are provided in Section 10.3.1.

5.4 CHROMATOGRAPHIC COLUMN--400 mm long x 19 mm ID Chromaflex, equipped with coarse fritted bottom plate and PTFE stopcock. (Kontes K-420540-0224 or equivalent).

CHROMATOGRAPHIC COLUMN--300 mm long x 10 mm ID, equipped with coarse fritted bottom plate and PFTE stopcock (Kontes K-430540-0213 or equivalent).

5.5 DRYING COLUMN--Approximately 400 mm long x 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--two-liter, equipped with PTFE stopcock.

5.6.3 Water bath--heated with concentric ring cover, capable of temperature control (±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 Soxhlet extract overnight with methylene chloride.

6. REAGENTS AND CONSUMABLE MATERIALS

6.1 REAGENTS

6.1.1 Acetone, hexane, ethanol and methylene chloride--demonstrated to be free of analytes.

6.1.2 Ethyl ether--Nanograde, redistilled in glass if necessary. Must be free of peroxides as indicated by EM Quant test strips. (Available from Scientific Products Co., Cat. No. P1126-8, and other suppliers.) Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethyl alcohol preservative must be added to each liter of ether.

6.1.3 Florisil--PR grade (60/100 mesh). Purchase activated at 1250°C and store in dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate

each batch overnight at 130°C in foil-covered glass container.

6.1.4 Silica gel--Activate approximately 100 grams of silica gel at 200°C for 16 hours in a tared 500-mL Erlenmeyer flask with ground glass stopper. Allow to cool to room temperature, and determine the weight of activated silica gel. Deactivate by adding 3 percent by weight of distilled water. Restopper the flask, and shake on a wrist-action shaker for at least 1 hour. Allow to equilibrate for 3 or more hours at room temperature.

6.1.5 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.

6.1.6 Sodium hydroxide (NaOH) solution (10N)--dissolve 40 g NaOH in reagent water and dilute to 100 mL.

6.1.7 Sodium sulfate--granular, anydrous. Condition by heating at 400°C for 4 hours in a shallow tray.

6.1.8 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 grams of pure material. Dissolve the material in hexane or other suitable solvent 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. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before extraction. If the samples will not be extracted within 48 hours of collection, the sample should be adjuted to a pH range of 6.0 to 8.0 with sodium hydroxide or sulfuric acid.

7.3 All samples must be extracted within 7 days of collection, and 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 EDL (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, standard solutions should be prepared at concentrations representing 0.3 µg/L, 5 µg/L, and 10 µg/L of the analytes.

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.

8.2 FflorisiL STANDARDIZATION

8.2.1 Florisil from different batches or sources may vary in absorptive capacity. To standardize the amount of Florisil which may be used in the cleanup procedure (Section 10.2.2) use of the lauric acid value (7) is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing this factor into 110 and multiplying by 20 g.

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 one-liter 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 standrd 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 6.3, 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. (8)

9.2.1.2 Laboratory Control Standard - using a pipet, add 1.00 mL of the laboratory control standard concentrate to a one-liter 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:

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

where S_i = the analytical results from the laboratory control standard, in µg/L; and
T_i = the 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 (RR_i) with the equation:

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

where R_i = the absolute difference between the duplicate measurements X_1 and X_2, in µg/L; and

X_i = the average concentration found ($[X_1 + X_2]/2$), 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-liter 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 methylene chloride 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 methylene chloride 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 the extract 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 (60 to 65°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 about 3 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

10.1.6 Increase the temperature of the hot water bath to about 80 to 85°C. Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Pour about 1 mL of hexane into the top of the Snyder column, and concentrate the solvent extract as before. Elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches about 3 mL, remove the K-D apparatus, and allow it to drain at least 10 minutes while cooling. Remove the Snyder column, rinse the flask and the lower joint into the concentrator tube with 1 to 2 mL of hexane, and adjust the volume to 10 mL. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube, and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than 2 days, they should be transferred to Teflon-sealed screw-cap bottles. If the sample extract requires no cleanup, proceed with gas chromatographic analysis.

10.1.7 If the sample requires cleanup, the extract obtained must be divided into two fractions. One of the fractions is eluted through Florisil for the analysis of dicloran and DCPA. The other fraction is eluted through silica gel for the analysis of chlorothalonil, methoxychlor, and the permethrins.

10.1.8 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000 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 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 *Florisil Column Cleanup.*

10.2.2.1 Add a weighed amount of Florisil, about 21 grams, to a chromatographic column. The exact weight should be determined by calibration. (7) Tap the column to settle the Florisil. Add a 1- to 2-cm layer of sodium sulfate above the Florisil. Rinse the Florisil and sodium sulfate by adding 60 mL of hexane to the column. Just prior to exposure of the sodium sulfate to air, stop the draining of the hexane by closing the stopcock on the column. Discard the eluate.

10.2.2.2 Quantitatively, add the fraction of extract chosen for the analysis of dichloran and DCPA to the column. Drain the column into the flask, stopping just prior to exposure of the sodium sulfate layer.

10.2.2.3 Elute the column with 200 mL of 6-percent ethyl ether in hexane (Fraction 1) using a drip rate of about 5 mL/minute. Remove and discard. Perform a second elution using 200 mL of 15-percent ethyl ether in hexane (Fraction 2), collecting the eluant in a 500 mL K-D flask equipped with a 10 mL concentrator tube.

10.2.2.4 Concentrate the eluate by standard K-D techniques (Paragraph 10.1.5), substituting hexane for methylene chloride, and using the water bath at about 85°C. Adjust the final volumes to 10 mL with hexane. Analyze by gas chromatography.

10.2.3 Silica Gel Column Cleanup.

10.2.3.1 Prepare silica gel columns using a 300-mm by 10-mm ID glass column.

Rinse column with hexane. Add approximately 50 mL of hexane to the empty column. Add 3.5 grams of 3-percent deactivated silica gel (Paragraph 6.1.4). Pack by rotating slowly to release air bubbles. Top with 1.5 cm of Na_2SO_4. Drain hexane to the top of the Na_2SO_4.

10.2.3.2 Add the fraction of extract chosen for the analysis of chlorothalonil, methoxychlor, and the permethrins to the column. Open the stopcock and allow it to drain to the surface of the sodium sulfate. Elute with the following solutions:

1st fraction--25 mL of hexane,
2nd fraction--25 mL of 6-percent $MeCl_2$ in hexane (volume/volume), and
3rd fraction--25mL of 50-percent $MeCl_2$ in hexane.

10.2.3.3 Collect the third fraction in a 500 mL K-D flask equipped with a 10 mL concentrator tube, and add 50 mL of hexane. Concentrate on an 85°C water bath to 10.0 mL as described in Section 10.1.5.

10.2.4 The elution profiles obtained in these studies are listed in Tables 3 and 4 for the convenience of the analyst. The analyst must determine the elution profiles and demonstrate that the recovery of each compound of interest is no less than that reported in Table 2 before the analysis of any samples utilizing these cleanup procedures.

10.2.5 Proceed with gas chromatography.

10.3 GAS CHROMATOGRAPHIC ANALYSIS

10.3.1 Recommended columns and detector for the gas chromatographic 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 by Column 1 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 percent 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 (9). Record the volume injected to the nearest 0.05 µL, the total extract volume, the fraction

of total extract utilized in each cleanup scheme 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 µg/L with the equation:

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

where A = amount of material injected, in nanograms;

V_i = volume of extract injected, µL;

V_t = volume of total extract, µL;

V_s = volume of water extracted, mL;

V_c = volume of final extract after cleanup (µL)

V_f = volume of extract utilized for cleanup scheme (µ/L)

11.2 Report the results for the unknown samples in µg/L. Round off the results of 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(10). The detection limits were calculated from the minimum detectable response of the EC detector equal to 5 times the background noise, assuming a 10.0-mL final extract volume of a 1-liter sample and a GC injection of 5 µL.

12.2 Single laboratory accuracy and precision studies were conducted by Environmental Science and Engineering, Inc. (6), using spiked 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 compound. 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.(11)

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.(12)

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 nanograms 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-percent relative abundance in the mass spectrum of the standard must be present in the mass spectrum of the sample with agreement to plus or minus 10 percent. For example, if the relative abundance of an ion is 30 percent 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 percent.

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 alternate packed or capillary GC columns or additional cleanup.

REFERENCES

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TABLE 1
GAS CHROMATOGRAPHY OF ORGANOCHLORINE PESTICIDES

Parameter	Retention Time (minutes) Column 1*	Column 2**	Estimated Detection Limit (µg/L)
Chlorothalonil	3.40	4.69	0.001
DCPA	4.19	5.44	0.003
Dicloran	2.23	2.62	0.002
Methoxychlor	22.35	10.85	0.04
cis-Permethrin***	18.52	16.04	0.2
trans-Permethrin***	20.02	17.53	0.2

* Column 1: 180 cm long by 2 mm ID, glass, packed with 1.5-percent OV-17/1.95-percent OV 210 on Chromosorb W-HP (100/120 mesh) or equivalent; 5-percent methane/95-percent Argon carrier gas at 30 mL/min flow rate. Column temperature is 200°C, detector--electron capture.

** Column 2: 180 cm long by 2 mm ID, glass, packed with 4-percent SE-30/6-percent SP-2401 on Supelcoport (100/120 mesh) or equivalent; 5-percent methane/95-percent Argon carrier gas at 60 mL/min flow rate. Column temperature is 200°C, detector--electron capture.

*** Column temperature is 220°C.

TABLE 2
SINGLE LABORATORY ACCURACY AND PRECISION

Parameter	Matrix Type*	Spike Range (µg/L)	Number of Replicates	Average Percent Recovery	Standard Deviation (%)
Chlorothalonil	1	37.8	7	84.1	16.4
	2	2,300	7	94.9	22.5
DCPA	1	16	7	77.6	25.7
	2	10,540	7	89.5	11.0
Dicloran	1	37.5	7	98.6	8.4
	2	21,200	7	90.8	20.3
Methoxychlor	1	24.5	7	102.4	12.4
	2	2,600	7	102.2	10.2
cis-Permethrin	1	6.3	7	99.5	18.8
	2	317	7	77.5	10.6
trans-Permethrin	1	5.7	7	78.8	16.1
	2	297	7	88.9	19.6

* 1 = Low-level industrial effluent.
  2 = High-level industrial effluent.

TABLE 3

ELUTION PROFILES FOR FLORISIL CLEANUP

Parameter	Percent Recovery by Fraction*		
	1	2	3
DCPA	0	99.3	0
Dicloran	0	96.3	0

* Eluting solvent composition for each fraction given in Section 10.2.2.3.

TABLE 4

ELUTION PROFILES FOR SILICA GEL* CLEANUP

Parameter	Percent Recovery by Fraction**		
	1	2	3
Chlorothalonil	0	0	93.8
Methoxychlor	0	0	93.8
Cis-permethrin	0	0	107.2
Trans-Permethrin	0	0	92.5

* 3-Percent deactivated.
**Eluting solvent composition for each fraction given in Sections 10.2.3.2 and 10.2.3.3.

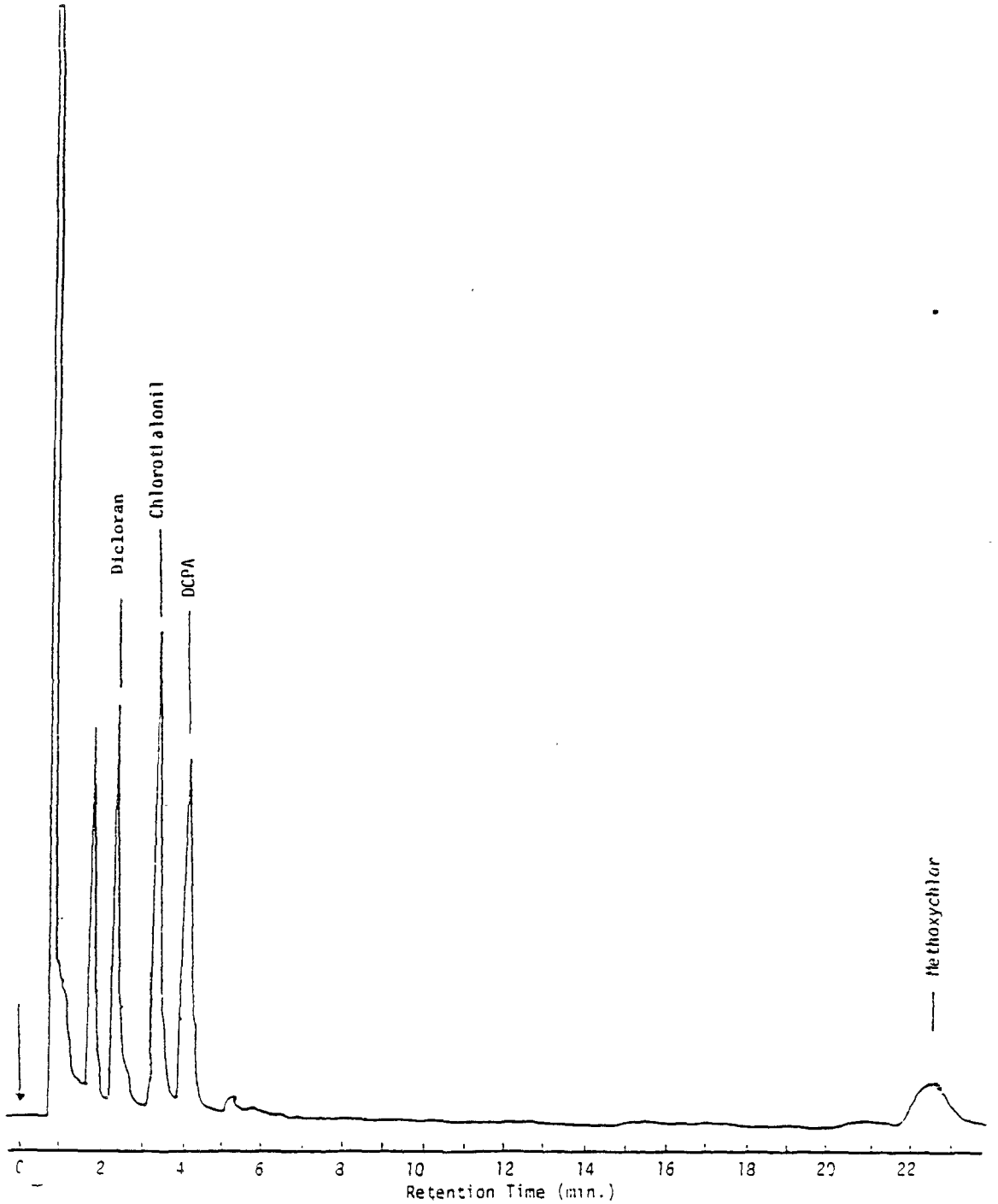

FIGURE 1. GAS CHROMATOGRAM OF CHLOROTHALONIL, DCPA, DICLORAN, AND METHOXYCHLOR IN A WASTEWATER EXTRACT, COLUMN 1.

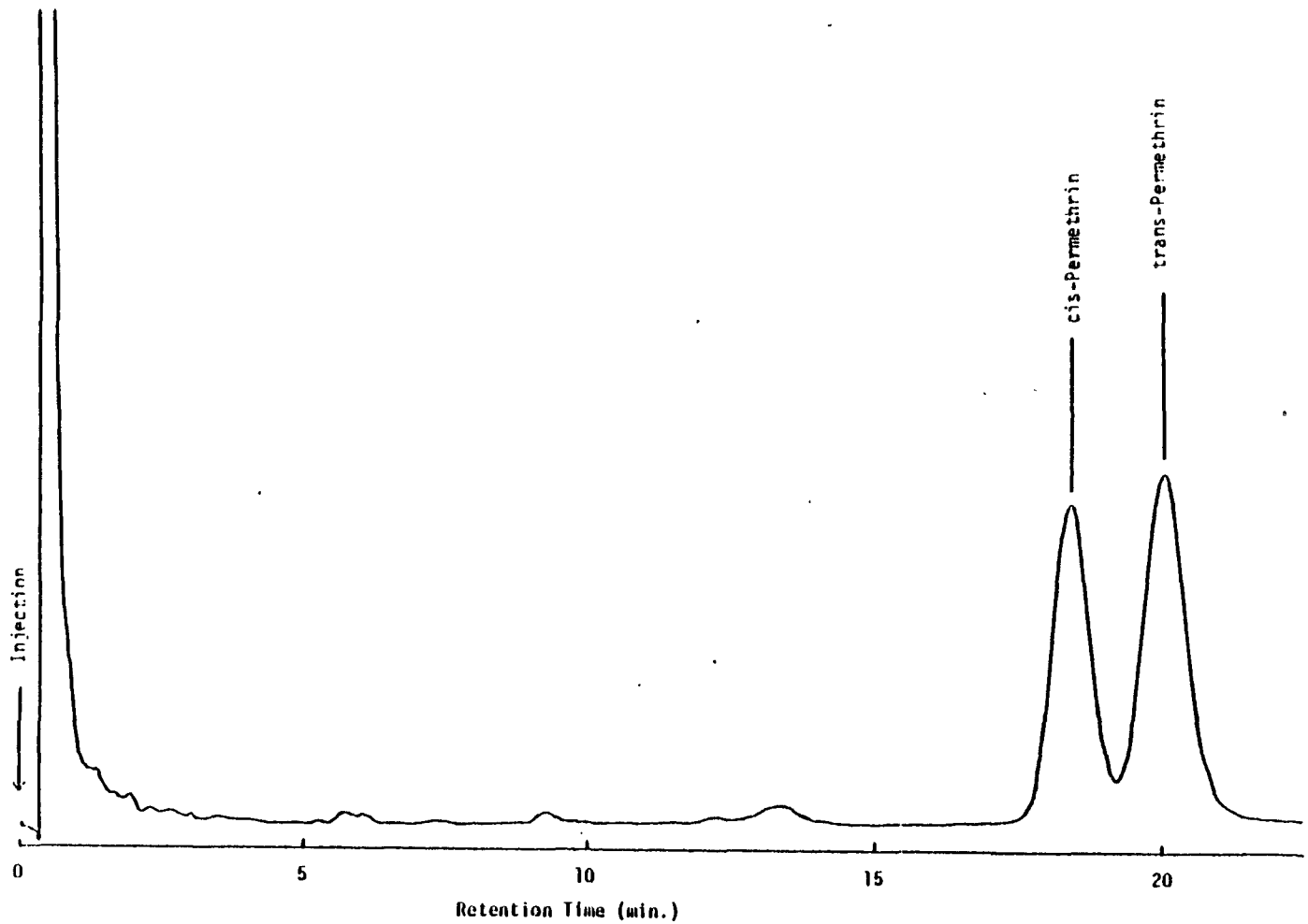

FIGURE 2. GAS CHROMATOGRAM OF PERMETHRIN SAMPLE, COLUMN 1.