

METHOD 505

**ANALYSIS OF ORGANOHALIDE PESTICIDES AND
COMMERCIAL POLYCHLORINATED BIPHENYL (PCB) PRODUCTS
IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY**

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T. W. Winfield -- Method 505, Revision 1.0 (1986)

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ANALYSIS OF ORGANOHALIDE PESTICIDES AND COMMERCIAL POLYCHLORINATED BIPHENYL (PCB) PRODUCTS IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

- 1.1 This method is applicable to the determination of the following analytes in finished drinking water, drinking water during intermediate stages of treatment, and the raw source water:¹⁻³

Analyte	Chemical Abstract Services Registry Number
Alachlor	15972-60-8
Aldrin	309-00-2
Atrazine	1912-24-9
Chlordane	57-74-9
alpha-Chlorodane	5103-71-9
gamma-Chlorodane	5103-74-2
Dieldrin	60-57-1
Endrin	72-20-8
Heptachlor	76-44-8
Heptachlor Epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorocyclopentadiene	77-74-4
Lindane	58-89-9
Methoxychlor	72-43-5
cis-Nonachlor	5103-73-1
trans-Nonachlor	39765-80-5
Simazine	122-34-9
Toxaphene	8001-35-2
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5

- 1.2 For compounds other than the above mentioned analytes or for other sample sources, the analyst must demonstrate the applicability of the method by collecting precision and accuracy data on fortified samples (i.e., groundwater, tap water) and provide qualitative confirmation of results by Gas Chromatography/Mass Spectrometry (GC/MS), or by GC analysis using dissimilar columns.⁴⁻⁵

- 1.3 Method detection limits (MDL)⁶ for the above organohalides and Aroclors have been experimentally determined (Section 13.1). Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system used (e.g., column type, age, and proper conditioning; detector condition; and injector mode and condition).
- 1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of GC and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 11.0.
- 1.5 Analytes that are not separated chromatographically, i.e., analytes which have very similar retention times, cannot be individually identified and measured in the same calibration mixture or water sample unless an alternative technique for identification and quantitation is used (Section 11.4).
- 1.6 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications should be confirmed by at least one additional qualitative technique.
- 1.7 Degradation of Endrin, caused by active sites in the injection port and GC columns, may occur. This is not as much a problem with new capillary columns as with packed columns. However, high boiling sample residue in capillary columns will create the same problem after injection of sample extracts.

2.0 SUMMARY OF METHOD

- 2.1 Thirty-five mL of sample are extracted with 2 mL of hexane. Two μL of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis. Aqueous calibration standards are extracted and analyzed in an identical manner in order to compensate for possible extraction losses.
- 2.2 The extraction and analysis time is 30-50 minutes per sample depending upon the analytes and the analytical conditions chosen. (See Section 6.9.)

3.0 DEFINITIONS

- 3.1 Laboratory Duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
- 3.2 Field Duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a

measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

- 3.3 Laboratory Reagent Blank (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.
- 3.4 Field Reagent Blank (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.
- 3.5 Laboratory Performance Check Solution (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.
- 3.6 Laboratory Fortified Blank (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.
- 3.7 Laboratory Fortified Sample Matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.
- 3.8 Stock Standard Solution -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.
- 3.9 Primary Dilution Standard Solution -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.
- 3.10 Calibration Standard (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

- 3.11 Quality Control Sample (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

4.0 INTERFERENCES

- 4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 10.2.
- 4.1.1 Glassware must be scrupulously cleaned.² Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for one hour. Do not heat volumetric ware. Thermally stable materials might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.
- 4.1.2 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. WARNING: When a solvent is purified, stabilizers put into the solvent by the manufacturer are removed thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives put into the solvent by the manufacturer are removed thus potentially reducing the shelf-life.
- 4.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the sample syringe and associated equipment with hexane can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of hexane should be made to ensure that accurate values are obtained for the next sample.
- 4.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. Also, note that all the analytes listed in the scope and application section are not resolved from each other on any one column, i.e., one analyte of interest may be an interferent for another analyte of interest. The extent of matrix interferences will vary considerably from source to source, depending upon the water sampled. Cleanup of sample extracts may be necessary. Positive identifications should be confirmed (Section 11.4).

- 4.4 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.
- 4.5 Caution must be taken in the determination of endrin since it has been reported that the splitless injector may cause endrin degradation⁷. The analyst should be alerted to this possible interference resulting in an erratic response for endrin.
- 4.6 Variable amounts of pesticides and commercial PCB products from aqueous solutions adhere to glass surfaces. It is recommended that sample transfers and glass surface contacts be minimized.
- 4.7 Aldrin, hexachlorocyclopentadiene and methoxychlor are rapidly oxidized by chlorine. Dechlorination with sodium thiosulfate at time of collection will retard further oxidation of these compounds.

WARNING: An interfering, erratic peak has been observed within the retention window of heptachlor during many analyses of reagent, tap, and groundwater. It appears to be related to dibutyl phthalate; however, the specific source has not yet been definitively determined. The observed magnitude and character of this peak randomly varies in numerical value from successive injections made from the same vial.

5.0 SAFETY

- 5.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst.⁸⁻¹⁰
- 5.2 The following organohalides have been tentatively classified as known or suspected human or mammalian carcinogens: aldrin, commercial PCB products, chlordane, dieldrin, heptachlor, hexachlorobenzene, and toxaphene. Pure standard materials and stock standard solutions of these compounds should be handled in a hood or glovebox.

WARNING: When a solvent is purified, stabilizers put into the solvent by the manufacturer are removed thus potentially making the solvent hazardous.

6.0 APPARATUS AND EQUIPMENT

- 6.1 Sample Containers -- 40 mL screw cap vials (Pierce #13075 or equivalent) each equipped with a size 24 cap with a flat, disc-like TFE facing backed with a polyethylene film/foam extrusion (Fisher #02-883-3F or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place the vials in a 400°C oven for one hour, then remove and allow to cool in an area known to be free of organics.
- 6.2 Vials -- auto sampler, screw cap with septa, 1.8 mL, Varian #96-000099-00 or equivalent or any other autosampler vials not requiring more than 1.8 mL sample volumes.
- 6.3 Auto Sampler -- Hewlett-Packard 7671A, or equivalent.
- 6.4 Micro Syringes -- 10 and 100 µL.
- 6.5 Micro Syringe -- 25 µL with a 2-inch by 0.006-inch needle - Hamilton 702N or equivalent.
- 6.6 Pipettes -- 2.0 and 5.0 mL transfer.
- 6.7 Volumetric Flasks -- 10 and 100 mL, glass stoppered.
- 6.8 Standard Solution Storage Containers -- 15 mL bottles with PTFE-lined screw caps.
- 6.9 Gas Chromatograph -- Analytical system complete with temperature programmable GC suitable and split/splitless injector for use with capillary columns and all required accessories including syringes, analytical columns, gases, a linearized electron capture detector and stripchart recorder. A data system is recommended for measuring peak areas. Table 1 lists retention times observed for method analytes using the columns and analytical conditions described below.
- 6.9.1 Three gas chromatographic columns are recommended. Column 1 (Section 6.9.2) should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Validation data presented in this method were obtained using this column. Columns 2 and 3 are recommended for use as confirmatory columns when GC/MS confirmation is not available. Alternative columns may be used in accordance with the provisions described in Section 10.3.
- 6.9.2 Column 1 (Primary Column) -- 0.32 mm ID x 30 M long fused silica capillary with chemically bonded methyl polysiloxane phase (DB-1, 1.0 µm film, or equivalent). Helium carrier gas flow is about 25 cm/sec linear velocity, measured at 180° with 9 psi column head pressure. The

oven temperature is programmed from 180-260°C at 4°C/min and held at 260°C until all expected compounds have eluted. Injector temperature: 200°C. Splitless Mode: 0.5 minutes. Detector temperature: 290°C. Sample chromatograms for selected pesticides are presented in Figures 1 and 2. Chromatograms of the Aroclors, toxaphene, and technical chlordane are presented in Figures 3 through 11.

- 6.9.3 Column 2 (alternative column 1) -- 0.32 mm ID x 30 M long fused silica capillary with a 1:1 mixed phase of dimethyl silicone and polyethylene glycol (Durawax-DX3, 0.25 µm film, or equivalent). Helium carrier gas flow is about 25 cm/sec linear velocity and oven temperature is programmed from 100-210°C at 8°C/min, and held at 210°C until all expected compounds have eluted. Then the post temperature is programmed to 240°C at 8°C/min for five minutes.
- 6.9.4 Column 3 (alternative column 2) -- 0.32 mm ID x 25 M long fused silica capillary with chemically bonded 50:50 Methyl-Phenyl silicone (OV-17, 1.5 µm film thickness, or equivalent). Helium carrier gas flow is about 40 cm/sec linear velocity and oven temperature is programmed from 100-260°C at 4°C/min and held at 260°C until all expected compounds have eluted.

7.0 REAGENTS AND CONSUMABLE MATERIALS

WARNING: When a solvent is purified stabilizers put into the solvent by the manufacturer are removed thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives put into the solvent by the manufacturer are removed thus potentially making the shelf-life short.

7.1 Reagents

- 7.1.1 Hexane extraction solvent -- UV grade, Burdick and Jackson #216 or equivalent.
- 7.1.2 Methyl alcohol -- ACS reagent grade, demonstrated to be free of analytes.
- 7.1.3 Sodium chloride, NaCl -- ACS reagent grade, for pretreatment before use, pulverize a batch of NaCl and place in a muffle furnace at room temperature. Increase the temperature to 400°C and hold for 30 minutes. Place in a bottle and cap.
- 7.1.4 Sodium thiosulfate, Na₂S₂O₃ -- ACS reagent grade, for preparation of solution (0.04 g/mL), mix 1 g of Na₂S₂O₃ with reagent water and bring to 25 mL volume in a volumetric flask.

- 7.2 Reagent Water -- Reagent water is defined as water free of interference when employed in the procedure described herein.
- 7.2.1 A Millipore Super-Q Water System or its equivalent may be used to generate deionized reagent water.
- 7.2.2 Test reagent water each day it is used by analyzing it according to Section 11.0.
- 7.3 Stock Standard Solutions -- These solutions may be obtained as certified solutions or prepared from pure standard materials using the following procedures:
- 7.3.1 Prepare stock standard solutions (5000 µg/mL) by accurately weighing about 0.0500 g of pure material. Dissolve the material in methanol and dilute to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.
- 7.3.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.
- 7.3.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.
- 7.4 Primary Dilution Standard Solutions -- Use stock standard solutions to prepare primary dilution standard solutions that contain the analytes in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration standards (Section 9.1.1) that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration standards. The storage time described for stock standard solutions in Section 7.3.3 also applies to primary dilution standard solutions.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection

- 8.1.1 Collect all samples in 40 mL bottles into which 3 mg of sodium thiosulfate crystals have been added to the empty bottles just prior to shipping to the sampling site. Alternately, 75 µL of freshly prepared

sodium thiosulfate solution (0.04 g/mL) may be added to empty 40 mL bottles just prior to sample collection.

8.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 minutes). Adjust the flow to about 500 mL/min and collect samples from the flowing stream.

8.1.3 When sampling from a well, fill a wide-mouth bottle or beaker with sample, and carefully fill 40 mL sample bottles.

8.2 Sample Preservation

8.2.1 The samples must be chilled to 4°C at the time of collection and maintained at that temperature until the analyst is prepared for the extraction process. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to insure that they will be maintained at 4°C until arrival at the laboratory.

8.3 Sample Storage

8.3.1 Store samples and extracts at 4°C until extraction and analysis.

8.3.2 Extract all samples as soon as possible after collection. Results of holding time studies suggest that all analytes with the possible exception of heptachlor were adequately stable for 14 days when stored under these conditions. In general, heptachlor showed inconsistent results. If heptachlor is to be determined, samples should be extracted within seven days of collection. Analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Establish GC operating parameters equivalent to those indicated in Section 6.9.

WARNING: Endrin is easily degraded in the injection port if the injection port or front of the column is dirty. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems by injecting a mid-level standard containing only endrin. Look for the degradation products of endrin (endrin ketone and endrin aldehyde). If degradation of endrin exceeds 20%, take corrective action before proceeding with calibration. Calculate percent breakdown as follows:

$$\frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)}}{\text{Total endrin peak area (endrin + endrin aldehyde + endrine ketone)}} \times 100$$

- 9.2 At least three calibration standards are needed; five are recommended. One should contain analytes at a concentration near but greater than the method detection limit for each compound; the other two should be at concentrations that bracket the range expected in samples. For example, if the MDL is 0.01 µg/L, and a sample expected to contain approximately 0.10 µg/L is to be analyzed, aqueous standards should be prepared at concentrations of 0.02 µg/L, 0.10 µg/L, and 0.20 µg/L.
- 9.2.1 To prepare a calibration standard (CAL), add an appropriate volume of a secondary dilution standard to a 35 mL aliquot of reagent water in a 40 mL bottle. Do not add less than 20 µL of an alcoholic standard to the reagent water. Use a 25 µL micro syringe and rapidly inject the alcoholic standard into the middle point of the water volume. Remove the needle as quickly as possible after injection. Mix by inverting and shaking the capped bottle several times. Aqueous standards must be prepared fresh daily.
- 9.2.2 Starting with the standard of lowest concentration, prepare, extract, and analyze each calibration standard beginning with Section 11.2 and tabulate peak height or area response versus the concentration in the standard. The results are to be used to prepare a calibration curve for each compound by plotting the peak height or area response versus the concentration. Alternatively, if the ratio of concentration to response (calibration factor) is a constant over the working range (20% RSD or less), linearity to the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.
- 9.2.3 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 an analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve or use a single point calibration standard as described in Section 9.2.4.
- 9.2.4 Single point calibration is an acceptable alternative to a calibration curve. Prepare single point standards from the secondary dilution standard solutions. The single point calibration standard should be prepared at a concentration that produces a response close (±20% or less) to that of the unknowns. Do not use less than 20 µL of the secondary dilution standard solution to produce a single point calibration standard in reagent water.

- 9.3 Instrument Performance -- Check the performance of the entire analytical system daily using data gathered from analyses of laboratory reagent blanks (LRB), (CAL), laboratory duplicate samples (LD1 and LD2), and the laboratory performance check solution (LPC) (Section 10.6).
- 9.3.1 Significant peak tailing in excess of that shown for the target compounds in the method chromatograms (Figures 1 through 11) must be corrected. Tailing problems are generally traceable to active sites on the GC column, improper column installation, or operation of the detector.
- 9.3.2 Check the precision between replicate analyses. Poor precision is generally traceable to pneumatic leaks, especially at the injection port. If the GC system is apparently performing acceptably but with decreased sensitivity, it may be necessary to generate a new curve or set of calibration factors to verify the decreased responses before searching for the source of the problem.
- 9.3.3 Observed relative area responses of endrin (See Section 4.5) must meet the following general criteria:
- 9.3.3.1 The breakdown of endrin into its aldo and keto forms must be adequately consistent during a period in which a series of analyses is made. Equivalent relative amounts of breakdown should be demonstrated in the LRB, LPC, LFB, CAL and QCS. Consistent breakdown resulting in these analyses would suggest that the breakdown occurred in the instrument system and that the methodology is in control.
- 9.3.3.2 Analyses of laboratory fortified matrix (LFM) samples must also be adequately consistent after corrections for potential background concentrations are made.

10.0 QUALITY CONTROL

- 10.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, analysis of laboratory reagent blanks (LRB), laboratory fortified blanks (LFB), laboratory fortified sample matrix (LFM), and quality control samples (QCS).
- 10.2 Laboratory Reagent Blanks -- Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, an LRB must be analyzed. If within the retention time window of any analyte the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

- 10.3 Initial Demonstration of Capability
- 10.3.1 Select a representative concentration (about 10 times MDL or at the regulatory Maximum Contaminant Level, whichever is lower) for each analyte. Prepare a primary dilution standard solution (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 35 μ L of the concentrate to each of at least four 35 mL aliquots of reagent water, and analyze each aliquot according to procedures beginning in Section 11.0.
- 10.3.2 For each analyte the recovery value should for at least three out of four consecutively analyzed samples fall in the range of $R \pm 30\%$ (or within $R \pm 3S_r$ if broader) using the values for R and S_r for reagent water in Table 2. For those compounds that meet the acceptance criteria, performance is considered acceptable and sample analysis may begin. For those compounds that fail these criteria, initial demonstration procedures should be repeated.
- 10.3.3 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.
- 10.4 The analyst is permitted to modify GC columns, GC conditions, or detectors to improve separations or lower analytical costs. Each time such method modifications are made, the analyst must repeat the procedures in Section 10.3.
- 10.5 Assessing Laboratory Performance -- Laboratory Fortified Blank (LFB)
- 10.5.1 The laboratory must analyze at least one LFB per sample set (all samples extracted within a 24-hour period). If the sample set contains more than 20 samples, analyze one LFB for every 20 samples. The fortifying concentration of each analyte in the LFB sample should be 10 times MDL or the MCL, whichever is less. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Section 10.5.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.
- 10.5.2 Until sufficient data become available from within their own laboratory, usually a minimum of results from 20-30 analyses, the laboratory may assess laboratory performance against the control limits in Section 10.3.2 that are derived from the data in Table 2. When sufficient internal performance data becomes available, develop control limits from the mean percent recovery (\bar{X}) and standard deviation (S) of the percent recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = \bar{X} + 3S$$
$$\text{LOWER CONTROL LIMIT} = \bar{X} - 3S$$

After each 5-10 new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points.

- 10.5.3 It is recommended that the laboratory periodically determine and document its detection limit capabilities for analytes of interest.

CAUTION: No attempts to establish low detection limits should be made before instrument optimization and adequate conditioning of both the column and the GC system. Conditioning includes the processing of LFB and LFM samples containing moderate concentration levels of these analytes.

- 10.5.4 At least each quarter the laboratory should analyze quality control samples (QCS) (if available). If criteria provided with the QCS are not met, corrective action should be taken and documented.

10.6 Assessing Analyte Recovery -- Laboratory Fortified Sample Matrix (LFM)

- 10.6.1 The laboratory must add a known concentration to a minimum of 10% of the routine samples or one LFM per set, whichever is greater. The fortified concentration should not be less than the background concentration of the sample selected for fortification. Ideally the LFM concentration should be the same as that used for the LFB (Section 10.5). Periodically, samples from all routine sample sources should be fortified.

- 10.6.2 Calculate the percent recovery (R_i) for each analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the control limits established in Section 10.5.2 from the analyses of LFBs.

- 10.6.3 If the recovery of any such analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (Section 10.5), the recovery problem encountered with the dosed sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

- 10.7 The laboratory may adopt additional quality control practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

11.0 PROCEDURE

11.1 Sample Preparation

11.1.1 Remove samples from storage and allow them to equilibrate to room temperature.

11.1.2 Remove the container caps. Withdraw and discard a 5 mL volume using a 10 mL graduated cylinder. Replace the container caps and weigh the containers with contents to the nearest 0.1 g and record these weights for subsequent sample volume determinations (Section 11.3).

11.2 Extraction and Analysis

11.2.1 Remove the container cap of each sample, and add 6 g NaCl (Section 7.1.3) to the sample bottle. Using a transfer or automatic dispensing pipet, add 2.0 mL of hexane. Recap and shake vigorously by hand for 1 min. Invert the bottle and allow the water and hexane phases to separate.

11.2.2 Remove the cap and carefully transfer approximately 0.5 mL of hexane layer into an autosampler vial using a disposable glass pipet.

11.2.3 Transfer the remaining hexane phase, being careful not to include any of the water phase, into a second autosampler vial. Reserve this second vial at 4°C for an immediate reanalysis if necessary.

11.2.4 Transfer the first sample vial to an autosampler set up to inject 1-2 μ L portions into the gas chromatograph for analysis (See Section 6.9 for GC conditions). Alternately, 1-2 mL portions of samples, blanks, and standards may be manually injected, although an autosampler is strongly recommended.

11.3 Determination of Sample Volume in Bottles Not Calibrated

11.3.1 Discard the remaining sample/hexane mixture from the sample bottle. Shake off the remaining few drops using short, brisk wrist movements.

11.3.2 Reweigh the empty container with original cap and calculate the net weight of sample by difference to the nearest 0.1 g (Section 11.1.2 minus Section 11.3.2). This net weight (in grams) is equivalent to the volume (in mL) of water extracted (Section 12.3). By alternately using 40 mL bottles precalibrated at 35 mL levels, the gravimetric steps can be omitted, thus increasing the speed and ease of this extraction process.

11.4 Identification of Analytes

11.4.1 Identify a sample component by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then identification is considered positive.

11.4.2 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 a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.4.3 Identification requires expert judgement when sample components are not resolved chromatographically. When peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), or any time doubt exists over the identification of a peak on a chromatogram, appropriate alternative techniques to help confirm peak identification need be employed. For example, more positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used, e.g., mass spectrometry, or the use of a second chromatography column. Suggested alternative columns are described in Section 6.9.

12.0 CALCULATIONS

12.1 Identify the organohalides in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards and the laboratory fortified blanks. Identify the multicomponent compounds using all peaks that are characteristic of the specific compound from chromatograms generated with individual standards. Select the most sensitive and reproducible peaks to obtain a sum for calculation purposes (See Table 1).

12.2 Use the single point calibration (Section 9.2.4) or use the calibration curve or calibration factor (Section 9.2.3) to directly calculate the uncorrected concentration (C_i) of each analyte in the sample (e.g., calibration factor \times response).

12.3 Calculate the sample volume (V_s) as equal to the net sample weight:

$V_s = \text{gross weight (Section 11.1.2)} - \text{bottle tare (Section 11.3.2)}$.

12.4 Calculate the corrected sample concentration as:

$$\text{Concentration, } \mu\text{g/L} = \frac{50(c_i)}{(V_s)}$$

12.5 Results should be reported with an appropriate number of significant figures. Experience indicates that three significant figures may be used for concentrations above 99 $\mu\text{g/L}$, two significant figures for concentrations between 1-99 $\mu\text{g/L}$, and 1 significant figure for lower concentrations.

13.0 ACCURACY AND PRECISION

13.1 Single laboratory (EMSL-Cincinnati) accuracy and precision at several concentrations in reagent, ground, and tap water matrices are presented in Table 2.¹¹ These results were obtained from data generated with a DB-1 column.

13.2 This method has been tested by 10 laboratories using reagent water and groundwater fortified at three concentration levels. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and virtually independent of the sample matrix. Linear equations to describe the relationships are presented in Table 3.¹²

14.0 REFERENCES

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8. "Carcinogens-Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute of Occupational Safety and Health, Publication No. 77-206, August 1977.
9. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).
10. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
11. Winfield, T., et al. "Analysis of Organohalide Pesticides and Commercial PCB Products in Drinking Water by Microextraction and Gas Chromatography." In preparation.
12. Multilaboratory Method Validation Study #40, conducted by the Quality Assurance Branch, EMSL-Ci. Report in progress.

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

Analyte	Retention Time (min) ^a		
	Primary	Confirm. 1	Confirm. 2
Hexachlorocyclopentadiene	5.5	6.8	5.2
Simazine	10.9	25.7	19.9
Atrazine	11.2	22.6	19.6
Hexachlorobenzene	11.9	13.4	15.6
Lindane	12.3	18.4	18.7
Alachlor	15.1	19.7	21.1
Heptachlor	15.9	17.5	20.0
Aldrin	17.6	18.4	21.4
Heptachlor Epoxide	19.0	24.6	24.6
gamma-Chlordane	19.9	25.9	26.0
alpha-Chlordane	20.9	26.6	26.6
trans-Nonachlor	21.3	24.8	26.3
Dieldrin	22.1	45.1	27.8
Endrin	23.2	33.3	29.2
cis-Nonachlor	24.3	39.0	30.4
Methoxychlor	30.0	58.5	36.4
	Primary ^b		
Aroclor 1016	13.6, 14.8, 15.2, 16.2, 17.7		
Aroclor 1221	7.7, 9.0, 15.9, 19.1, 24.7		
Aroclor 1232	11.2, 14.7, 13.6, 15.2, 17.7		
Aroclor 1242	11.2, 13.6, 14.7, 15.2, 17.7, 19.8		
Aroclor 1248	14.8, 16.2, 17.1, 17.7, 19.8, 22.0		
Aroclor 1254	19.1, 21.9, 23.4, 24.9, 26.7		
Aroclor 1260	23.4, 24.9, 26.7, 28.2, 29.9, 32.6		
Chlordane	15.1, 15.9, 20.1, 20.9, 21.3		
Toxaphene	21.7, 22.5, 26.7, 27.2		

^aColumns and analytical conditions are described in Sections 6.9.2, 6.9.3, and 6.9.4.

^bColumn and conditions described in Section 6.9.2. More than one peak listed does not implicate the total number of peaks characteristic of the multi-component analyte. Listed peaks indicate only the ones chosen for summation in the quantification.

**TABLE 2. SINGLE LABORATORY ACCURACY, PRECISION AND METHOD
DETECTION LIMITS (MDLS) FOR ANALYTES FROM REAGENT WATER,
GROUNDWATER, AND TAP WATER^a**

Analyte	Accuracy and Standard Deviation Data							
	µg/L	Concentration* µg/L	Reagent Water		Groundwater		Tap Water	
			R ^c	SR ^d	R	S _R	R	S _R
Aldrin	0.075	0.15	86	9.5	100	11.0	69	9.0
Alachlor	0.225	0.50	102	13.4	–	–	–	–
Aldrin	0.007	0.05	106	20.0	86	16.3	–	–
Atrazine	2.4	5.0	85	16.2	95	7.3	108	10.9
		20.0	95	5.2	86	9.1	91	3.1
alpha-Chlordane	0.006	0.06	95	3.5	83	4.4	85	7.1
		0.35	86	17.0	94	10.2	91	2.4
gamma-Chlordane	0.012	0.06	95	0.4	86	5.3	83	14.7
		0.35	86	18.5	95	14.5	91	6.0
Chlordane	0.14	0.17	NA	8.0	–	–	105	12.4
		3.4	NA	3.6	–	–	95	9.6
Dieldrin	0.012	0.10	87	17.1	67	10.1	92	15.7
		3.6	114	9.1	94	8.6	81	14.0
Endrin	0.063	0.10	119	29.8	94	20.2	106	14.0
		3.6	99	6.5	100	11.3	85	12.4
Heptachlor	0.003	0.032	77	10.2	37	6.8	200	22.6
		1.2	80	7.4	71	9.8	106	16.8
Heptachlor Epoxide	0.004	0.04	100	15.6	90	14.2	112	7.5
		1.4	115	6.6	103	6.9	81	5.9
Hexachlorobenzene	0.002	0.003	104	13.5	91	10.9	100	15.6
		0.09	103	6.6	101	4.4	88	13.4
Hexachlorocyclopentadiene	0.13	0.15	73	5.1	87	5.1	191	18.5
		0.35	73	11.7	69	4.8	109	14.3
Lindane	0.003	0.03	91	6.5	88	7.7	103	8.1
		1.2	111	5.0	109	3.4	93	18.4
Methoxychlor	0.96	2.10	100	21.0	–	–	–	–
		7.03	98	10.9	–	–	–	–
cis-Nonachlor	0.027	0.06	110	15.2	101	7.2	93	14.3
		0.45	82	21.3	93	18.3	87	5.4
trans-Nonachlor	0.011	0.06	95	9.6	83	7.1	73	4.1
		0.35	86	21.8	94	17.2	86	5.1
Simazine	6.8	25	99	8.3	97	9.2	102	13.4
		60	65	3.6	59	18.0	67	6.2
Toxaphene	1.0	10	NA	12.6	–	–	110	9.5
		80	NA	15.3	–	–	114	13.5
Aroclor 1016	0.08	1.0	NA	6.6	–	–	97	7.5
Aroclor 1221	15.0	180	NA	8.3	–	–	92	9.6
Aroclor 1232	0.48	3.9	NA	13.5	–	–	86	7.3

TABLE 2. SINGLE LABORATORY ACCURACY, PRECISION AND METHOD DETECTION LIMITS (MDLS) FOR ANALYTES FROM REAGENT WATER, GROUNDWATER, AND TAP WATER^a

Analyte	Accuracy and Standard Deviation Data							
	µg/L	Concentration* µg/L	Reagent Water		Groundwater		Tap Water	
			R ^c	SR ^d	R	S _R	R	S _R
Aroclor 1242	0.31	4.7	NA	6.0	-	-	96	7.4
Aroclor 1248	0.102	3.6	NA	11.5	-	-	-	-
		3.4	-	-	-	-	84	9.9
Aroclor 1254	0.102	1.8	NA	10.4	-	-	-	-
		1.7	-	-	-	-	85	11.8
Aroclor 1260	0.189	2.0	NA	20.7	-	-	-	-
		1.8	NA	-	-	-	88	19.8

NA = Not applicable. A separate set of aqueous standards was not analyzed, and the response factor for reagent water was used to calculate a recovery for the tap water matrix.

^aData corrected for amount detected in blank and represent the mean of five to eight samples.

^bMDL = method detection limit in sample in µg/L; calculated by multiplying standard deviation (S) times the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

^cR = average percent recovery.

^dS_R = Standard deviation about percent recovery.

*Refers to concentration levels used to generate R and S_R data for the three types of water Matrices, not for MDL determinations.

- = No analyses conducted.

TABLE 3. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 505

REAGENT WATER						
Parameter	Applicable Conc. Range (µg/L)	Accuracy as Recovery X (µg/L)	Single Analyst Precision S _r (µg/L)		Overall Precision S (µg/L)	
Atrazine	(3.06-45.90)	1.122C+0.97	0.000	+1.21	0.045	+2.23
Simazine	(12.55-50.20)	0.892C+1.446	-0.049	+3.52	0.209	+1.23
Hexachlorobenzene	(0.01-0.37)	1.028C-0.00	0.108	+0.00	0.227	+0.00
Lindane	(0.04-1.39)	1.009C-0.00	0.057	+0.01	0.142	+0.00
Alachlor	(0.50-37.50)	1.004C-0.08	0.077	+0.10	0.105	+0.16
Heptachlor	(0.04-1.41)	1.002C+0.02	0.107	+0.01	0.211	+0.02
Aldrin	(0.04-1.42)	1.066C+0.00	0.031	+0.02	0.264	-0.00
Heptachlor epoxide	(0.04-1.42)	0.952C+0.00	0.032	+0.02	0.129	+0.02
Dieldrin	(0.10-7.53)	1.027C+0.00	0.091	+0.01	0.198	+0.02
Endrin	(0.10-7.50)	0.958C+0.01	0.116	+0.01	0.136	+0.02
Methoxychlor	(0.20-15.00)	0.950C+0.15	0.115	+0.12	0.125	+0.20
Chlordane	(0.51-50.90)	1.037C+0.06	0.084	+0.06	0.125	+0.19
Toxaphene	(5.63-70.40)	1.087C+0.24	0.131	-0.31	0.269	+0.69
X PCB-1016	(0.50-49.80)	0.856C+0.31	0.106	+0.31	0.147	+0.45
PCB-1254	(0.50-50.40)	0.872C-0.01	0.122	+0.11	0.281	+0.05

*The concentration range applicable to the multi-laboratory study from which the data was generated.

~~X~~

~~X~~

~~X~~

505-22

505-23

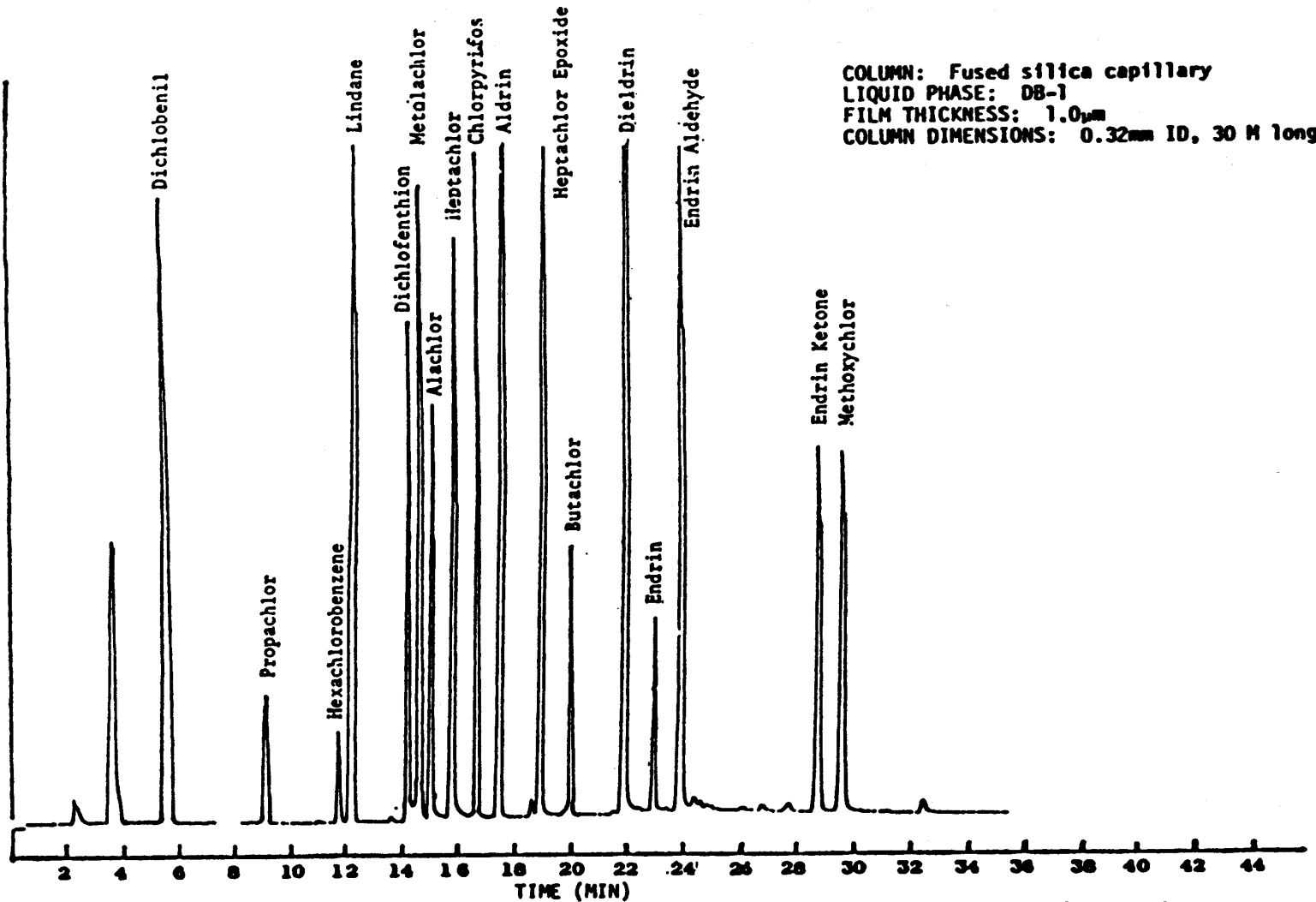


Figure 1. Hexane spiked at 7.71 ug/L with heptachlor and lindane; 9.14 ug/L with heptachlor epoxide; 11.4 ug/L with aldrin and hexachlorobenzene; 23 ug/L with butachlor, chlorpyrifos, chlorpyrifos-methyl, dichlobenil, dieldrin, endrin, metolachlor, and propachlor; and 44.9 ug/L with methoxychlor.

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0um
COLUMN DIMENSIONS: 0.32mm ID,
30 M long

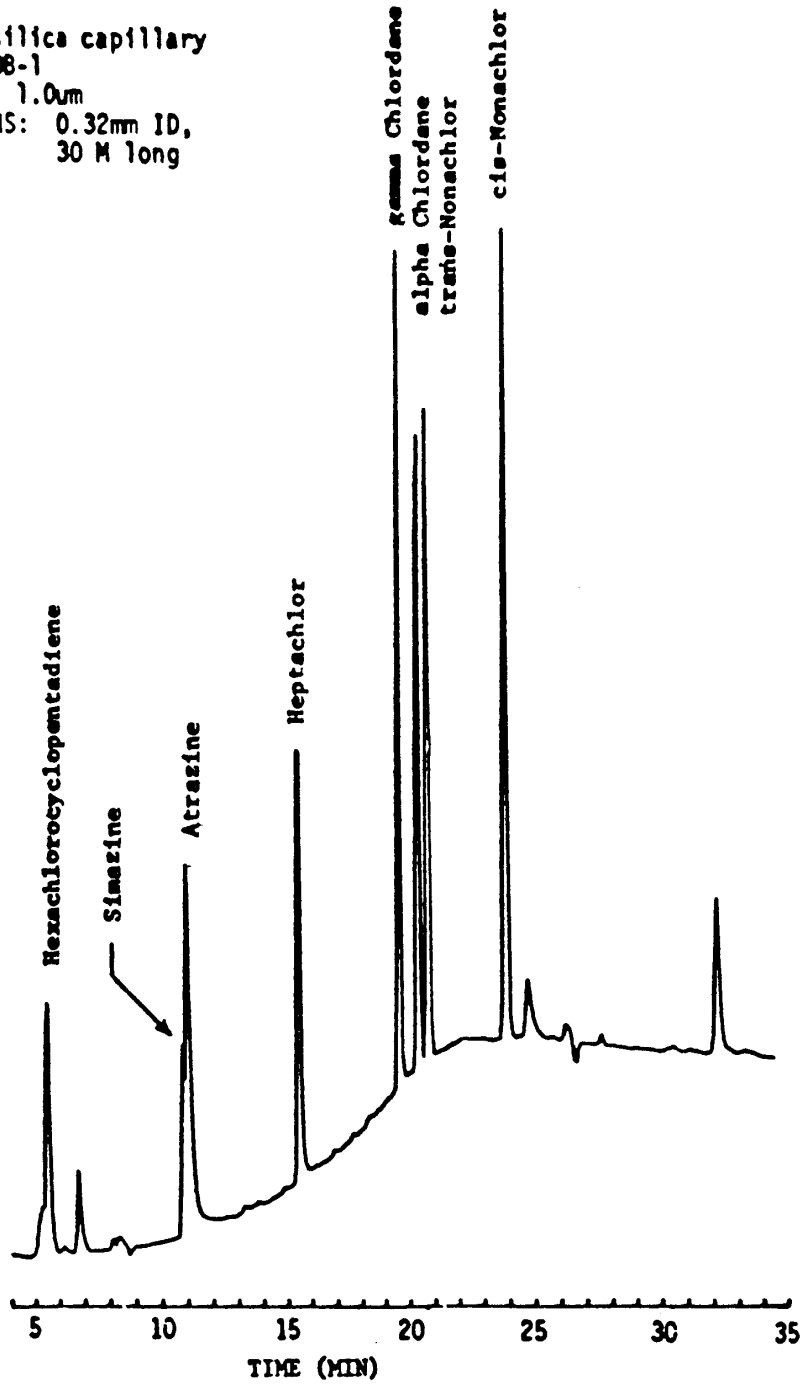


Figure 2. Extract of reagent water spiked at 20 ug/L with atrazine, 60 ug/L with simazine, 0.45 ug/L with cis-nonachlor, and 0.35 ug/L with hexachlorocyclopentadiene, heptachlor, alpha chlordane, gamma chlordane, and trans-nonachlor.

505-25

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0 μ m
COLUMN DIMENSIONS: 0.32mm ID, 30 M long

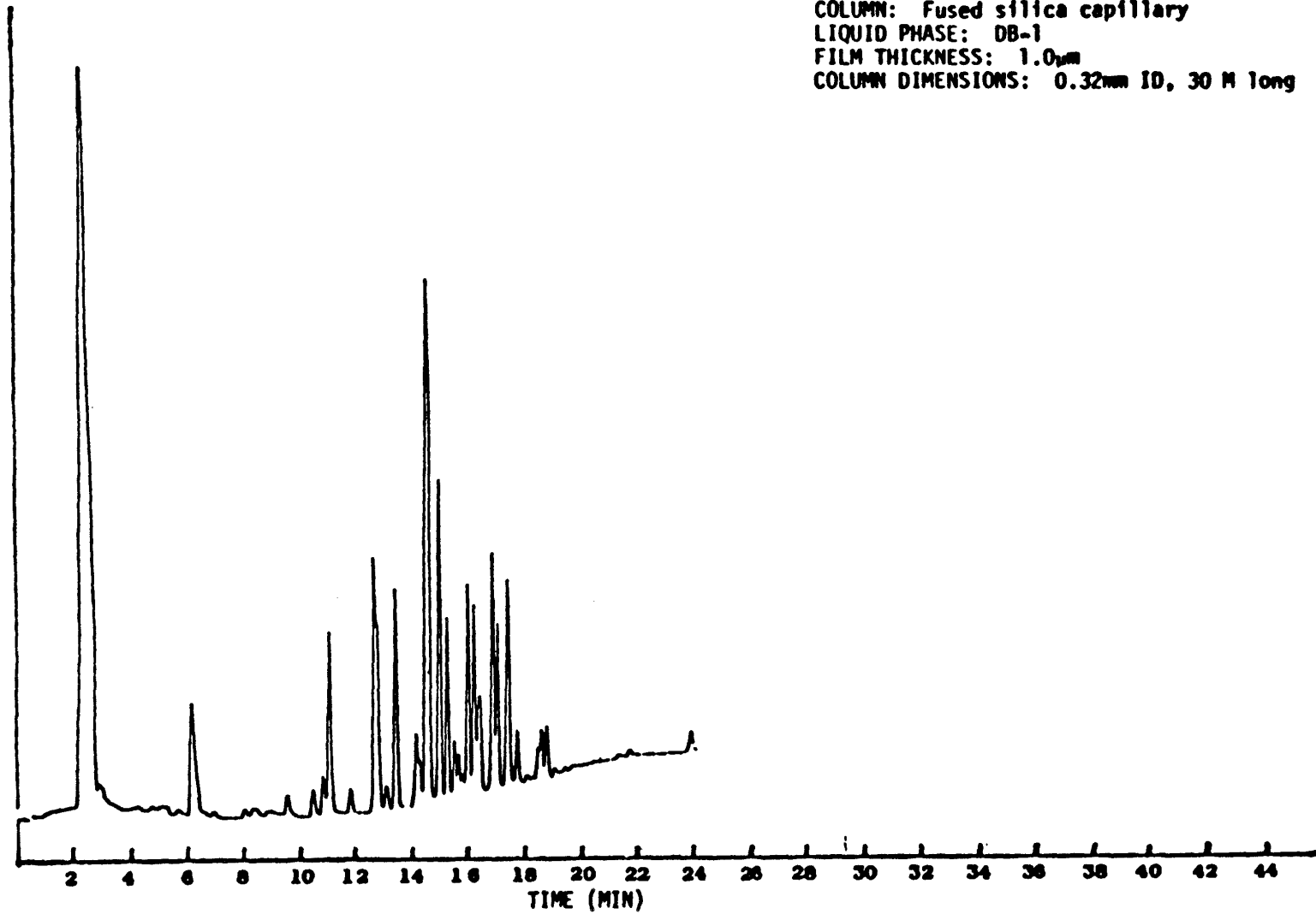


Figure 3. Hexane spiked at 11.4 ug/L with Aroclor 1016.

505-26

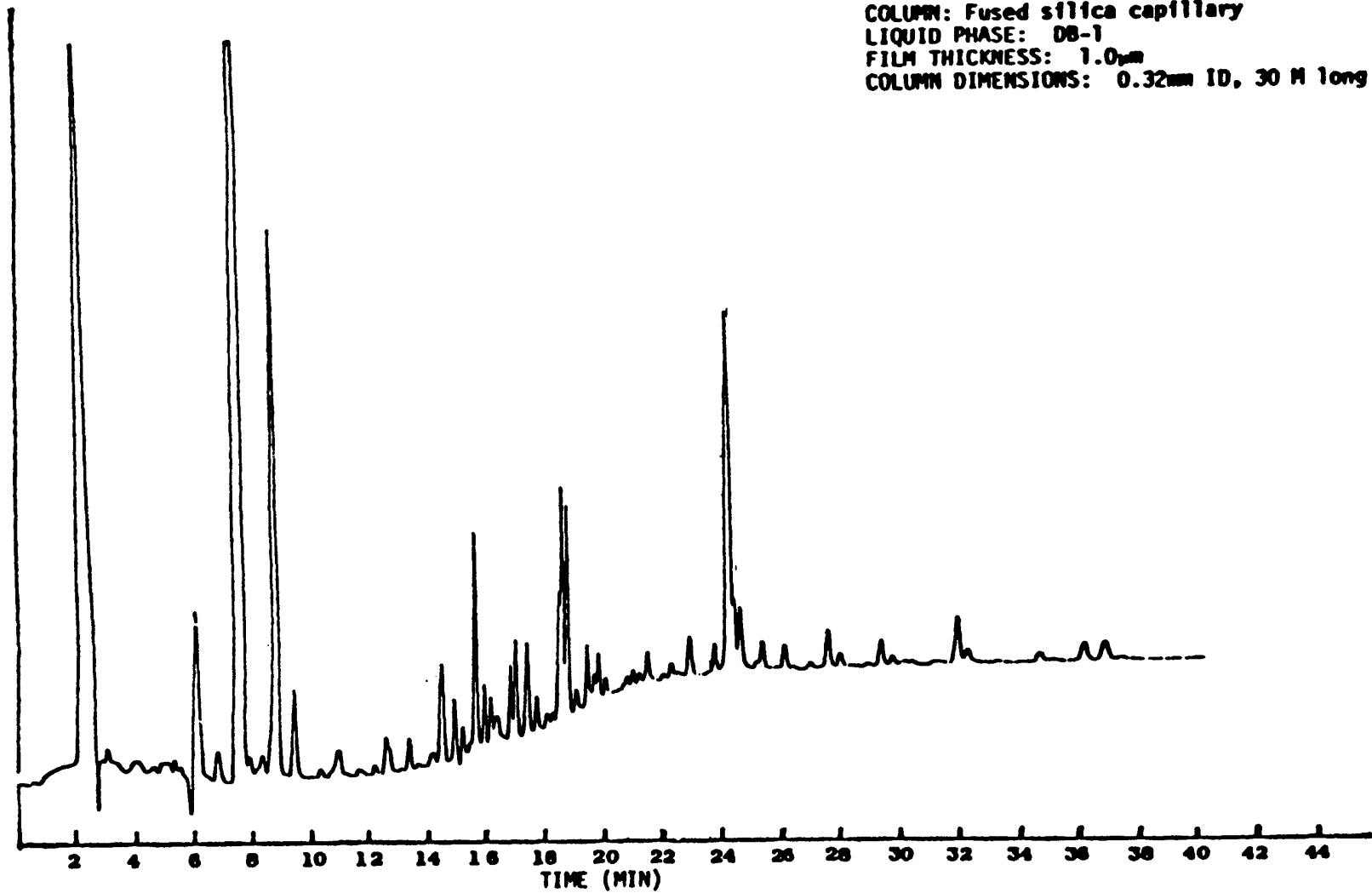


Figure 4. Hexane spiked at 171.4 ug/L with Aroclor 1221.

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0 μ m
COLUMN DIMENSIONS: 0.32mm ID, 30 M long

505-27

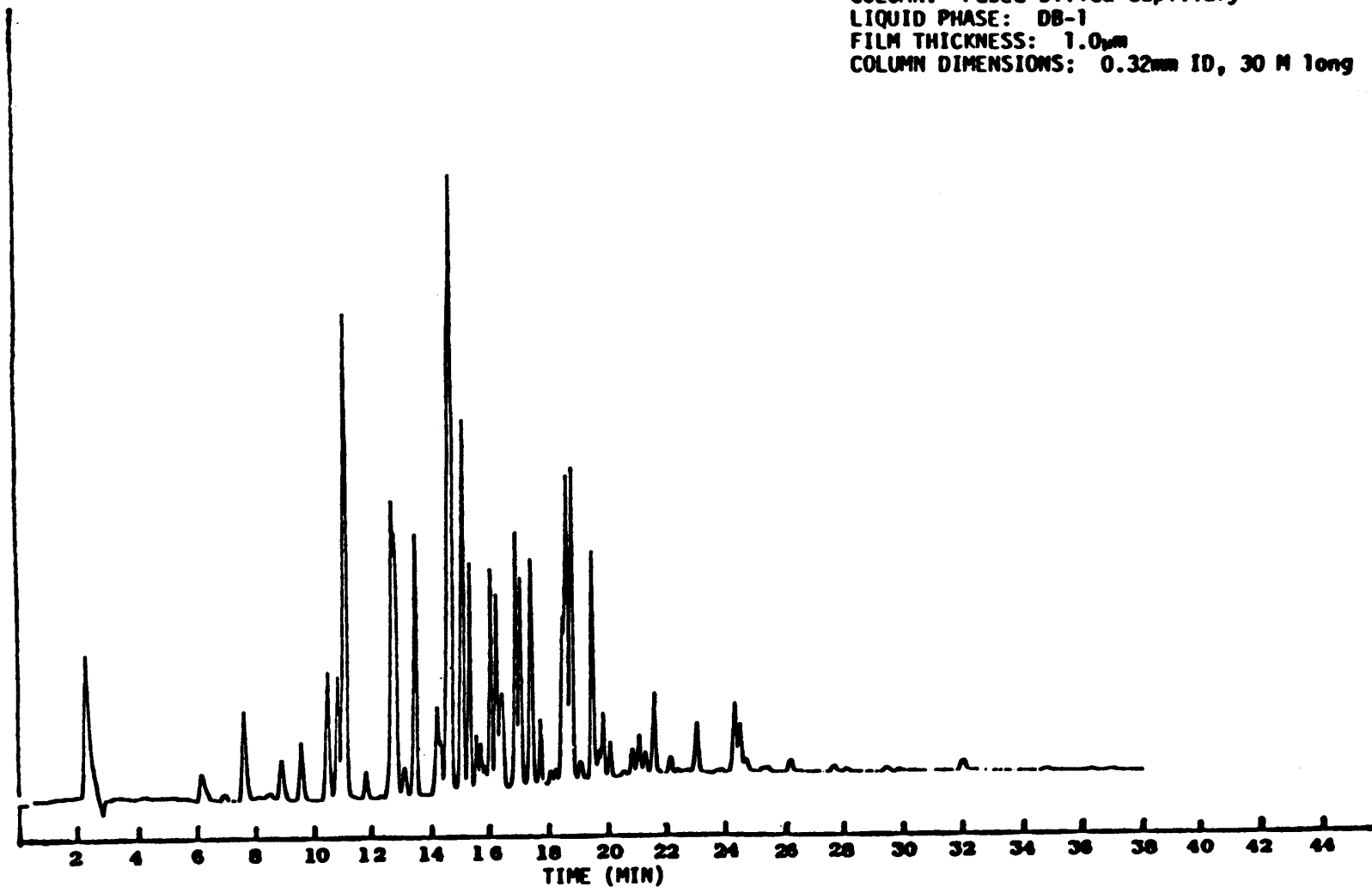


Figure 5. Hexane spiked at 57.1 ug/L with Aroclor 1232.

505-28

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0 μ m
COLUMN DIMENSIONS: 0.32mm ID, 30 M long

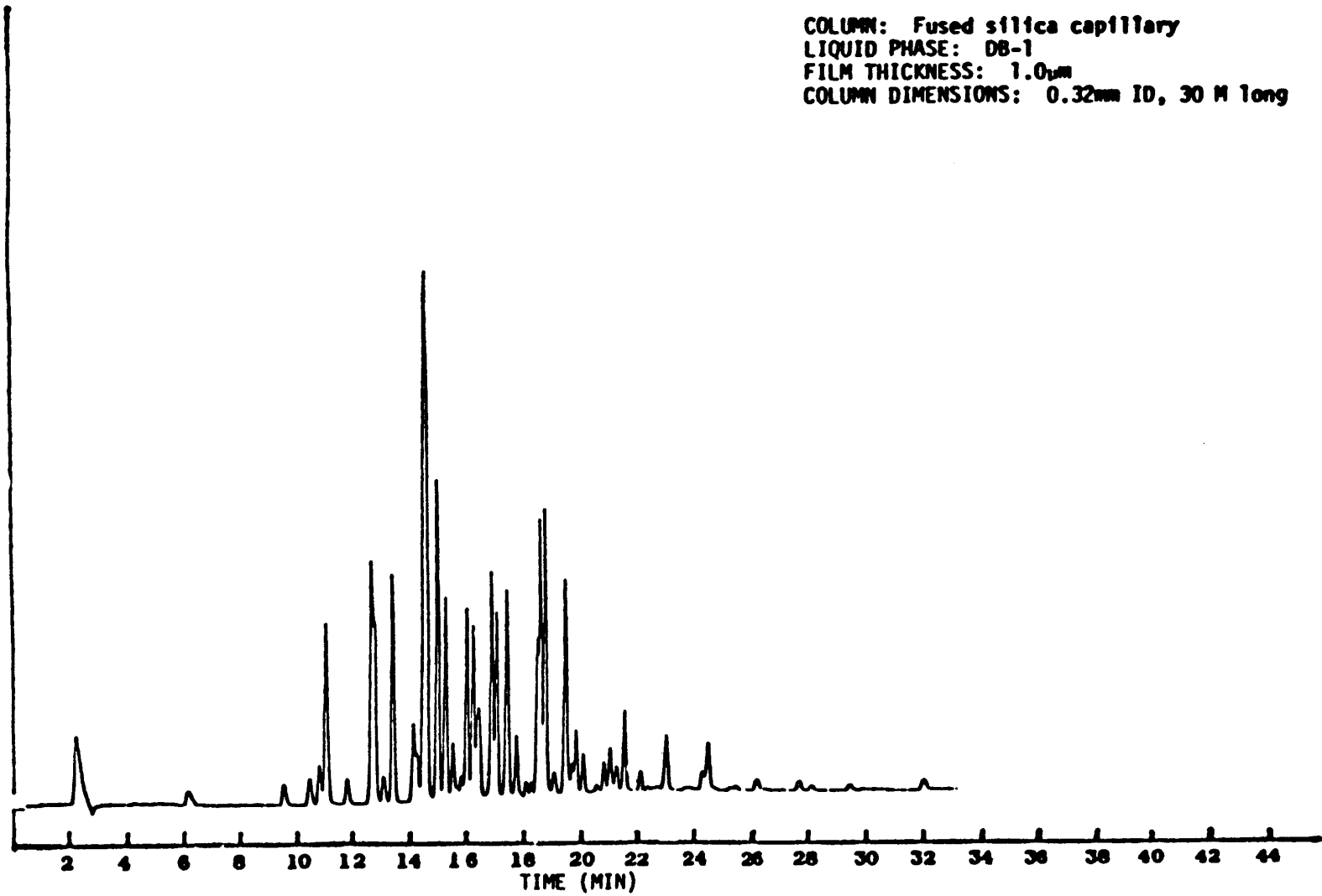


Figure 6. Hexane spiked at 57.1 ug/L with Aroclor 1242.

505-29

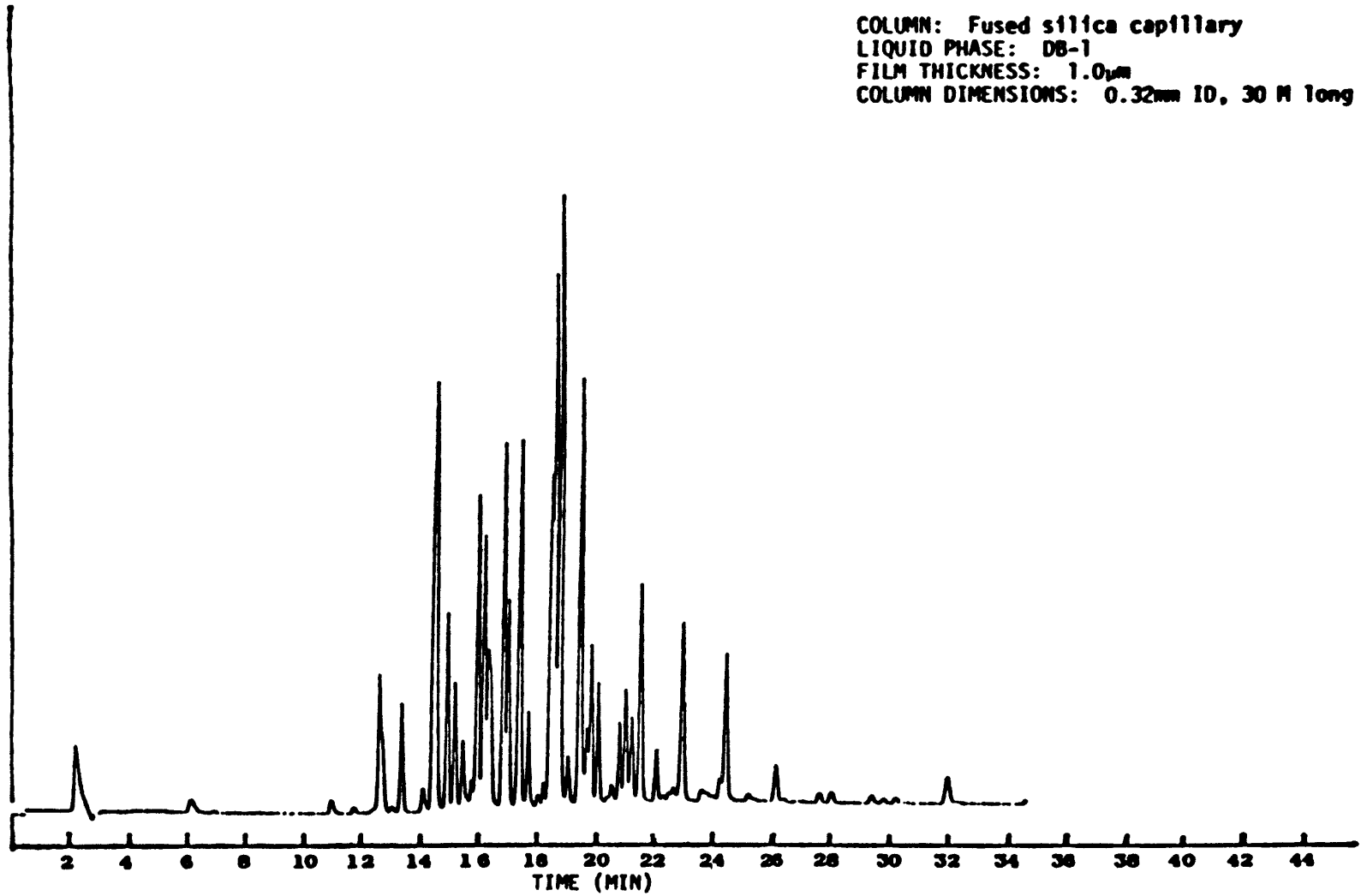


Figure 7. Hexane spiked at 57.1 ug/L with Aroclor 1248.

505-30

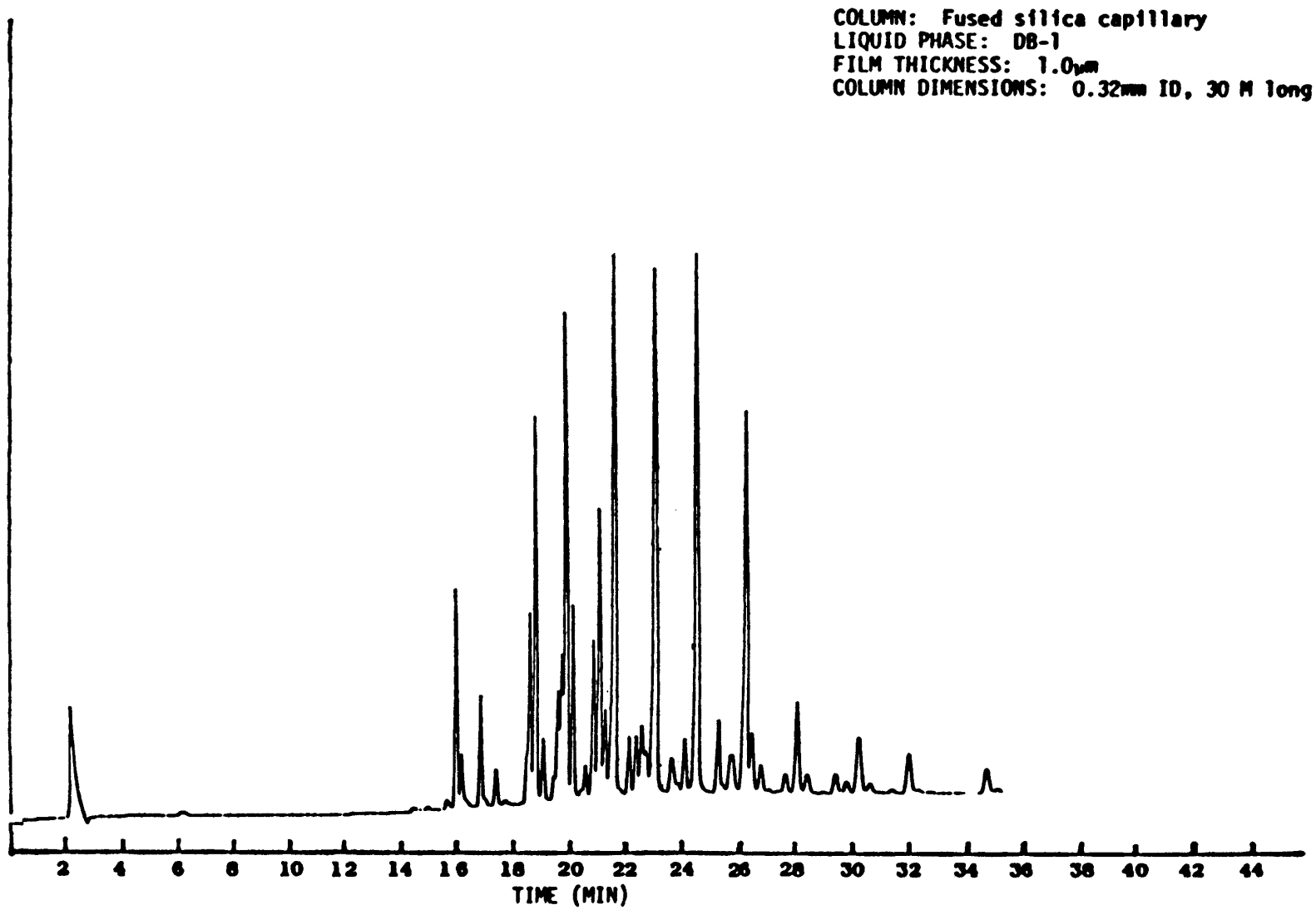


Figure 8. Hexane spiked at 42.9 ug/L with Aroclor 1254.

505-31

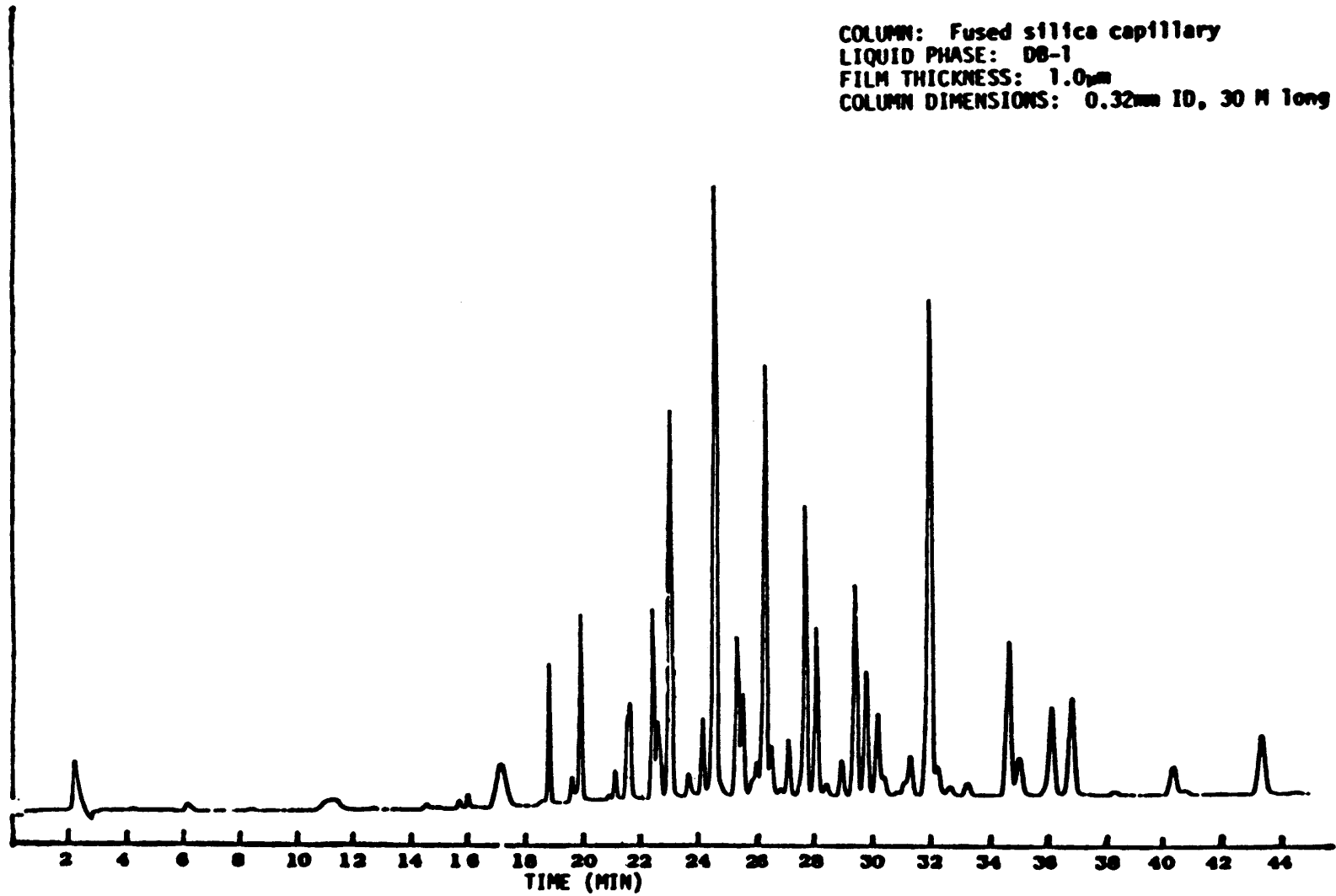


Figure 9. Hexane spiked at 34.3 ug/L with Aroclor 1260.

505-32

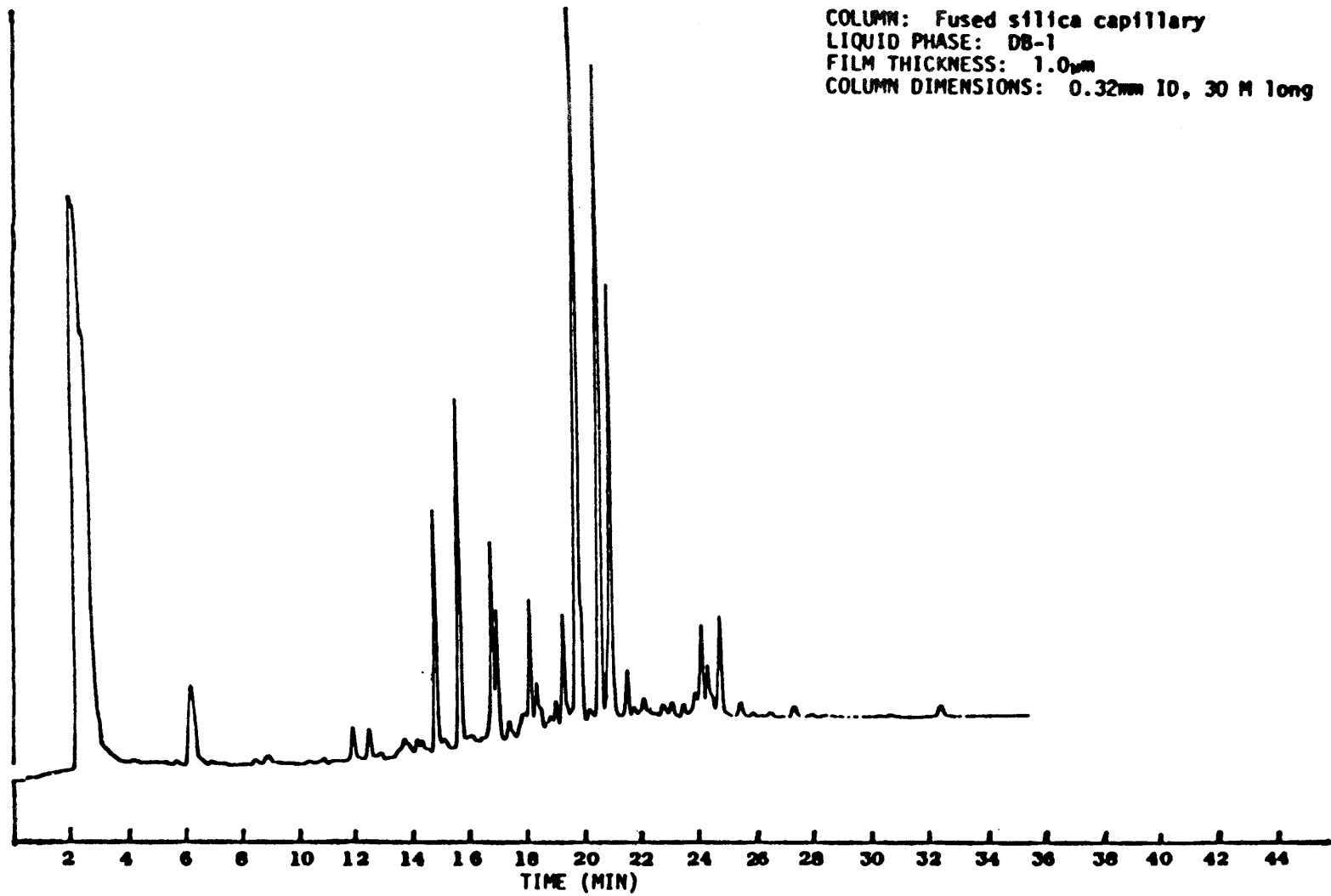


Figure 10. Hexane spiked at 28.6 ug/L with chlordane.

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0 μ m
COLUMN DIMENSIONS: 0.32mm ID, 30 M long

505-33

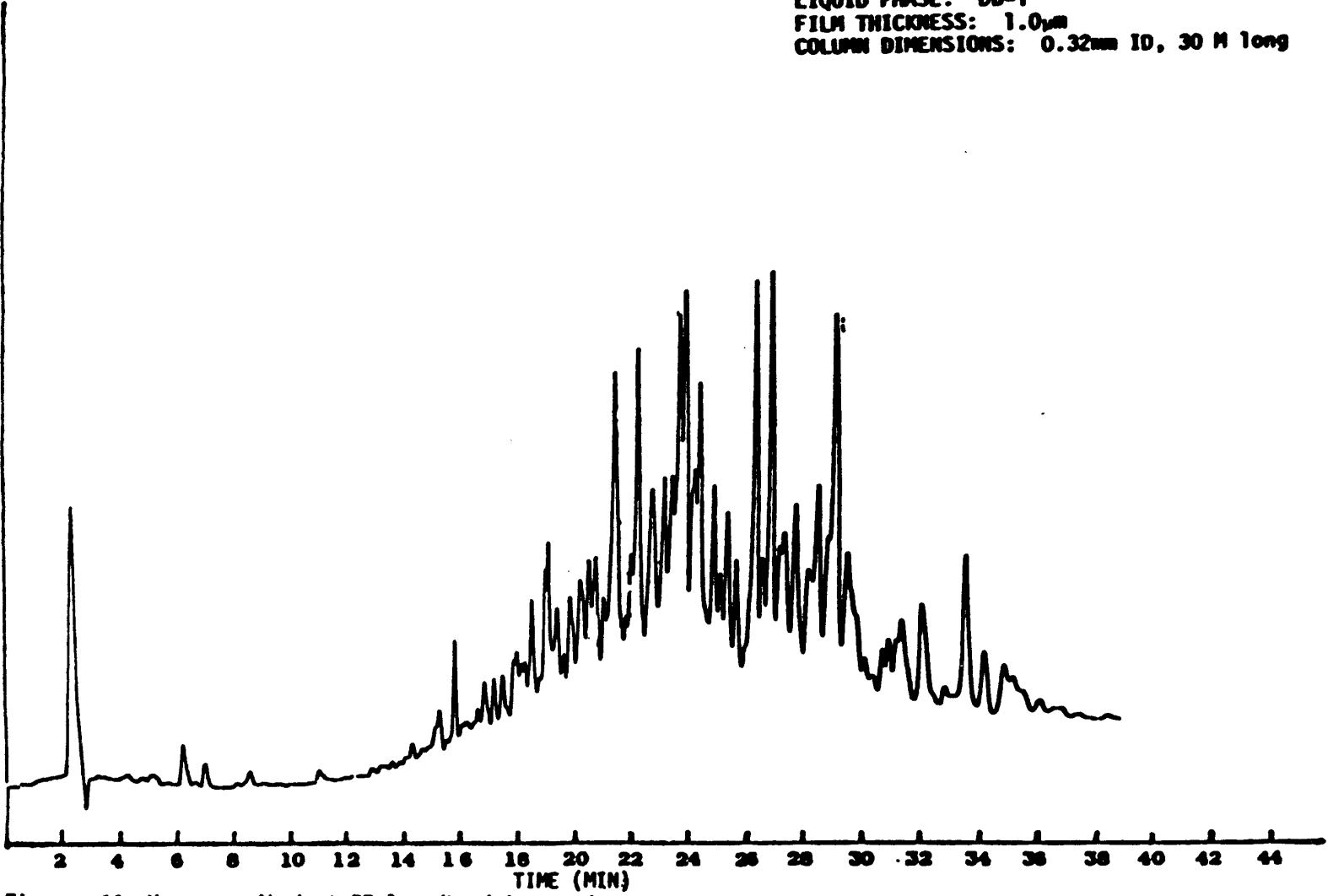


Figure 11. Hexane spiked at 57.1 ug/L with toxaphene.