METHOD 508.1

DETERMINATION OF CHLORINATED PESTICIDES, HERBICIDES, AND ORGANOHALIDES BY LIQUID-SOLID EXTRACTION AND ELECTRON CAPTURE GAS CHROMATOGRAPHY

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METHOD 508.1

DETERMINATION OF CHLORINATED PESTICIDES, HERBICIDES, AND ORGANOHALIDES IN WATER USING LIQUID-SOLID EXTRACTION AND ELECTRON CAPTURE GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method utilizes disk liquid-solid extraction and gas chromatography with an electron capture detector to determine twenty nine chlorinated pesticides, three herbicides, and four organohalides in drinking water, ground water, and drinking water in any treatment stage. Liquid solid extraction cartridges may also be used to carry out sample extractions. Single laboratory accuracy, precision, and method detection limit data have been determined for the following compounds:

Analyte	Chemical Abstract Services Registry Number
Alachlor	15972-60-8
Aldrin	309-00-2
Atrazine	1912-24-9
Butachlor	23184-66-9
Chlordane-alpha	5103-71-9
Chlordane-gamma	5103-74-2
Chloroneb	2675-77-6
Chlorbenzilate	510-15-6
Chlorthalonil	1897-45-6
Cyanazine	21725-46-2
DCPA	1861-32-1
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan Sulfate	1031-07-8
Endrin	72-20-8
Endrin Aldehyde	7421-93-4
Etridiazole	2593-15-9
HCH-alpha	319-84-6
HCH-beta	319-85-7
HCH-delta	319-86-8
HCH-gamma (Lindane)	58-89-9
Heptachlor	76-44-8
Heptachlor Epoxide	1024-57-3

Analyte	Chemical Abstract Services Registry Number
Hexachlorobenzene	118-74-1
Hexachlorocylcopentadiene	77-47-4
Methoxychlor	72-43-5
Metoachlor	51218-45-2
Metribuzin	21087-64-9
cis-Permethrin	61949-76-6
trans-Permethrin	61949-77-7
Propachlor	1918-16-7
Simazine	122-34-9
Toxaphene	8001-35-2
Trifluralin	1582-09-8
Aroclor 1016	12674-11-1
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 This method has been validated in a single laboratory and method detection limits have been determined for each analyte listed above. The method detection limit (MDL) is defined as the statistically calculated minimum amount that can be measured with 99% confidence that the reported value is greater than zero[1]. For the listed analytes (except multi-component analytes), MDLs which range from 0.001-0.015 µg/L are listed in Table 3. MDLs for multi-component analytes (Aroclors and toxaphene) range from 0.01-0.13 µg/L.

2.0 SUMMARY OF METHOD

2.1 The analytes are extracted from the water sample by passing 1 L of sample through a preconditioned disk or cartridge containing a solid inorganic matrix coated with a chemically bonded C_{18} organic phase (liquid-solid extraction, LSE). The analytes are eluted from the LSE disk or cartridge with small volumes of ethyl acetate and methylene chloride, and this eluate is concentrated by evaporation of some of the solvent. The sample components are separated, identified, and measured by injecting micro-liter quantities of the eluate into a high resolution fused silica capillary column of a gas chromatograph/electron capture detector (GC/ECD) system.

3.0 DEFINITIONS

3.1 Internal Standard (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution.

3.2 Surrogate Analyte (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 Laboratory Reagent Blank (LRB) -- A aliquot of reagent water or other blank matrix 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 Instrument Performance Check Solution (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.5 Laboratory Fortified Blank (LFB) -- An aliquot of reagent water or other blank matrix 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.

3.6 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.

3.7 Stock Standard Solution -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.8 Primary Dilution Standard Solution (PDS) -- 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.

3.9 Quality Control Sample (QCS) -- A solution of method analytes of known concentrations which are used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.10 Method Detection Limit (MDL) -- The statistically calculated minimum amount of an analyte that can be measured with 99% confidence that the reported value is greater than zero[1].

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated baselines in gas chromatograms.

4.2 Interfering contamination may occur when a sample containing low concentrations of compounds is analyzed immediately after a sample containing relatively high concentrations of compounds. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed. After analysis of a sample containing high concentrations of compounds, a laboratory reagent blank should be analyzed to ensure that accurate values are obtained for the next sample.

4.3 It is important that samples and standards be contained in the same solvent, i.e., the solvent for final 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.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each chemical and reagent used in this method has not been precisely defined. However, each one must be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining a current awareness of OSHA regulations regarding safe handling of the chemicals used in this method. Additional references to laboratory safety are cited[2-4].

5.2 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

6.0 EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers and brand names are included for illustration only.)

6.1 All glassware, including sample bottles, must be meticulously cleaned. This may be accomplished by washing with detergent and water, rinsing with tap water, distilled water, or solvent, air-drying, and heating (where appropriate)

in a muffle furnace for two hours at 400°C. Volumetric glassware must never be heated in a muffle furnace.

6.2 Sample Containers -- 1 L or 1 quart amber glass bottles fitted with Teflon-lined screw caps. Amber bottles are highly recommended since some of the method analytes are sensitive to light and are oxidized or decomposed upon exposure.

6.3 Volumetric Flasks -- Various sizes.

6.4 Micro Syringes -- Various sizes.

6.5 Vials -- Various sizes of amber vials with Teflon-lined screw caps.

6.6 Drying Column -- The drying tube should contain about 5-7 g of anhydrous sodium sulfate to prohibit residual water from contaminating the extract. Any small tube may be used, such as a syringe barrel, a glass dropper, etc., as long as no sodium sulfate passes through the column into the extract.

6.7 Fused Silica Capillary Gas Chromatography Column -- Any capillary column that provides adequate resolution, capacity, accuracy, and precision may be used. A 30 m X 0.25 mm ID fused silica capillary column coated with a 0.25 µm bonded film of polyphenylmethylsilicone (J&W DB-5) was used to develop this method. Any column which provides analyte separations equivalent to or better than this column may be used.

6.8 Gas Chromatograph -- Must be capable of temperature programming, be equipped for split/splitless injection, and be equipped with an electron capture detector. On-column capillary injection is acceptable if all the quality control specifications in Section 9.0 and Section 10.0 are met. The injection system should not allow the analytes to contact hot stainless steel or other hot metal surfaces that promote decomposition.

6.9 Vacuum Manifold -- A manifold system or a commercially available automatic or robotic sample preparation system designed for disks or cartridges should be utilized in this method. Ensure that all quality control requirements discussed in Section 9.0 are met. A standard all glass or Teflon lined filter apparatus should be used for disk or cartridge extraction when an automatic system is not utilized.

7.0 REAGENTS AND STANDARDS

7.1 Helium Carrier Gas -- As contaminant free as possible.

7.2 Extraction Disks and Cartridges -- Containing octadecyl bonded silica uniformly enmeshed in an inert matrix. The disks used to generate the data in this method were 47 mm in diameter and 0.5 mm in thickness. Larger disk sizes are acceptable. The disks should not contain any organic compounds, either from the matrix or the bonded silica, that will leach into the ethyl

acetate and methylene chloride eluant. Cartridges should be made of inert, non-leaching plastic or glass, and must not leach plasticizers or other organic compounds into the eluting solvent. Cartridges contain about 1 g of silica or other inert inorganic support whose surface is modified by chemically bonding octadecyl C_{18} groups.

7.3 Solvents -- Methylene chloride, ethyl acetate, and methanol, high purity pesticide quality or equivalent.

7.4 Reagent Water -- Water in which an interferant is not observed at the MDL of the compound of interest. Prepare reagent water by passing tap or distilled water through a filter bed containing activated carbon, or by using a water purification system. If necessary, store reagent water in clean bottles with Teflon-lined screw caps.

7.5 Hydrochloric Acid -- 6N.

7.6 Sodium Sulfate -- Anhydrous, muffled at 400°C for a minimum of four hours and stored in an air-tight clean glass container at ambient temperature.

7.7 Sodium Sulfite -- Anhydrous.

7.8 Pentachloronitrobenzene, ≥98% purity -- For use as the internal standard.

7.9 4,4-dibromobiphenyl, ≥96% purity -- For use as the surrogate compound.

7.10 Stock Standard Solutions -- Individual solutions of analytes may be purchased from commercial suppliers or prepared from pure materials. These solutions are usually available at a concentration of 500 µg/mL. These solutions are used to make the primary dilution standard. They should be stored in amber vials in a refrigerator or freezer. Stock standard solutions should be replaced if ongoing quality control checks indicate a problem.

7.11 Primary Dilution Standards (PDS) -- Prepare the solution(s) to contain all method analytes, but not the internal standard or surrogate compound, at a concentration of 2.5 µg/mL in ethyl acetate.

7.12 Instrument Performance Check Solution -- Prepare by accurately weighing 0.0010 g each of chlorothalonil, chlorpyrifos, DCPA, and HCH-delta. Dissolve each analyte in MTBE and dilute to volume in individual 10 mL volumetric flasks. Combine 2 µL of the chlorpyrifos stock solution, 50 µL of the DCPA stock solution, 50 µL of the chlorothalonil stock solution, and 40 µL of the HCH-delta stock solution to a 100 mL volumetric flask and dilute to volume with ethyl acetate. Transfer to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC (Section 9.0) indicates a problem.

7.13 Calibration Solutions -- Using the primary dilution standards, prepare calibration solutions at six concentrations in ethyl acetate. The calibration range is dependent upon the instrumentation used, and expected analyte concentrations in the samples to be analyzed. A suggested concentration range of calibration solutions is 0.002-1.0 µg/mL.

Note: Calibration standards for toxaphene and each of the Aroclors must be prepared individually.

7.14 Internal Standard Solution -- Prepare this solution of pentachloronitrobenzene by itself in ethyl acetate at a concentration of 10 µg/mL.

7.15 Surrogate Compound Solution -- Prepare this solution of 4,4'-dibromobiphenyl by itself in ethyl acetate at a concentration of 10 µg/mL. Other surrogate compounds may be used if it can be demonstrated that they are not in any samples and are not interfered with by any analyte or other sample component.

7.16 GC Degradation Check Solution -- Prepare a solution in ethyl acetate containing endrin and 4,4'-DDT each at a concentration of 1 µg/mL. This solution will be injected to check for undesirable degradation of these compounds in the injection port by looking for endrin aldehyde and endrin ketone or for 4,4'-DDE and 4,4'-DDD.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (generally one to two minutes). Adjust the flow to about 500 mL/min. and collect the sample from the flowing stream. Keep sample sealed from collection time until analysis. When sampling from a body of water, fill the sample container with water from a representative area. Sampling equipment, including automatic samplers, must not use plastic tubing, plastic gaskets, or any parts that may leach interfering analytes into the sample. Automatic samplers that composite samples over time should use refrigerated glass sample containers.

8.2 Residual chlorine in the sample should be reduced by adding 50 mg/L of sodium sulfite (this may be added as a solid with stirring or shaking until dissolved, or as a prepared solution).

8.3 Adjust the sample to pH ≤2 by adding 6N HCl. It may require up to 4 mL to accomplish this. It is very important that the sample be dechlorinated (Section 8.2) before adding the acid to lower the pH of the sample. Adding sodium sulfite and HCl to the sample bottles prior to shipping the bottles to the sampling site is not permitted. HCl should be added at the sampling site to retard any microbiological degradation of method analytes.

8.4 Samples must be iced or refrigerated at 4°C from the time of collection until extraction. Preservation study results show that the analytes (except cyanazine) are stable for 14 days in samples that are preserved as described in Section 8.2 and Section 8.3. Refrigerated sample extracts may be stored up to 30 days.

8.5 If cyanazine is to be determined, a separate sample must be collected. Cyanazine degrades in the sample when it is stored under acidic conditions or when sodium sulfite is present in the stored sample. Samples collected for cyanazine determination MUST NOT be dechlorinated or acidified when collected. They should be iced or refrigerated as described above and analyzed within 14 days. However, these samples must be dechlorinated and acidified immediately prior to fortification with the surrogate standard and extraction using the same quantities of acid and sodium sulfite described above.

9.0 QUALITY CONTROL

9.1 Quality control requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrix samples. The laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended. Determination of a MDL is also required.

9.2 Before any samples are analyzed or any time a new supply of disks or cartridges are received from a supplier, it must be demonstrated that a laboratory reagent blank is reasonably free of contamination that would prevent the determination of any analyte of concern. Both disks and cartridges could contain trace quantities of phthalate esters or silicon compounds that could prevent the determination of method analytes at low concentrations. Other sources of background contamination are impure solvents, impure reagents, and contaminated glassware. In general, background from method analytes should be below method detection limits.

9.3 Initial Demonstration of Capability

9.3.1 To demonstrate initial laboratory capability, analyze a minimum of four replicate laboratory fortified blanks containing each analyte of concern at a suggested concentration in the range of 0.01-0.5 µg/L. Prepare each reagent water replicate by adding sodium sulfite (Section 8.2) and HCl (Section 8.3) to each sample, then adding an appropriate aliquot of the primary dilution standard solution(s). Analyze each replicate according to the procedures described in Section 11.0.

9.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, the mean accuracy (as mean percentage of true value) for each analyte, and the

precision (as relative standard deviation, RSD) of the measurements for each analyte.

9.3.3 For each analyte, the mean accuracy, expressed as a percentage of the true value, should be 70-130% and the RSD should be ≤30%.

9.3.4 To determine the MDL, analyze a minimum of seven replicate laboratory fortified blanks which have been fortified with all analytes of interest at approximately 0.01 µg/L (Use a higher concentration for multi-component analytes). Calculate the MDL of each analyte using the procedure described in Section 13.2[1]. It is recommended that these analyses be carried out over a period of three or four days to produce more realistic limits.

9.3.5 Develop a system of control charts to plot the precision and accuracy of analyte and surrogate compound recoveries as a function of time. Charting of surrogate compound recoveries, which are present in every sample, will form a significant record of data quality. When surrogate recovery from a sample, a LFB, or a LFM is <70% or >130%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the cause cannot be determined, reanalyze the sample. If the surrogate recovery from an LFB is still is <70% or >130%, remedial action (Section 10.8) will likely be necessary. If the surrogate recovery from a field sample or LFM is still is <70% or >130%, and LFBs are in control, a matrix effect is suspected.

9.4 Assessing the Internal Standard -- The analyst should monitor the internal standard response (peak area units) of all samples and LFBs during each work shift. The IS area should not deviate from the latest continuing calibration check (Section 10.7) by more than 30%, or from the initial calibration by more than 50%. If this criteria cannot be met, remedial action (Section 10.8) must be taken. When method performance has been restored, reanalyze any extracts that failed Section 9.4 criteria.

9.5 With each group or set of samples processed within a 12-hour work shift, analyze a LRB to determine background contamination. Any time a new batch of LSE disks or cartridges are received, or a new supply of reagents are used, repeat Section 9.2.

9.6 Assessing Laboratory Performance -- With each group or set of samples processed within a 12-hour work shift, analyze a LFB containing each analyte of interest at a concentration of 0.01-0.5 µg/L. If more than 20 samples are included in a set, analyze a LFB for every 20 samples. Use the criteria in Section 9.3.3 to evaluate the accuracy of the measurements. If acceptable accuracy cannot be achieved, the problem must be located and corrected before additional samples are analyzed. Maintain control charts to document data quality.

Note: It is suggested that one multi-component analyte (an Aroclor or toxaphene) LFB also be analyzed with each sample set. By selecting a different multi-component analyte for this LFB each work shift, LFB data can be obtained for all of these analytes over the course of several days.

9.7 Assessing Sample Matrix Effects -- In an attempt to ascertain any detrimental matrix effects, analyze a LFM for each type of matrix (i.e., tap water, ground water, surface water). This need not be done with every group of samples unless matrices are vastly different. The LFM should contain each analyte of interest at a concentration similar to that selected in Section 9.6. Results from a LFM should be within 65-135% of the fortified amount. If these criteria are not met, then a matrix interference is suspected and must be documented.

9.8 Assessing Instrument Performance -- Instrument performance should be monitored each 12-hour work shift by analysis of the IPC sample and GC degradation check solution.

9.8.1 The IPC sample contains compounds designed to indicate appropriate instrument sensitivity, column performance (primary column) and chromatographic performance. IPC sample components and performance criteria are listed in Table 2. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the instrument system.

9.8.2 Inject the GC degradation check solution. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and the degradation products of endrin (endrin aldehyde, EA and endrin ketone, EK). For 4,4'-DDT, these products will elute just before the parent, and for endrin, the products will elute just after the parent. If degradation of either DDT or endrin exceeds 20%, resilanize the injection port liner and/or break off a meter from the front of the column. The degradation check solution is required in each 12-hour workshift in which analyses are performed.

$$\text{\% degrade of 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE+DDD)}}{\text{Total DDT peak area (DDT+DDE+DDD)}} \times 100$$

$$\text{\% degrade of endrin} = \frac{\text{Total EA + EK peak area}}{\text{Total endrin + EA + EK area}} \times 100$$

Note: If the analyst can verify that 4,4'-DDT, endrin, their breakdown products, and the analytes in the IPC solution are all resolved, the IPC solution and the GC degradation check solution may be prepared and analyzed as a single solution.

9.9 At least quarterly, analyze a QCS from an external source. If measured analyte concentrations are not of acceptable accuracy as described in Section 9.3.3, check the entire analytical procedure to locate and correct the problem.

9.10 Numerous other quality control measures are incorporated into other parts of this method, and serve to alert the analyst to potential problems.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration are required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration has been successfully accomplished, at least one continuing calibration check is required each 12-hour work shift in which analyses are performed.

10.2 Establish GC operating parameters equivalent to those below:

Injector temperature	-- 250°C
Detector temperature	-- 320°C
Injection volume	-- 2 µL, splitless for 45 seconds
Temperature program	-- Inject at 40°C and hold one minute
	-- program at 20°C/min. to 160°C hold three minutes
	-- program at 3°C/min. to 275°C with no hold
	-- program at 20°C/min. to 310°C with no hold

Using the above conditions and the column in Section 6.7, the total run time is about 50 minutes. The last eluting analyte is trans-permethrin which elutes at 267°C with a retention time of 45.4 minutes. Table 1 lists all method analytes and their retention times using the above conditions. It should be noted that some method analytes elute very close together. If there are unresolved peaks using the above temperature program, the analyst should modify the program to achieve resolution.

10.3 Analyze the instrument performance check sample and GC degradation check sample, and evaluate as described in Section 9.8. If acceptance criteria are met, proceed with calibration. If criteria are not met, take remedial action (Section 10.8).

10.4 Prepare calibration solutions containing all analytes of interest according to Section 7.13 in ethyl acetate. The calibration standard concentrations should bracket the expected concentration range of each analyte in sample extracts, or define the working range of the detector. Each standard must contain the internal standard, pentachloronitrobenzene, at a concentration of 0.5 µg/mL. The surrogate should also be present in each solution at that concentration.

Note: Calibration standards of multi-component analytes must be prepared and analyzed as separate solutions

10.5 Analyze each calibration standard using the suggested conditions in Section 10.2. Tabulate peak area versus concentration for each compound and the internal standard. Calculate the response factor (RF) for each analyte and the surrogate using the following equation.

$$RF = \frac{(A_s)\ (C_{is})}{(A_{is})\ (C_s)}$$

where: A_S = response for the analyte to be measured
A_{IS} = response for the internal standard
C_{IS} = concentration of the internal standard (µg/mL)
C_S = concentration of the analyte to be measured (µg/mL)

Note: To calibrate for multi-component analytes, one of the following methods should be used.
Option 1 - Calculate an average response factor or linear regression equation for each multi-component analyte using the combined area of all the component peaks in each of the calibration standard chromatograms.

Option 2 - Calculate an average response factor or linear regression equation for each multi-component analyte using the combined areas of three to six of the most intense and reproducible peaks in each of the calibration standard chromatograms.

10.6 If the RF over the working range is constant (≤30% RSD), the average RF can be used for calculations. Alternatively, use the results to generate a linear regression calibration for each analyte using response ratios (A_S/A_{IS}) vs. C_S.

10.7 The linear regression calibration or RF must be verified on each work shift (not to exceed 12 hours) by measuring one or more calibration standards. Additional periodic calibration checks are good laboratory practice. It is highly recommended that an additional calibration check be performed at the end of any cycle of continuous instrument operation, so that each set of field samples is bracketed by calibration check standards. Varying the concentration of continuing calibration standards from shift to shift is recommended, to evaluate the accuracy of the calibration at more than one point. Calculate the RF for each analyte from the data measured in the continuing calibration check. The RF for each analyte must be within 30% of the mean value measured in the initial calibration. If a linear regression calibration is being used, the measured amount for each analyte from the calibration verification test must be within 30% of the true value. If these conditions do not exist, remedial action should be taken which may require recalibration. For those analytes that failed the calibration verification, results from field samples analyzed since the last passing calibration should be considered suspect. Reanalyze sample extracts for these analytes after acceptable calibration is restored.

Note: It is suggested that a calibration verification standard of one multi-component analyte (an Aroclor or toxaphene) also be analyzed each work shift. By selecting a different multi-component analyte for this calibration verification each work shift, continuing calibration data can be obtained for all of these analytes over the course of several days.

10.8 The following are suggested remedial actions which may improve method performance:

10.8.1 Check and adjust GC operating conditions and temperature programming parameters.

10.8.2 Clean or replace the splitless injector liner. Silanize a cleaned or new liner.

10.8.3 Break off a short portion of the GC column from the end near the injector, or replace GC column. Breaking off a portion of the column will somewhat shorten the analyte retention times.

10.8.4 Prepare fresh calibration solutions and repeat the initial calibrations.

10.8.5 Replace any components in the GC that permit analytes to come in contact with hot metal surfaces.

11.0 PROCEDURE

11.1 Disk Extraction

11.1.1 This procedure may be carried out in the manual mode or in the automatic mode using a robotic or automatic sample preparation device. If an automatic system is used to prepare samples, follow the manufacturer's instructions, but follow this procedure. If the manual mode is used, the setup of the extraction apparatus described in EPA Method 525.2[5] may be used. This procedure was developed using the standard 47 mm diameter disks. Larger disks (i.e., 90 mm) may be used if special matrix problems are encountered. If larger disks are used, the washing solvent volume is 15 mL and the elution solvent volumes are two 15 mL aliquots.

11.1.2 Insert the disk into the filter apparatus or sample preparation unit. Wash the disk with 5 mL of a 1:1 mixture of ethyl acetate (EtAC) and methylene chloride ($MeCl_2$) by adding the solvent to the disk, then drawing it through very slowly to ensure adequate contact time between solvent and disk. Soaking the disk may not be desirable when disks other than Teflon are used.

11.1.3 Add 5 mL methanol to the disk and draw some of it through slowly. A layer of methanol must be left on the surface of the disk which must not be allowed to go dry from this point until the end of the sample extraction. **This is critical for uniform flow and good analyte recoveries.**

11.1.4 Rinse the disk with 5 mL reagent water by adding the water to the disk and drawing most through, again leaving a layer on the surface of the disk.

11.1.5 Add 5 mL methanol to the sample and mix well. Mark the water meniscus on the side of the sample bottle for later determination of sample volume.

11.1.6 Add 50 µL of the surrogate compound solution (Section 7.15) and shake well.

11.1.7 Draw the sample through the disk while maintaining sufficient vacuum. One L of drinking water may pass through the disk in as little as five minutes without reducing analyte recoveries. Drain the entire sample from the container through the disk. Determine the original sample volume by refilling the sample bottle to the mark with tap water and transferring the water to a 1000 mL graduated cylinder. Measure to the nearest 5 mL.

11.1.8 Dry the disk by drawing air or nitrogen through the disk for about 10 minutes.

11.1.9 Remove the filtration glassware, but do not disassemble the reservoir and fritted base. Insert a collection tube into the vacuum manifold. If a suction flask is being used, empty the water from the flask and insert a suitable collection tube to contain the eluate. The only constraint on the collection tube is that it fit around the drip tip of the fritted base. Reassemble the apparatus.

11.1.10 Rinse the inside walls of the sample bottle with 5 mL EtAC then transfer the solvent to the disk using a syringe or disposable pipet. Rinse the inside walls of the glass filtration reservoir with this EtAC. Draw the solvent through the disk very slowly to allow adequate contact time between disk and solvent for good analyte recoveries.

11.1.11 Repeat the above step (Section 11.10) with 5 mL $MeCl_2$.

11.1.12 Using the syringe or disposable pipet, rinse the filtration reservoir with two 3 mL portions of 1:1 EtAc:$MeCl_2$. Pour all combined eluates through the drying tube containing about 5-7 g of anhydrous sodium sulfate. Rinse the drying tube and the sodium

sulfate with two 3 mL portions of 1:1 EtAc/$MeCl_2$. Collect all eluate and washings in a concentrator tube.

11.1.13 Concentrate the extract to approximately 0.8 mL under a gentle stream of nitrogen while warming gently in a water bath or heating block. Rinse the inside walls of the concentrator tube two or three times with EtAC during concentration. Fortify the extract with 50 µL of the IS fortifying solution (Section 7.14). Adjust the extract volume to 1.0 mL with EtAc.

11.1.14 Inject a 1-2 µL aliquot into the gas chromatograph using the GC conditions used for initial calibration (Section 10.2). Table 1 lists retention times for method analytes using these conditions.

11.1.15 Identify a method analyte in the sample extract by comparing its gas chromatographic retention time to the retention time of the known analyte in a reference standard chromatogram, a calibration standard, or a laboratory fortified blank. If the retention time of the sample peak is within the pre-defined retention time window, identification is considered positive. The width of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards during the course of a work shift. It is suggested that three times the standard deviation of the retention times obtained when the system is calibrated be used to calculate the window. The experience of the analyst should be an important factor in the interpretation of a gas chromatogram. Confirmation may be performed by analysis on a second column, or if concentrations are sufficient, by GC/MS.

Note: Identify multi-component analytes by comparison of the sample chromatogram to the corresponding calibration standard chromatograms of toxaphene and the Aroclors. Identification of multi-component analytes is made by pattern recognition, in which the experience of the analyst is an important factor. Figures 1-8 illustrate patterns that can be expected from these analytes at low concentrations. The peaks indicated on the chromatograms are those that were used for quantitation. Other peaks may be selected at the discretion of the analyst.

11.2 Cartridge Extraction

11.2.1 This procedure may be carried out in the manual mode or in the automatic mode using a robotic or automatic sample preparation device. If an automatic system is used to prepare samples, follow the manufacturer's instructions, but follow this procedure. If the manual mode is used, the setup of the extraction apparatus described in EPA Method 525.2[5] may be used.

11.2.2 Elute each cartridge with a 5 mL aliquot of ethyl acetate followed by a 5 mL aliquot of methylene chloride. Let the cartridge drain dry after each flush. Then elute the cartridge with a 10 mL aliquot of methanol, but DO NOT allow the methanol to elute below the top of the cartridge packing. Add 10 mL of reagent water to the cartridge and elute, but before the reagent water level drops below the top edge of the packing, begin adding sample to the solvent reservoir.

11.2.3 Pour the water sample into the 2 L separatory funnel with the stopcock closed, add 5 mL methanol and the surrogate standard, and mix well. If a vacuum manifold is used instead of the separatory funnel, the sample may be transferred directly to the cartridge after the methanol and surrogate standard are added to the sample.

11.2.4 Drain the sample into the cartridge being careful not to overflow the cartridge. Maintain the packing material in the cartridge immersed in water at all times. After all the sample has passed through the LSE cartridge, draw air or nitrogen through the cartridge for 10 minutes.

11.2.5 If the setup in Method 525.2[5] is being used, transfer the 125 mL solvent reservoir and LSE cartridge to the elution apparatus. The same reservoir is used for both apparatus. Rinse the inside of the separatory funnel and the sample jar with 5 mL ethyl acetate and elute the cartridge with this rinse into the collection tube. Wash the inside of the separatory funnel and the sample jar with 5 mL methylene chloride and elute the cartridge, collecting the rinse in the same collection tube. Small amounts of residual water from the sample container and the LSE cartridge may form am immiscible layer with the eluate. Pass the eluate through the drying column which is packed with approximately 5-7 g of anhydrous sodium sulfate and collect in a second tube. Wash the sodium sulfate with at least 2 mL methylene chloride and collect in the same tube. Proceed according to steps in Sections 11.1.13 through 11.1.15 above.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calculate the concentration (C) of the analyte in the sample using the response factor (RF) determined in Section 10.5 and the equation below.

$$C\ (\mu g/L) = \frac{(A_s)\ (I_s)}{(A_{is})\ (RF)\ (V_o)}$$

where: A_S = peak area for the analyte to be measured
A_{IS} = peak area for the internal standard
I_S = amount of internal standard added (µg)
V_o = volume of water extracted (L)

If a linear regression calibration is used, use the regression equation to calculate the amount of analyte in the sample. All samples containing analytes outside the calibration range must be diluted and reanalyzed. When diluting, add additional internal standard to maintain its concentration at 0.5 µg/mL in the diluted extract.

12.2 To quantitate multi-component analytes, one of the following methods should be used.

Option 1 - Calculate an average response factor or linear regression equation for each multi-component analyte using the combined area of all the component peaks in each of the calibration standard chromatograms.

Option 2 - Calculate an average response factor or linear regression equation for each multi-component analyte using the combined areas of three to six of the most intense and reproducible peaks in each of the calibration standard chromatograms.

When quantifying multi-component analytes in samples, the analyst should use caution to include only those peaks from the sample that are attributable to the multi-component analyte. Option 1 should not be used if there are significant interference peaks within the Aroclor or toxaphene pattern.

13.0 METHOD PERFORMANCE

13.1 Method performance data was obtained using the GC column and conditions described in Sections 6.7 and 10.2. Retention times are listed in Table 1. All data presented here were obtained with the liquid-solid extraction disk option. Previous method development research has shown no significant performance differences between cartridges and disks. Method 525.2 shows comparative recovery data for Method 508.1 analytes using both cartridges and disks.

13.2 Method detection limits (MDL) for all method analytes (except Aroclors and toxaphene) were determined by analyzing seven reagent water samples which were fortified with the analytes at a concentration of 0.01 µg/L. The mean and standard deviation were calculated for each analyte. The MDL was calculated by multiplying the standard deviation by the students-t value for n-1 and a 99% confidence interval[1]. The students-t value for seven replicates (n-1=6) is 3.143. The mean recoveries and the standard deviations along with the MDLs are listed in Table 3. Aroclor and toxaphene data in Table 3 were calculated using Option 2 in Section 12.2.

13.3 Method accuracy and precision were determined by analyzing two sets of eight reagent water samples fortified with method analytes (except the multi-component analytes) at approximately five and 10 times the average MDL. The fortification concentrations for these samples were calculated by averaging the analyte MDLs and multiplying that average by five and 10. Thus the concentrations used were 0.03 µg/L and 0.048 µg/L. Results of these analyses

are listed in Tables 4 and 5. An additional set of samples was analyzed at approximately 20 times the average MDL (0.096µg/L). This set of samples was extracted from an artificial matrix containing 1 mg/L fulvic acid. The fulvic acid served to mimic the naturally occurring organic material found in many water sources. The results of these analyses are listed in Table 6.

13.4 Atrazine, hexachlorocyclopentadiene, and metribuzin appear to be problem analytes. Atrazine displays low peak response when compared to most of the other method analytes, and requires manual peak area integration even at the 0.048 µg/L level. Hexachlorocyclopentadiene, while displaying relatively high peak response, showed poor recovery. The resulting mean recoveries were 50.8%, 52.6%, and 21.7%, respectively for the three levels. It is suspected that the higher volatility of hexachlorocyclopentadiene causes the problem. Very careful, very slow nitrogen blowdown may produce higher recoveries of this compound[5]. It is suspected that Metribuzin was recovered poorly due to breakthrough on C-18 media[5].

14.0 POLLUTION PREVENTION

14.1 This method utilizes liquid-solid extraction (LSE) technology to remove the analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes. This eliminates the potential hazards to both the analyst and the environment that are present when large volumes of solvents are used in conventional liquid-liquid extractions.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less Is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.0 WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", also available from the American Chemical Society at the address in Section 14.2.

16.0 REFERENCES

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2. "Carcinogens - Working With Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

3. "OSHA Safety and Health Standards, General Industry", (29CFR1910), Occupational Safety and Health Administration, OSHA 2206 (Revised January 1976).

4. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

5. Munch, J. W. "Method 525.2-Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Chromatography/Mass Spectrometry" in Methods for the Determination of Organic Compounds in Drinking Water; Supplement 3 (1995). USEPA, National Exposure Research Laboratory, Cincinnati, Ohio 45268.

7.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES USING THE GC COLUMN IN SECTION 6.7 AND THE GC CONDITIONS IN SECTION 10.2

Analyte	Retention Time (Min)
Hexachlorocyclopentadiene	9.64
Etridiazole	11.41
Chloroneb	12.39
Propachlor	14.69
Trifluralin	16.29
HCH-alpha	17.01
Hexachlorobenzene	17.44
Simazine	17.86
Atrazine	18.23
HCH-beta	18.33
HCH-gamma	18.71
HCH-delta	19.21
Chlorthalonil	20.27
Metribuzin	21.88
Heptachlor	22.78
Alachlor	22.86
Aldrin	24.81
Metolachlor	25.02
Cyanazine	25.21
DCPA	26.49
Heptachlor Epoxide	27.20
Chlordane-gamma	28.65
Endosulfan I	29.36
Chlordane-alpha	29.58
Dieldrin	30.95
4,4'-DDE	31.97
Endrin	32.24
Butachlor[a]	32.65
Endosulfan II	32.81
Chlorbenzilate	32.98
4,4'-DDD	33.49
Endrin Aldehyde	33.96
Endosulfan Sulfate	35.43
4,4'-DDT	35.80
Methoxychlor	39.38
cis-Permethrin	44.98
trans-Permethrin	45.42
Toxaphene[a]	33.53, 36.48, 39.12[b]
Aroclor 1016[a]	18.93, 22.55, 24.83[b]
Aroclor 1221[a]	13.67, 18.02, 19.93[b]
Aroclor 1232[a]	18.93, 22.55, 24.83[b]
Aroclor 1242[a]	35.65, 41.38, 43.08[b]

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES USING THE GC COLUMN IN SECTION 6.7 AND THE GC CONDITIONS IN SECTION 10.2

Analyte	Retention Time (Min)
Aroclor 1248[a]	24.15, 24.83, 31.40[b]
Aroclor 1254[a]	31.80, 34.12, 38.88[b]
Aroclor 1260[a]	35.65, 41.38, 43.08[b]
Pentachlorointrobenzene (IS):	19.02 minutes
4,4-Dibromobiphenyl (SUR):	25.64 minutes

[a]Retention time was determined with the following GC conditions:

Injector temperature -- 250°C
Detector temperature -- 320°C
Injection volume -- 2 µL, splitless for 45 seconds
Temperature program -- Inject at 60°C and hold one minute
-- program at 20°C/min. to 160°C hold three minutes
-- program at 3°C/min. to 275°C with no hold
-- program at 20°C/min. to 310°C with no hold

The IS retention time using these conditions is 21.15 minutes. The SUR retention time using these conditions is 28.18 minutes.

[b]The retention times listed do not reflect the total number of peaks characteristic of the multi-component analyte. Listed peaks indicate those chosen for quantitation. Quantitative data is in Table 3.

TABLE 2. LABORATORY PERFORMANCE CHECK SOLUTION

Test	Analyte	Conc. µg/mL	Requirements
Sensitivity	Chlorpyrifos	0.0020	Detection of analyte; S/N >3
Chromatographic performance	DCPA	0.0500	PGF between 0.80 and 1.15[a]
Column performance	Chlorothalonil	0.0500	
	HCH-delta	0.0400	Resolution >0.15[b]

[a]PGF -- peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where: W(1/2) = the peak width at half height in seconds
W(1/10) = the peak width in seconds at 10th height

[b]Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where: t = the difference in elution times between the two peaks
W = the average peak width, at the baseline, of the two peaks

TABLE 3. MDL STATISTICAL RESULTS FOR SEVEN REPLICATES IN REAGENT WATER

Analyte	Fortified Conc. (µg/L)	Mean µg/L	% REC	Std. Dev. µg/L	% RSD	Calc. MDL
Alachlor	0.01	0.008	80	0.0030	37.5	0.009
Aldrin	0.01	0.008	80	0.0030	37.5	0.009
Atrazine	0.01	0.014	140	0.0010	7.14	0.003
Butachlor	0.5	0.43	86	0.023	5.5	0.07
Chlorbenzilate	0.01	0.008	80	0.0007	8.75	0.002
Chlordane-alpha	0.01	0.007	70	0.0012	17.1	0.004
Chlordane-gamma	0.01	0.006	60	0.003	50.0	0.001
Chloroneb	0.01	0.012	120	0.0019	15.8	0.006
Chlorothalonil	0.01	0.007	70	0.0007	10.0	0.002
Cyanazine	0.01	0.010	100	0.0022	22.0	0.007
DCPA	0.01	0.010	100	0.0028	28.0	0.009
4,4'-DDD	0.01	0.009	90	0.0008	8.89	0.003
4,4'-DDE	0.01	0.008	80	0.0009	11.2	0.003
4,4'-DDT	0.01	0.012	120	0.0011	9.17	0.004
4,4'-Dibromobiphenyl (Surrogate)	0.01	0.440	88.0	0.027	6.14	
Dieldrin	0.01	0.007	70	0.0009	12.9	0.003
Endosulfan I	0.01	0.007	70	0.0019	27.1	0.006
Endosulfan II	0.01	0.007	70	0.0003	42.9	0.001
Endosulfan Sulfate	0.01	0.007	70	0.0010	14.3	0.003
Endrin	0.01	0.015	150	0.0023	15.3	0.007
Endrin Aldehyde	0.01	0.008	80	0.0012	15.0	0.004
Etridiazole	0.01	0.011	110	0.0045	40.9	0.014
HCH-alpha	0.01	0.007	70	0.0003	42.8	0.001
HCH-beta	0.01	0.009	90	0.0029	32.2	0.009
HCH-delta	0.01	0.008	80	0.0014	17.5	0.004
HCH-gamma	0.01	0.007	70	0.0020	28.6	0.006
Heptachlor	0.01	0.009	90	0.0016	17.8	0.005
Heptachlor Epoxide	0.01	0.006	60	0.0003	5.0	0.001

TABLE 3. MDL STATISTICAL RESULTS FOR SEVEN REPLICATES IN REAGENT WATER

Analyte	Fortified Conc. (µg/L)	Mean µg/L	% REC	Std. Dev. µg/L	% RSD	Calc. MDL
Hexachlorobenzene	0.01	0.010	100	0.0004	4.0	0.001
Hexachlorocyclopentadie	0.01	0.004	40	0.0013	32.5	0.004
ne	0.01	0.006	60	0.0009	15.0	0.003
Methoxychlor	0.01	0.013	130	0.0049	37.7	0.015
Metolochlor	0.01	0.009	90	0.0028	31.1	0.009
Metribuzin	0.01	0.007	70	0.0030	42.9	0.009
cis-Permethrin	0.01	0.011	110	0.0022	20.0	0.007
trans-Permethrin	0.01	0.008	80	0.0027	33.8	0.008
Propachlor	0.01	0.009	90	0.0025	27.8	0.008
Simazine	0.01	0.006	60	0.0003	5.0	0.001
Trifluralin	1.0	0.81	81	0.041	5.1	0.13
Toxaphene	0.2	0.16	82	0.009	5.7	0.029
Aroclor 1016	0.2	0.17	85	0.012	6.8	0.037
Aroclor 1221	0.2	0.18	90	0.010	5.8	0.033
Aroclor 1232	0.2	0.20	100	0.014	6.9	0.043
Aroclor 1242	0.2	0.18	88	0.014	8.0	0.044
Aroclor 1248	0.2	0.16	82	0.012	7.0	0.036
Aroclor 1254	0.2	0.16	82	0.004	2.4	0.012
Aroclor 1260						

TABLE 4. EIGHT REPLICATES IN REAGENT WATER ANALYTE CONCENTRATIONS 0.03 µg/L

Analyte	Mean µg/L	% REC	Std. Dev. µg/L	% RSD
Alachlor	0.031	103	0.005	16.1
Aldrin	0.025	81.9	0.005	20.2
Atrazine	0.021	70.4	0.002	11.4
Chlorbenzilate	0.024	81.5	0.006	23.1
Chlordane-alpha	0.025	83.4	0.005	18.8
Chlordane-gamma	0.025	82.3	0.007	28.8
Chloroneb	0.026	88.3	0.006	24.3
Chlorothalonil	0.032	106	0.006	19.5
Cyanazine	0.029	95.2	0.004	12.8
DCPA	0.026	85.2	0.004	14.1
4,4'-DDD	0.027	89.1	0.004	16.4
4,4'-DDE	0.023	78.0	0.005	20.0
4,4'-DDT	0.028	93.8	0.005	17.4
4,4'-Dibromobiphenyl (Surrogate)	0.466	93.2	0.032	6.97
Dieldrin	0.027	91.5	0.004	15.8
Endosulfan I	0.028	92.6	0.005	17.8
Endosulfan II	0.026	87.9	0.005	18.6
Endosulfan Sulfate	0.032	106	0.004	11.5
Endrin	0.029	96.5	0.004	13.9
Endrin Aldehyde	0.030	98.8	0.004	13.7
Etridiazole	0.028	95.3	0.008	27.1
HCH-alpha	0.026	88.4	0.007	24.9
HCH-beta	0.028	95.0	0.004	13.9
HCH-delta	0.034	114	0.004	11.1
HCH-gamma	0.033	110	0.004	11.3
Heptachlor Epoxide	0.027	90.6	0.005	17.4
Heptachlor	0.026	85.6	0.006	22.1
Hexachlorobenzene	0.032	107	0.006	20
Hexachlorocyclopentadiene	0.015	50.8	0.007	44.8
Methoxychlor	0.024	92.7	0.003	10.7

TABLE 4. EIGHT REPLICATES IN REAGENT WATER ANALYTE CONCENTRATIONS 0.03 µg/L

Analyte	Mean µg/L	% REC	Std. Dev. µg/L	% RSD
Metolochlor	0.034	113	0.006	18.2
Metribuzin	0.012	39.5	0.002	15.8
cis-Permethrin	0.033	81.2	0.004	17.8
trans-Permethrin	0.033	111	0.004	13.4
Propachlor	0.028	93.0	0.005	17.4
Simazine	0.020	68.4	0.002	11.5
Trifluralin	0.024	80.5	0.004	18.0

TABLE 5. EIGHT REPLICATES IN REAGENT WATER ANALYTE CONCENTRATIONS 0.048 µg/L

Analyte	Mean µg/L	% REC	Std. Dev. µg/L	% RSD
Alachlor	0.044	91.1	0.002	3.70
Aldrin	0.034	69.8	0.004	11.5
Atrazine	0.036	74.9	0.002	6.60
Chlorbenzilate	0.051	107	0.004	8.40
Chlordane-alpha	0.047	97.7	0.002	4.80
Chlordane-gamma	0.044	92.6	0.003	5.40
Chloroneb	0.055	155	0.004	6.70
Chlorothalonil	0.059	123	0.004	6.00
Cyanazine	0.045	94.5	0.000	3.60
DCPA	0.042	88.5	0.001	2.90
4,4'-DDD	0.052	108	0.003	5.80
4,4'-DDE	0.046	94.8	0.004	8.30
4,4'-DDT	0.056	116	0.004	7.20
4,4'-Dibromobiphenyl (Surrogate)	0.474	94.7	0.032	6.79
Dieldrin	0.048	101	0.002	4.00
Endosulfan I	0.049	102	0.004	7.50
Endosulfan II	0.051	106	0.004	7.80
Endosulfan Sulfate	0.056	117	0.005	9.30
Endrin	0.053	111	0.004	8.20
Endrin Aldehyde	0.047	98.5	0.005	10.7
Etridiazole	0.051	107	0.003	6.46
HCH-alpha	0.052	109	0.005	10.0
HCH-beta	0.044	90.7	0.002	3.60
HCH-delta	0.058	120	0.005	8.80
HCH-gamma	0.053	111	0.007	13.3
Heptachlor Epoxide	0.040	82.6	0.004	9.80
Heptachlor	0.048	100	0.003	6.60
Hexachlorobenzene	0.044	90.7	0.005	11.8
Hexachlorocyclopentadiene	0.025	52.6	0.005	19.1
Methoxychlor	0.052	109	0.005	9.50

TABLE 5. EIGHT REPLICATES IN REAGENT WATER ANALYTE CONCENTRATIONS 0.048 µg/L

Analyte	Mean µg/L	% REC	Std. Dev. µg/L	% RSD
Metolochlor	0.060	126	0.002	3.60
Metribuzin	0.033	67.7	0.006	18.1
cis-Permethrin	0.049	102	0.009	18.9
trans-Permethrin	0.056	117	0.007	11.7
Propachlor	0.049	102	0.002	3.33
Simazine	0.039	82.2	0.003	6.69
Trifluralin	0.0043	89.9	0.002	4.71

TABLE 6. EIGHT REPLICATES IN REAGENT WATER ANALYTE CONCENTRATIONS 0.096 µg/L

Analyte	Mean µg/L	% REC	Std. Dev. µg/L	% RSD
Alachlor	0.093	96.6	0.012	13.2
Aldrin	0.071	73.6	0.006	8.90
Atrazine	0.069	71.9	0.005	9.30
Chlorbenzilate	0.086	89.9	0.009	10.4
Chlordane-alpha	0.088	91.9	0.004	4.90
Chlordane-gamma	0.072	74.5	0.006	7.50
Chloroneb	0.082	85.4	0.008	9.70
Chlorothalonil	0.079	82.5	0.007	9.20
Cyanazine	0.085	89.0	0.011	12.5
DCPA	0.075	78.6	0.004	4.90
4,4'-DDD	0.091	95.0	0.009	10.3
4,4'-DDE	0.095	96.5	0.005	5.00
4,4'-DDT	0.082	85.0	0.008	9.50
4,4'-Dibromobiphenyl (Surrogate)	0.046	91.2	0.030	6.64
Dieldrin	0.089	92.3	0.009	9.90
Endosulfan I	0.088	91.8	0.008	8.60
Endosulfan II	0.088	92.0	0.006	7.40
Endosulfan Sulfate	0.094	98.3	0.007	7.30
Endrin	0.098	102	0.010	10.3
Endrin Aldehyde	0.067	69.8	0.003	5.20
Etridiazole	0.095	98.9	0.009	9.80
HCH-alpha	0.092	95.4	0.006	6.70
HCH-beta	0.088	91.2	0.007	7.80
HCH-delta	0.094	97.6	0.006	5.90
HCH-gamma	0.102	106	0.007	7.10
Heptachlor Epoxide	0.068	71.4	0.007	9.80
Heptachlor	0.088	91.6	0.007	7.80
Hexachlorobenzene	0.063	65.3	0.006	8.90
Hexachlorocyclopentadiene	0.021	21.7	0.008	40.1
Methoxychlor	0.092	96.1	0.010	12.0

TABLE 6. EIGHT REPLICATES IN REAGENT WATER ANALYTE CONCENTRATIONS 0.096 µg/L

Analyte	Mean µg/L	% REC	Std. Dev. µg/L	% RSD
Metolochlor	0.110	115	0.012	11.1
Metribuzin	0.039	40.7	0.004	9.50
cis-Permethrin	0.078	81.3	0.009	11.1
trans-Permethrin	0.082	85.2	0.008	11.1
Propachlor	0.098	102	0.017	17.4
Simazine	0.076	78.8	0.005	6.10
Trifluralin	0.074	77.4	0.010	13.3

Figure 1. Aroclor 1016. Chromatogram of LFB at 0.2 ug/L

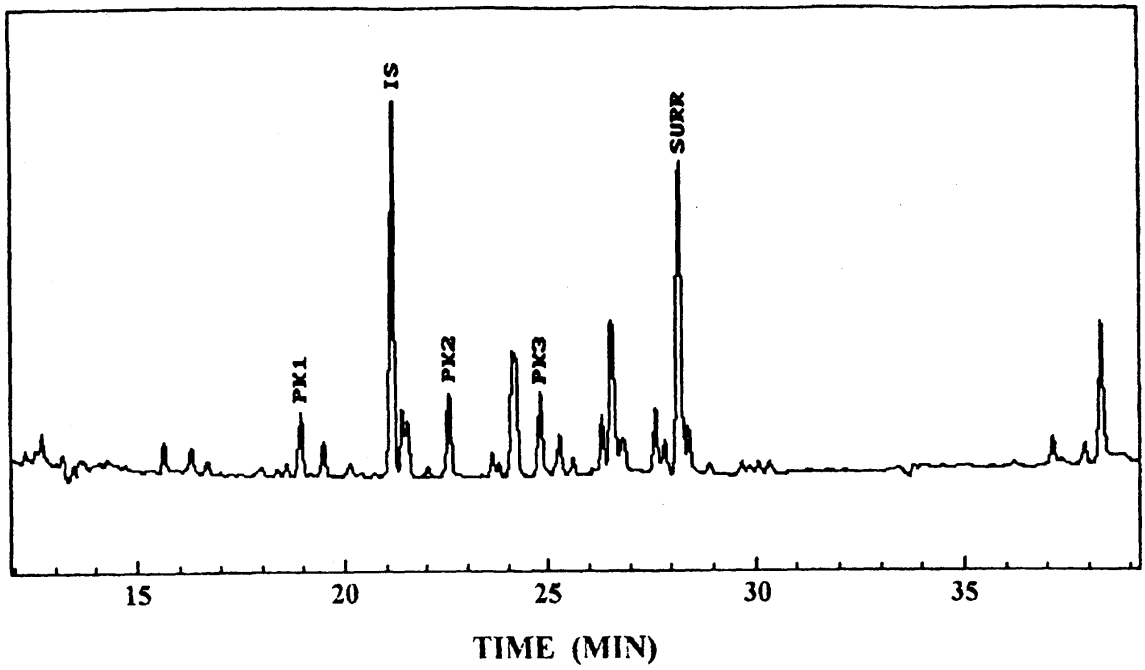

Figure 2. Aroclor 1221. Chromatogram of LFB at 0.2 ug/L

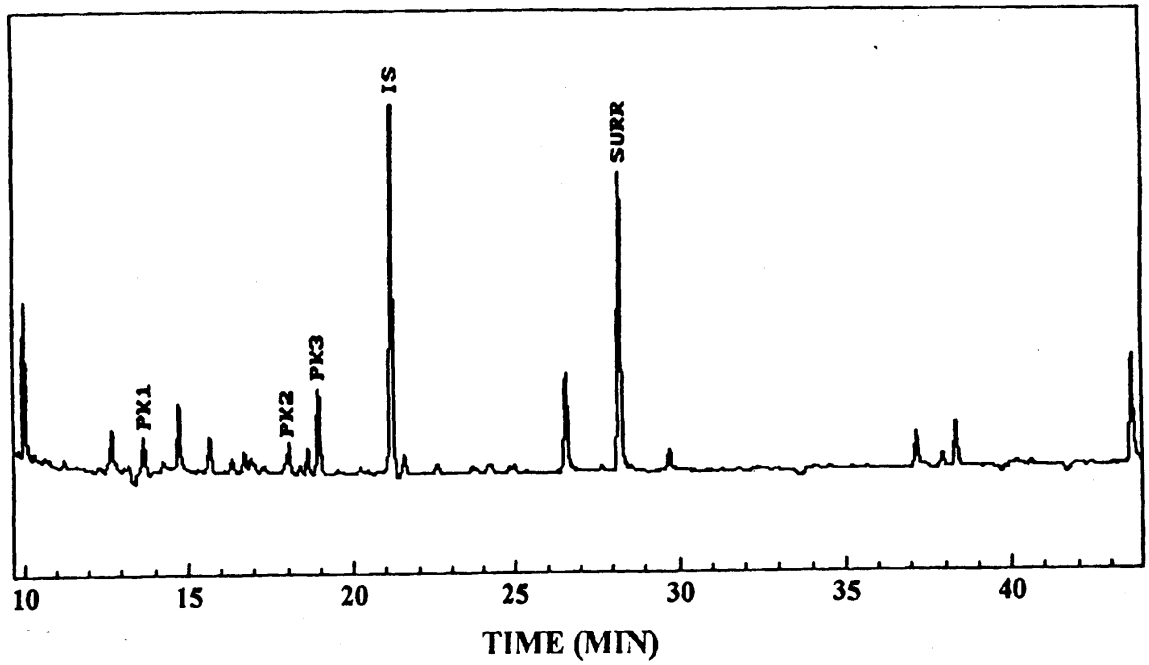

Figure 3. Aroclor 1232. Chromatogram of LFB at 0.2ug/L

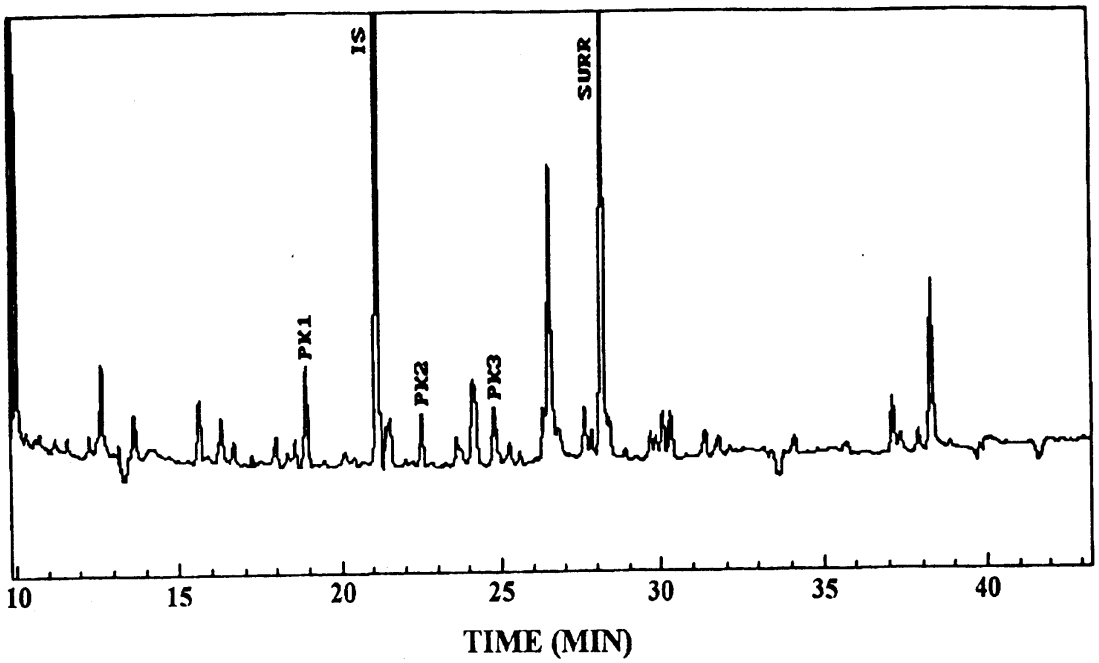

Figure 4. Aroclor 1242. Chromatogram of LFB at 0.2ug/L

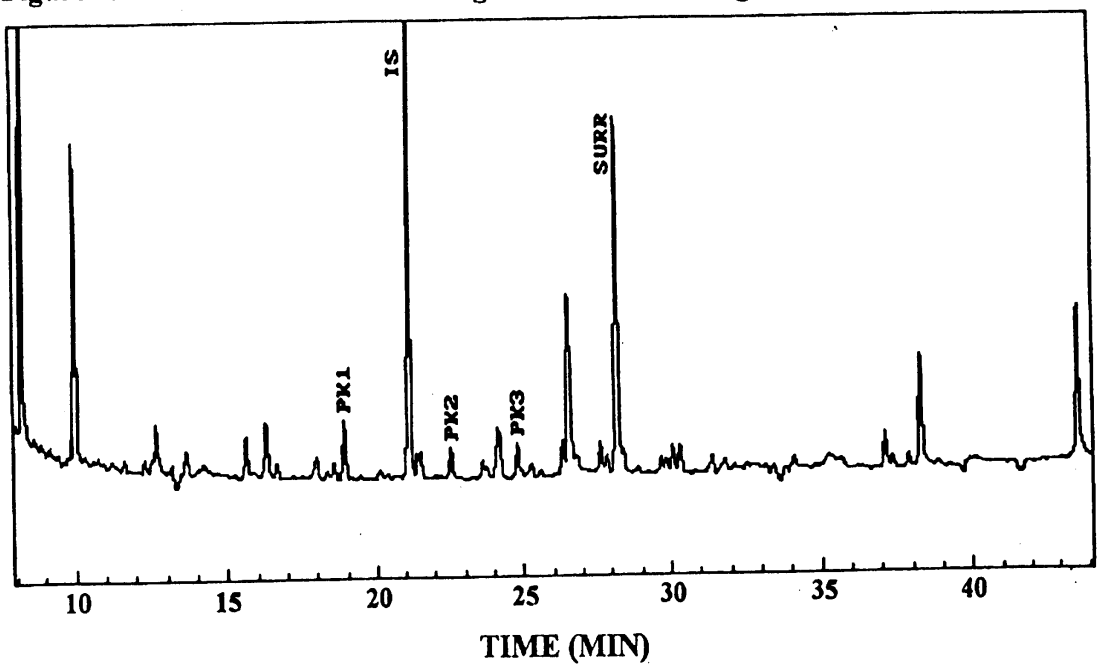

Figure 5. Aroclor 1248. Chromatogram of LFB at 0.2ug/L

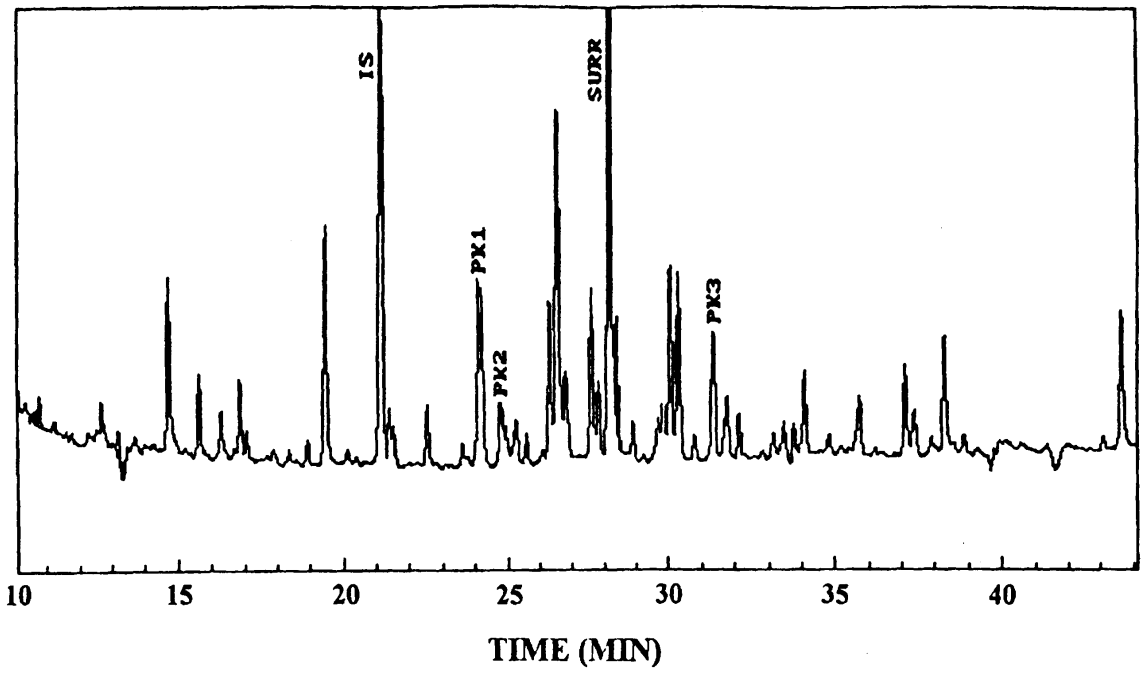

Figure 6. Aroclor 1254. Chromatogram of LFB at 0.2ug/L

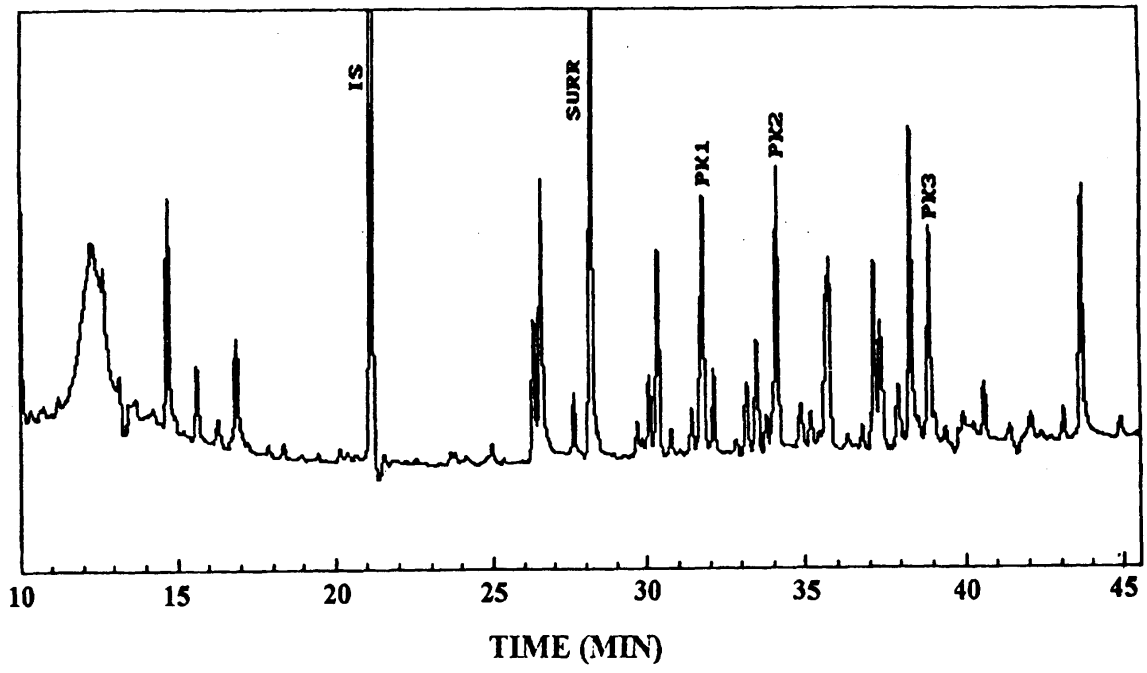

Figure 7. Aroclor 1260. Chromatogram of LFB at 0.2ug/L

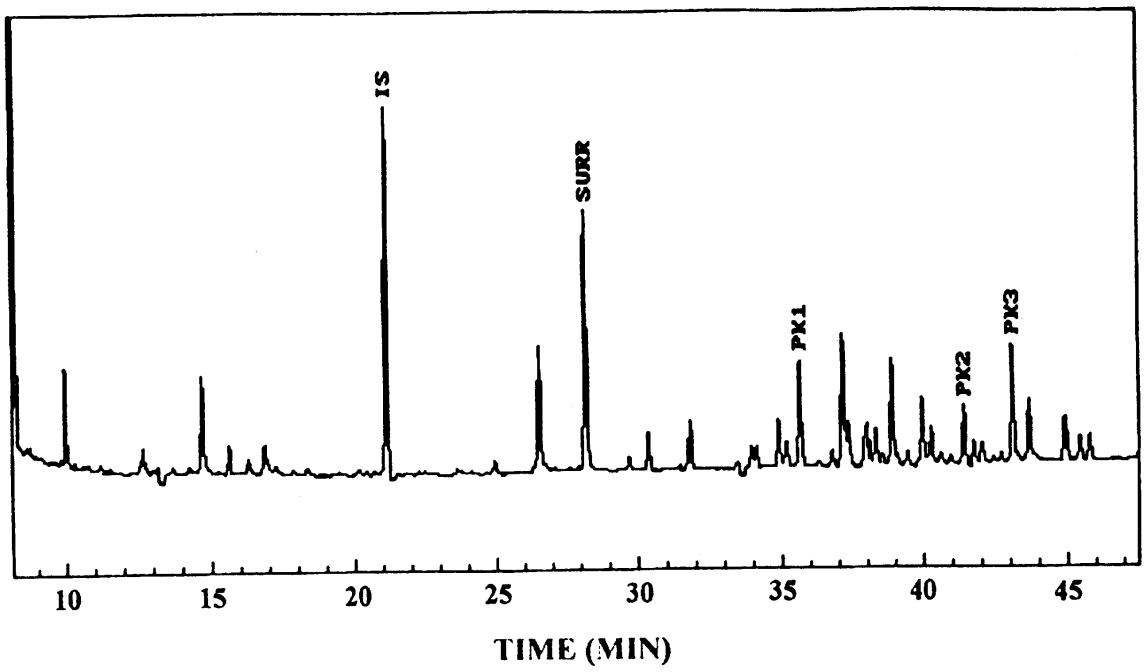

Figure 8. Toxaphene. Chromatogram of LFB at 0.2ug/L