METHOD 508. DETERMINATION OF CHLORINATED PESTICIDES IN WATER BY GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

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METHOD 508

DETERMINATION OF CHLORINATED PESTICIDES IN WATER BY GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

1. SCOPE AND APPLICATION

1.1 This is a gas chromatographic (GC) method applicable to the determination of certain chlorinated pesticides in groundwater and finished drinking water. The following compounds can be determined using this method:

Analyte	Chemical Abstract Services Registry Number
Aldrin	309-00-2
Atrazine	5103-71-9
Chlordane-alpha	5103-74-2
Chlordane-gamma	2675-77-6
Chlorneb	501-15-6
Chlorobenzilate[a]	2921-88-2
Chlorothalonil	1861-32-1
DCPA	72-54-8
4,4'-DDD	72-55-9
4,4'-DDE	50-29-3
4,4'-DDT	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[a]	319-86-8
HCH-gamma (Lindane)	58-89-9
Heptachlor	76-44-8
Heptachlor Epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Methoxychlor	72-43-5
cis-Permethrin	52645-53-1
trans-Permethrin	52645-53-1
Propachlor	1918-16-7
Trifuluralin	1582-09-8
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

Toxaphene*	8001-35-2
Chlordane*	57-74-9

* The extraction conditions of this method are comparable to USEPA Method 608, which does measure the multicomponent constituents: commercial polychlorinated biphenyl (PCB) mixtures (Aroclors), toxaphene, and chlordane. The extract derived from this procedure may be analyzed for these constituents by using the GC conditions prescribed in either Method 608 (packed column) or Methods 505, 508.1 or 525.2 (capillary column)(1). The columns used in this method may well be adequate, however, no data were collected for these constituents during methods development.

(a) Chlorbenzilate and HCH-delta are only qualitatively identified and are not quantitated because control over precision has not been accomplished.

1.2 This method has been validated in a single laboratory and estimated detection limits (EDLs) and method detection limits (MDLs) have been determined for the analytes above (Sect. 13). Observed detection limits may vary between waters, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.

1.3 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 Sect. 9.3.

1.4 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 exist (Sect. 11.5).

1.5 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications must be confirmed by at least one additional qualitative technique.

2. SUMMARY OF METHOD

2.1 A measured volume of sample of approximately 1 L is solvent extracted with methylene chloride by shaking in a separatory funnel or mechanical tumbling in a bottle. The methylene chloride extract is isolated, dried and concentrated to a volume of 5 mL after solvent substitution with methyl tert-butyl ether (MTBE). Chroma-tographic conditions are described which permit the separation and measurement of the analytes in the extract by capillary column GC with an electron capture detector (ECD).

3. DEFINITIONS

3.1 INTERNAL STANDARD -- A pure analyte(s) added to a 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. The internal standard must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE -- 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 and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 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.

3.4 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.

3.5 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.

3.6 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.

3.7 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.

3.8 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.

3.9 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.

3.10 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.

3.11 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.

3.12 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.

3.13 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. 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 Sect. 9.2.

4.1.1 Glassware must be scrupulously cleaned (2). Clean all glass-ware 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 1 hour. Do not heat volumetric glassware. Thermally stable materials such as PCBs 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 added by the manufacturer are removed thus

potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed thus potentially reducing the shelf-life.

4.2 Interferences by phthalate esters can pose a major problem in pesti-cide analysis when using the electron capture detector. These compounds generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalates that are easily extracted or leached during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

4.3 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 MTBE can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MTBE should be made to ensure that accurate values are obtained for the next sample.

4.4 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 interferant for another analyte of interest. The extent of matrix interferences will vary considerably from source to source, depending upon the water sampled. Analyte identifications should be confirmed (Sect. 11.5).

4.5 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. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. Accordingly, exposure to these chemicals must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (3-5) for the information of the analyst.

5.2 WARNING: When a solvent is purified stabilizers added by the manufacturer are removed thus potentially making the solvent hazardous.

6. EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLE BOTTLE -- Borosilicate, 1-L volume with graduations (Wheaton Media/Lab bottle 219820 or equivalent), fitted with screw caps lined with TFE-fluorocarbon. Protect samples from light. Amber bottles may be used. The container must be washed and dried as described in Sect. 4.1.1 before use to minimize contamination. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

6.2 GLASSWARE

6.2.1 Separatory funnel -- 2000-mL, with TFE-fluorocarbon stopcock, ground glass or TFE-fluorocarbon stopper.

6.2.2 Tumbler bottle 1.7-L (Wheaton Roller Culture Vessel or equivalent), with TFE-fluorocarbon lined screw cap. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

6.2.3 Flask, Erlenmeyer -- 500-mL.

6.2.4 Concentrator tube, Kuderna-Danish (K-D) 10- or 25-mL, graduated (Kontes K-570050-1025 or K-570050-2525 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stoppers are used to prevent evaporation of extracts.

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

6.2.6 Snyder column, K-D three-ball macro (Kontes K-503000-0121 or equivalent).

6.2.7 Snyder column, K-D two-ball micro (Kontes K-569001-0219 or equivalent).

6.2.8 Vials -- Glass, 5- to 10-mL capacity with TFE-fluorocarbon lined screw cap.

6.3 SEPARATORY FUNNEL SHAKER -- Capable of holding 2-L separatory funnels and shaking them with rocking motion to achieve thorough mixing of separatory funnel contents (available from Eberbach Co. in Ann Arbor, MI or other suppliers).

6.4 TUMBLER -- Capable of holding tumbler bottles and tumbling them end-over-end at 30 turns/min (Associated Design and Mfg. Co., Alexandria, VA or other suppliers.).

6.5 BOILING STONES CARBORUNDUM, #12 granules (Arthur H. Thomas Co. #1590-033 or equivalent). Heat at 400°C for 30 min prior to use. Cool and store in a desiccator.

6.6 WATER BATH -- Heated, capable of temperature control ($\pm$ 2°C). The bath should be used in a hood.

6.7 BALANCE -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.8 GAS CHROMATOGRAPH -- Analytical system complete with temperature programmable GC suitable for use with capillary columns and all required accessories including syringes, analytical columns, gases, 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.

6.8.1 Column 1 (Primary column) -- 30 m long x 0.25 mm I.D. DB-5 bonded fused silica column, 0.25 µm film thickness (J&W Scientific). Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60°C to 300°C at 4°C/min. Data presented in this method were obtained using this column. The injection volume was 2 µL splitless mode with a 45 sec. delay. The injector temperature was 250°C and the detector temperature was 320°C. Column performance criteria are presented in Table 4 (See Section 9.9). Alternative columns may be used in accordance with the provisions described in Sect. 9.4.

6.8.2 Column 2 (Alternative column) -- 30 m long x 0.25 mm I.D.DB-1701 bonded fused silica column, 0.25 µm film thickness (J&W Scientific). Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60°C to 300°C at 4°C/min.

6.8.3 Detector -- Electron capture. This detector has proven effective in the analysis of fortified reagent and artificial ground waters.

7. <u>REAGENTS AND STANDARDS</u> - - WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed thus potentially reducing the shelf-life.

7.1 ACETONE, methylene chloride, MTBE -- Distilled-in-glass quality or equivalent.

7.2 PHOSPHATE BUFFER, pH 7 Prepare by mixing 29.6 mL 0.1 N HCl and 50 mL 0.1 M dipotassium phosphate.

7.3 SODIUM CHLORIDE, crystal, ACS grade. Heat treat in a shallow tray at 400°C for a minimum of 4 hours to remove interfering organic substances. Store in a glass bottle (not plastic) to avoid phthalate contamination.

7.4 SODIUM SULFATE, granular, anhydrous, ACS grade. Heat treat in a shallow tray at 450°C for a minimum of 4 hours to remove interfering organic substances. Store in a glass bottle (not plastic) to avoid phthalate contamination.

7.5 SODIUM THIOSULFATE, granular, anhydrous, ACS grade.

7.6 PENTACHLORONITROBENZENE (PCNB) 98% purity, for use as internal standard.

7.7 DECACHLOROBIPHENYL (DCB) 96% purity, for use as surrogate standard (available from Chemicals Procurement Inc.).

7.8 MERCURIC CHLORIDE -- ACS grade -- for use as a bactericide (optional).

7.9 REAGENT WATER -- Reagent water is defined as water that is reasonably free of contamination that would prevent the determination of any analyte of interest. Reagent water used to generate the validation data in this method was distilled water obtained from the Magnetic Springs Water Co., Columbus, Ohio.

7.10 STOCK STANDARD SOLUTIONS (1.00 µg/µL) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

7.10.1 Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in MTBE and dilute to volume in a 10-mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.10.2 Transfer the stock standard solutions into TFE-fluoro-carbon-sealed screw cap amber vials. Store at room temper-ature and protect from light.

7.10.3 Stock standard solutions should be replaced after two months or sooner if comparison with laboratory fortified blanks, or QC samples indicate a problem.

7.11 INTERNAL STANDARD SOLUTION -- Prepare an internal standard fortifying solution by accurately weighing approximately 0.0010 g of pure PCNB. Dissolve the PCNB in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the internal standard solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 5 µL of the internal standard fortifying solution to 5 mL of sample extract results in a final internal standard concentration of 0.1 µg/mL. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem. Note that PCNB has been shown to be an effective internal standard for the method analytes, but other compounds may be used if the quality control requirements in Section 9 are met.

7.12 SURROGATE STANDARD SOLUTION -- Prepare a surrogate standard fortifying solution by accurately weighing approximately 0.0050 g of pure DCB. Dissolve the DCB in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the surrogate standard fortifying solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 50 µL of the surrogate standard fortifying solution to a 1-L sample prior to extraction results in a surrogate standard concentration in the sample of 25 µg/L and, assuming quantitative recovery of DCB, a surrogate standard concentration in the final extract of 5.0 µg/mL. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem. Note DCB has been shown to be an effective surrogate standard

for the method analytes, but other compounds may be used if the quality control requirements in Section 9 are met.

7.13 LABORATORY 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 chloropyrifos 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 MTBE. Transfer to a TFE-fluorcarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC indicates a problem.

7.14 GC DEGRADATION CHECK SOLUTION -- Prepare a solution in MTBE 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. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Grab samples must be collected in glass containers. Conventional sampling practices (6) should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION

8.2.1 If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample to the sample bottle prior to collecting the sample.

8.2.2 After adding the sample to the bottle containing sodium thiosulfate, seal the sample bottle and shake until dissolved.

8.2.3 Samples must be iced or refrigerated at 4°C from the time of collection until extraction. Preservation study results indicate that most of the target analytes present in the samples are stable for 7 days when stored under these conditions. Preservation data for the analytes chlorthalonil, alpha-HCH, delta-HCH, gamma-HCH, cis-permethrin, trans-permethrin, and trifluralin are nondefinitive, and therefore if these are analytes of interest, it is recommended that the samples be analyzed immediately. Analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

8.2.4 All performance data presented in this method are from samples preserved with mercuric chloride. No suitable preservation agent (biocide) has been found other than mercuric chloride. However, the use of mercuric chloride is not required due to its toxicity and potential harm to the environment.

8.2.5 In some circumstances where biological degradation of target pesticides might be expected, use of mercuric chloride may be appropriate to minimize the possibility of false-negative results. If mercuric chloride is to be used, add it to the sample bottle in

amounts to produce a concentration of 10 mg/L. Add 1 mL of a solution containing 10 mg/mL of mercuric chloride in reagent water to the sample bottle at the sampling site or in the laboratory before shipping to the sampling site. A major disadvantage of mercuric chloride is that it is a highly toxic chemical; mercuric chloride must be handled with caution, and samples containing mercuric chloride must be disposed of properly.

8.3 EXTRACT STORAGE

8.3.1 Sample extracts should be stored at 4°C away from light. A 14-day maximum extract storage time is recommended. However, analyte stability may be affected by the matrix; therefore, the analyst should verify appropriate extract holding times applicable to the samples under study.

9. QUALITY CONTROL

9.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank (when internal standard calibration procedures are being employed), analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks, and QC samples. An MDL for each analyte must also be determined.

9.2 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, a laboratory reagent blank (LRB) must be analyzed. If within the retention time window of any analyte of interest 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.

9.3 INITIAL DEMONSTRATION OF CAPABILITY

9.3.1 Select a representative fortified concentration (about 10 times EDL or at a concentration that represents a mid-point of the calibration range for each analyte. Prepare a primary dilution standard (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 1 mL of the concentrate to each of four to seven 1-L aliquots of reagent water, and analyze each of these LFBs according to procedures beginning in Section 11.

9.3.2 For each analyte, the recovery value for all replicates must fall in the range of R ± 30% using the value for R demonstrated for reagent water in Table 2. The precision of the measurements, calculated as relative standard deviation (RSD), must be 20% or less. For those compounds that fail these criteria, this procedure must be repeated using four fresh samples until satisfactory performance has been demonstrated.

9.3.3 For each analyte, determine the MDL. Prepare a minimum of 7 LFBs at a low concentration. Fortification concentration in Table 3 may be used as a guide, or use calibration data obtained in Section 10 to estimate a concentration for each analyte that will produce a peak with a 3-5 times signal to noise response. Extract and analyze each

replicate according to Sections 11 and 12. It is recommended that these LFBs be prepared and analyzed over a period of several days, so that day to day variations are reflected in the precision data. Calculate mean recovery and standard deviation for each analyte. Use the equation given in Table 3 to calculate the MDL.

9.3.4 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.

9.4 The analyst is permitted to modify GC columns, GC conditions, concentration techniques (i.e. evaporation techniques), internal standards or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Section 9.3.

9.5 ASSESSING SURROGATE RECOVERY

9.5.1 When surrogate recovery from a sample or method blank is <70% or >130%, check calculations to locate possible errors, fortifying solutions for degradation, contamination or other obvious abnormalities, and instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

9.5.2 If a LRB extract reanalysis fails the 70-130% recovery criterion, the problem must be identified and corrected before continuing.

9.5.3 If sample extract reanalysis meets the surrogate recovery criterion, report only data for the reanalyzed extract. If sample extract reanalysis continues to fail the surrogate recovery criterion, report all data for that sample as suspect.

9.6 ASSESSING THE INTERNAL STANDARD

9.6.1 When using the internal standard calibration procedure, the analyst must monitor the IS response (peak area or peak height) of all samples during each analysis day. The IS response for any sample chromatogram should not deviate from the daily calibration check standards IS response by more than 30%.

9.6.2 If >30% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

9.6.2.1 If the reinjected aliquot produces an acceptable internal standard response report results for that aliquot.

9.6.2.2 If a deviation of greater than 30% is obtained for the re-injected extract, analysis of the sample should be repeated beginning with Section 11, provided the sample is still available. Otherwise, report results obtained from the re-injected extract, but annotate as suspect.

9.6.3 If consecutive samples fail the IS response acceptance criterion, immediately analyze a calibration check standard.

9.6.3.1 If the check standard provides a response factor (RF) within 20% of the predicted value, then follow procedures itemized in Section 9.6.2 for each sample failing the IS response criterion.

9.6.3.2 If the check standard provides a response factor which deviates more than 20% of the predicted value, then the analyst must recalibrate, as specified in Section 10. After calibration is restored, reanalyze sample extracts that failed Sect 9.6.2 criteria.

9.7 ASSESSING LABORATORY PERFORMANCE - LABORATORY FORTIFIED BLANK

9.7.1 The laboratory must analyze at least one laboratory fortified blank (LFB) sample with every twenty samples or one per sample set (all samples extracted within a 24-h period) whichever is greater. The fortified concentration of each analyte in the LFB should be 10 times EDL or a concentration that represents a mid-point of the calibration range. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Sect. 9.7.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

Note: It is suggested that one multi-component analyte (toxaphene, chlordane or an Aroclor) 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.

9.7.2 Until sufficient data becomes available from within their own laboratory, usually a minimum of results from 20 to 30 analyses, the laboratory should assess laboratory performance against the control limits in Sect. 9.3.2 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 five to ten new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points. These calculated control limits should not exceed those established in Sect. 9.3.2.

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

9.7.4 At least quarterly, analyze a QC sample from an outside source.

9.8 ASSESSING METHOD PERFORMANCE - LABORATORY FORTIFIED SAMPLE MATRIX

9.8.1 The laboratory must add a known concentration to a minimum of 10% of the routine samples or one sample per set, whichever is greater. The added concentration should not be less then the background concentration of the sample selected for fortification. Ideally, the fortified analyte concentrations should be the same as that used for the LFB (Section 9.7). Over time, samples from all routine sample sources should be fortified.

9.8.2 Calculate the percent recovery, P, of the concentration for each analyte, after correcting the analytical result, X, from the fortified sample for the background concentration, b, measured in the unfortified sample, i.e.,:

P = 100 (X - b) / fortifying concentration,

and compare these values to reagent water recoveries listed in Table 2. The calculated value of P must fall in the range of R ± 35%. If P exceeds this control limit, and the laboratory performance for that analyte is shown to be in control (Sect. 9.7), 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.

9.9 ASSESSING INSTRUMENT SYSTEM - LABORATORY PERFORMANCE CHECK (LPC)

9.9.1 Laboratory performance check (LPC). After initial demonstration of capability, instrument performance should be monitored on a daily basis by analysis of the LPC sample. The LPC sample contains compounds designed to monitor instrument sensitivity, column performance (primary column) and chromatographic performance. LPC sample components and performance criteria are listed in Table 4. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the instrument system. The sensitivity requirements are set based on the EDLs published in this method. If laboratory EDLs differ from those listed in this method, concentrations of the LPC standard compounds must be adjusted to be compatible with the laboratory EDLs.

9.9.2 Degradation of DDT and endrin caused by active sites in the injection port and GC columns may occur. This should be checked on a daily basis by injecting 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 each day 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.

9.10 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 asses contamination of samples under site conditions, transportation and storage.

10. CALIBRATION

10.1 Establish GC operating parameters equivalent to those indicated in Sect. 6.8. The GC system must be calibrated using the internal standard technique (Sect. 10.2) or the external standard technique (Sect. 10.3). Perform the endrin and DDT degradation check described in Sect. 9.9.2. If degradation of either DDT or endrin exceeds 20%, take corrective action before proceeding with calibration.

10.2 INTERNAL STANDARD CALIBRATION PROCEDURE -- To use this approach, the analyst must select one or more internal standards compatible in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. PCNB has been identified as a suitable internal standard. Data presented in this method were generated using the internal standard calibration procedure.

10.2.1 Prepare calibration standards at a minimum of three (recommend five) concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more of the internal standards, and dilute to volume with MTBE. Guidance on the number of standards is as follows: A minimum of three calibration standards are required to calibrate a range of a factor of 20 in concentration. For a factor of 50, use at least four standards, and for a factor of 100, at least five standards. The lowest standard should represent analyte concentrations near, but above, their respective EDLs. The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector. The calibration standards must bracket the analyte concentration found in the sample extracts. NOTE: Calibration standard solutions must be prepared such that no unresolved analytes are mixed together, and calibration standards for toxaphene, chlordane and each of the Aroclors must be prepared individually.

10.2.2 Analyze each calibration standard according to the procedure (Sect. 11.4). Tabulate response (peak height or area) against concentration for each compound and internal standard. Calculate the response factor (RF) for each analyte and surrogate using Equation 1. RF is a unitless value.

$$RF = \frac{(A_s)\ (C_{is})}{(A_{is})\ (C_s)} \qquad \text{Equation 1}$$

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/L).
C_s = Concentration of the analyte to be measured (µg/L).

Note: For options on calculating response factors for multi-component analytes refer to Sect. 12.4.

10.2.3 If the RF value over the working range is constant (20% RSD or less) the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios (A_s/A_{is}) vs. C_s.

10.2.4 The working calibration curve or calibration factor must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the calibration curve. For extended periods of analysis (greater than 8 hrs.), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analyses. If the response for any 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. 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. WARNING: A dirty injector insert will cause poor sensitivity for the late eluting analytes.

NOTE: It is suggested that a calibration verification standard of one multi-component analyte also be analyzed each day or work shift. By alternating the selection of the multi-component analyte chosen, continuing calibration data can be obtained for all of these analytes over a period of several days.

10.2.5 Verify calibration standards periodically, recommend at least quarterly, by analyzing a standard prepared from reference material obtained from an independent source (QCS). Results from these analyses must be within the limits used to routinely check calibration (Sect. 10.2.4).

10.3 EXTERNAL STANDARD CALIBRATION PROCEDURE

10.3.1 Prepare calibration standards as in Section 10.2.1, omitting the use of the internal standard.

10.3.2 Starting with the standard of lowest concentration, analyze each calibration standard according to Sect. 11.4 and tabulate response (peak height or area) versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (20% RSD or less), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

Note: For options on calulating a calibration factor for multi-component analytes, refer to Sect. 12.4.

10.3.3 The working calibration curve or calibration factor must be verified on each working day by the procedures described in Section 10.2.4. Note: It is suggested that one multi-component analyte calibration be verified each day or work shift. By alternating the selection of the analyte (an Aroclor or toxaphene), calibration verification data can be obtained for all these analytes over a period of several days.

10.3.4 Verify calibration standards periodically (at least quarterly), by analyzing a QCS.

11. PROCEDURE

11.1 EXTRACTION (MANUAL METHOD)

11.1.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume (Sect. 11.1.6). Add preservative to LRBs and LFBs. Fortify the sample with 50 µL of the surrogate standard fortifying solution. Pour the entire sample into a 2-L separatory funnel.

11.1.2 Adjust the sample to pH 7 by adding 50 mL of phosphate buffer. Check pH: add H_2SO_4 or NaOH if necessary.

11.1.3 Add 100 g NaCl to the sample, seal, and shake to dissolve salt.

11.1.4 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner walls. Transfer the solvent to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the

emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 500-mL Erlenmeyer flask.

11.1.5 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

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

11.2 AUTOMATED EXTRACTION METHOD -- Data presented in this method were generated using the automated extraction procedure with the mechanical tumbler.

11.2.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume (Sect. 11.2.6). Add preservative to LRBs and LFBs. Fortify the sample with 50 µL of the surrogate standard fortifying solution. If the mechanical separatory funnel shaker is used, pour the entire sample into a 2-L separatory funnel. If the mechanical tumbler is used, pour the entire sample into a tumbler bottle.

11.2.2 Adjust the sample to pH 7 by adding 50 mL of phosphate buffer. Check pH: add H_2SO_4 or NaOH if necessary.

11.2.3 Add 100 g NaCl to the sample, seal, and shake to dissolve salt.

11.2.4 Add 300 mL methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner walls. Transfer the solvent to the sample contained in the separatory funnel or tumbler bottle, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during venting. Reseal and place sample container in appropriate mechanical mixing device (separatory funnel shaker or tumbler). Shake or tumble the sample for 1 hour. Complete mixing of the organic and aqueous phases should be observed within about 2 min after starting the mixing device.

11.2.5 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 500-mL Erlenmeyer flask.

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

11.3 EXTRACT CONCENTRATION

11.3.1 Assemble a K-D concentrator by attaching a 25-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if the requirements of Sect. 9.3 are met.

11.3.2 Dry the extract by pouring it through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate. Collect the extract in the K-D concentrator, and rinse the column with 20-30 mL methylene chloride. Add this rinse to the extract. Alternatively, add about 5 g anhydrous sodium sulfate to dry the extract in the Erlenmeyer flask; swirl the flask to dry extract and allow to sit for 15 min. Decant the methylene chloride extract into the K-D concentrator. Rinse the remaining sodium sulfate with two 25-mL portions of methylene chloride and decant the rinses into the K-D concentrator.

11.3.3 Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath, 65 to 70°C, so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

11.3.4 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of MTBE. Add 5-10 mL of MTBE and a fresh boiling stone. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 mL of MTBE to the top. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 min. When the apparent volume of liquid reaches 2 mL, remove the micro K-D from the bath and allow it to drain and cool. Add 5-10 mL MTBE to the micro K-D and reconcentrate to 2 mL. Remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column, and rinse the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE.

11.3.5 Transfer extract to an appropriate-sized TFE-fluorocarbon- sealed screw-cap vial and store, refrigerated at 4°C, until analysis by GC-ECD.

11.4 GAS CHROMATOGRAPHY

11.4.1 Sect. 6.8 summarizes the recommended operating conditions for the gas chromatograph. Included in Table 1 are retention times observed using this method. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 9.3 are met.

11.4.2 Calibrate or verify the system calibration daily as described in Sect. 10. The standards and extracts must be in MTBE.

11.4.3 If the internal standard calibration procedure is used, add 5 µL of the internal standard fortifying solution to the sample extract, seal, and shake to distribute the internal standard.

11.4.4 Inject 2 µL of the sample extract. Record the resulting peak size in area units.

11.4.5 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze. If internal standard calibration has been used, add an appropriate amount of additional internal standard to maintain the a concentration of 0.1 μg/mL.

11.5 IDENTIFICATION OF ANALYTES

11.5.1 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.

11.5.2 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.

11.5.3 Identification requires expert judgment when sample components are not resolved chromatographically. When GC 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 alternate techniques, to help confirm peak identification, need to 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 (Method 525.2) (1), or the use of a second chromatography column. A suggested alternative column is described in Sect. 6.8.

Note: Identify multi-component analytes by comparison of the sample chromatogram to the corresponding calibration standard chromatograms of chlordane, 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.

12. CALCULATIONS

12.1 Calculate analyte concentrations in the sample from the response for the analyte using one of the multi-point calibration procedures described in Sect. 10. Do not use the daily calibration verification standard to calculate the amount of method analytes in samples.

12.2 If the internal standard calibration procedure is used, calculate the concentration (C) in the sample using the calibration curve or response factor (RF) determined in Sect. 10.2 and Equation 2. RF is a unitless value.

$$C\ (\mu g/L) = \frac{(A_s)\ (I_s)}{(A_{is})\ (RF)\ (V_o)} \qquad \text{Equation 2}$$

where:

A_s = Response for the parameter to be measured.
A_{is} = Response for the internal standard.
I_s = Amount of internal standard added to each extract (µg).
V_o = Volume of water extracted (L).

12.3 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 10.3. The concentration (C) in the sample can be calculated from Equation 3.

$$C\ (\mu g/L) = \frac{(A_s)\ (I_s)}{(A_{is})\ (RF)\ (V_o)} \qquad \text{Equation 3}$$

where:

A = Amount of material injected (ng).
V_i = Volume of extract injected (µL).
V_t = Volume of total extract (µL).
V_s = Volume of water extracted (mL).

12.4 To quantitate multi-component analytes, one of the following methods should be used. Option 1- Calculate an average response factor, calibration 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, calibration factor or linear regression equation for each multi-component analyte using the combined areas of 3-6 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 chlordane, Aroclor or toxaphene pattern.

13. PRECISION AND ACCURACY

13.1 In a single laboratory, analyte recoveries from reagent water were used to determine analyte MDLs, EDLs (Table 3) and demonstrate method range. Analytes were divided into two fortified groups for recovery studies. Analyte recoveries and standard deviation about the percent recoveries at one concentration are given in Tables 2 and 3.

13.2 In a single laboratory, analyte recoveries from two standard synthetic ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices. Analyte recoveries from the two synthetic matrices are given in Table 2.

14. POLLUTION PREVENTION

14.1 This method uses significant volumes of organic solvents. It is highly recommended that laboratories use solvent recovery systems to recover used solvent as sample extracts are being concentrated. Recovered solvents should be recycled or properly disposed of.

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 Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15. 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 Sect. 14.2.

16. REFERENCES

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2. ASTM Annual Book of Standards, Part 11, Volume 11.02, D3694-82, "Standard Practice for Preparation of Sample Containers and for Preservation," American Society for Testing and Materials, Philadelphia, PA, 1986.

3. "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, Aug. 1977.

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

6. ASTM Annual Book of Standards, Part 11, Volume 11.01, D3370-82, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, 1986.

17. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

	Retention Time[a] (minutes)	
	Primary	Alternative
Etridiazole	23.46	22.78
Chlorneb	25.50	26.18
Propachlor	28.90	30.94
Trifluralin	31.62	(b)
HCH-alpha	31.62	32.98
Hexachlorobenzene	31.96	(b)
HCH-beta	33.32	40.12
HCH-gamma	33.66	35.36
PCNB (internal standard)	34.00	34.00
HCH-delta	35.02	41.48
Chlorthalonil	35.36	39.78
Heptachlor	37.74	36.72
Aldrin	40.12	38.08
Chlorpyrifos	40.6	(b)
DCPA	41.14	41.14
Heptachlor Epoxide	42.16	42.16
Chlordane-gamma	43.52	43.86
Endosulfan I	44.20	43.52
Chlordane-alpha	44.54	44.54
4,4'-DDE	45.90	44.88
Dieldrin	45.90	45.90
Endrin	46.92	(b)
Endosulfan II	47.60	51.68
Chlorobenzilate	47.94	48.28
4,4'-DDD	48.28	46.92
Endrin Aldehyde	48.62	46.92
Endosulfan Sulfate	49.98	49.30
4,4'-DDT	50.32	50.32
Methoxychlor	53.38	53.72
cis-Permethrin	58.48	(b)
trans-Permethrin	58.82	(b)
DCB	64.10	(b)

[a] Columns and analytical conditions are described in Sect. 6.8.1 and 6.8.2.
[b] Data not available.

TABLE 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR ANALYTES FROM REAGENT WATER AND SYNTHETIC GROUNDWATERS[a]

Analyte	Fortified Conc. µg/L	Reagent Water		Synthetic Water 1[d]		Synthetic Water 2[e]	
		R[b]	S_r[c]	R	S_R	R	S_R
Aldrin	0.15	86	9.5	100	11.0	69	9.0
Chlordane-alpha	0.15	99	11.9	96	12.5	99	7.9
Chlordane-gamma	0.15	99	11.9	96	12.5	99	6.9
Chlorneb	5.0	97	11.6	95	6.7	75	8.3
Chlorobenzilate	10	108	5.4	98	10.8	102	9.2
Chlorthalonil	0.25	91	8.2	103	10.3	71	9.2
DCPA	0.25	103	12.4	100	13.0	101	6.1
4,4'-DDD	0.25	107	6.4	96	8.6	101	7.1
4,4'-DDE	0.10	99	11.9	96	12.5	99	6.9
4,4'-DDT	0.60	112	16.8	98	11.8	84	8.4
Dieldrin	0.20	87	8.7	103	9.3	82	7.4
Endosulfan I	0.15	87	8.7	102	8.2	84	8.4
Endosulfan Sulfate	0.15	102	15.3	94	1.3	72	12.2
Endrin	0.15	88	8.8	98	9.8	104	9.4
Endrin Aldehyde	0.25	88	7.9	103	11.3	84	9.2
Endosulfan II	0.15	92	10.1	98	10.8	76	6.8
Etridiazole	0.25	103	6.2	91	6.4	98	3.9
HCH-alpha	0.05	92	10.1	106	7.4	86	7.7
HCH-beta	0.10	95	6.7	92	5.5	100	6.0
HCH-delta	0.10	102	11.2	99	11.9	103	6.2
HCH-gamma	0.15	89	9.8	115	6.9	85	7.7
Heptachlor	0.10	98	11.8	85	11.1	85	7.7
Heptachlor Epoxide	0.15	87	8.7	103	7.2	82	9.8
Hexachlorobenzene	0.05	99	21.8	82	9.8	68	4.8
Methoxychlor	0.5	105	13.7	101	10.1	104	6.2
cis-Permethrin	5.0	91	9.1	96	11.5	86	9.5
trans-Permethrin	5.0	111	6.7	97	9.7	102	7.1
Propachlor	5.0	103	9.3	116	4.6	95	7.6
Trifluralin	0.25	103	5.2	86	10.3	87	9.6

TABLE 2. (Continued)

[a] Data corrected for amount detected in blank and represent the mean of 7-8 samples.

[b] R = average percent recovery.

[c] S_R = standard deviation of the percent recovery.

[d] Corrected for amount found in blank; Absopure Nature Artesian Spring Water Obtained from the Absopure Water Company in Plymouth, Michigan.

[e] Corrected for amount found in blank; reagent water fortified with fulvic acid at the 1 mg/L concentration level. A well-characterized fulvic acid, available from the International Humic Substances Society (associated with the United States Geological Survey in Denver, Colorado), was used.

TABLE 3. SINGLE LABORATORY ACCURACY, PRECISION, METHOD DETECTION LIMITS (MDLs) AND ESTIMATED DETECTION LIMITS(EDLs) FOR ANALYTES FROM REAGENT WATER

	Fortified Conc. µg/L	N[a]	Recovery %	RSD %	MDL[b] µg/L	EDL[c] µg/L
Aldrin	0.075	7	66	9	0.014	0.075
Chlordane-alpha	0.015	7	117	8	0.0041	0.0015
Chlordane-gamma	0.015	7	109	3	0.0016	0.0015
Chlorneb	0.50	7	47	34	0.25	0.5
Chlorobenzilate	5.0	8	99	5	2.2	5.0
Chlorothalonil	0.025	7	119	12	0.011	0.025
DCPA	0.025	7	112	4	0.0032	0.025
4,4'-DDD	0.025	7	115	5	0.0044	0.025
4,4'-DDE	0.010	7	127	6	0.0025	0.01
4,4'-DDT	0.060	7	87	23	0.039	0.06
Dieldrin	0.020	7	77	22	0.011	0.02
Endosulfan I	0.015	7	78	25	0.0092	0.015
Endosulfan Sulfate	0.015	7	129	4	0.0024	0.015
Endrin	0.015	7	72	18	0.0062	0.015
Endrin Aldehyde	0.025	7	95	15	0.011	0.025
Endosulfan II	0.015	7	148	35	0.024	0.024
Etridiazole	0.025	7	96	17	0.013	0.025
HCH-alpha	0.025	8	94	8	0.0053	0.025
HCH-beta	0.010	7	95	12	0.0036	0.01
HCH-delta	0.010	7	84	7	0.0020	0.01
HCH-gamma	0.015	7	80	16	0.0060	0.015
Heptachlor	0.010	7	67	7	0.0015	0.01
Heptachlor Epoxide	0.015	7	71	18	0.0059	0.015
Hexachlorobenzene	0.0050	7	115	43	0.0077	0.0077
Methoxychlor	0.050	7	120	11	0.022	0.05
cis-Permethrin	0.50	7	64	24	0.25	0.50
trans-Permethrin	0.50	7	122	9	0.18	0.50
Propachlor	0.50	7	90	18	0.25	0.50
Trifluralin	0.025	7	108	3	0.0026	0.025

[a]N = Number of replicates.

[b]With these data, the method detection limits (MDL) in the tables were calculated using the formula:

$$MDL = S\, t_{(n-1,\ 1-alpha\ =\ 0.99)}$$

where: $t_{(n-1,\ 1-alpha\ =\ 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom.
n = number of replicates.
S = standard deviation of replicate analyses.

[c]EDL = estimated detection limit; defined as either MDL (Appendix B to 40 CFR Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11) or a level of compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

TABLE 4. 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 HCH-delta	0.0500 0.0400	Resolution >0.50[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) is the peak width at half height in secs, and W(1/10) is the peak width in secs. at tenth height.

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

$$R = t / W$$

where t is the difference in elution times between the two peaks and W is the average peak width, at the baseline, of the two peaks.

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