Empore™
Extraction Disks

EPA METHOD 608 ATP 3M0222

An alternative test procedure for the measurement of organochlorine pesticides and polychlorinated biphenyls in waste water.

Promulgated
Federal Register/Vol. 60, No. 148
August 2, 1995

Printed in U.S.A.

Organochlorine Pesticides and PCBs In Wastewater Using Empore™ Disk

1. SCOPE AND APPLICATION

1.1 This method is designed as an alternate test procedure for EPA Method 608.[19] The Empore disk is used in place of the liquid-liquid extraction. This method covers the determination of certain organochlorine pesticides and PCBs. The following parameters can be determined by this method:

Parameter	STORET No.	CAS No.
Aldrin	39330	309-00-2
alpha-BHC	39337	319-84-6
beta-BHC	39338	319-85-7
delta-BHC	34259	319-86-8
gamma-BHC	39340	58-89-9
Chlordane	39350	57-74-9
4,4'-DDD	39310	72-54-8
4,4'-DDE	39320	72-55-9
4,4'-DDT	39300	50-29-3
Dieldrin	39380	60-57-1
Endosulfan I	34361	959-98-8
Endosulfan II	34356	33212-65-9
Endosulfan sulfate	34351	1031-07-8
Endrin	39390	72-20-8
Endrin aldehyde	34366	7421-93-4
Heptachlor	39410	76-44-8
Heptachlor epoxide	39420	1024-57-3
Methoxychlor	39480	72-43-5
Toxaphene	39400	8001-35-2
PCB-1016	34671	12674-11-2
PCB-1221	39488	1104-28-2
PCB-1232	39492	11141-16-5
PCB-1242	39496	53469-21-9
PCB-1248	39500	12672-29-6
PCB-1254	39504	11097-69-1
PCB-1260	39508	11096-82-5

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column.

1.3 The method detection limit (MDL, defined in Section 13.1)[1] for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 9.2.

2. SUMMARY OF METHOD

2.1 A measured volume of sample, approximately 1-L, is extracted using a 90 mm Empore disk. The disk is eluted with acetone followed by methylene chloride. The eluant is dried and exchanged to hexane during concentration to a volume of 10 mL or less. The eluant is separated by gas chromatography and the analytes are then measured with an electron capture detector.[2]

2.2 The method provides a Florisil column cleanup procedure and an elemental sulfur removal procedure to aid in the elimination of interferences that may be encountered.

3. DEFINITIONS

3.1 INTERNAL STANDARD (IS) – A pure analytes(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 (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 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 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 the sampling site, 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 SPIKE – Spike means either:

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.

or

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.

3.9 STOCK STANDARD SOLUTION (SSS) – 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.

3.10 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.

3.11 CALIBRATION STANDARD (CAL) – A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.12 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 hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 9.1.3.

4.1.1 Glassware must be scrupulously cleaned.[3] Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400°C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store 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.

4.2 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. These compounds generally appear in the chromatogram as large late eluting peaks, especially in the 15 and 50% fractions from Florisil. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials 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.[4,5] The interferences from phthalate esters can be avoided by using a microcoulometric or electrolytic conductivity detector.

4.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures in Section 11.2 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level

by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[6-8] for the information of the analyst.

5.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the PCBs. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6. EQUIPMENT AND SUPPLIES

6.1 Sampling equipment, for discrete or composite sampling.

6.1.1 Grab sample bottle – 1-L or 1-qt. amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

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

6.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

6.2.1 Drying column – Chromatographic column, approximately 400 mm long x 19 mm ID.

6.2.2 Concentrator tube, Kuderna-Danish – 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

6.2.3 Evaporative flask. Kuderna-Danish – 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

6.2.4 Snyder column, Kuderna/Danish – Three-ball macro (Kontes K-503000-0121 or equivalent).

6.2.5 Vials – 10 to 15 mL, amber glass, with Teflon-lined screw cap.

6.2.6 Collection tube, for single extractions, a large test tube; for multiple extractions, a 40 mL screw cap vial. Collection tube must fit around drip tip of filter apparatus.

6.3 Boiling chips – Approximately 10/40 mesh. Heat to 400°C for 30 min or Soxhlet extract with methylene chloride.

6.4 Water bath – Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

6.5 Balance – Analytical, capable of accurately weighing 0.0001 g.

6.6 Gas chromatograph – An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

6.6.1 Column 1 – DB 608, 30 m x 0.53 mm x 0.83 µm or equivalent. This column was used to develop the method performance statements in Section 13. Guidelines for the use of alternate column packing are provided in Section 11.3.

6.6.2 Column 2 – DB 1701, 30m x 0.53 mm x 1 µm or equivalent.

6.6.3 Detector – Electron capture detector. This detector has proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1), and was used to develop the method performance statements in Section 13. Guidelines for the use of alternate detectors are provided in Section 11.3.

6.7 Standard 90 mm Filter Apparatus or multiposition manifold.

6.8 Prefiltering aids – 90 mm 1 µm glass fiber filter or Empore Filter Aid 400.

7. REAGENTS AND STANDARDS

7.1 Reagent water – Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

7.2 Sodium hydroxide solution (10 N) – Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

7.3 Sodium thiosulfate – (ACS) Granular.

7.4 Sulfuric acid (1 + 1) – Slowly, add 50 mL to H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

7.5 Acetone, hexane, isooctane, methylene chloride – Pesticide quality or equivalent.

7.6 Ethyl ether – Pesticide quality or equivalent, redistilled in glass if necessary.

7.6.1 Ethyl ether must be free of peroxides before it is used as indicated by EM Laboratories Quant test strips. (Available from Scientific Products Co., Cat. No. P1126-8 and other suppliers.)

7.6.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

7.7 Sodium sulfate – (ACS) Granular, anhydrous. Purify by heating at 400°C for 4 h in a shallow tray.

7.8 Florisil – PR grade (60/100 mesh). Purchase activated at 1250°F and store in the dark in glass containers with ground glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 h at 130°C in a foil-covered glass container and allow to cool.

7.9 Mercury – Triple distilled.

7.10 Copper powder – Activated.

7.11 Stock standard solutions (1.00 µg/µL) – Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

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

7.11.2 Transfer the stock standard solutions into Teflon-sealed, screw-cap bottles. Store at 4°C and protect from light. Stock standards solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.11.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

7.12 Quality control check sample concentrate – See Section 9.2.1.

7.13 The Empore extraction disks contain 2 g of 8 µm octadecyl bonded silica uniformly enmeshed in a matrix of inert PTFE fibrils. The size of the disks is 90 mm x 0.5 mm. The disks should not contain any organic compounds, either from the PTFE or the bonded silica, which will leach into the methylene chloride eluant. One liter of reagent water should pass through the disks in 2-5 minutes using a vacuum of at least 25 inches of mercury.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

8.2 All samples must be iced or refrigerated at 4°C from the time of collection until extraction. If the samples will not be extracted within 72 h of collection, the sample should be adjusted to a pH range of 5.0 to 9.0 with sodium hydroxide solution or sulfuric acid. Record the volume of acid or base used. If aldrin is to be determined, add sodium thiosulfate when residual chlorine is present. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.[12] Field test kits are available for this purpose.

8.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.[2]

9. QUALITY ASSURANCE

9.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

9.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 11.1.4, 11.2.1, and 11.3.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 9.2.

9.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

9.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 9.3.

9.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 9.4. The frequency of the check standards analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 9.3) meet all specified quality control criteria.

9.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 9.5.

9.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

9.2.1 A quality control (QC) check sample concentrate is required containing each single-component parameter of interest at the following concentrations in acetone: 4,4'-DDD, 10 µg/mL; 4,4'-DDT, 10 µg/mL; endosulfan II, 10 µg/mL; endosulfan sulfate, 10 µg/mL; endrin, 10 µg/mL; any other single-component pesticide, 2 µg/mL. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 µg/mL in acetone. The QC check sample concentrate must be obtained from an external source. If not available from an external source, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

9.2.2 Using a pipes, prepare QC check samples at the test concentrations shown in Table 3 by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

9.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

9.2.4 Calculate the average recovery (X) in µg/mL, and the standard deviation of the recovery (s) in µg/mL, for each parameter using the four results.

9.2.5 For each parameter compare s and X with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 3. If s and X for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, the system performance is unacceptable for that parameter.

NOTE: The large number of parameters in Table 3 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

9.2.6 When one or more of the parameters tested fails at least one of the acceptance criteria, the analyst must proceed according to Section 9.2.6.1 or 9.2.6.2.

9.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 9.2.2.

9.2.6.2 Beginning with Section 9.2.2, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 9.2.2.

9.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

9.3.1 The concentration of the spike in the sample should be determined as follows:

9.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 9.3.2, whichever concentration would be larger.

9.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at the test concentration in Section 9.2.2 or 1 to 5 times higher than the background concentration determined in Section 9.3.2, whichever concentration would be larger.

9.3. 1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the test concentration in Section 9.2.2.

9.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 9.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as 100(A–B)%/T, where T is the known true value of the spike.

9.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 3. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.[10] If spiking was performed at a concentration lower than the test concentration in Section 9.2.2, the analyst must use either the QC acceptance criteria in Table 3, or optional QC acceptance criteria calculated for the specific spike concentration using the procedures described in Method 608.

9.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 9.4.

9.4 If any parameter fails the acceptance criteria for recovery in Section 9.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of parameters in Table 3 must be measured in the sample in Section 9.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

9.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Section 9.2.1 or 9.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 9.3.

9.4.2 Analyze the QC check standards to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as 100 (A/T)% where T is the true value of the standard concentration.

9.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 3. Only parameters that failed the test in Section 9.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for the parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

9.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 9.3, calculate the average percent recovery (P) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $P - 2s_p$ to $P + 2s_p$. If P = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70 – 110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

9.6 It is recommended that the laboratory adopt additional quality assurance 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. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10. CALIBRATION AND STANDARDIZATION

10.1 Establish gas chromatographic operating conditions equivalent to those given in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 10.2) or the internal standard technique (Section 10.3).

10.2 External standard calibration procedure:

10.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to a volume with isooctane. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

10.2.2 Using injections of 1 to 2 µL, analyze each calibration standard according to Section 11.3 and tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

10.3 Internal standard calibration procedure – To use this approach, the analyst must select one or more internal standards that are similar 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. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

10.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter 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 internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

10.3.2 Using injections of 1 to 2 µL, analyze each calibration standard according to Section 11.3 and tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each compound as:

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

where:
A_s=Response for the parameter to be measured.
A_{is}=Response for the internal standard.
C_{is}=Concentration of the internal standard (µg/L).
C_s= Concentration of the parameter to be measured (µg/L).
If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant and 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. RF.

10.4 The working calibration curve, calibration factor, or RF must be verified on each working day

by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±15%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

10.5 The cleanup procedure in Section 11.2.2 utilizes Florisil column chromatography. Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value[9] is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g.

10.6 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

11. PROCEDURE

11.1 SAMPLE EXTRACTION

11.1.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. If the sample contains particulates, let stand to settle out the particulates before extraction.

11.1.2 Extract the sample as follows:

11.1.2.1 Place a 90 mm standard filter apparatus on a vacuum filtration flask or manifold and attach to a vacuum source. The vacuum gauge should read at least 25 in. of mercury when all valves are closed. Position a 90 mm C18 Empore extraction disk onto the filter screen. Wet the entire disk with methanol. To aid in filtering samples with particulates, a 1µm glass fiber filter or Empore Filter Aid 400 can be placed on the top of the Empore disk and wetted with methanol. Install the reservoir and clamp. Resume vacuum to dry the disk. Interrupt the vacuum. Wash the disk and reservoir with 20 mL of methylene chloride. Resume the vacuum briefly to pull methylene chloride through the disk. Interrupt the vacuum and allow the disk to soak for about a minute. Resume vacuum and completely dry the disk.

11.1.2.2 Condition the disk with 20 mL of methanol. Apply vacuum until nearly all the solvent has passed through the disk, interrupting it while solvent remains on the disk. Allow the disk to soak for about a minute. Resume vacuum to pull most of the methanol through, but interrupting it to leave a layer of methanol on the surface of the disk. Do not allow disk to dry. For uniform flow and good recovery, it is critical the disk not be allowed to dry from now until the end of the extraction. Discard waste solvent. Rinse the disk with 20 mL of deionized water. Resume vacuum to pull most of the water through, but interrupt it to leave a layer of water on the surface of the disk. Do not allow the disk to dry. If disk does dry, recondition with methanol as above.

11.1.2.3 Add the water sample to the reservoir and immediately apply the vacuum. If particulates have settled in the sample, gently decant the clear layer into the apparatus until most of the sample has been processed. Then pour the remainder including the particulates into the reservoir. Empty the sample bottle completely. When the filtration is complete, dry the disk for three minutes. Turn off the vacuum.

11.1.3 Discard sample filtrate. Insert tube to collect the eluant. The tube should fit around the drip tip of the base. Reassemble the apparatus. Add 5.0 mL of acetone to the center of the disk, allowing it to spread evenly over the disk. Turn the vacuum on and quickly off when the filter surface nears dryness but still remains wet. Allow to soak for 15

seconds. Add 20 mL of methylene chloride to the sample bottle, seal and shake to rinse the inside of the bottle. Transfer the methylene chloride from the bottle to the filter. Resume the vacuum slowly so as to avoid splashing. Interrupt the vacuum when the filter surface nears dryness but still remains wet. Allow disk to soak in solvent for 20 seconds. Rinse the reservoir glass and disk with 10 mL of methylene chloride. Resume vacuum slowly. Interrupt vacuum when disk is covered with solvent. Allow to soak for 20 seconds. Resume vacuum to dry the disk. Remove the sample tube.

11.1.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 9.2 are met.

11.1.5 Prior to pouring sample onto drying column, slowly add about *10 mL of sodium sulfate to the collection tube to remove the excess water. (Excess water may cause the drying column to plug.) Pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the collection tube and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer. After all the methylene chloride has drained, remove the column. Add 10 mL of hexane to the K-D concentrator.

11.1.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (80°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 with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

11.1.7 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for the operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis (Section 11.3). If the sample requires further cleanup, proceed to Section 11.2.2.

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

11.2 CLEANUP AND SEPARATION

11.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst may use either procedure below or any other appropriate procedure. However, the analyst first must demonstrate that the requirements of Section 9.2 can be met using the method as revised to incorporate the cleanup procedure. The Florisil column allows for a select fractionation of the compounds and will eliminate polar interferences. Elemental sulfur, which interferes with the electron capture gas chromatography of certain pesticides, can be removed by the technique described in Section 11.2.2.6.

*Approximately 16.5 gms granular anhydrous sodium sulfate. A graduated cylinder was used for dispensing the dry chemical.

11.2.2 Florisil column cleanup:

11.2.2.1 Place a weight of Florisil (nominally 20 g) predetermined by calibration (Section 10.5), into a chromatographic column. Tap the column to settle the Florisil and add 1 to 2 cm of anhydrous sodium sulfate to the top.

11.2.2.2 Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate layer to the air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate.

11.2.2.3 Adjust the sample extract volume to 10 mL with hexane and transfer it from the K-D concentrator tube onto the column. Rinse the tube twice with 1 to 2 mL of hexane, adding each rinse to the column.

11.2.2.4 Place a 50-mL K-D flask and clean concentrator tube under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of 6% ethyl ether in hexane (V/V) (Fraction 1) at a rate of about 5 mL/min. Remove the K-D flask and set it aside for later concentration. Elute the column again, using 200 mL of 15% ethyl ether in hexane (V/V) (Fraction 2) into a second K-D flask. Perform the third elution using 200 mL of 50% ethyl ether in hexane (V/V) (Fraction 3). The elution patterns for the pesticides and PCBs are shown in Table 2.

11.2.2.5 Concentrate the fractions as in Section 11.1.6, except use hexane to prewet the column and set the water bath at about 85°C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the volume of each fraction to 10 mL with hexane and analyze by gas chromatography (Section 11.3).

11.2.2.6 Elemental sulfur will usually elute entirely in Fraction 1 of the Florisil column cleanup. To remove sulfur interference from this fraction or the original extract, pipet 1.00 mL of the concentrated extract into a clean concentrator tube or Teflon-sealed vial. Add one to three drops of mercury and seal.[13] Agitate the contents of the vial for 15 to 30 s. Prolonged shaking (2 h) may be required. If so, this may be accomplished with a reciprocal shaker. Alternatively, activated copper powder may be used for sulfur removal.[14] Analyze by gas chromatography.

11.3 GAS CHROMATOGRAPHY

11.3.1 Table 1 summarizes the recommended operating conditions for the gas chromatography. Included in this table are retention times and MDL that can be achieved under these conditions. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 9.2 are met.

11.3.2 Calibrate the system daily as described in Section 10.

11.3.3 If the internal standard calibration procedure is being used, the internal standard must be added to the sample extract and mixed thoroughly immediately before injection into the gas chromatograph.

11.3.4 Inject 1 to 2 µL of the sample extract or standard into the gas chromatograph using the solvent-flush technique.[15] Smaller (1.0 µL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL, the total extract volume, and the resulting peak size in area or peak height units.

1 1.3.5 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. 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 for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

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

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

12. DATA ANALYSIS AND CALCULATIONS

12.1 Determine the concentration of individual compounds in the sample.

12.1.1 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 10.2.2. The concentration in the sample can be calculated from Equation 2.

$$Concentration\ (\mu g/L) = \frac{(A)(V_t)}{(V_i)(V_s)} \qquad \text{Equation 2}$$

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).

12.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 10.3.2 and Equation 3.

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

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).

12.2 When it is apparent that two or more PCB (Aroclor) mixtures are present, the Webb and McCall procedure[16] may be used to identify and quantify the Aroclors.

12.3 For multicomponent mixtures (chlordane, toxaphene, and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

12.4 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

13. METHOD PERFORMANCE

13.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.[1] The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

13.2 This method was tested by a single laboratory using industrial wastewaters spiked at three different concentrations, ranging from 0.2 to 15 µg/L for single component pesticides and from 2.0 to 250 µg/L for multicomponent parameters. PCB 1254 was the only PCB evaluated in the laboratory. The percent accuracy and precision of the wastewater analyses are summarized in Table 4.

14. POLLUTION PREVENTION

14.1 This method utilizes the new 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, thereby eliminating the potential hazards to both the analyst and the environment involved with the use of large volumes of organic solvents in conventional liquid-liquid extractions.

14.2 For more 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 Section 14.2.

16. REFERENCES

1. 40 CFR part 136, appendix B.

2. "Determination of Pesticides and PCBs in Industrial and Municipal Wastewaters," EPA 600/4-82-023, National Technical Information Service, PB82-214222, Springfield, Virginia 22161, April 1982.

3. ASTM Annual Book of Standards, Part 31, D3694-78. "Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.

4. Giam, C.S., Chan,H.S., and Nef, G.S., "Sensitive Method for Determination of Phthalate Ester Plasticizers in Open Ocean Biota Samples," *Analytical Chemistry, 47,* 2225 (1975).

5. Giam, C.S., Chan, H.S., "Control of Blanks in the Analysis of Phthalates in Air and Ocean Biota Samples," U.S. National Bureau of Standards, Special Publication 442, pp. 701-708, 1976.

6. "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.

7. "OSHA Safety and Health Standards, General Industry," (29 CFR part 1910), Center for Disease Control, Occupational Safety and Heath Administration, OSHA 2206 (Revised, January 1976).

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

9. Mills, P.A. "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns," *Joumal of the Association of Official Analytical Chemists, 51,* 29, (1968).

10. Provost, L.P., and Elder, R.S. "Interpretation of Percent Recovery Data," American Laboratory, 15, 58-63 (1983). (The value 2.44 used in the equation in Section 8.3.3 is two times the value 1.22 derived in this report.)

11. ASTM Annual Book of Standards, Part 31, D3370-76. "Standard Practices for Sampling Water," American Society for Testing and Materials, Philadelphia.

12. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotmetric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

13. Goerlitz, D.F., and Law, L.M. *Bulletin for Environmental Contamination and Toxicology,* 6, 9 (1971).

14. "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples," EPA-600/8-80-038, U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, North Carolina.

15. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis: Some Practical Aspects," *Joumal of the Association of Official Analytical Chemists, 48,* 1037 (1965).

16. Webb, R.G., and McCall, A.C. "Quantitative PCB Standards for Electron Capture Gas Chromatography," *Joumal of Chromatographic Science, 11,* 366 (1973).

17. TABLES, VALIDATION DATA

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	**Retention Time Col. 1 (min)**	**Retention Time Col. 2 (min)**	**Method Detection Limit (µg/L)**
Aldrin	19.15	18.84	0.008
alpha-BHC	14.86	15.28	0.005
beta-BHC	16.79	19.61	0.021
Chlordane	mr	mr	0.070
delta-BHC	18.28	20.58	0.011
Dieldrin	23.88	23.71	0.008
Endosulfan I	22.71	22.38	0.008
Endosulfan II	25.93	26.13	0.043
Endosulfan sulfate	27.59	30.39	0.048
Endrin	25.27	24.45	0.068
Endrin aldehyde	27.14	27.57	0.015
gamma-BHC	16.50	16.87	0.004
Heptachlor	17.82	17.75	0.020
Heptachlor epoxide	21.35	21.34	0.010
Methoxychlor	30.14	28.68	0.027
Toxaphene	mr	mr	0.610
4,4’-DDD	25.60	25.84	0.083
4,4’-DDE	23.51	23.04	0.022
4,4’-DDT	26.71	26.46	0.071
PCB-1016	mr	mr	nd
PCB-1221	mr	mr	nd
PCB-1232	mr	mr	nd
PCB-1242	mr	mr	nd
PCB-1248	mr	mr	nd
PCB-1254	mr	mr	0.260
PCB-1260	mr	mr	nd

Column 1 conditions: DB-608, 30 m x 0.53 mm x 0.8 µm film thickness, with helium carrier gas at 3 cc/min constant flow rate. Temperature program at 135°C - 275°C, rate at 5°C/min, hold 17 min.
Column 2 conditions: DB 1707, 30 m x 0.53 mm x 1 mm film thickness, with helium carrier gas at 3 cc/min constant flow rate. Temperature program at 135°C - 275°C, rate at 5°C/min, hold 17 min.
mr= multiple peak response
nd=not determined

TABLE 2. DISTRIBUTION OF CHLORINATED PESTICIDES AND PCBs IN FLORISIL COLUMN FRACTIONS

Parameter	Percent Recovery Fraction 1*	Percent Recovery Fraction 2*	Percent Recovery Fraction 3*
Aldrin	100		
alpha-BHC	100		
beta-BHC	97		
delta-BHC	98		
gamma-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95		
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

*Eluant composition: Fraction 1 – 6% ethyl ether in hexane.
Fraction 2 – 15% ethyl ether in hexane.
Fraction 3 – 50% ethyl ether in hexane.

TABLE 3. QC ACCEPTANCE CRITERIA – METHOD 608

Parameter	Test Conc. (µg/L)	Limit for s (µg/L)	Range for X (µg/L)	Range for P, P_s(%)
Aldrin	2.0	0.42	1.08- 2.24	42 - 122
alpha-BHC	2.0	0.48	.98- 2.44	37 - 134
beta-BHC	2.0	0.64	0.78- 2.60	17 - 147
delta-BHC	2.0	0.72	1.01- 2.37	19 - 140
gamma-BHC	2.0	0.46	0.86- 2.82	32 - 127
Chlordane	50	10.0	27.6 -54.3	45 - 119
4,4'-DDD	10	2.8	4.8 -12.6	31 - 141
4,4'-DDE	2.0	0.55	1.08- 2.60	30 - 145
4,4'-DDT	10	3.6	46 -13.7	25 - 160
Dieldrin	2.0	0.76	1.15- 2.49	36 - 146
Endosulfan 1	2.0	0.49	1.14- 2.82	45 - 153
Endosulfan 11	10	6.1	2.2 -17.1	D - 202
Endosulfan sulfate	10	2.7	3.8 -13.2	26 - 144
Endrin	10	3.7	5.1 -12.6	30 - 147
Heptachlor	2.0	0.40	0.86- 2.00	34 - 111
Heptachlor epoxide	2.0	0.41	1.13- 2.63	37 - 142
Toxaphene	50	12.7	27.8 -55.6	41 - 126
PCB-1016	50	10.0	30.5 -51.5	50 - 114
PCB-1221	50	24.4	22.1 -75.2	15 - 178
PCB-1232	50	17.9	14.0 -98.5	10 - 215
PCB-1242	50	12.2	24.8 -69.6	39 - 150
PCB-1248	50	15.9	29.0 -70.2	38 - 158
PCB-1254	50	13.8	22.2 -57.9	29 - 131
PCB-1260	50	10.4	18.7 -54.9	8 - 127

s = Standard deviation of four recovery measurements, in µg/L (Section 9.2.4).
X = Average recovery for four recovery measurements, in µg/L (Section 9.2.4).
P,P_s= Percent recovery measured (Section 9.3.2, Section 9.4.2).
D = Detected; result must be greater than zero.

NOTE: These criteria are based directly on the method performance data in Table 4 of EPA Method 608. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to the concentrations below those used to develop the cited source table.

TABLE 4. SINGLE ANALYST PRECISION AND ACCURACY IN WASTE WATER SAMPLES

Analyte	Industry	SIC Code	Conc µg/l	Mean Recovery µg/l	Mean Recovery %	Std Dev µg/l	RSD %	Conc µg/l	Mean Recovery µg/l	Mean Recovery %	Std Dev µg/l	RSD %	Conc µg/l	Mean Recovery µg/l	Mean Recovery %	Std Dev µg/l	RSD %
ALDRIN	CHEMICAL	2869A	0.2	0.22	108	0.04	16.2	1.0	0.76	76	0.03	3.5	5.0	3.42	68	0.18	5.2
	CHEMICAL	2869B	0.2	0.26	130	0.01	3.8	1.0	0.85	85	0.01	0.7	5.0	4.66	93	0.11	2.4
	PAPER	2621A	0.2	0.27	133	0.01	4.3	1.0	0.73	73	0.05	6.5	5.0	3.93	79	0.18	4.7
	PAPER	2621C	0.2	0.23	113	0.01	2.5	1.0	0.62	62	0.03	4.9	5.0	3.77	75	0.06	1.5
	PHARMACEUTICAL	2833A	0.2	0.20	102	0.01	2.8	1.0	0.71	71	0.01	0.8	5.0	4.40	88	0.12	2.7
	PHARMACEUTICAL	2833B	0.2	0.30	148	0.01	1.9	1.0	0.76	76	0.03	3.3	5.0	3.44	69	0.19	5.5
	REFUSE	4953B	0.2	0.29	145	0.00	0.0	1.0	0.84	84	0.01	0.7	5.0	4.54	91	0.06	1.3
	REFUSE	4953G	0.2	0.26	132	0.02	5.8	1.0	0.61	61	0.02	3.4	5.0	3.06	61	0.28	9.3
	SEWERAGE	4952A	0.2	0.21	103	0.01	2.8	1.0	0.75	75	0.01	0.8	5.0	4.04	81	0.05	1.3
	SEWERAGE	4952B	0.2	0.19	93	0.01	3.1	1.0	0.62	62	0.05	7.7	5.0	3.79	76	0.04	1.1
ALPHA-BHC	CHEMICAL	2869A	0.2	0.24	118	0.02	6.5	1.0	0.74	74	0.04	4.8	5.0	3.71	74	0.12	3.1
	CHEMICAL	2869B	0.2	0.30	148	0.01	3.9	1.0	0.93	93	0.01	0.6	5.0	4.95	99	0.01	0.1
	PAPER	2621A	0.2	0.87	435	0.04	5.0	1.0	1.49	149	0.05	3.1	5.0	5.13	103	0.18	3.5
	PAPER	2621C	0.2	0.27	135	0.00	0.0	1.0	0.73	73	0.03	4.4	5.0	4.59	92	0.05	1.0
	PHARMACEUTICAL	2833A	0.2	0.21	107	0.01	2.7	1.0	0.77	77	0.00	0.0	5.0	4.71	94	0.12	2.5
	PHARMACEUTICAL	2833B	0.2	0.27	137	0.01	2.1	1.0	0.81	81	0.02	1.9	5.0	4.85	97	0.18	3.7
	REFUSE	4953B	0.2	0.32	160	0.00	0.0	1.0	0.90	90	0.01	0.6	5.0	4.94	99	0.06	1.2
	REFUSE	4953G	0.2	0.31	155	0.00	0.0	1.0	0.90	90	0.02	2.2	5.0	4.38	88	0.12	2.7
	SEWERAGE	4952A	0.2	0.25	123	0.01	2.3	1.0	0.87	87	0.01	1.3	5.0	4.57	91	0.08	1.7
	SEWERAGE	4952B	0.2	0.25	127	0.01	2.3	1.0	0.72	72	0.06	8.3	5.0	4.62	92	0.12	2.5
BETA-BHC	CHEMICAL	2869A	0.2	0.24	118	0.01	2.4	1.0	0.81	81	0.03	3.7	5.0	3.68	74	0.15	3.9
	CHEMICAL	2869B	0.2	0.26	132	0.02	5.8	1.0	0.95	95	0.01	0.6	5.0	4.86	97	0.02	0.4
	PAPER	2621A	0.2	0.59	293	0.10	16.6	1.0	1.36	136	0.04	2.7	5.0	5.06	101	0.23	4.5
	PAPER	2621C	0.2	0.24	120	0.00	0.0	1.0	0.79	79	0.03	3.6	5.0	4.70	94	0.02	0.4
	PHARMACEUTICAL	2833A	0.2	0.21	103	0.01	2.8	1.0	0.91	91	0.01	0.6	5.0	4.99	100	0.11	2.1
	PHARMACEUTICAL	2833B	0.2	0.24	120	0.00	0.0	1.0	0.89	89	0.01	1.3	5.0	4.93	99	0.06	1.2
	REFUSE	4953B	0.2	0.29	145	0.00	0.0	1.0	0.97	97	0.01	0.6	5.0	5.06	101	0.08	1.5
	REFUSE	4953G	0.2	0.33	167	0.01	1.7	1.0	1.01	101	0.02	2.1	5.0	4.55	91	0.08	1.7
	SEWERAGE	4952A	0.2	0.22	110	0.00	0.0	1.0	0.95	95	0.01	0.6	5.0	4.58	92	0.10	2.1
	SEWERAGE	4952B	0.2	0.25	127	0.01	2.3	1.0	0.84	84	0.05	5.5	5.0	4.95	99	0.10	2.0
CHLORDANE	CHEMICAL	2869A	2.0	0.91	46	0.03	3.5	10.0	2.48	25	0.35	14.1	50.0	26.98	54	2.63	9.8
	CHEMICAL	2869B	2.0	2.53	127	0.01	0.4	10.0	8.93	89	0.03	0.3	50.0	49.14	98	1.03	2.1
	PAPER	2621A	2.0	2.10	105	0.03	1.3	10.0	7.09	71	0.16	2.2	50.0	34.16	68	0.83	2.4
	PAPER	2621C	2.0	2.07	103	0.03	1.6	10.0	8.26	83	0.14	1.7	50.0	44.08	88	0.03	0.1
	PHARMACEUTICAL	2833A	2.0	1.65	83	0.02	1.3	10.0	8.69	87	0.15	1.7	50.0	46.54	93	2.38	5.1
	PHARMACEUTICAL	2833B	2.0	2.15	108	0.02	1.0	10.0	8.13	81	0.12	1.5	50.0	44.17	88	0.81	1.8
	REFUSE	4953B	2.0	2.25	112	0.05	2.1	10.0	8.48	85	0.05	0.6	50.0	46.44	93	0.62	1.3
	REFUSE	4953G	2.0	2.27	114	0.01	0.5	10.0	8.21	82	0.24	2.9	50.0	41.52	83	0.59	1.4
	SEWERAGE	4952A	2.0	1.48	74	0.05	3.2	10.0	5.57	56	0.14	2.5	50.0	27.06	54	0.45	1.7
	SEWERAGE	4952B	2.0	1.75	88	0.05	3.0	10.0	7.27	73	0.07	0.9	50.0	37.51	75	0.26	0.7
DELTA-BHC	CHEMICAL	2869A	0.2	0.23	113	0.03	11.1	1.0	0.79	79	0.04	4.4	5.0	4.24	85	0.18	4.3
	CHEMICAL	2869B	0.2	0.35	175	0.01	2.9	1.0	0.96	96	0.01	0.6	5.0	5.26	105	0.02	0.3
	PAPER	2621A	0.2	0.41	203	0.02	3.8	1.0	1.33	133	0.06	4.6	5.0	6.68	134	0.22	3.2
	PAPER	2621C	0.2	0.32	158	0.01	1.8	1.0	0.79	79	0.03	4.4	5.0	4.87	97	0.02	0.3
	PHARMACEUTICAL	2833A	0.2	0.28	138	0.01	2.1	1.0	0.86	86	0.01	1.2	5.0	5.08	102	0.09	1.7
	PHARMACEUTICAL	2833B	0.2	0.32	160	0.00	0.0	1.0	0.88	88	0.01	1.1	5.0	4.95	99	0.37	7.4
	REFUSE	4953B	0.2	0.36	180	0.00	0.0	1.0	0.94	94	0.01	0.6	5.0	5.18	104	0.06	1.1
	REFUSE	4953G	0.2	0.41	203	0.01	1.4	1.0	1.06	106	0.02	1.4	5.0	4.83	97	0.14	2.8
	SEWERAGE	4952A	0.2	0.22	108	0.01	5.3	1.0	1.37	137	0.03	2.5	5.0	6.58	132	0.13	1.9
	SEWERAGE	4952B	0.2	0.36	182	0.01	1.6	1.0	0.90	90	0.10	10.6	5.0	5.41	108	0.23	4.3
4,4’-DDD	CHEMICAL	2869A	1.0	0.93	93	0.01	1.2	5.0	4.47	89	0.20	4.5	15.0	11.53	77	0.47	4.1
	CHEMICAL	2869B	1.0	1.15	115	0.05	4.3	5.0	6.06	121	0.11	1.7	15.0	16.14	108	0.19	1.2
	PAPER	2621A	1.0	0.94	94	0.05	4.9	5.0	4.32	86	0.33	7.6	15.0	13.37	89	0.29	2.2
	PAPER	2621C	1.0	0.96	96	0.01	1.0	5.0	4.41	88	0.24	5.4	15.0	13.89	93	0.17	1.2
	PHARMACEUTICAL	2833A	1.0	0.80	80	0.01	1.4	5.0	4.53	91	0.04	0.9	15.0	14.45	96	0.36	2.5
	PHARMACEUTICAL	2833B	1.0	0.57	57	0.00	0.0	5.0	3.77	75	0.09	2.4	15.0	11.74	78	0.32	2.7
	REFUSE	4953B	1.0	1.02	102	0.02	1.5	5.0	5.62	112	0.05	0.9	15.0	15.84	106	0.19	1.2
	REFUSE	4953G	1.0	1.05	105	0.02	1.5	5.0	4.74	95	0.09	1.9	15.0	13.12	87	0.79	6.1
	SEWERAGE	4952A	1.0	1.06	106	0.02	1.6	5.0	4.97	99	0.05	1.0	15.0	14.66	98	0.20	1.3
	SEWERAGE	4952B	1.0	0.65	65	0.02	2.7	5.0	3.15	63	0.23	7.2	15.0	10.59	71	0.07	0.7

TABLE 4. SINGLE ANALYST PRECISION AND ACCURACY IN WASTE WATER SAMPLES (cont'd)

Analyte	Industry	SIC Code	Conc µg/l	Mean Recovery µg/l	Mean Recovery %	Std Dev µg/l	RSD %	Conc µg/l	Mean Recovery µg/l	Mean Recovery %	Std Dev µg/l	RSD %	Conc µg/l	Mean Recovery µg/l	Mean Recovery %	Std Dev µg/l	RSD %
4.4'-DDE	CHEMICAL	2869A	0.2	0.18	88	0.01	3.3	1.0	0.75	75	0.03	4.0	5.0	3.50	70	0.18	5.2
	CHEMICAL	2869B	0.2	0.41	203	0.01	2.8	1.0	1.07	107	0.02	1.4	5.0	5.40	108	0.21	3.9
	PAPER	2621A	0.2	0.41	205	0.02	4.9	1.0	0.90	90	0.07	7.9	5.0	4.00	80	0.09	2.3
	PAPER	2621C	0.2	0.27	133	0.01	2.2	1.0	0.68	68	0.04	5.3	5.0	3.89	78	0.05	1.3
	PHARMACEUTICAL	2833A	0.2	0.23	115	0.00	0.0	1.0	0.74	74	0.01	0.8	5.0	4.61	92	0.12	2.6
	PHARMACEUTICAL	2833B	0.2	0.28	140	0.00	0.0	1.0	0.80	80	0.01	1.4	5.0	4.38	88	0.17	4.0
	REFUSE	4953B	0.2	0.37	183	0.01	1.6	1.0	1.00	100	0.02	1.5	5.0	5.06	101	0.11	2.2
	REFUSE	4953G	0.2	0.32	158	0.01	1.8	1.0	0.74	74	0.01	1.6	5.0	3.67	73	0.35	9.5
	SEWERAGE	4952A	0.2	0.22	110	0.00	0.0	1.0	0.80	80	0.01	1.3	5.0	4.18	84	0.08	1.8
	SEWERAGE	4952B	0.2	0.32	158	0.01	1.8	1.0	0.86	86	0.06	6.4	5.0	4.50	90	0.07	1.6
4,4'-DDT	CHEMICAL	2869A	1.0	0.87	87	0.06	6.7	5.0	4.08	82	0.18	4.4	15.0	11.63	78	0.57	4.9
	CHEMICAL	2869B	1.0	1.04	104	0.09	8.2	5.0	5.28	106	0.07	1.3	15.0	14.74	98	0.44	3.0
	PAPER	2621A	1.0	0.89	89	0.03	3.0	5.0	3.78	76	0.30	8.0	15.0	12.75	85	0.29	2.3
	PAPER	2621C	1.0	0.82	82	0.02	1.9	5.0	3.65	73	0.22	6.0	15.0	11.80	79	0.13	1.1
	PHARMACEUTICAL	2833A	1.0	0.71	71	0.01	0.8	5.0	3.89	78	0.03	0.8	15.0	13.37	89	0.30	2.3
	PHARMACEUTICAL	2833B	1.0	0.80	80	0.01	0.7	5.0	4.06	81	0.09	2.2	15.0	12.69	85	0.24	1.9
	REFUSE	4953B	1.0	0.90	90	0.02	1.9	5.0	5.05	101	0.06	1.2	15.0	15.80	105	0.37	2.4
	REFUSE	4953G	1.0	0.69	69	0.02	2.5	5.0	3.32	66	0.05	1.4	15.0	10.69	71	1.00	9.3
	SEWERAGE	4952A	1.0	0.81	81	0.03	3.3	5.0	3.46	69	0.03	0.8	15.0	9.70	65	0.06	0.6
	SEWERAGE	4952B	1.0	0.86	86	0.01	1.2	5.0	3.88	78	0.45	11.5	15.0	12.02	80	0.49	4.0
DIELDRIN	CHEMICAL	2869A	0.2	0.15	75	0.00	0.0	1.0	0.75	75	0.03	3.3	5.0	3.81	76	0.18	4.8
	CHEMICAL	2869B	0.2	0.23	113	0.01	5.1	1.0	0.80	80	0.01	0.7	5.0	4.46	89	0.03	0.7
	PAPER	2621A	0.2	0.63	315	0.11	16.7	1.0	1.03	103	0.06	5.7	5.0	5.09	102	0.13	2.5
	PAPER	2621C	0.2	0.21	105	0.00	0.0	1.0	0.65	65	0.03	5.0	5.0	4.22	84	0.05	1.2
	PHARMACEUTICAL	2833A	0.2	0.20	98	0.01	2.9	1.0	0.73	73	0.01	0.8	5.0	4.39	88	0.10	2.2
	PHARMACEUTICAL	2833B	0.2	0.21	105	0.00	0.0	1.0	0.71	71	0.02	2.4	5.0	3.90	78	0.22	5.8
	REFUSE	4953B	0.2	0.26	132	0.01	2.2	1.0	0.78	78	0.00	0.0	5.0	4.38	88	0.04	0.9
	REFUSE	4953G	0.2	0.32	158	0.01	1.8	1.0	0.79	79	0.02	1.9	5.0	3.80	76	0.23	6.0
	SEWERAGE	4952A	0.2	0.21	105	0.00	0.0	1.0	0.84	84	0.01	1.4	5.0	4.53	91	0.09	1.9
	SEWERAGE	4952B	0.2	0.20	100	0.00	0.0	1.0	0.61	61	0.04	6.7	5.0	4.01	80	0.09	2.1
ENDOSULFAN I	CHEMICAL	2869A	0.2	0.39	197	0.01	1.5	1.0	0.93	93	0.03	3.4	5.0	4.08	82	0.19	4.7
	CHEMICAL	2869B	0.2	0.20	98	0.01	5.9	1.0	0.72	72	0.01	0.8	5.0	3.64	73	0.03	0.8
	PAPER	2621A	0.2	0.25	127	0.04	14.9	1.0	0.89	89	0.04	4.0	5.0	5.31	106	0.12	2.3
	PAPER	2621C	0.2	0.19	95	0.00	0.0	1.0	0.61	61	0.02	3.8	5.0	3.56	71	0.03	0.7
	PHARMACEUTICAL	2833A	0.2	0.15	73	0.01	3.9	1.0	0.59	59	0.00	0.0	5.0	4.66	93	0.10	2.1
	PHARMACEUTICAL	2833B	0.2	0.19	95	0.00	0.0	1.0	0.66	66	0.01	1.7	5.0	3.73	75	0.19	5.2
	REFUSE	4953B	0.2	0.22	108	0.01	2.7	1.0	0.67	67	0.00	0.0	5.0	3.58	72	0.05	1.3
	REFUSE	4953G	0.2	0.18	90	0.00	0.0	1.0	0.58	58	0.02	2.6	5.0	2.87	57	0.14	4.8
	SEWERAGE	4952A	0.2	0.20	98	0.01	2.9	1.0	1.07	107	0.01	0.5	5.0	5.62	112	0.10	1.8
	SEWERAGE	4952B	0.2	0.18	90	0.00	0.0	1.0	0.58	58	0.03	5.3	5.0	3.69	74	0.06	1.7
ENDOSULFANII	CHEMICAL	2869A	1.0	0.88	88	0.03	2.9	5.0	3.99	80	0.14	3.6	15.0	10.97	73	0.49	4.5
	CHEMICAL	2869B	1.0	0.75	75	0.07	8.8	5.0	4.09	82	0.02	0.4	15.0	13.85	92	0.06	0.4
	PAPER	2621A	1.0	0.85	85	0.04	4.8	5.0	4.07	81	0.28	6.8	15.0	15.40	103	0.43	2.8
	PAPER	2621C	1.0	0.75	75	0.02	2.0	5.0	3.45	69	0.15	4.4	15.0	12.86	86	0.16	1.2
	PHARMACEUTICAL	2833A	1.0	0.68	68	0.01	1.7	5.0	3.49	70	0.01	0.2	15.0	13.54	90	0.35	2.6
	PHARMACEUTICAL	2833B	1.0	0.75	75	0.01	1.3	5.0	3.77	75	0.10	2.6	15.0	13.56	90	0.31	2.3
	REFUSE	4953B	1.0	0.69	69	0.00	0.0	5.0	3.84	77	0.03	0.7	15.0	14.36	96	0.11	0.7
	REFUSE	4953G	1.0	0.62	62	0.01	1.6	5.0	3.15	63	0.04	1.4	15.0	11.75	78	0.49	4.2
	SEWERAGE	4952A	1.0	0.82	82	0.02	1.9	5.0	5.17	103	0.02	0.3	15.0	15.16	101	0.27	1.8
	SEWERAGE	4952B	1.0	0.74	74	0.01	0.8	5.0	3.34	67	0.17	5.2	15.0	13.05	87	0.24	1.8
ENDOSULFANSULFATE	CHEMICAL	2869A	1.0	0.98	98	0.01	1.2	5.0	4.21	84	0.18	4.3	15.0	12.57	84	0.64	5.1
	CHEMICAL	2869B	1.0	1.05	105	0.08	8.0	5.0	5.14	103	0.01	0.1	15.0	15.02	100	0.07	0.5
	PAPER	2621A	1.0	0.93	93	0.03	2.8	5.0	4.94	99	0.31	6.3	15.0	16.18	108	0.53	3.3
	PAPER	2621C	1.0	0.93	93	0.01	1.2	5.0	4.18	84	0.19	4.6	15.0	14.01	93	0.09	0.6
	PHARMACEUTICAL	2833A	1.0	0.87	87	0.03	2.9	5.0	4.65	93	0.02	0.4	15.0	14.26	95	0.29	2.0
	PHARMACEUTICAL	2833B	1.0	0.86	86	0.01	1.2	5.0	5.27	105	0.11	2.0	15.0	14.78	99	0.55	3.7
	REFUSE	4953B	1.0	0.96	96	0.02	1.6	5.0	5.10	102	0.04	0.9	15.0	15.76	105	0.12	0.8
	REFUSE	4953G	1.0	0.98	98	0.00	0.0	5.0	4.67	93	0.06	1.2	15.0	13.76	92	0.57	4.1
	SEWERAGE	4952A	1.0	1.03	103	0.02	2.2	5.0	5.10	102	0.01	0.2	15.0	14.04	94	0.25	1.8
	SEWERAGE	4952B	1.0	1.15	115	0.02	1.3	5.0	5.17	103	0.37	7.2	15.0	16.49	110	0.27	1.6

TABLE 4. SINGLE ANALYST PRECISION AND ACCURACY IN WASTE WATER SAMPLES (cont'd)

Analyte	Industry	SIC Code	Conc µg/l	Mean Recovery µg/l	Mean Recovery %	Std Dev µg/l	RSD %	Conc µg/l	Mean Recovery µg/l	Mean Recovery %	Std Dev µg/l	RSD %	Conc µg/l	Mean Recovery µg/l	Mean Recovery %	Std Dev µg/l	RSD %
ENDRIN	CHEMICAL	2869A	1.0	1.04	104	0.02	2.0	5.0	4.77	95	0.18	3.7	15.0	13.07	87	0.61	4.7
	CHEMICAL	2869B	1.0	1.07	107	0.09	8.1	5.0	5.53	111	0.02	0.3	15.0	15.69	105	0.13	0.8
	PAPER	2621A	1.0	0.92	92	0.04	4.7	5.0	4.29	86	0.29	6.9	15.0	14.51	97	0.42	2.9
	PAPER	2621C	1.0	0.87	87	0.02	2.3	5.0	4.08	82	0.18	4.5	15.0	13.92	93	0.14	1.0
	PHARMACEUTICAL	2833A	1.0	0.81	81	0.02	2.5	5.0	4.70	94	0.02	0.5	15.0	14.48	97	0.23	1.6
	PHARMACEUTICAL	2833B	1.0	0.93	93	0.01	1.2	5.0	4.77	95	0.08	1.6	15.0	14.88	99	0.16	1.1
	REFUSE	4953B	1.0	0.97	97	0.02	1.6	5.0	5.40	108	0.12	2.2	15.0	17.07	114	0.24	1.4
	REFUSE	4953G	1.0	0.93	93	0.02	1.9	5.0	4.56	91	0.08	1.7	15.0	13.04	87	0.49	3.8
	SEWERAGE	4952A	1.0	0.90	90	0.02	1.7	5.0	4.67	93	0.01	0.2	15.0	13.36	89	0.26	2.0
	SEWERAGE	4952B	1.0	1.12	112	0.02	1.5	5.0	4.35	87	0.40	9.2	15.0	13.97	93	0.56	4.0
ENDRINALDEHYDE	CHEMICAL	2869A	0.2	0.49	247	0.02	4.2	1.0	0.22	22	0.03	11.6	5.0	0.53	11	0.03	5.7
	CHEMICAL	2869B	0.2	0.19	97	0.01	3.0	1.0	0.84	84	0.03	3.8	5.0	3.79	76	0.02	0.5
	PAPER	2621A	0.2	0.13	67	0.01	4.3	1.0	0.66	66	0.04	6.6	5.0	3.72	74	0.13	3.5
	PAPER	2621C	0.2	0.19	95	0.00	0.0	1.0	0.67	67	0.03	3.9	5.0	3.94	79	0.04	1.0
	PHARMACEUTICAL	2833A	0.2	0.21	107	0.01	2.7	1.0	0.94	94	0.00	0.0	5.0	4.82	96	0.11	2.2
	PHARMACEUTICAL	2833B	0.2	0.17	83	0.01	3.5	1.0	0.69	69	0.03	3.8	5.0	2.96	59	0.15	5.0
	REFUSE	4953B	0.2	0.28	138	0.01	2.1	1.0	1.22	122	0.03	2.5	5.0	5.49	110	0.07	1.3
	REFUSE	4953G	0.2	0.23	115	0.01	4.3	1.0	0.99	99	0.01	0.6	5.0	4.75	95	0.18	3.8
	SEWERAGE	4952A	0.2	0.16	82	0.01	3.5	1.0	0.67	67	0.01	1.7	5.0	2.71	54	0.09	3.2
	SEWERAGE	4952B	0.2	0.15	73	0.01	3.9	1.0	0.58	58	0.02	2.6	5.0	3.73	75	0.20	5.4
GAMMA-BHC	CHEMICAL	2869A	0.2	0.22	110	0.01	4.5	1.0	0.74	74	0.03	4.1	5.0	3.52	70	0.11	3.0
	CHEMICAL	2869B	0.2	0.28	142	0.02	5.4	1.0	0.96	96	0.00	0.0	5.0	5.06	101	0.02	0.5
	PAPER	2621A	0.2	1.31	657	0.08	6.1	1.0	1.95	195	0.08	4.1	5.0	5.86	117	0.24	4.0
	PAPER	2621C	0.2	0.25	125	0.00	0.0	1.0	0.75	75	0.03	4.6	5.0	4.69	94	0.03	0.7
	PHARMACEUTICAL	2833A	0.2	0.21	105	0.00	0.0	1.0	0.83	83	0.00	0.0	5.0	4.91	98	0.10	2.1
	PHARMACEUTICAL	2833B	0.2	0.26	132	0.01	2.2	1.0	0.85	85	0.01	1.2	5.0	5.00	100	0.19	3.8
	REFUSE	4953B	0.2	0.31	155	0.00	0.0	1.0	0.95	95	0.01	0.6	5.0	5.02	100	0.05	1.0
	REFUSE	4953G	0.2	0.40	198	0.01	1.5	1.0	1.01	101	0.02	1.5	5.0	4.59	92	0.12	2.6
	SEWERAGE	4952A	0.2	0.23	115	0.00	0.0	1.0	0.93	93	0.02	1.9	5.0	4.56	91	0.08	1.8
	SEWERAGE	4952B	0.2	0.27	137	0.01	4.2	1.0	0.79	79	0.06	7.6	5.0	4.85	97	0.13	2.7
HEPTACHLOR	CHEMICAL	2869A	0.2	0.16	78	0.01	3.7	1.0	0.68	68	0.03	4.4	5.0	3.03	61	0.15	4.9
	CHEMICAL	2869B	0.2	0.32	162	0.02	4.7	1.0	1.37	137	0.02	1.5	5.0	5.79	116	0.07	1.2
	PAPER	2621A	0.2	0.24	122	0.02	6.3	1.0	0.80	80	0.06	7.1	5.0	3.64	73	0.12	3.2
	PAPER	2621C	0.2	0.25	127	0.01	2.3	1.0	0.74	74	0.04	5.1	5.0	4.31	86	0.10	2.2
	PHARMACEUTICAL	2833A	0.2	0.21	107	0.01	2.7	1.0	0.96	96	0.04	4.5	5.0	4.49	90	0.09	1.9
	PHARMACEUTICAL	2833B	0.2	0.34	168	0.01	1.7	1.0	1.57	157	0.02	1.3	5.0	5.80	116	0.10	1.8
	REFUSE	4953B	0.2	0.34	172	0.01	1.7	1.0	1.31	131	0.01	0.8	5.0	5.81	116	0.07	1.1
	REFUSE	4953G	0.2	0.23	113	0.01	2.5	1.0	0.77	77	0.02	2.0	5.0	3.44	69	0.28	8.2
	SEWERAGE	4952A	0.2	0.24	120	0.00	0.0	1.0	0.76	76	0.01	1.5	5.0	3.39	68	0.07	2.1
	SEWERAGE	4952B	0.2	0.23	113	0.01	2.5	1.0	0.87	87	0.06	7.0	5.0	4.54	91	0.07	1.5
HEPTACHLOR EPOXIDE	CHEMICAL	2869A	0.2	0.18	88	0.01	3.3	1.0	0.76	76	0.03	4.0	5.0	3.54	71	0.17	4.8
	CHEMICAL	2869B	0.2	0.23	113	0.01	2.5	1.0	0.99	99	0.01	0.6	5.0	5.01	100	0.02	0.4
	PAPER	2621A	0.2	1.18	592	0.12	9.9	1.0	1.77	177	0.07	3.8	5.0	5.28	106	0.10	1.9
	PAPER	2621C	0.2	0.26	128	0.01	2.2	1.0	0.80	80	0.03	4.0	5.0	4.65	93	0.05	1.1
	PHARMACEUTICAL	2833A	0.2	0.18	92	0.01	3.1	1.0	0.88	88	0.01	0.7	5.0	4.78	96	0.09	1.9
	PHARMACEUTICAL	2833B	0.2	0.21	105	0.00	0.0	1.0	0.87	87	0.02	1.8	5.0	4.68	94	0.22	4.7
	REFUSE	4953B	0.2	0.27	137	0.01	2.1	1.0	0.96	96	0.01	0.6	5.0	4.92	98	0.06	1.1
	REFUSE	4953G	0.2	0.24	120	0.00	0.0	1.0	0.87	87	0.02	1.7	5.0	4.12	82	0.17	4.2
	SEWERAGE	4952A	0.2	0.20	100	0.00	0.0	1.0	0.88	88	0.00	0.0	5.0	4.28	86	0.08	1.8
	SEWERAGE	4952B	0.2	0.21	103	0.01	2.8	1.0	0.77	77	0.05	6.0	5.0	4.63	93	0.09	1.9
METHOXYCHLOR	CHEMICAL	2869A	0.2	0.31	153	0.01	1.9	1.0	1.18	118	0.05	4.0	5.0	5.08	102	0.17	3.4
	CHEMICAL	2869B	0.2	0.43	215	0.02	4.7	1.0	1.38	138	0.02	1.7	5.0	6.21	124	0.07	1.1
	PAPER	2621A	0.2	0.35	177	0.01	3.3	1.0	0.98	98	0.07	7.1	5.0	4.77	95	0.22	4.6
	PAPER	2621C	0.2	0.34	170	0.00	0.0	1.0	1.01	101	0.04	4.3	5.0	5.15	103	0.02	0.3
	PHARMACEUTICAL	2833A	0.2	0.25	125	0.00	0.0	1.0	0.98	98	0.02	2.1	5.0	5.02	100	0.09	1.7
	PHARMACEUTICAL	2833B	0.2	0.36	180	0.00	0.0	1.0	1.16	116	0.03	2.5	5.0	5.44	109	0.27	4.9
	REFUSE	4953B	0.2	0.43	213	0.01	1.4	1.0	1.27	127	0.03	2.4	5.0	6.32	126	0.07	1.1
	REFUSE	4953G	0.2	0.38	190	0.03	7.0	1.0	1.28	128	0.22	17.2	5.0	4.99	100	0.18	3.7
	SEWERAGE	4952A	0.2	0.11	57	0.01	5.1	1.0	0.75	75	0.01	0.8	5.0	3.49	70	0.03	0.7
	SEWERAGE	4952B	0.2	0.48	240	0.00	0.0	1.0	1.28	128	0.11	8.4	5.0	5.99	120	0.25	4.1

TABLE 4. SINGLE ANALYST PRECISION AND ACCURACY IN WASTE WATER SAMPLES (cont'd)

Analyte	Industry	SIC Code	Conc µg/l	Mean Recovery µg/l	Mean Recovery %	Std Dev µg/l	RSD %	Conc µg/l	Mean Recovery µg/l	Mean Recovery %	Std Dev µg/l	RSD %	Conc µg/l	Mean Recovery µg/l	Mean Recovery %	Std Dev µg/l	RSD %
PCB	CHEMICAL	2869A	2.0	2.39	120	0.41	17.2	10.0	8.75	88	1.07	12.2	100	81.72	82	1.46	1.8
	CHEMICAL	2869B	2.0	0.56	28	0.03	5.4	10.0	8.08	81	0.06	0.7	100	89.71	90	0.66	0.7
	PAPER	2621A	2.0	3.00	150	0.56	18.5	10.0	8.88	89	0.71	7.9	100	73.73	74	3.94	5.3
	PAPER	2621C	2.0	2.30	115	0.08	3.7	10.0	10.14	101	0.15	1.4	100	95.26	95	1.89	2.0
	PHARMACEUTICAL	2833A	2.0	1.52	78	0.03	1.7	10.0	9.19	92	0.24	2.6	100	86.41	86	1.95	2.3
	PHARMACEUTICAL	2833B	2.0	1.02	51	0.03	2.9	10.0	8.42	84	0.17	2.0	100	79.16	79	3.92	4.9
	REFUSE	4953B	2.0	0.54	27	0.04	6.7	10.0	8.80	88	0.49	5.6	100	85.70	86	1.59	1.9
	REFUSE	4953G	2.0	0.63	31	0.10	16.0	10.0	8.00	80	1.44	18.0	100	71.50	72	1.61	2.2
	SEWERAGE	4952A	2.0	1.92	96	0.15	7.8	10.0	9.52	95	0.07	0.8	100	87.76	88	1.76	2.0
	SEWERAGE	4952B	2.0	2.10	105	0.04	1.8	10.0	8.18	82	0.17	2.1	100	80.59	81	0.40	0.5
TOXAPHENE	CHEMICAL	2869A	10.0	9.84	98	0.54	5.5	50.0	45.44	91	3.81	8.4	250	141.06	56	34.88	24.7
	CHEMICAL	2869B	10.0	10.13	101	0.93	9.2	50.0	42.99	86	0.47	1.1	250	222.52	89	4.78	2.1
	PAPER	2621A	10.0	34.85	349	4.30	12.3	50.0	64.23	128	7.91	12.3	250	179.12	72	9.04	5.0
	PAPER	2621C	10.0	20.42	204	0.02	0.1	50.0	55.63	111	2.95	5.3	250	244.58	98	3.14	1.3
	PHARMACEUTICAL	2833A	10.0	10.82	108	0.90	8.3	50.0	29.67	59	17.53	59.1	250	217.29	87	2.54	1.2
	PHARMACEUTICAL	2833B	10.0	8.73	87	0.52	6.0	50.0	49.22	98	0.74	1.5	250	196.22	78	6.64	3.4
	REFUSE	4953B	10.0	10.94	109	0.09	0.8	50.0	45.34	91	1.06	2.3	250	226.00	90	3.93	1.7
	REFUSE	4953G	10.0	26.17	262	0.50	1.9	50.0	54.19	108	3.07	5.7	250	189.47	76	4.42	2.3
	SEWERAGE	4952A	10.0	13.22	132	0.57	4.3	50.0	39.99	80	0.65	1.6	250	203.78	82	2.14	1.0
	SEWERAGE	4952B	10.0	12.60	126	0.23	1.8	50.0	38.49	77	0.50	1.3	250	189.07	76	3.64	1.9