ALLOWAY

STANDARD OPERATING PROCEDURE FOR METHOD 508

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

EPA Method: 508 Revision 3.1, 1995

Alloway Revision 9

Originator: Date:
Section Supervisor: Date:
QA Manager: Date:
Section 1.0 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:

<table>
<thead>
<tr>
<th>Analyte</th>
<th>CAS NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin</td>
<td>309-00-2</td>
</tr>
<tr>
<td>Gamma-BHC (Lindane)</td>
<td>58-89-9</td>
</tr>
<tr>
<td>Chlordane-total</td>
<td>57-74-9</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>60-57-1</td>
</tr>
<tr>
<td>Endrin</td>
<td>72-20-8</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>76-44-8</td>
</tr>
<tr>
<td>Heptachlor Epoxide</td>
<td>1024-57-3</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>118-74-1</td>
</tr>
<tr>
<td>Hexachlorocyclopentadiene</td>
<td>77-47-4</td>
</tr>
<tr>
<td>Methoxychlor</td>
<td>72-43-5</td>
</tr>
<tr>
<td>Propachlor</td>
<td>1918-16-7</td>
</tr>
<tr>
<td>Toxaphene</td>
<td>8001-35-2</td>
</tr>
<tr>
<td>4,4'-DDD</td>
<td>72-54-8</td>
</tr>
<tr>
<td>4,4'-DDE</td>
<td>72-55-9</td>
</tr>
<tr>
<td>4,4'-DDT</td>
<td>50-29-3</td>
</tr>
<tr>
<td>Endrin Aldehyde</td>
<td>7421-93-4</td>
</tr>
<tr>
<td>Endrin Ketone</td>
<td>53494-70-5</td>
</tr>
<tr>
<td>Aroclor-1016</td>
<td>12674-11-2</td>
</tr>
<tr>
<td>Aroclor-1221</td>
<td>11104-28-2</td>
</tr>
<tr>
<td>Aroclor-1232</td>
<td>11141-16-5</td>
</tr>
<tr>
<td>Aroclor-1242</td>
<td>53469-21-9</td>
</tr>
<tr>
<td>Aroclor-1248</td>
<td>12672-29-6</td>
</tr>
<tr>
<td>Aroclor-1254</td>
<td>11097-69-1</td>
</tr>
<tr>
<td>Aroclor-1260</td>
<td>11096-82-5</td>
</tr>
</tbody>
</table>

1.2 This method is restricted to use by or under the supervision of analysts experienced in the use of GC and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 10.2.
Section 2.0 Summary of Method

2.1 A measured volume of sample of approximately 1 liter is extracted with Methylene chloride by shaking in separatory funnel. The Methylene chloride extract is isolated, dried and concentrated to a volume of 2 ml during a solvent exchange to methyl tert-butyl ether (MTBE). Chromatographic 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).

Section 3.0 Definitions

3.1 Acceptance Criteria – specified limits placed on characteristics of an item, process, or service defined in required documents.

3.2 Analytical Batch – composed of prepared environmental samples which are analyzed together as a group. It can include prepared sample originating from various environmental matrices and can exceed 20 samples.

3.3 Calibration – to determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter, instrument, or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

3.4 Calibration Curve – the graphical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response.

3.5 Calibration Standard (CAL) -- A solution prepared from the primary dilution standard solution. The CAL is used to calibrate an instrument.

3.6 Field Blank or Trip Blank – blank prepared in the field or laboratory by filling a clean container with pure de-ionized water and appropriate preservative, if any, for the specific sampling activity being undertaken.

3.7 High Quality Pure Reagent Water – water in which no target analytes or interferences are detected as required by the analytical method.

3.8 Holding Times (Maximum Allowable Holding Times) – the maximum times that samples may be held prior to analysis and still be considered valid or not compromised.
3.9 **Internal Standard** – a known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

3.10 **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.

3.11 **Laboratory Fortified Blank (LFB)** -- An aliquot of reagent water to which a known quantity of the method analyte is added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.12 **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.

3.13 **Matrix** – the component or substrate that contains the analyte of interest.

3.14 **Matrix Spike (MS) or Laboratory Fortified Matrix (LFM)** – a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Used to determine the effect of the matrix on a method’s recovery efficiency. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured value in the LFM corrected for background concentration.

3.15 **Matrix Spike Duplicate (MSD) or Laboratory Fortified Matrix Duplicate (LFMD)** – a second replicate of spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

3.16 **Primary Dilution Standard Solution (PDS)** - A solution of several analytes purchased from a commercial source and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.17 **Procedural Standard Calibration** - A calibration method where aqueous calibration standards are prepared and processed (e.g., purged, extracted, and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses compensates for any inefficiencies in the processing procedure.
3.18 **Quality Control** – the overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

3.19 **Raw Data** – any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report activity.

3.20 **Reference Method** – a method of known and documented accuracy and precision issued by an organization recognized as competent to do so.

3.21 **Standard Operating Procedures (SOPs)** – a written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

3.22 **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.

3.23 **Surrogate** – a substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes. Calculated as percent recovery.

**Section 4.0 Interferences**

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated baselines in gas chromatograms. The LRB is used as a tool to monitor for the presence of interferences.

4.2 Glassware must be carefully cleaned as detailed in the laboratory’s Standard Operating Procedure for Glassware Preparation.

4.3 Interfering contamination may occur when a sample containing low concentrations of compounds is analyzed immediately after a sample containing relatively high concentrations of compounds. Syringes and injection port liners must be cleaned carefully or replaced as needed. After analysis of a sample containing high concentrations of compounds, a solvent blank or an LRB is analyzed to ensure that accurate values are obtained for the next sample. If suspicion of carryover exists, reanalysis of the affected samples is performed.
4.4 Samples and standards must be contained in the same solvent to ensure chromatographic comparability.

4.5 Sample matrix interferences: A confirmation column or another analytical technique, such as GC/MS, may be used to confirm the presence of a compound or may be used to separate a matrix interferent from the target compound.

Section 5.0 Safety

5.1 The toxicity or carcinogenicity of each chemical and reagent used in this method has not been precisely defined. However, each one must be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each analyst is responsible for adherence to the procedures outlined in the Chemical Hygiene Plan. Material Safety Data Sheets are stored in the Quality Assurance Section of the laboratory.

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

5.3 Safety glasses, gloves, and lab coats must be worn when handling samples and solvents. Safety glasses must be worn when handling glassware and chromatographic columns. Safety glasses must be worn when handling equipment within the laboratory.

Section 6.0 Equipment and Supplies

6.1 Sample Bottle -- Borosilicate, 1-L volume fitted with screw caps lined with PTFE-fluorocarbon. Protect samples from light. Cap liners are also used.

6.2 Glassware

   6.2.1 Separatory funnel -- 2,000-mL, with TFE-fluorocarbon stopcock, ground glass or TFE-fluorocarbon stopper.

   6.2.2 Erlenmeyer Flask -- 250-mL.

   6.2.3 Concentrator tube, Kuderna-Danish (K-D) -- 10 or 25-mL, graduated. Calibration must be checked at the volumes employed in the test. Ground glass stoppers are used to prevent evaporation of extracts.
6.2.4 Evaporative flask, K-D -- 500-mL. Attach to concentrator tube with springs.

6.2.5 Snyder column, K-D -- Three-ball macro.

6.2.6 Vials -- glass, 10 –40 AND 60-mL capacity with TFE-fluorocarbon lined screw cap for standard preparation.

6.2.7 Graduated cylinder --- 1000 ML

6.2.8 Glass funnel

6.2.9 Volumetrics

6.3 **Separatory funnel mechanical shaker** -- Capable of holding 2-L separatory funnels and shaking them with rocking motion to achieve thorough mixing of separatory funnel contents.

6.4 **Boiling stones** -- Carborundum, #12 granules.

6.5 **Water bath** -- Heated, capable of temperature control (±2°C). The bath should be used in a hood.

6.6 **Balance** -- Analytical, capable of accurately weighing to the nearest 0.001 g.

6.7 **Muffle Furnace**

6.8 **N-EVAP**

6.9 **Thermometer**

6.10 **Metal spatula**

6.11 **Rinsed glass wool**

6.12 **Permanent ink marker**

6.13 **Prep sheet**

6.14 **1 ml autosampler vial**

6.15 **Crimp caps**

6.16 **Crimper**
6.17  Rubber pipette bulb

6.18  Disposable pasteur pipettes

6.19  pH paper

6.20  Glass rods

6.21  Syringes (of various sizes)

6.22  DI water

6.23  Bottle top dispenser for solvent bottles

6.24  Gas Chromatograph – Varian CP-3800 GC system, temperature programmable for use with capillary columns and all required accessories including syringes, analytical columns, liners with glass wool inside, gases, detector and data system.

6.24.1  Column 1 (RTX-CLPesticides) -- 30 m long x 0.32 mm, 0.50 µm film thickness or equivalent.

6.24.2  Column 2 (RTX CLPesticides II) -- 30 m long x 0.32 mm, 0.25 µm film thickness or equivalent.

6.24.3  Helium carrier gas flow is established at 34 cm/sec linear velocity and oven temperature is programmed from 120°C to hold for 1 minute, then to 300°C at 9°C/min. with a final hold of 3 minutes. The injection volume is 2 µL. The injector temperature is 225°C and the detector temperature is 310°C.

6.24.4  Detector – Electron Capture Detector (ECD). An ECD was used to generate the validation data presented in this method. Alternative detectors, including a mass spectrometer, may be used.

6.24.5  Data Collection – Varian Galaxie Chromatography data system software

Section 7.0  Reagents and Calibration Standards

7.1  Acetone, Methylene chloride, methyl tert-butyl ether (MTBE), Hexane -- Distilled-in-glass quality or equivalent.

7.2  Phosphate buffer, pH 7 – Purchased in 20 Liter container from VWR.
7.3 Sodium chloride (NaCl), crystal, ACS grade -- Heat treat in a shallow tray at 450°C for a minimum of 4 hours to remove interfering organic substances.

7.4 Sodium sulfate, granular, anhydrous, ACS grade -- Heat in beakers ¾ full setting in a shallow pan for a minimum of 4 hours at 450°C to remove interfering organic substances.

7.5 Sodium thiosulfate, granular anhydrous, ACS grade.

7.6 10N NaOH

7.7 Nitrogen

7.8 Helium (carrier gas)

7.9 High Quality Pure Reagent Water

7.10 Stock Standard Solutions- Stock standard solutions are purchased as certified solutions and should be replaced after the manufacturer’s expiration date or sooner if comparison with laboratory fortified blanks, or QC samples indicate a problem. They are purchased as follows:

7.10.1 Ultra Scientific custom mix in MTBE contains the following:

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration (µg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin</td>
<td>50</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>50</td>
</tr>
<tr>
<td>4,4'-DDE</td>
<td>100</td>
</tr>
<tr>
<td>4,4'-DDD</td>
<td>100</td>
</tr>
<tr>
<td>4,4'-DDT</td>
<td>100</td>
</tr>
<tr>
<td>Endrin</td>
<td>50</td>
</tr>
<tr>
<td>Endrin aldehyde</td>
<td>100</td>
</tr>
<tr>
<td>Endrin ketone</td>
<td>100</td>
</tr>
<tr>
<td>Gamma-BHC (Lindane)</td>
<td>50</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>50</td>
</tr>
<tr>
<td>Heptachlor epoxide</td>
<td>50</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>50</td>
</tr>
<tr>
<td>HCCPD</td>
<td>100</td>
</tr>
<tr>
<td>Methoxychlor</td>
<td>100</td>
</tr>
<tr>
<td>Propachlor</td>
<td>100</td>
</tr>
</tbody>
</table>

7.10.2 Ultra Scientific chlordane-solution in methanol contains the following:

Chlordane at 5000 µg/ml
7.10.3 Ultra Scientific Toxaphene-solution in methanol contains the following:

Toxaphene at 1000 µg/ml

7.10.4 Ultra Scientific AROCLOR SOLUTIONS contain the following:

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration (µg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aroclor 1016/1260</td>
<td>1000</td>
</tr>
<tr>
<td>Aroclor 1221</td>
<td>1000</td>
</tr>
<tr>
<td>Aroclor 1232</td>
<td>1000</td>
</tr>
<tr>
<td>Aroclor 1242</td>
<td>1000</td>
</tr>
<tr>
<td>Aroclor 1248</td>
<td>1000</td>
</tr>
<tr>
<td>Aroclor 1254</td>
<td>1000</td>
</tr>
</tbody>
</table>

7.11 Surrogate Standard Solution -- Surrogate standard solutions are purchased as certified solutions.

7.11.1 Ultra Scientific Pest Surrogate Std. Spiking Solution contain the following:

DCB at 200 µg/ml
TCMX at 200 µg/ml

* Solution should be replaced when ongoing QC indicates a problem.

7.12 Laboratory Performance/Degradation check Solution - a mix out of Ultra Scientific purchased LPC solutions and single compound Endrin and DDT solution. It contains those compounds and concentrations listed in Table 2.

7.12.1 Transfer to a PTFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC indicates a problem.

7.12.2 This solution is injected to check for undesirable degradation of Endrin and DDT in the injection port by looking for Endrin aldehyde and Endrin ketone and for 4,4’-DDE and 4,4’-DDD and to monitor instrument sensitivity, column performance and chromatographic performance instrument performance will be checked on a daily basis.

Section 8.0 Sample Collection, Preservation, Shipment, 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 pre-washed with sample before collection.
8.2 If residual chlorine is present, add 80 mg of Sodium Thiosulfate per liter of sample to the sample bottle prior to collecting the sample. After the sample is collected in a bottle containing preservative, seal the bottle and shake vigorously for 1 minute.

8.3 The samples must be iced or refrigerated at 0.5 - 6°C away from light from the time of collection until extraction. Preservation study results indicate that most method analytes present in samples are stable for seven days when stored under these conditions.

8.4 Extracts should be stored at 0.5 - 6°C away from light. A 14-day maximum extract storage time is recommended.

Section 9.0 Calibration and Standardization

Establish GC operating parameters equivalent to those indicated in Section 6.24. The GC system is calibrated using the external standard technique.

9.1 External Standard Calibration Procedure

9.1.1 Prepare calibration standards, calibration check standards (CCVs), report limit check standards (RDLs), and laboratory performance check standards (LPCs) as outlined in Reagent Traceability under the heading “508 Chlorinated Pesticides”. Be sure to prepare those labeled for Toxaphene and Chlordane as well as Pesticides.

9.1.2 Prepare calibration standards and CCVs as outlined in Reagent Traceability under the heading “608/8082 Pesticides/PCBs”. These will be used for the PCB screen, as well as for quantitation of any PCB hits that are not specifically slated for method 508A.

9.1.3 Inject the LPC standard (See Appendices). If degradation of either DDT or Endrin exceeds 20%, take corrective action before proceeding with calibration. This would include resilanizing or replacing the injection port liner and/or breaking off approximately 1 meter from the front of the column.

9.1.4 Starting with the standard of lowest concentration, analyze each calibration standard and tabulate response (peak height or area) versus the concentration in the standard (See Section 12.0). The results of 6 points (or at least 5 points) are 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.
9.2 Continuing Calibration Verification (CCV)

9.2.1 One of two mid range calibration check standards containing all of the single component pesticides must be analyzed alternating every 10 injections. A mid range calibration check standard for one of the two multi-component pesticides (Toxaphene or Chlordane) must accompany them.

9.2.1.1 If the reanalyzed CCV meets the requirements of 80-120% recovery then analysis may proceed.

9.2.1.2 If the reanalyzed CCV is high (>120%) and the results of samples are below the reporting levels, the results of the samples can be reported without qualification.

9.2.1.3 If the reanalyzed CCV is high (>120%) indicating a high bias, and the results of samples are detected at or above the reporting limit the samples need to be reanalyzed following the acceptance of a new calibration curve or a completed corrective action.

9.2.1.4 If the reanalyzed CCV is low (<80%) indicating a low bias, results for samples exceeding a regulatory limit may be reported and qualified using the statement: The CCV was below the lowest limit indicating a low bias. This result exceeds the regulatory limit and is considered a reportable value under the TNI standards.

9.2.1.5 If the reanalyzed CCV is biased low (<80%) and the results of the samples do not exceed a regulatory limit then the samples must be reanalyzed after acceptance of a new calibration curve.

9.2.2 The CCV must be from a different source than that of the standard used in the initial calibration curve.

Note: It is suggested that the multi-component analytes be alternated for each batch.

9.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of calibration check standards. A Reporting Limit Check (RLC) standard must be analyzed at a minimum of one time every 24 hours that samples are ran and a new curve is not established. The reporting limit is from the lowest point in the curve and must fall between 50% and 150% recovery.

9.3.1 An extracted RLC must be analyzed at least once every 3 months or at least 10% of extracted sample sets, whichever is greater. The limits are 50% to 150% of true value.
Section 10.0 Quality Control

10.1 Minimum quality control (QC) requirements are:

Initial demonstration of capability and detection limit studies and ongoing analysis of laboratory reagent blanks (LRB), laboratory performance check solutions (LPC), laboratory fortified sample matrix (LFM), laboratory fortified blanks (LFB), and quality control samples (QCS) to evaluate and document data quality. Determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank not to exceed ±30%. (when internal standard calibration procedures are being employed).

10.1.1 An MDL for each analyte. A MDL study for the front and back columns must be performed if each column is used as the primary column from time to time.

10.1.2 Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

10.2 Initial Demonstration of Capability

10.2.1 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. Analyze 4 LFB’s according to procedures beginning in section 11.0.

10.2.2 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 1. 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.

10.2.3 For each analyte, determine the MDL. Prepare a minimum of seven LFBs at a low concentration. The LFB’s should be prepared over a period of several days so that day to day variations are reflected in precision measurements. Use calibration data obtained in Section 9 to estimate a concentration for each analyte that will produce a peak with a three to five times signal to noise response. Extract and analyze each replicate according to Sections 11.0 and 12.0. The formula for the MDL is in section 12.5.
10.2.4 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.

10.3 **Assessing Instrument System -- Laboratory Performance Check (LPC)**

10.3.1 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 that check for undesirable degradation of Endrin and DDT in the injection port by looking for Endrin aldehyde and Endrin ketone and for 4,4'-DDE and 4,4'-DDD and to monitor instrument sensitivity, column performance and chromatographic performance. Instrument performance LPC sample components and performance criteria are listed in Table 1. 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.

If degradation of either DDT or Endrin exceeds 20% replace the injection port liner and/or cut off a meter from the front of the column.

10.4 **Laboratory Reagent Blanks (LRB) --** 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 LRB must be analyzed. For any analytes of interest found in the LRB the following applies:

10.4.1 Samples can be reported if any analyte of interest is found in the LRB below the reporting limit.

10.4.2 If the analyte is detected at or above the reporting level, samples that are below the reporting limit can be reported with a qualifying statement.

10.4.3 If an analyte is detected at or above the reporting limit, instrument results that are 10 times higher than the LRB results can be reported using the following qualifying statement: Analyte detected in the LRB is \( \leq \frac{1}{10} \) of the amount found in the sample. Associated data may be biased high, evaluate data accordingly.

10.4.4 If an analyte is detected at or above the reporting limit, instrument results that are not 10 times higher than the LRB should be re-analyzed or if
reported the following qualification statement must be used: Analyte detected in the LRB >1/10 of the amount detected in the sample. Evaluate data accordingly.

10.4.5 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.

10.5 Assessing Surrogate Recovery

10.5.1 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.

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

10.5.3 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, qualify all data as estimated with either a high or low bias.

10.6 Assessing Laboratory Performance -- Laboratory Fortified Blank (LFB)

10.6.1 The laboratory must analyze at least one laboratory fortified blank (LFB) sample with every 20 samples or one per sample set (all samples extracted within a 24 hour period) whichever is greater. The concentration of the LFB should be midrange of the calibration curve and/or 10 times the EDL. Calculate the accuracy as percent recovery (X). The recovery (X) should be between 70% and 130% of the expected value.

- If the LFB meets limits the results can be reported.
- If the initial LFB fails the 70-130% recovery criteria then it can be analyzed a second time.
- If the reanalyzed LFB meets requirements then analysis may proceed.
- If the reanalyzed LFB is exceeded high (>130%) and the results of the samples are below the reporting level, then the results can be reported using the following qualification statement: The LFB was above the upper limit indicating a high bias. This non-detect result is not affected by the high bias of the LFB.
- If the reanalyzed LFB is exceeded high (>130%) and the results of the sample are detected at or above the reporting level then the
samples need to be re-analyzed following acceptance of a new calibration curve or following corrective action.

- If the reanalyzed LFB is exceeded low (<70%), indicating a low bias, then the results for samples that exceed a regulatory limit may be reported using the following qualifying statement: The LFB was below the lower limit indicating a low bias. This sample result exceeds the regulatory limit and is considered reportable under the TNI standards.
- If the reanalyzed LFB is exceeded low, indicating a low bias then the results for samples that do not exceed a regulatory limit need to be reanalyzed following acceptance of a new calibration curve or following corrective action.
- LCS Marginal Exceedance (ME) – between 3 and 4 standard deviations around the mean (upper and lower). The following table documents the number of Marginal Exceedances (ME) that is acceptable for the specific number of analytes present in the LCS. Use the following qualification statement in the LIMS for each analyte that is determined to be a marginal Exceedance: The LCS was (above the upper limit or below the lower limit) but met the Marginal Exceedance requirement therefore data is reportable.

<table>
<thead>
<tr>
<th>Number of Analytes in LCS</th>
<th>Number of Allowed Marginal Exceadnces</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 90</td>
<td>5</td>
</tr>
<tr>
<td>71-90</td>
<td>4</td>
</tr>
<tr>
<td>51-70</td>
<td>3</td>
</tr>
<tr>
<td>31-50</td>
<td>2</td>
</tr>
<tr>
<td>11-30</td>
<td>1</td>
</tr>
<tr>
<td>&lt;11</td>
<td>0</td>
</tr>
</tbody>
</table>

NOTE: MARGINAL EXCEEDANCE DOES NOT APPLY TO POTABLE WATER SAMPLES. IT APPLIES ONLY TO NON-POTABLE WATER SAMPLES.

10.6.1 Spike solutions can be found in Reagent Traceability under the heading “508 Chlorinated Pesticides”. Given a final extract volume of 2 mL, a spike amount of 200 μL will yield a final concentration of 50/100 μg/L for the pesticide spike and 500 μg/L for both the toxaphene and chlordane spikes.

10.6.2 The laboratory should determine and document detection limit capabilities for the analytes of interest yearly and whenever significant method or instrument modifications are made (as outlined in section 10).
10.7 Assessing Method Performance -- Laboratory Fortified Sample Matrix

10.7.1 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 than the background concentration of the sample selected for fortification. The fortified analyte concentrations are the same as that used for the LFB (Section 10.6). Over time, samples from all routine sample sources should be fortified.

10.7.2 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., $P = \frac{100(X - b)}{\text{fortifying concentration}}$, and compare these values to reagent water recoveries listed in the method. The calculated value of P must fall in the range of 0±35%. If P exceeds this control limit, and the laboratory performance for that analyte is shown to be in control (Section 10.6), 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. The following qualification statement should be used: The matrix spike fell outside method limits (biased high or biased low). The result for this sample should be evaluated accordingly.

10.8 The analyst is permitted to modify GC columns, GC conditions, concentration techniques (i.e., evaporation techniques), and internal standards or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Section 10.2.

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

Section 11.0 Analytical Procedures

11.1 Extraction

11.1.1 Turn on water bath heater and set thermostat to 85°C.
11.1.2 Fill a preserved amber quart bottle with 900 mL of D.I. water for each reagent blank/laboratory fortified blank. Allow QC and sample bottles to reach room temperature.

11.1.3 Measure 900mL of each sample into a class “A” graduated cylinder. Discard remaining sample and add the 900mL back into the amber quart bottle. Record sample volume on the prep sheet.

11.1.4 Add 50mL phosphate buffer to each sample to neutralize pH. Cap and shake to mix. Check with pH paper. If sample is not neutral, it must be titrated to pH 7.0 (+/- 0.5) with NaOH/H2SO4.

11.1.5 Using a gas-tight Hamilton syringe, add 200μL “508 Surrogate Spike Solution” to each sample. Add 200μL “508 Spike Solution” to the LFB-1 and Matrix Spike-1. Add 200μL of either toxaphene or chlorodane spike solution (alternate with successive batches) to the LFB-2 and Matrix Spike-2. Cap bottles tightly and swirl to mix.

11.1.6 Add 100g baked sodium chloride to each bottle and shake to dissolve.

11.1.7 Prepare drying funnels by placing a pyrex funnel in a clean 250mL flask for each bottle. Plug funnels loosely with a small amount of glass wool and fill each about half-way with baked sodium sulfate (Na2SO4).

11.1.8 Use methylene chloride/dichloromethane (MeCl2) to rinse the Teflon separatory funnels, the drying funnels, and the 250mL flasks. Discard the rinsate. Label funnels and flasks.

11.1.9 After making sure the petcocks are closed, transfer the samples and QC from the amber quart bottles to the rinsed and labeled sep-funnels.

11.1.10 Rinse each bottle thoroughly with 60mL Methylene chloride and add rinsate to samples in the sep-funnels. Discard empty bottles.

11.1.11 Cap sep-funnels tightly. Hand shake the samples and vent to release pressure until venting is no longer necessary. Secure funnels in mechanical shaker and shake for 2 minutes.

11.1.12 Remove funnels from shaker and return to rack. Wait for solvent layers to separate and drain the lower MeCl2 layer through the drying funnel into the 250mL flask.

11.1.13 Repeat steps 11.1.10 through 11.1.12 twice more, adding the 60mL of MeCl2 directly to the sep-funnel.
11.1.14 Rinse a K-D, receiver, and 3-ball Snyder column for each extraction with MeCl₂. Discard rinsate. Affix receivers to the K-Ds and add a boiling chip to each.

11.1.15 Examine the 250mL flask closely. If any water drops are apparent, either floating on top of the MeCl₂ or sticking to the glass, then prepare and rinse an additional drying funnel for that sample. The wet extracts should be added to the K-Ds through the freshly prepared drying funnels. Dry extracts can be added directly to the K-Ds.

11.1.16 Affix the Snyder columns to the K-Ds and place in the water bath so that the receiver is in the water, and the bottom of the flask is bathed in steam. We the Snyder columns by adding 3 or 4mL of MeCl₂ or MTBE to the top of each.

11.1.17 Let the extract boil down until the sample can no longer be seen bubbling out of the receiver. **DO NOT LET THE SAMPLE GO DRY!** This should take about 15-20 minutes. Add 30mL of MTBE through the top of the Snyder column and concentrate down to an apparent volume of 5 mL (**DO NOT LET THE SAMPLE GO DRY!**) and remove from water bath to cool for 5-10 minutes. NOTE: The volume of the sample in the receiver will increase markedly as the flask and column cool and drain into it. The final level of the extract must remain a couple of centimeters below the top of the receiver. If the sample exceeds this volume, it must be returned to the water bath and concentrated further.

11.1.18 Carefully remove the receivers from the K-D taking care that no water drips into the sample. A bit of paper towel should be used to blot the ground glass joint before opening if it is still wet. Transfer the receivers to an N-EVAP set at ~50°C. Under a gentle stream of nitrogen, concentrate the extracts to about 1mL. **DO NOT LET THE SAMPLE GO DRY!** Transfer the sample and rinse the receiver with MTBE into a 2mL volumetric flask. Vial and inject.

11.1.19 Review prep sheet and make sure all reagents/solutions are accounted for.

### 11.2 Gas Chromatography

11.2.1 Section 6.24 summarizes the recommended operating conditions for the gas chromatograph.

11.2.2 Calibrate the system daily as described in Section 9.

11.2.3 Inject 2 µL of the sample extract. Record the resulting peak size in area units.
11.2.4 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

11.2.5 Routine maintenance is performed on the GC. Usually septa are changed approximately every 200 injections. At this time, the lines are inspected along with the detectors. Column maintenance is also performed at this time. Gases are checked daily for adequate pressure.

11.3 Setting up the sequence

11.3.1 Check cooler to see which samples must be analyzed

11.3.2 Prepare vials for curve (if being analyzed that day); check standards and laboratory performance check (LPC).

11.3.3 Take samples from cooler and load all appropriate vials on the tray (including check standards every ten samples).

11.3.4 On computer, pull down Sequence Scroll and choose Sequence Table.

11.3.5 Using the same order that the vials are in the tray, fill in the table with all necessary information.

11.3.6 Pull down Sequence Scroll and choose Save Sequence As. Save the sequence with the date that the run is started.

11.3.7 Pull down Sequence Scroll and choose Sequence Paramaters. Change the subdirectory to the date that is being used for the sequence.

11.3.8 Pull down the Sequence Scroll and choose Print Sequence. Click in the boxes in front of sequence parameters, method, and injection port. Choose print and 2 copies (one for data folder and one for sequence folder).

11.3.9 Prepare instrument for the analysis.

11.3.10 After instrument is ready, choose Start Sequence.

11.4 Reviewing Data

11.4.1 Load Method
11.4.2 If a curve was run, choose the correct curve for the method. Work the curve according to Section 9.0 to make sure that it meets all criteria. If all criteria is met, save the new curve. If a curve was not run, go to Section 11.4.3.

11.4.3 Examine all check standards and quality control samples before any samples to ensure that the data is reportable. Use manual integrations if necessary (printing a before and after copy and including the reason code, date, and initials).

11.4.4 Load Data File

11.4.5 After Data File is loaded, all samples will be listed on the left-hand side of the box. Double click on each sample to pull it up on the screen. If a sample is clean, print only a copy from the column that was used for the check standards. If a target compound is detected, copies from both columns must be printed.

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 on both the primary and confirmation columns, then identification is considered positive. GC/MS confirmation should be employed if analyte concentrations are high enough.

11.5.2 As Stated in the Federal register, EPA method 508 is used to screen for the presence of seven individual Arochlors. If the analysis of a sample shows no detects, then the analysis is complete and analysis by Method 508A is not required. In this case the test is reported as <0.1-μg/L. If any of the PCB Arochlors are detected in the sample, then EPA Method 508A is performed in order quantify PCBs as Decachlorobiphenyl.

With method 508, results are not to be quantified. A detect with method 508 is based on the ability to recognize a chromatogram pattern.

Method 508A can sometimes yield false positives. Both the screening test (Method 508) and Method 508A must show positive results before the results can be reported as PCBs as Decachlorobiphenyl. Therefore when a “positive” arochlor pattern is identified via the screening method, it is required that the same sample be analyzed via Method 508A. The result from 508A is then reported to the client.
Section 12.0  Calculations and Quantitative Analysis

12.1  Calculate analyte concentrations in the sample from the response for the analyte using the calibration procedure described in Section 9. The concentration (C) in the sample can be calculated from the following equation:

\[ C = C_1 \times \frac{V_e}{V_i} \times DF \]

\( C_1 \) = Concentration from instrument
\( C \) = Concentration in µg/L
\( V_e \) = Volume of total extract (µl)
\( V_i \) = Volume of water extracted (ml)

12.2  To quantitate multi-component analytes, the following method should be used. 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. 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. This method should not be used if there are significant interference peaks within the chlordane, Aroclor or Toxaphene pattern.

12.3  The peaks in each chromatogram must be appropriately integrated. Peaks should be present without excessive tailing so that integration is easily accomplished typically by the software and not manually. Typically, a peak is integrated from the baseline at the beginning of the peak to the baseline at the end of the peak. If peaks are distorted as occurs with some sample matrixes, the integration should be accomplished using the judgement of the analyst with a review of the integrations by the supervisor. These unusual integrations should be documented by the analyst.

12.4  After adequate training of an analyst, (which includes an initial demonstration of capability and successful completion of at least 1 PE sample), the analyst’s supervisor should review the raw data, including chromatograms. This review should occur at least once per month until it is clear that the analyst is experienced enough to consistently report valid and defensible data.
12.5 Additional formulas:

12.5.1 *Method Detection Limit (MDL)*

\[ \text{MDL} = S \cdot t(n-1,1-\alpha=0.99) \]

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
- \( S \) = the standard deviation of the replicate analyses

Section 13.0 Data Assessment

13.1 The primary analyst bears the responsibility of producing accurate data. A documented review is performed that includes a check of the following parameters:

- Calibration verification
- QC criteria
- Calculation checks
- Data entry using the LIMS worksheet
- Review of all data to ensure proper peak integration

The initial data review is documented on a checklist that is initiated and dated by the primary analyst. A secondary review must be performed by an individual trained to the standard operating procedure.

13.2 Data qualifiers are used whenever deviations occur while analyzing the samples. The qualifiers are included on the Certificate of Analysis that is presented to the client. Qualifiers include: samples that were not properly preserved, failed surrogate recovery, failed LFM recovery, qualified due to LRB contamination, estimated or elevated reporting limit due to sample matrix interference, calibration failure (high bias) but sample was <RL for the compound.

Section 14.0 Report Generation

14.1 A report is generated after each analysis run is complete. The report includes the US EPA Method number, sample identification, date acquired, acquisition method, date processed, processing method, analyst’s name, chromatogram and quantitative results. If any manipulation is performed, the result is saved and another report is printed and added to the original.
Section 15.0 Pollution Prevention and Waste Management

15.1 (For information about pollution prevention that may be applicable to laboratory practices, 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.)

15.2 “The Waste Management Manual for Laboratory Personnel”, also available from the American Chemical Society at the address above.

15.3 It is the laboratory’s responsibility to comply with the requirements as stated in the Chemical Hygiene Plan for waste disposal.

Section 16.0 References


Section 17.0 Revision History

17.1 Revision 5 issued to update format, numbering and add Revision History section.

17.2 Revision 6 issued to specify the calibration check concentration must be alternated (Section 9.1.9), the control charts are calculated on 20 data points and not 50 (Section 10.6.1), and the reporting level check must be analyzed once per every 24 hours (Section 9.1.9).

17.3 Revision 7 issued to update equipment used, calibration procedure, lab fortified blanks acceptance limits, analytical procedures, and degradation check requirements.

17.4 Revision 8 issued to update the following sections: Section 9.2 CCV was added. Section 10.0 was reformatted with Section 10.4 LRB expanded and adding section 10.6 LRB. Section 9.2 CCV was added to Calibration and Standardization. Section 18.0 Data Assessment and acceptance criteria were added to the SOP. Section 10.6 Marginal Exceedances added to SOP.

17.5 Revision 9 issued to revise sections 8.3 & 8.4 regarding temperature from 4°C to 0.5-6°C, added requirement to perform MDL on both front and back columns, added note about Marginal Exceedance in section 10.6.1. Revised reference numbers in table for sample holding time and extract holding time to 8.3 and 8.4 respectively. Revised section references throughout SOP.
Section 18.0 Data Assessment and Acceptance Criteria for Quality Control Measures

<table>
<thead>
<tr>
<th>SOP Reference</th>
<th>Requirement</th>
<th>Specification and Frequency</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Section 9.1</td>
<td>Initial Calibration</td>
<td>Use external standard calibration technique to generate an average RRF, first or second order calibration curve only.</td>
<td>When average response is used, the %RSD must be less than 20%. When first or second order regression is used, the correlation coefficient must be greater than 0.995. A minimum of 5 standards are required for a linear regression. A minimum of 6 standards is required for second order regression. If criteria are not met corrective action is required such as injection port maintenance, new column, and/or recalibration.</td>
</tr>
</tbody>
</table>
| Section 9.2     | Continuing Calibration Verification (CCV) | Verify initial calibration by analyzing a calibration verification standard (second source) at the beginning of an analytical run, after every 10 samples, and at the end of the analytical run. | If Average response is used for the calibration then the response of the analyte should be ± 20% of the average response in the curve. If first or second order regression is used, then the recovery should be ±20% of the true value.  
1. If the recovery is below criteria, then the results for the analysis must be considered invalid.  
2. If the recovery is above criteria, and there are NO detections in the sample then the results can be reported with a qualifier, otherwise the results should be considered invalid. |
<table>
<thead>
<tr>
<th>Section</th>
<th>Procedure</th>
<th>Frequency</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.3</td>
<td>Reporting Limit Standard (RLC)</td>
<td>Daily, prior to the analysis of field samples.</td>
<td>The recoveries of the analytes should meet the criteria 50-150%, if the recovery is high and no target analytes are detected in the sample then the results can be reported. If the recovery is low then the system does not meet the required sensitivity and analysis cannot proceed until corrective action is taken to restore system sensitivity.</td>
</tr>
<tr>
<td>10.4</td>
<td>Laboratory Reagent Blank / Method Blank (LRB)</td>
<td>Daily, or with each extraction batch of up to 10 samples (1 in 10), whichever is more frequent.</td>
<td>Demonstrate that all target analytes are below the PQL, and confirm that possible interferences do not prevent quantification of method Analytes. If target analytes are detected in the method blank then extraction must be considered invalid if the analytes are detected in the samples.</td>
</tr>
<tr>
<td>10.6</td>
<td>Laboratory Fortified Blank (LFB)</td>
<td>Daily, or with each extraction batch of 10 samples or at a rate of 1 in 10 samples</td>
<td>Results of LFB analyses at medium and high fortifications should be 70-130% of the true value for each analyte.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1. If the recovery is below method criteria. Then the results for that extraction batch should be considered invalid.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2. If the recovery is above criteria, and there are NO detections in the sample then the results can be reported with a qualifier, otherwise the results should be considered invalid.</td>
</tr>
<tr>
<td>Section 10.7</td>
<td>Laboratory Fortified Sample Matrix (LFSM)</td>
<td>Analyze one LFSM per analysis batch (10 samples or less) fortified with method analytes at a concentration close to but greater than the native concentration. Calculate LFSM recoveries.</td>
<td>Recoveries that are not within 65-135% of the fortified amount may indicate a matrix effect and must be qualified.</td>
</tr>
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<td>---------------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Section 8.3</td>
<td>Sample Holding Time</td>
<td>7 days with appropriate preservation and storage</td>
<td>Sample results are valid only if samples are extracted within sample hold time.</td>
</tr>
<tr>
<td>Section 8.4</td>
<td>Extract Holding Time</td>
<td>14 days with appropriate preservation and storage</td>
<td>Sample results are valid only if extracts are analyzed within extract hold time.</td>
</tr>
</tbody>
</table>
Appendices

Table 1: Laboratory performance /degradation check solution

<table>
<thead>
<tr>
<th>Test</th>
<th>Analyte</th>
<th>Conc. (µg/mL)</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity</td>
<td>Chloropyrifos</td>
<td>0.0020</td>
<td>Detect analyte, S/N &gt;3</td>
</tr>
<tr>
<td>Chromatographic Performance</td>
<td>DCPA</td>
<td>0.0500</td>
<td>PGF between 0.80 and 1.15</td>
</tr>
<tr>
<td>Column Performance</td>
<td>Chlorothalonil</td>
<td>0.0500</td>
<td>Resolution &gt; 0.50</td>
</tr>
<tr>
<td></td>
<td>HCH-delta</td>
<td>0.0400</td>
<td></td>
</tr>
<tr>
<td>%Degradation of 4,4'-DDT</td>
<td>4,4'-DDT</td>
<td>1.0</td>
<td>&lt; 20%</td>
</tr>
<tr>
<td>%Degradation of Endrin</td>
<td>Endrin</td>
<td>1.0</td>
<td>&lt; 20%</td>
</tr>
</tbody>
</table>

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

\[
\text{% Degradation of Endrin} = \frac{\text{Total\text{-}Endrin\text{-}peak\text{-}area} (\text{EA + EK})}{\text{Total\text{-}peak\text{-}area} (\text{En + EA + EK})} \times 100
\]

Where: En = Endrin, EA = EndrinAldehyde, EK = EndrinKetone

Peak Gaussian Factor (PGF)

\[
\text{PGF} = \frac{1.83 \times W\left(\frac{1}{2}\right)}{W\left(\frac{1}{10}\right)}
\]

Where: \(W\left(\frac{1}{2}\right)\) = the peak width that half height in seconds

\(W\left(\frac{1}{10}\right)\) = the peak width at 10\textsuperscript{th} height in seconds

Resolution

\[
\text{Resolution} = \frac{t}{W}
\]

Where: \(t\) = the difference in elution times between the two peaks

\(W\) = the average peak width at the baseline of the two peaks