ROUTINE ANALYSIS OF TOXAPHENE IN WATER AND SOIL/SEDIMENT SAMPLES BY GC/ECD

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CONTENTS (cont'd)

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1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) is applicable to the determination of toxaphene in water and soil/sediment matrices including treated bioremediation or other engineering processes samples. The analysis is conducted using a gas chromatograph (GC) with a narrow-bore fused silica column and an electron capture detector (ECD). The typical quantitation limits for toxaphene in water and soil/sediment matrices are found in Table 1, Appendix A.

2.0 METHOD SUMMARY

2.1 Water Samples

Approximately 1 liter (L) of a water sample is serially extracted at a neutral pH with methylene chloride. The extract is concentrated to 10 milliliters (mL), then 60 mL of hexane is added as an exchange solvent, and the extract is concentrated to a final volume of 1 mL. The extracts are analyzed for toxaphene using GC/ECD. A second column confirmation is optional for Toxaphene analysis.

2.2 Soil Samples

Approximately 30 grams (g) of a soil/sediment sample and 30 g of anhydrous sodium sulfate is extracted with 300 mL of 1:1 acetone/hexane using a Soxhlet extractor for 16 hours. The extract is concentrated to 10 mL, then 60 mL of hexane is added as an exchange solvent, and the extract is concentrated to a final volume of 5 mL. Some projects may require concentrating the extract to various final volumes depending on the concentration of toxaphene in the solid material or matrix effects. The extracts are analyzed for toxaphene using GC/ECD. A second column confirmation is optional for Toxaphene analysis.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

3.1 Sample Storage

Water samples should be collected in 1-L amber glass containers fitted with Teflon®-lined caps. Soil samples should be collected in wide-mouth glass containers with Teflon-lined caps.

From the time of sample collection until after analysis, extracts and unused samples must be protected from light and refrigerated at 4 degrees Celsius (°C) ± 2°C for the periods specified by the Scientific, Engineering, Response and Analytical Services (SERAS) Task Leader and/or U.S. EPA/Environmental Response Team (ERT) Work Assignment Manager (WAM).

Samples, sample extracts, and standards must be stored separately in an atmosphere free of all potential contaminants.

3.2 Holding Times

Extraction of water and soil/sediment samples must be completed within 7 days from the date of collection and analysis completed within 40 days of sample extraction.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences in the sample extracts for analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks on a routine basis. Interferences co-extracted from the samples may vary considerably from sample to sample. Cleanup procedures may be necessary if the extract contains analytes that interfere with quantitation or peak separation.

Phthalate esters are present in many types of products commonly found in the laboratory. Some plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

Soap residue on glassware may cause degradation of certain analytes. This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem.

Elemental sulfur is encountered in many sediment samples such as marine algae and some industrial wastes. Sulfur will be quite evident in gas chromatograms obtained from electron capture detectors. If the GC is operated at the normal conditions for toxaphene analysis, the sulfur interference can completely mask the region from the solvent peak through most of the toxaphene peaks. Two techniques [activated copper powder or tetrabutylammonium (TBA) sulfite] for the elimination of sulfur may be used. Florisil cleanup may be used to reduce matrix interferences caused by polar compounds.

5.0 EQUIPMENT/APPARATUS

The following equipment/apparatus is required:

- Separatory funnel, 2000 mL with stopcock (glass or Teflon)
- Erlenmeyer flasks, 500 mL
- Graduated cylinder, 1L
- Buchner funnels
- Bench top shaker (Glas-Col) or equivalent
- Soxhlet extractor, 40 millimeter (mm) inner diameter (ID), with 500-mL round bottom flask, fits

45/50 condenser

- Teflon boiling chips, approximately 10/40 mesh, rinsed three times with methylene chloride
- Spoon and/or spatula, stainless steel or Teflon
- Balance, capable of accurately weighing 100 g to the nearest 0.01 g
- Glass container(s)
- Glass wool, Pyrex baked at 400°C for 2 hours or equivalent
- Kuderna-Danish (K-D) apparatus, consisting of a 10-mL graduated concentrator tube, 500-mL evaporation flask, and three-ball macro Snyder column
- Water bath, heated with concentric ring cover, capable of maintaining temperature within ±2°C. The bath should be used in a hood.
- Disposable glass Pasteur pipettes
- Nitrogen evaporation device, equipped with a water bath that can be maintained at 35-40°C (N-Evap by Organomation Associations Model Number 111 or equivalent)
- TurboVap II concentrator, with six positions for concentrating extracts
- TurboVap II concentrator cells, 200 mL
- TurboVap II concentrator cell rack
- Clean Bath solution, for use in TurboVap II concentrator
- TurboVap LV concentrator cells, 60 mL or equivalent
- Test tube rack
- Drying oven
- Desiccator
- Concentrator tubes, 25 mL
- Vials and caps, 2 mL for GC autosampler
- Vial(s) with screw top(s), 4 mL

- Test tubes with screw caps, 25 mL
- pH paper wide range.
- Ring Stand.
- Gas chromatograph - An analytical system complete with GC and all required accessories including syringes, autosampler, analytical columns, gases, an electron capture detector, and data system. A data system is required for measuring peak areas or peak heights and recording retention times.
- DB-608 fused silica capillary column, 30 meter (m) x 0.32 mm ID, 0.50 micron (um) film thickness or equivalent
- RTX - CLPesticides fused silica capillary column, 30 m x 0.32 mm ID, 0.50 um film thickness or equivalent
- Florisil cartridge (12 mL tube, Supelco CAT # 57155 or equivalent)
- Visiprap SPE Vacuum manifold, 12 port or equivalent
- Valve liners, disposable or equivalent.
- Syringes, miscellaneous
- Class "S" weight for balance calibration

6.0 REAGENTS

1. Sodium Sulfate, anhydrous granular reagent grade, heated at 400 C for four hours, cooled in a desiccator, and stored in a glass bottle
2. Methylene Chloride, pesticide residue analysis grade or equivalent
1. Hexane, pesticide residue analysis grade or equivalent
4. Acetone, pesticide residue analysis grade or equivalent
5. Methanol, pesticide residue analysis grade or equivalent
6. 2-Propanol, pesticide residue analysis grade or equivalent
7. Tetrabutylammonium sulfite solution - Prepare by dissolving 3.39 g of tetrabutylammonium hydrogen sulfate in 100 mL of reagent water. Extract this solution three times with 20 mL

portions of hexanes to remove any impurities. Discard the hexane layer and add 25g of sodium sulfite to the aqueous layer. Store this solution at room temperature.

8. Copper powder, activated (purchased activated)

9. Toxaphene stock calibration standards, 1000 micrograms/milliliter (µg/mL), commercially available

10. Toxaphene Calibration Standards - Prepare at a minimum of five concentration levels [0.5, 1.0, 2.0, 5.0 and 10 milligrams/liter (mg/L)]. Each calibration standard must contain surrogates at a concentration range of 20, 50, 100, 200 and 500 micrograms/liter (µg/L). Care must be taken to maintain the integrity of all standard solutions. Transfer all prepared standard solutions to crimp-top amber bottles with Teflon liners and store at below 4°C when not in use. All prepared standards must be documented in accordance with SERAS SOP #1012, *Preparation of Standard Solutions*.

11. Surrogate Stock Standard, 200 mg/L, commercially available. This stock solution may be used as the spiking solution without dilution in instances where the final volume of the extract is greater than described in this method.

12. Surrogate Working Solution - Prepare a solution containing decachlorobiphenyl (DCBP) and 2,4,5,6-tetrachloro-meta-xylene (TCMX)at a concentration of 0.2 µg/mL (for water) and 2 µg/mL in methanol, acetone or hexane (for soil). Store the surrogate solutions at 4 C ± 2 C in Teflon®-sealed containers. These solutions must be replaced every six months or sooner if any contamination or degradation is observed. All prepared standards must be documented in accordance with SERAS SOP #1012, *Preparation of Standard Solutions*.

13. Stock Toxaphene Matrix Spiking Solution, 1000 mg/L and 25,000 mg/L, commercially available

14. Matrix Spike Working Solution - Prepare a spiking solution of toxaphene in methanol, acetone, or hexane at a concentration of 20 µg/mL. Depending on the project, varying concentrations may be used for the matrix spike. Store the spiking solutions at $4^{O}C$ ($\pm 2^{O}C$) in Teflon-sealed containers. These solutions must be replaced after six months, or sooner, if any contamination or degradation is observed. All prepared standards must be documented in accordance with SERAS SOP #1012, *Preparation of Standard Solutions*.

15. Sodium hydroxide (NaOH), 10 Normal (N) - Weigh out 40 g of NaOH and dissolve in 100 mL of deionized water.

16. Sulfuric acid, 1:1 - Add an equal volume of concentrated sulfuric acid to an equal volume of deionized water.

17. Deionized water

7.0 PROCEDURES

7.1 Sample Preparation and Extraction for Water

1. Transfer the sample container into a fume hood. Mark the meniscus on the sample bottle with an indelible marker, and pour the sample into a 2-L separatory funnel. Check the pH of the sample with wide-range pH paper and record it on the extraction log. Adjust the pH to between 5 and 9 with 10 N sodium hydroxide and/or 1:1 sulfuric acid solution. Refill the sample bottle with tap water to the mark. Measure the volume of tap water using a 1-L graduated cylinder and record the volume in the extraction log.

2. Prepare a method blank by measuring out 1 L of deionized water into a separate 2-L separatory funnel. A method blank must be prepared with every batch not to exceed 20 samples.

3. Measure out two additional 1-L portions of the sample chosen for spiking as the matrix spike and matrix spike duplicate (MS/MSD) at a rate of one sample for every 10 samples per project or 10%.

NOTE: This sample may be specified on the chain of custody record for this purpose by the SERAS Task Leader.

4. Add 1 mL of the 0.2 µg/mL surrogate working solution to the method blank, MS/MSD, and all the samples in the batch, or add sufficient volume to result in a final concentration of 200 parts per billion (ppb) in the final extract.

5. Add 100 µL of the 20 µg/mL matrix spike working solution to the MS/MSD or add a sufficient volume to result in a final concentration of 2 parts per million (ppm) in the extract if a higher extract volume will be obtained.

6. Rinse the empty sample bottle with 60 mL methylene chloride; transfer the rinsate to the separatory funnel and extract the sample by shaking the funnel by hand for two minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the extraction chemist must employ mechanical techniques to complete the phase separation. The optimal techniques employed depend upon the sample, and may include: stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means. If using a bench top shaker, vent and release excess pressure, place it on shaker and shake for 5 minutes.

7. Filter the extract (usually the bottom layer) through a funnel containing glass wool and anhydrous sodium sulfate into a 500-mL Erlenmeyer flask. Add a second 60-mL portion of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. After the third extraction rinse the sodium sulfate in the funnel with sufficient methylene chloride. If using the bench top shaker, shake the

sample(s) for 3 minutes for the 2nd and 3rd extractions.

7.2 Sample Preparation and Extraction for Soil

11 In a fume hood, place 300 mL of 1:1 acetone/hexane into a 500-mL round bottom flask containing 3 or more clean boiling chips. Attach the flask to the Soxhlet extractor.

12 Transfer the sample container into the fume hood. Open the sample bottle and properly discard any foreign objects such as sticks, leaves, and rocks. Mix the sample thoroughly.

13 Calibrate the balance with Class "S" weights prior to weighing samples or on a daily basis when the balance is in use. The balance should be calibrated with a weight that is similar to the weight used to extract the samples (i.e., 30g)

14 Weigh approximately 30 g of each sample to the nearest 0.1g into a glass container and add a sufficient amount (approximately 30-100g) of anhydrous granular sodium sulfate. Mix well. The sample should have a sandy texture at this point. A method blank must be prepared using 30 g of sand (or baked sodium sulfate) according to the same procedure as the samples at the frequency of one per 20 samples.

15 Cut a piece of baked glass wool and place it in the Soxhlet extractor so it covers the bottom of the inner diameter and add some sodium sulfate to hold the glass wool in place. This will prevent any soil/sediment from getting caught and clogging the soxhlet. Add the blended sample and anhydrous sodium sulfate into the soxhlet extractor on top of glass wool and sodium sulfate.

16 Weigh two additional 30 g portions of the sample chosen for spiking to the nearest 0.1 g for use as a MS/MSD at a rate of one per ten samples per project or ten percent.

NOTE: This sample may be specified on the Chain-of-Custody record for this purpose by the SERAS Task Leader.

17 Add 0.5 mL of the 2 µg/mL surrogate working solution to the method blank, the MS/MSD and all the samples or add sufficient volume to result in a final concentration of 200 ppb in the final extract.

8. Add 0.5 mL of the 20 µg/mL matrix spike working solution to the MS/MSD or add sufficient volume to achieve a final concentration of 2 ppm in the final extract..

9. Attach the condenser to the extractor and flask, and extract the sample(s) for 16 hours.

NOTE: Care must be taken to supervise the beginning of the extraction to ensure that the condenser is cooling the evaporating solvent efficiently to guarantee that the solvent will condense and continue to extract the sample in a continuous cycle for the entire 16 hours. Allow

the extract to cool after the extraction is complete.

7.3 Sample Concentration for Water and Soil Extracts

1. If concentrating using a TurboVap apparatus, skip to step 5. Otherwise, assemble a Kuderna-Danish (K-D) apparatus by attaching a 10 mL concentrator tube to a 500-mL evaporation flask. Transfer the extract to the K-D concentrator.

2. Add one or two clean boiling chips to the evaporation flask and attach a three-ball Snyder column. Place the K-D apparatus on a hot water bath (70 to 75^{O}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. Add approximately 1 mL of hexane to the top of Snyder column. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration. 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 below 10 mL add another 60 mL of hexane and evaporate down to below 10 mL. Remove the K-D apparatus, and allow it to drain and cool.

   NOTE: DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS.

3. Remove the Snyder column; use 1-2 mL of hexane to rinse the flask and its lower joint into the concentrator tube. Remove the concentrator tube and place it onto the N-Evap preheated to 35^{O}C.

4. Evaporate the extract to a final volume of 1 mL for water and 5 mL for soil. During evaporation rinse the wall of the concentrator tube with 1-2 mL of hexane. Continue with step 7.

NOTE: DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS.

5. If using the TurboVap concentrator, fill the TurboVap water bath with approximately one gallon of deionized water mixed with 10-15 drops of Clean Bath solution. Set the water bath temperature at 55 C.

6. Transfer as much of the extract(s) into 200 mL cells in the hood. Begin concentrating by blowing a gentle stream of nitrogen into the cells so that no solvent is splashed out. As the solvent level is reduced, add any remaining extract and rinse the flask with hexane and add the rinsate to the concentration cell. Once all extract is in the cell and the solvent level is well below the 200-mL mark, the flow of nitrogen can be increased to speed up the concentration. Periodically rinse the cell with hexane. Concentrate the extract below 10 mL, add 60 mL of hexane and concentrate it down to a final volume of 1 mL for water and 5 mL for soil.

NOTE: DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS.

7. For projects requiring a final volume of 300 mL for sample extracts, adjust the volume to 300 mL with hexane. Take a 5-mL aliquot, add 60 mL of hexane and solvent exchange by following Section 7.3 Steps 2-4 or 5-6.

8. Take a 2-mL aliquot of the soil sample extract from Steps 4 or 6 or 7 and if needed, proceed to the optional Florisil cleanup described in Section 7.5 and/or optional tetrabutylammonium (TBA)-sulfite cleanup described in Section 7.6 or optional copper cleanup described in Section 7.7. Store the remaining extract(s) at 4 C± 2^{O}C.

9. Note: Record the date in the extraction log when the extract is taken through the cleanup procedures.

7.4 Total Solids

The sample aliquots for total solids are weighed in conjunction with the samples for the extraction. The total solids for the MS/MSD are based on the corresponding sample. The blank is assumed to be 100 percent (%) total solids.

Determine the percent total solids by drying in an oven that is placed inside of a fume hood overnight. Weigh and record (in the percent solid log book) an empty aluminum sample dish to the nearest 0.01 g. Weigh at least 10 g of the soil/sediment into the aluminum dish and record the weight. Preheat the oven to 103 – 105^{O}C. Place the aluminum dishes in the oven and record the initial temperature in the logbook. In the morning, record the final temperature of the oven in the log book. Turn off the oven and allow the dishes to cool in the desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of the soil or sediment. Calculate the percent total solids using the following equation:

$$\%\,Total\,Solids = \frac{Weight\ of\ Dried\ Sample\ with\ Dish\ (g) - Dish\ Weight\ (g)}{Weight\ of\ Wet\ Sample\ with\ Dish\ (g) - Dish\ Weight\ (g)}$$

7.5 Florisil Cleanup Procedure

Florisil cleanup significantly reduces matrix interferences caused by polar compounds.

1. Place one Florisil cartridge into the manifold for each sample extract to be subjected to cleanup.

2. Prior to cleanup of samples, the cartridges must be washed with hexane/acetone (90:10). This is accomplished by passing through at least 10 mL of the hexane/acetone solution through the each cartridge. Note: DO NOT ALLOW THE CARTRIDGES TO DRY AFTER THEY HAVE BEEN WASHED.

3. After the cartridges in the manifold are washed, a rack containing labeled 25 mL concentrator tubes is placed inside the manifold. Care must be taken to ensure that the solvent line for each cartridge is placed inside of the appropriate concentrator tube as the manifold top is replaced.

4. After the concentrator tubes are in place, add approximately 1 mL of the mobile solution (90:10 hexane/acetone) to the florisil bed in the cartridge. Allow the solvent to pass into the sorbent bed and immediately transfer 2 mL from each sample, blank and MS/MSD extract from Section 7.3, Step 8 to the top of the florisil bed in the appropriate florisil cartridge.

5. The extracts are then eluted through the cartridge with 18 mL of hexane/acetone (90:10) and are collected into the 25-mL concentrator tubes held in the rack inside the manifold. NOTE: Be sure to add the 18 mL of mobile solution right after the 2-mL extract crosses the florisil bed.

6. The concentrator tubes from Step 5 are transferred to Turbo Vap LV and the extracts concentrated down to a final volume of 2.0 mL using nitrogen blow down.

7.6 Tetrabutylammonium-Sulfite Cleanup

Elemental sulfur is encountered in many soil/sediment samples. The solubility of sulfur in the extraction and exchange solvents are very similar to the toxaphene; therefore, the sulfur interferes with the toxaphene. If the GC is operated at the normal conditions for toxaphene analysis, the sulfur interference can completely mask the region where most of toxaphene peaks elute. TBA-sulfite is used to remove the sulfur interference.

1. Transfer 2-mL of extract from Section 7.3, Step 8 or Section 7.5, Step 6, to a 25-mL test tube.
2. Add 2 mL of TBA-sulfite reagent and 2 mL of 2-propanol; cap and shake vigorously with a mechanical shaker such as Vortex for at least one minute. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears add more TBA - sulfite reagent until a solid residue remains after repeated shaking.

3. Add 6 mL of deionized water and shake for at least two minutes. Allow the sample to stand for 5-10 minutes. Transfer the hexane layer (top) to two 1-mL injection vials. The extracts may be analyzed by GC/ECD.

7.7 Copper Cleanup

Copper cleanup requires that the copper powder be very reactive.

1. Transfer 2 mL of sample extract from Section 7.3 Step 8, Section 7.5, step 6 or Section

7.6 Step 3, to a 4-mL screw-top vial.

2. Add approximately 0.5 to 2 g of copper powder (depends on the color and viscosity sample) to the vial. Vigorously mix the extract and copper powder for at least 1 minute on a mechanical shaker such as Vortex. Allow the phases to separate.

3. Separate the extract from the copper by drawing off the extract with a disposable glass pipet into two 1-mL injection vials.

7.8 GC/ECD Conditions

Sample analyses are performed using a Hewlett Packard (HP) 6890 GC/ECD, equipped with dual injector, column, and electron capture detector capabilities.

The HP 6890 conditions used for the toxaphene analysis are listed below:

Injector Temperature	200°C
Oven Temperature Program	120°C hold for 1 minute (min) 9°C/min to 285°C, 10 min at 285°C
Detector Temperature	300°C
Carrier Gas	Helium
Make-up Gas	Argon/Methane
Column Flow Rate	DB-608 3.1 milliliters/minute (mL/min); RTX-CLPesticides 1.9 mL/min
Head Pressure	DB-608 1-3 pounds per square inch (psi); RTX-CLPesticides 2.5-4 psi
Amount Injected	1 microliter (µL)
Data System	HP Chem Station

The instrument conditions listed above are guidelines to be used for standards and sample analysis on a HP 6890 GC/ECD system. Any suitable conditions may be used as long as QA/QC criteria and peak separation is achieved.

7.9 Retention Time Windows

Due to advances in electronic pressure controls in modern GCs such as the HP6890, the retention times (RTs) usually remain constant and may exhibit a negligible shift (nearly zero) over the traditional 72-hour period. A default standard value of 0.030 minutes will be used for the two surrogates. These default values will be applied unless the instrument and EPC unit cannot maintain constant retention times. If the instrument cannot maintain reproducible RTs, the analyst must investigate the cause and implement corrective action. New RT windows must be calculated whenever a new column is installed.

7.10 Standard and Sample Analysis

The analytical sequence listed in Appendix B must be followed.

1. Inject each of the five toxaphene calibration standards and tabulate the total toxaphene peak area for each standard concentration. Calculate the response factor (RF) for toxaphene at each standard concentration. The average RF and percent relative standard deviation (%RSD) must also be calculated.

$$RF = \frac{Total\ Peak\ Area\ of\ Toxaphene}{Mass\ Injected\ (ng)}$$

For surrogates, calculate RF from peak heights of the analytes.

$$RF = \frac{Peak\ Height\ of\ the\ Surrogate}{Mass\ Injected\ (ng)}$$

The %RSD of the RF for toxaphene must be less than or equal to (≤) 20.0%, and the two surrogates must be ≤ 30.0%.

$$\%RSD = \frac{SD}{RRF_{average}} x\ 100$$

$$SD = \sqrt{\frac{\sum_{i=}^{n} (i - F_{average})^2}{n -}}$$

where:

Note: The initial curve must be run every six months at a minimum or sooner if the daily calibration check doesn't meet the required percent difference (%D) as specified in Section 7.10.1, Step 3.

3. Every 12 hours of sample analysis, inject the 2 ppm continuing calibration check standard, which is the mid-point of the curve. Calculate and tabulate the %D of all compounds using the following equation. The percent difference must be ≤ 25.0%.

$$Percent\ Difference\ (\%D) = \frac{ARF_{INT} - RF_{CALC}}{A_{INT}} x\ 100$$

where:

ARF_{INT} = Initial Average Response Factor
RF_{CALC} = Calculated Response Factor

4. Inject a group of sample extracts. It is good laboratory practice to inject a method blank first to monitor any possible carryover or laboratory contamination. All sample extracts must be analyzed within 12 hours of the injection of the continuing calibration standard (step 3).

   Repeat steps 3 and 4, if necessary, until the %D requirement of the continuing calibration check fails.

   End the sequence with the continuing calibration check standard.

7.11 Evaluation of Chromatograms

All standard and sample chromatograms must be evaluated to decide if re-injection and/or dilution is necessary.

7.11.1 Standard/Sample Chromatograms

The following requirements apply to all data presented for toxaphene analysis.

1. The toxaphene chromatograms must display the multi-component analytes present in each standard or sample at greater than (>) 25% and less than (<) 100% of full scale. The chromatogram must be printed in landscape mode with the time scale of the chromatogram from approximately 5 (before the TCMX) to 25 minutes (after the DCBP peak). If the time scale is modified, all chromatograms will be scaled the same for comparative purposes.

2. If an extract is diluted, chromatograms must display multi-component toxaphene between 10% and 100% of full scale.

3. If a chromatogram is re-plotted electronically to meet requirements, the scaling factor used must be displayed on the chromatogram.

4. If a chromatogram indicates carryover from a previous injection, subsequent sample extract(s) must be re-analyzed.

5. The retention time of each surrogate must fall within the RT window criteria in Section 7.9. If the RT window has shifted in the thousandth place (>0.030 but <0.040), professional judgment may be used to determine the acceptability of the data. If the RT is shifted by more than 0.040 minutes, the analytical sequence (acquisition) must be interrupted for corrective action. After

corrective action, acquisition of data can be resumed only after an acceptable 2 ppm toxaphene standard is obtained.

6. If a confirmed pesticide peak is present, that area is subtracted from the total area used for quantitation of the toxaphene.

7. If a sample chromatogram has interfering peaks, a high baseline, or off-scale peaks, the sample extract must be re-analyzed using a dilution, further cleanup, or re-extraction. Samples that do not meet acceptance criteria after one re-extraction and cleanup must be reported in the case narrative and do not require further analysis.

8. If it is determined that the matrix may be causing a RT shift, the MS/MSD in conjunction with the original sample chosen for spiking may be used to assess matrix effects.

9. If manual integrations have been performed, refer to SERAS SOP #1001, *Chromatographic Peak Integration Procedures* for appropriate documentation.

7.11.2 Toxaphene Identification

The identification of toxaphene is primarily based on pattern recognition, which can only be verified from an on-scale chromatogram. A second column confirmation is optional for toxaphene analysis.

7.12 Sample Dilution

Target compound concentrations must not exceed the initial calibration range. If toxaphene is detected in the extract at a level greater than the highest calibration standard, the extract must be diluted (to a maximum of 1:100,000) or until the analyte response is within the linear range established during calibration. Guidance in performing dilutions and exceptions to this requirement are given below.

1. If the analyst has reason to believe that diluting the final extracts will be necessary based on historical data or visual observation of the extracts, an undiluted run may not be required. However, if no peaks are detected above 25% of full scale on the diluted sample, analysis of a 10 times more concentrated sample extract or the undiluted sample extract is required.

2. If the response is still above the highest calibration point after the dilution of 1:100,000, the analyst should contact the Organic Group Leader immediately for further instruction.

3. The results of the original analysis are used to determine the approximate dilution factor required to bring the largest analyte peak within the initial calibration range.

4. The dilution factor chosen should keep the response of the largest peak for a target compound in the initial calibration range of the instrument.

5. Submit data for any reportable analyses.

6. All chromatograms for the dilution analyses must meet the requirements described in Section 7.11.1

8.0 CALCULATIONS

Quantitation of target compounds and surrogates can be performed on any column that passed all the quality control (QC) criteria specified in this SOP. In order to be quantitated, the detector response (peak area or peak height) of all the analytes must lie within the calibration range.

8.1 Quantitation Limit (QL) for Water

$$QL\,(\mu g/L) = \frac{(C_{STD})(V_T)(DF)}{(V_O)}$$

where:

C_{STD} = Concentration of the lowest standard in the calibration range (µg/mL)
V_T = Volume of the extract (mL)
DF = Dilution factor (if any)
V_o = Volume of water extracted (L)

8.2 Quantitation Limit for Soil

$$QL\,(\mu g/kg)\ Dry\ Weight = \frac{(C_{STD})(V_T)(DF)}{(W)(S)}$$

where:

C_{STD} = Concentration of the lowest standard in the calibration range (µg/mL)
V_T = Volume of the extract (mL)
DF = Dilution factor (if any)
W = Weight of soil/sediment extracted, kilograms (kg)
S = Decimal percent solid

8.3 Sample Concentration for Water

$$Concentration\ (\mu g/L) = \frac{(A_X)(V_T)(DF)}{(RF_{avg})(V_O)(V_I)}$$

where:

A_X	=	Pattern peak area or peak height for the compound to be measured
V_T	=	Volume of the concentrated extract (mL)
DF	=	Dilution factor (if any)
RF_{avg}	=	Average response factor
V_o	=	Volume of water extracted in milliliters (mL)
V_I	=	Volume of extract injected (µL)

8.4 Sample Concentration for Soil

$$Concentration\ (\mu g/kg)\ dry\ weight = \frac{(A_X)(V_T)(DF)}{(RF_{avg})(W)(S)(V_i)}$$

where:

A_X	=	Pattern peak area or peak height for the compound to be measured
V_T	=	Volume of the concentrated extract (mL)
DF	=	Dilution factor (if any)
RF_{avg}	=	Average response factor
W	=	Weight of soil/sediment extracted (kg)
V_I	=	Volume of extract injected (µL)
S	=	Decimal percent solid

Note: If any analytes are detected below the quantitation limit, they are to be reported as present below the quantitation limit and flagged as estimated (J). However, it is the analyst judgment whether to report the peaks detected below the quantitation limit, because of the uncertainty involved with the identification of the compounds due to baseline noise and many interfering peaks at low concentration level.

8.5 Surrogate Spike Recoveries

$$Percent\ Recovery\ (\%R) = \frac{Q_D}{Q_A} \times 100$$

where:

Q_D = quantity determined by analysis
Q_A = quantity added to sample

8.6 Matrix Spike Recoveries

The percent recoveries and the relative percent difference (RPD) between the recoveries of the toxaphene matrix spike samples will be calculated and reported by using the following equation:

$$Matrix\ Spike\ Recovery\ (\%R) = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = spike sample result
SR = sample result
SA = spike added

$$RPD = \frac{|MSR - MSDR|}{(MSR + MSDR)/2} \times 100$$

where:

RPD = relative percent difference
MSR = matrix spike recovery
MSDR = matrix spike duplicate recovery

The vertical bars in the formula above indicate the absolute value of the difference; hence, RPD is always expressed as a positive value.

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

9.1 Holding Time

Extraction of water and soil/sediment samples should be completed within 7 days of sampling, and analysis completed within 40 days of sample extraction.

9.2 Identification of Target Compounds.

The identification of toxaphene is based primarily on pattern recognition, and secondary column confirmation is optional.

9.3 Initial Calibration for Toxaphene and Surrogates

Prior to the analysis of any sample, method blank, or MS/MSD, the GC/ECD system must be

initially calibrated at a minimum of five concentrations to determine the linearity range for toxaphene and surrogates. If reporting data from only one column, the RSDs will only be reported from that column. If reporting data from both columns, all corresponding calibrations will be required for both columns.

1. The concentration of all calibration standards that are specified in Section 6.0 must be used.

2. The standards are to be analyzed according to the procedures given in Section 7.10 using the GC operating conditions in Section 7.8.

3. The response factors are determined according to the procedure in Section 7.10.

4. The initial calibration is also evaluated on the basis of the stability of the response factors of each target compound and surrogate. The %RSD for toxaphene must not exceed 20.0%, and the %RSD for the two surrogates must not exceed 30.0%.

9.4 Continuing Calibration for Toxaphene and Surrogates

Once the GC/ECD system has been calibrated, the calibration must be verified each 12-hour time period using the midpoint 2ppm toxaphene calibration standard. If reporting data from only one column, the %D will be reported only for that column. If reporting data from both columns, all corresponding %Ds will be required for both columns.

1. The %D of all target compounds and surrogates must not exceed 25.0%.

2. The continuing calibration is evaluated on the GC column used for analysis in the instrument.

3. If the %D exceeds 25.0% for a specific analyte and the analyte is present in the sample extract, re-injection is required to ensure an accurate concentration.

4. If the %D for the end of sequence (EOS) standard exceeds 50.0%, the samples must be re-analyzed. If the EOS standard does not meet acceptance criteria after re-analysis, it must be documented and further analysis is not required. The analytical sequence may be altered on the reanalysis by introducing additional calibration check standards at a greater frequency.

9.5 Retention Time Windows

A default standard value of 0.030 minutes will be used for the two surrogates. Since the identification of toxaphene by GC methods is based primarily on pattern recognition of a group of peaks and the total area, specific retention time windows are not used for the individual toxaphene peaks.

1. The retention time shifts of the surrogates may be used to evaluate the stability of the GC system during the analysis of standards only.

2. Retention time windows must be established on both columns for the surrogates and submitted with the data package if both columns are used for reporting in a data package.

9.6 Analytical Sequence

The standards and samples analyzed by this SOP must be analyzed in a sequence outlined in Appendix B. This sequence includes requirements that apply to the initial and continuing calibrations, as well as, to the analysis of samples.

9.7 Method Blank Analysis

A method blank is a known volume of deionized water or weight of a clean reference matrix (sand or baked sodium sulfate) that is carried through the entire analytical procedure. The weight of the reference matrix must be approximately equal to the weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

1. A method blank must be prepared for at least each 20 samples and analyzed on each GC/ECD system used to analyze samples.

2. A method blank must not contain any of the compounds listed in Appendix A at a concentration greater than or equal to (≥) the quantitation limit.

3. All samples associated with an unacceptable method blank must be re-extracted and re-analyzed.

4. When sample extracts are subjected to cleanup procedures, the associated method blank must also be subjected to the sample cleanup procedure.

5. Method blank results must not be subtracted from any associated samples.

6. A solvent blank may be used to check for contamination or carryover from a previous sample. If an analyte present in the solvent blank is found in subsequent samples, the samples should be re-analyzed.

9.8 Surrogate Recoveries

1. Surrogates are added to each sample, blank, MS, and MSD prior to extraction at the concentrations described in Sections 6.0, 7.1 and 7.2

2. The surrogate spike recoveries are calculated according to the procedures in Section 8.5.

3. The quality control limit for both surrogate recoveries is 30 - 150%. These limits are only advisory, and no further action is required if the limits are exceeded. However, frequent failures to meet the limits for surrogate recovery warrant investigation by the laboratory.

9.9 Matrix Spike and Matrix Spike Duplicate Analysis

The purpose of spiking target compounds into two aliquots of a sample is to evaluate the effects of the sample matrix on the methods used in this SOP.

1. The MS/MSD must be prepared every 10 samples per matrix or per project, whichever is more frequent.

2. The mixture of toxaphene standard specified in Section 6.0 must be used and result in the concentration specified in Sections 7.1 and 7.2.

3. The recoveries of the MS compounds are calculated according to the procedures in Section 8.6. The relative percent difference (%RPD) for each spiked analyte are calculated between the results of the MS and the MSD according to the procedures in Section 8.6.

4. Dilution and re-analysis of the MS/MSD is required to bring the target analytes within the linear range of the calibration curve. Dilution and re-analysis of the MS/MSD is not performed for non-target analytes outside the calibration range.

5. The MS/MSD must be extracted and analyzed within holding time.

9.10 Dilution Analysis

If the concentration of any sample extract exceeds the initial calibration range, that sample extract must be diluted and re-analyzed as described in Section 7.12. If there are no peaks detected above 25% of the full scale in the dilution analysis, a lower dilution of the sample extract must be analyzed.

9.11 Quantitation Limit

The lowest concentration of the calibration standard that is analyzed during the initial calibration determines the method quantitation limit based on the initial volume or weight of the sample, final volume of extract obtained from the extraction and percent total solids, if appropriate.

9.12 Method Detection Limit

A method detection limit study is run on an annual basis to verify instrument sensitivity and calculated for both columns.

10.0 DATA VALIDATION

Data will be assessed in accordance with the guidelines set forth in the most recent version of the SERAS data validation SOPs. However, data is considered satisfactory for submission purposes when ALL the requirements mentioned below are met.

1. All samples must be analyzed as part of a valid analytical sequence, i.e., an acceptable initial calibration, and continuing calibration check at the required frequency.

2. All the QC requirements described in Section 9.0 must be met at all times. Any deviations or anomalous conditions should be discussed with the Organic Group Leader.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, refer to U.S. EPA, Occupational Safety and health Administration (OSHA) and corporate health and safety practices. More specifically, refer to SERAS SOP #3013, SERAS *Laboratory Safety Program* and SERAS SOP #1501, *Hazardous Waste Management*.

12.0 REFERENCES

United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1996. *Test Methods for Evaluating Solid Waste, SW-846*, 3rd ed.. Revision 3, Method 3510C.

United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1996. *Test Methods for Evaluating Solid Waste, SW-846*, 3rd ed.. Revision 3, Method 3540C.

United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1996. *Test Methods for Evaluating Solid Waste, SW-846*, 3rd ed.. Revision 2, Method 8000B.

United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1996. *Test Methods for Evaluating Solid Waste, SW-846*, 3rd ed.. Revision 1, Method 8081A.

United States Environmental Protection Agency, Contract Laboratory Program (CLP). 1999. *Statement of Work for Organic Analysis, OLM04.2.*

13.0 APPENDICES

A - Table
B - Figure

APPENDIX A
Table
SOP #1802
April 2003

TABLE 1. Toxaphene Typical Quantitation Limits

ANALYTE	QL (µg/L)	QL (µg/kg)
Toxaphene	0.5	83

QL denotes Quantitation Limits

APPENDIX B
Figure
SOP #1802
April 2003

FIGURE 1. Analytical Sequence for Toxaphene Analysis

Time	Injection #	Material Injected
0 hr.	1-5	Toxaphene Calibration (5-point)
12 hr. Sequence	n	1st Sample
	0	2 ppm Toxaphene Continuing Calibration Standard and/or End of Sequence
	n+1	1st Sample
	:	
another 12 hr.	○	2 ppm Toxaphene Continuing Calibration Standard and/or End of Sequence
	:	
	:	Samples
	:	
another 12 hr. Sequence	○	2 ppm Toxaphene Continuing Calibration Standard and/or End of
	:	
	:	Samples
	:	
another 12 hr.	○	2 ppm Toxaphene Continuing Calibration Standard and/or End of Sequence
	:	
	:	Samples :
	etc.	
	last	2 ppm Toxaphene End of Sequence

NOTE: All subsequent 12-hour periods are timed from the injection of the mid-point calibration standard. The analytical sequence must end with a continuing calibration check standard (2 ppm toxaphene). The mid-point calibration standard from the initial calibration curve can be used as the daily check.