Organochlorine & PCB (Arochlor) Pesticide Analysis by GC/ECD

Process Owner (TS/PM/OM/LM)

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Assignment

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1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentrations of various organochlorine pesticides, and polychlorinated biphenyls (PCBs) as Aroclors, in extracts from municipal and industrial discharges as provided under 40 CRF 136.1. A large number of compounds will give a response in the electron capture detector (ECD) using this method; performance data for the following compounds are provided as part of this method:

ANALYTE	CAS#
alpha-BHC	319-84-6
beta-BHC	319-85-7
delta-BHC	319-86-8
gamma-BHC (Lindane)	58-89-9
Heptachlor	76-44-8
Aldrin	309-00-2
Heptachlor epoxide	1024-57-3
Endosulfan I	959-98-8
Dieldrin	60-57-1
4,4'-DDE	72-55-9
endrin	72-20-8
Endosulfan II	33213-65-9
4,4'-DDD	72-54-8
Endosulfan sulfate	1031-07-8
4,4'-DDT	50-29-3

ANALYTE	CAS#
Methoxychlor	72-43-5
Endrin ketone	53494-70-5
Endrin aldehyde	53494-70-5
alpha-Chlordane	5103-71-9
gamma-Chlordane	5103-74-2
Technical Chlordane	12789-03-6
Toxaphene	8001-35-2
Aroclor-1016	12674-11-2
Aroclor-1221	11104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5

1.2 This capillary GC/ECD method allows the analyst to use 0.53-mm ID capillary columns (wide bore.)

1.3 Table 1 lists average retention times and Weyerhaeuser method detection limits (MDLs) for each single component analyte of interest for the wide-bore capillary column version of this method. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix and the final volume of the extract. Retention time information given in Table 1 was obtained on two wide-bore, open tubular columns connected to the injector port of a gas chromatograph through a single ferrule.

1.4 Compound identification is based on dual-column/dual-detector analysis. This method describes analytical conditions for a second gas chromatographic column that is used to confirm the measurements made with the primary column. Method 625 (GC/MS) provides additional confirmation on analytes of concentration levels applicable to that method.

1.5 Extracts suitable for analysis by this method may also be analyzed for phthalate esters (606,) Nitroaromatics and Isophorone (609,) Haloethers (611,) and Chlorinated Hydrocarbons (612.)

1.6 This method follows EPA Method 608.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, approximately 0.5 Liter, is extracted at neutral pH with methylene chloride using a separatory funnel extraction (AC G-3510.) The extract is dried and exchanged to hexane to a volume of 5 mL (1 mL for lower quantitation limits.) A variety of clean-up steps are applied to the extract, depending on (1) the nature of the co-extracted matrix interferences and (2) the target analytes. Florisil clean up is not mandatory. For samples being analyzed for Aroclors only, sulfuric acid cleanup is applied. If sulfur is detected or suspected, an additional sulfur removal procedure is used. For samples that are suspected of containing oils, GPC (gel permeation chromatography) is performed. After clean up, the extract is analyzed by injecting a 1 to 2-μL sample into a gas chromatograph with dual wide-bore fused silica capillary columns and dual electron capture detectors (GC/ECD.)

2.2 The MDLs achievable in routine analyses of complex samples, using this method, will usually be dependent on the degree of interference associated with the presence of co-eluting EDC-responding compounds rather than on the inherent limitations in detector performance or on the irreducible noise associated with instrument electronics. If interferences prevent identification and qualification of the analytes within quality control (QC) limits at relevant concentrations, this method may also be performed on samples that have undergone clean up. Procedure AC G-3640, Gel-Permeation Clean-up (GPC), is applicable for samples that contain high amounts of lipids, waxes, and other high molecular weight co-extractables.

3.0 INTERFERENCES

3.1 Refer to procedure AP E-8000.

3.2 Sources of interference in this method can be grouped into three broad categories: contaminated solvents, reagents or sample processing hardware; contaminated GC carrier gas, parts, column surfaces or detector surfaces; and the presence of co-eluting compounds in the sample matrix to which the ECD will respond. Knowledge of good laboratory practices is assumed, including steps to be followed in routine testing and clean up of solvents, reagents and sample processing hardware, and instrument maintenance. The discussion following focuses on sources of interference associated with the sample matrix and compound classes that represent common sources of interference, particularly phthalate esters, organosulfur compounds, lipids, and waxes. Interferences co-extracted from the samples will vary considerably from waste to waste. While general clean-up techniques are referenced or provided as part of this method, unique samples may require additional clean-up approaches to achieve desired degree of discrimination and quantitation.

3.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. These materials may be removed prior to analysis using Gel Permeation Cleanup - pesticide option (AC G-3640.) Common flexible plastics contain varying amounts of phthalate esters that are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination. Exhaustive clean up of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

3.4 The presence of elemental sulfur will result in large peaks that interfere with the detection of later eluting organochlorine pesticides. Procedure AC G-3660 is suggested for removal of sulfur, where mercury is used to remove sulfur.

3.5 Oils, waxes, lipids or other high molecular weight co-extractables can be removed by Gel-Permeation Clean up (AC G-3640.)

3.6 All pesticides extracts are subjected to florisil cartridge clean up (AC G-3620) to remove polar compounds.

3.7 It may be difficult to quantitate Aroclor patterns and single component pesticides together. Pesticides can be removed by sulfuric acid/permanganate clean up (AC G-3665.)

4.0 ESTIMATE OF ANALYTICAL TIME

4.1 Extraction of 1 sample and QC (method blank, Lab control spike, matrix spike and matrix spike duplicate) require about 2 hr (no emulsions formed), 3 hrs (with emulsions).

5.0 AMOUNT OF SAMPLE REQUIRED

5.1 For a sample that requires a matrix spike and duplicate, at least 2 liters of sample is required, otherwise 1 liter of sample is sufficient.

6.0 SAMPLE HANDLING, AND PRESERVATION

6.1 Water samples must be extracted 7 days from date of sampling. Samples are stored under refrigeration (4± 2 °C).

6.2 Extracts must be stored under refrigeration (4± 2 °C) and analyzed within 40 days of extraction.

7.0 EQUIPMENT REQUIRED

7.1 Glassware (see procedure AC G-3510 for requirements.)

7.2 GC vials.

7.3 Kuderna-Danish (K-D) apparatus.

7.4 Gas chromatograph analytical system complete with gas chromatograph (HP5890) suitable for on-column and split/splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detector, and data system (chemstation and chemserver with target). The columns are equipped with 5 m of deactivated 0.53-mm fused silica guard column.

7.4.1 Wide-bore columns

7.4.2 Column 1 - 30 m x 0.53-mm ID fused silica capillary column chemically bonded (Rtx-CLPesticides), 0.50-µm film thickness.

7.4.3 Column 2 – 30 m x 0.53-mm ID fused silica capillary column chemically bonded (Rtx-CLPesticides 2), 0.42-µm film thickness.

7.4.4 Alternate column 1 -30 m x 0.53-mm ID fused silica capillary column chemically bonded with 35 % phenyl methylpolysiloxane (DB 608,) 0.83-µm film thickness.

7.4.5 Alternate column 2 - 30 m x 0.53-mm ID fused silica capillary column chemically bonded with 50 % phenyl methylpolysiloxane (DB 1701,) 1.0-µm film thickness.

7.4.6 Wide-bore columns are installed in 6.35-mm (1/4-inch) injectors with Siltek Drilled Uniliner (Restek #21055-214.5) deactivated liner designed specifically for use with these columns.

7.4.7 5 meter retention gaps guard column.

7.4.8 De-activated angled glass “Y” connector.

7.5 GC injector ports can be of critical concern, especially in the analysis of DDT and Endrin. Injectors that are contaminated, chemically active, or too hot can cause the degradation ("breakdown") of the analytes. Endrin breaks down to endrin aldehyde and endrin ketone. DDT breaks down to DDD and DDE. Whenever such breakdown is observed, clean and deactivate the injector port (replace or clean liners, replace silicon 'O'-rings, replace bottom of injector port or rinse the whole injector body and silanize), break off at least 5 cm of the guard column (or replace the guard column) and remount it. Check the injector temperature and lower it to 200 °C, if required (200 °C is the minimum operating temperature of the injector). Endrin and DDT breakdown is less of a problem when ambient on-column injectors are used.

8.0 REAGENTS

8.1 Pesticide grade, or equivalent, solvents and reagents shall be used in all tests, unless otherwise indicated. All references to water in this method refer to Millipore water from lab 211S, which shall be organic free.

8.2 Solvents - as appropriate for procedure AC G-3510 - n-hexane, methylene chloride, acetone, and isooctane (2,2,4-trimethylpentane.) Each lot of solvent should be determined to be phthalate free.

DANGER: READ THE HAZARDS FOR SPECIFIC REAGENTS UNDER AP E-3520.

8.3 Stock standard solutions

WARNING: Many of the compounds in the mixed standards are extremely toxic. The practicality of providing hazard evaluation precludes supplying hazard warnings on each substance. Also, the interactive affect of the compounds make providing an overall evaluation impossible. However, most are at very low concentrations. The standards are also handled in a manner such that the likelihood of contact is very small. The greatest **hazard is probably associated with the ability of the solvent used to carry the material through the skin.** There should be little health risks if handled in accordance with safe working practices.

8.3.1 All standards are bought as pre-made solutions that have been tested by the manufacturer. These solutions are then diluted to the required concentration with hexane. The solutions are purchased from Accustandard, Restek, Crescent, and Ultra. Spiking solutions are purchased from different manufacturers than the solutions used for standard curves (i.e., the initial calibration standards). All solutions are purchased with quality control paperwork for the given solutions. Standards are cross- checked by purchasing different standards from different manufacturers (i.e., when individual mix A is replaced, a different source is used for the next new individual mix A).

NOTE: AC Q-StdRefMat for requirements for ordering standards.

8.3.2 Once the vials have been opened, transfer the stock standard solutions into bottles with Teflon-lined screw caps. Store at (4± 2 °C) and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

8.3.3 Stock standard solutions must be replaced after 1 year (or before the manufacturer's expiration date), or sooner if comparison with check standards indicates a problem.

8.4 Calibration standards:

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8.4.1 Calibration standards, at a minimum of five concentrations for each analyte of interest, are prepared through serial dilution of the stock standards with hexane. One of the concentrations should be at a concentration near, but above, the practical detection limit (PQL.) The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. All calibration solutions must contain the injection standard.

DANGER: All manipulations involving hexane must be performed within a fume hood. n-Hexane is highly flammable. It has a flash point of -23 °C (-9 °F), has explosive limits in air in the range of 1 - 7 %, and poses a serious fire risk when heated, or exposed to flame or spark (this includes static electricity). n-Hexane can react vigorously with oxidizing materials. Avoid breathing vapors. Exposure can cause dizziness, numbness of extremities, and intoxication. n-Hexane is a central nervous system depressant and neurotoxin. Acute exposure causes irritation, narcosis, and gastrointestinal tract irritation. Chronic inhalation causes peripheral neuropathy and can have neurotoxic effects. Avoid skin contact. n-Hexane is absorbed through the skin. Prolonged or repeated skin contact can cause irritation and dermatitis, through defatting of skin.

8.4.2 Calibration solutions must be replaced after 1 year (or before the stock expiration date) or sooner, if comparison with check standards indicates a problem.

8.4.3 Two calibration mixtures are prepared (by serial dilution of a purchased stock standard) for the single component analytes (i.e., Individual Mix A and B) of this method to eliminate potential resolution and quantitation problems.

8.5 Internal standards

The analyst selects one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Isodrin is used as the internal standard. This internal standard is used to check the injection of the sample. All of the calibration standards, instrument blanks and samples have this added. The peak height must be within 80 to 120 % recovery for the injection to be deemed as a good injection. Poor injection indicates that the Teflon plug on the syringe plunger may need to be replaced, that the needle is partially plugged, or that the sample is interfering with the internal standard.

8.6 Surrogate standards

The analyst should monitor the performance of the extraction, clean up (when used), and analytical system, and the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and water blank with pesticide surrogates. Because GC/ECD analyses are more subject to interference than GC/MS analysis, a secondary surrogate is to be used when sample interference is apparent. Decachlorobiphenyl is the primary surrogate, and should be used whenever possible. However, if recovery is low, or compounds interfere with decachlorobiphenyl, then 2,4,5,6-tetrachloro-m-xylene should be evaluated for acceptance. Proceed with corrective action when both surrogates are out of limits for a sample (part 10.3.1). Surrogate solutions are purchased at the concentration of 200μg/mL. This solution is diluted to 0.2 μg/mL in methanol.

9.0 PROCEDURE

9.1 Extraction:

9.1.1 In general, water samples are extracted with methylene chloride as a solvent using a separatory funnel extraction (procedure AC G-3510.)

9.1.2 Spiked samples (Matrix Spikes or MSs) and spiked blanks (Lab Control Spikes or LCSs) are used to verify the applicability of the chosen extraction technique to each new sample type. The spiked sample must be spiked with the compounds of interest to determine the percent recovery and the limit of detection for that sample.

Spiking of water samples should be performed by adding appropriate amounts of pesticide or PCB compounds, dissolved in methanol, to the water sample immediately prior to extraction. After addition of the spike, mix the samples manually for 1 to 2 min. Typical, spiking concentrations for water samples are: 0.5 to 1.0 μg/L for samples in which pesticides and PCBs were not detected; and 2 to 5 times the background concentration in those cases where pesticides and PCBs are present (use of mixtures of Aroclors other than 1016/1260 are not recommended with this method.) Weyerhaeuser uses the submitter's specified samples for spiking. If this is not available from the submitter, then the lab chooses at random which sample will be used for matrix spiking.

9.2 Clean up/Fractionation

9.2.1 Clean-up procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific clean-up procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. General guidance for sample extract clean up is provided in this part.

9.2.2 If a sample is suspected of containing oils or other high molecular compounds, the use of GPC clean up/pesticide option (AC G-3640) is followed by florisil cartridge clean up (AC G-3620.)

9.2.3 If only PCBs are to be measured in a sample, the sample is subjected to sulfuric acid clean up (AP E-3665, where only the sulfuric acid clean up is employed), followed by Florisil cartridge clean up (AC G-3620).

9.2.4 If both PCBs and pesticides are to be measured in the sample, isolation of the PCB fraction by silica gel fractionation (procedure AC G-3630) is recommended. This procedure has not been tested in the extraction lab and is only mentioned as an option for later development.

9.2.5 If only pesticides are to be measured, clean up by AC G-3620 is used.

9.2.6 Elemental sulfur, which may appear in certain industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur should be removed by the technique described in AC G-3660, Sulfur Clean up, using mercury.

9.3 Gas chromatography conditions (recommended):

Wide-bore columns (DB1701 and DB608):	
Carrier gas (He)	5-7 mL/min
Makeup gas (argon / 5 % methane)	100-150 mL/min
Injector temperature	200 °C
Detector temperature	320 °C
Initial temperature	110 °C, hold 0.5 min
Temperature program	110 °C to 270 °C at 9 °C/min
Final temperature	270 °C, hold 10 min.

Wide-bore columns (Rtx-CLPestides and Rtx-CLPesticides 2):	
Carrier gas (He)	18 mL/min
Makeup gas (argon / 5 % methane)	100-150 mL/min
Injector temperature	200 °C
Detector temperature	300 °C
Initial temperature	110 °C, hold 1.0 min
Temperature program	110 °C to 200 °C at 8 °C/min 200 °C to 270 °C at 8 °C/min
Final temperature	270 °C, hold 4.75 min.

9.4 Calibration:

9.4.1 Refer to AI G-8000 for proper calibration techniques. Table 2 is used for the lowest point on the calibration curve (i.e., the low standard is used for the quantitation limits.) If the laboratory is requested to use MDL, then Table 1 is used for the quantitation limits.

9.4.2 The procedure for internal calibration is used. Refer to AI G-8000 for a description for this procedure.

9.4.3 Two calibration mixtures are used in order to minimize the problem of co-elution. These calibration mixtures are also listed in Table 2, along with the low point concentration of each analyte in the mixture. The concentrations provided should be detectable on a GC/ECD suitable for use with this method. Mixtures of Aroclors other than 1016/1260 are not recommended for use with this method (i.e., all of the other Aroclors are individually analyzed.)

9.5 Gas chromatographic analysis:

9.5.1 Refer to AI G-8000. Add 10 μL of internal standard (i.e., injection standard) to the sample extract prior to injection.

9.5.2 Follow AI G-8000 for instruction on the analysis sequence, appropriate dilutions, establishing daily retention time windows, identification criteria, and analysis of a mid-concentration standard after each group of 10 samples.

9.5.3 Examples of GC/ECD chromatograms generated by instruments with wide-bore columns are presented in Figures 1 through 10.

9.5.4 The sample volume injected and the resulting peak sizes (in peak heights) are recorded via the chemstation software and transferred to the chemserver for processing via target software.

9.5.5 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted by the context in which the result is to be used. In reporting, these values will be 'J' flagged (detected but quantitation is only an estimate.)

9.5.6 If the peak response exceeds the working range of the system, dilute the extract and re-analyze. In reporting, these values will be 'E' flagged (detected at a value greater than the calibration curve and the value is only an estimate). Dilute the samples so that the response is at the mid calibration level.

9.5.7 Identification of mixtures (i.e., PCBs, technical chlordane and toxaphene) are based on the characteristic "fingerprint" retention time and shape of the indicator peak(s). Quantitation is based on the height of the characteristic peaks as compared to the height of the corresponding calibration peak(s) of the same retention time and shape generated using external calibration procedures (AI G-8000, 7.6.a). At least three peaks are used in the quantitation of multicomponent analytes.

9.5.8 Identify compounds in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. Due to the stability of megabore columns, the window will never be greater than 0.07 min.

9.5.9 Quantitation of the compound(s) of interest is premised on: 1) a linear response of the ECD to the ranges of concentrations of the compound(s) of interest encountered in the sample extract and the corresponding calibration extract; and 2) a direct linear proportionality between the magnitude of response of the ECD over the width(s) of the retention window(s) (the height of the characteristic or "fingerprint" peak[s]) in the sample and calibration extracts. Proper quantitation requires the appropriate selection of a baseline from which the height of the characteristic peak(s) can be calculated.

9.5.10 If compound identification or quantitation are precluded due to interference (e.g., broad, rounded peaks or ill-defined baseline are present) clean up or dilution of the extract is warranted. Running of instrument blanks followed by midpoint calibration checks are used to determine if the instruments integrity has been affected by the sample is necessary before further sample analysis can be continued. Refer to part 3.2 for the procedures to be followed in sample clean up. If a sample is suspected of being high concentration or high background, multiple instrument blanks are added after the sample. While these instrument blanks are not analyzed, they serve visually to demonstrate that there is no carryover into the next analyzed sample.

9.6 Quantitation of Multiple Component Analytes:

Scope (excerpted from U.S. FDA, PALM): Residues of mixtures of two or more components present problems in measurement. When they are found together, e.g., toxaphene and DDT, the problem of quantitation becomes even more difficult. The following parts are for handing quantitation of toxaphene, chlordane, PCB, DDT, and BHC.

9.6.1 <u>Toxaphene:</u> Quantitative calculation of toxaphene or Storbane is difficult, but reasonable accuracy can be obtained. To calculate toxaphene on GC/ECD, (a) adjust the sample size so that the major toxaphene peaks are 10 - 70 % of full-scale deflection (FSD); (b) inject a toxaphene standard that is estimated to be within $\pm$ 10 ng of the sample; and (c) quantitate using total area sum or sum of all peaks in the range of the standard. This procedure is made difficult by the fact that the relative heights and widths of the peaks in the sample will probably not be identical to the standard.

9.6.2 <u>Chlordane</u> is a technical mixture of at least 11 major components and 30, or more, minor components. Alpha and gamma chlordane are the two major components of technical chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

a. The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of: constituents from the technical chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factors such as water and sunlight.

b. When the chlordane residue does not resemble technical chlordane, but instead consists primarily of individual, identifiable peaks, quantitate the peaks of alpha-chlordane, gamma-chlordane, and heptachlor separately against the appropriate reference materials, and report the individual residues.

c. When the GC pattern of the residue resembles technical chlordane, the analyst may quantitate chlordane residues by comparing the height of the chlordane-chromatogram using the three major peaks (alpha and gamma chlordane and heptachlor). If heptachlor and/or heptachlor epoxide are much out of proportion, calculate these separately and subtract their height from the total area to give a corrected chlordane height. (Note that octachlor epoxide, a metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.)

d. To measure the height of the chlordane chromatogram, proceed as in toxaphene. Adjust the sample volume to produce a response in which alpha and gamma chlordane are approximately the same size as those in the initial calibration standard. Quantitate on at least three peaks.

9.6.3 <u>Polychlorinated biphenyls (PCBs)</u>: Quantitation of residues of PCB involves problems similar to those encountered in the quantitation of toxaphene, strobane, and chlordane. In each case, the chemical is made up of numerous compounds and so the chromatograms are multi-peak. Also, in each case, the chromatogram of the residue may not match that of the standard.

a. Mixtures of PCB of various chlorine contents were sold for many years in the U.S. by the Monsanto Co. under the tradename Aroclor (1200 series and 1016). Though these Aroclors are no longer marketed, the PCBs remain in the environment and are sometimes found as residues in foods, especially fish.

b. PCB residues are quantitated by comparison to one or more of the Aroclor materials, depending on the chromatographic pattern of the residue. A choice must be made as to which Aroclor, or mixture of Aroclors, will produce a chromatogram most similar to that of the residue. This may also involve a judgement about what proportion of the different Aroclors to combine to produce the appropriate reference material.

c. Quantitate PCB residues by comparing height of residue peaks to height of peaks from appropriate Aroclor(s) reference materials. Measure height response from common baseline under all peaks. Use only those peaks from sample that can be attributed to chlorobiphenyls. These peaks must also be present in the chromatogram of reference materials. Mixture of Aroclors may be required to provide best GC patterns of sample and reference.

9.6.4 <u>DDT</u>: DDT found in samples often consist of both o,p' and p,p' DDT. Residues of DDE and TDE are also frequently present. Each isomer of DDT and its metabolites should be quantitated using the pure standard of that compound and reported as such. Only the para para' isomers are quantitated in the lab.

9.6.5 <u>Hexachlorocyclohexane</u> (BHC, from the former name, benzene hexachloride): Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor. It consists of a mixture of six chemically distinct isomers and one or more heptachloro-cyclohexanes and octachloro-cyclohexanes.

a. Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. The elimination rate of the isomers fed to rats was 3 weeks for the alpha, gamma and delta isomers and 14 weeks for the beta isomers. Thus it may be possible to have any combination of these various isomers in different food commodities. BHC found in dairy products usually has a large percentage of beta isomer.

b. Alpha, gamma, and delta isomers show equal response on ECD, whereas beta isomer shows a much weaker electron affinity compared to the other isomers.

c. Quantitate each isomer separately against a standard of the respective pure isomer.

10.0 QUALITY CONTROL

10.1 Quality control to validate sample extraction is covered in AC G-3500 and in the extraction method utilized. If extract clean up is performed, follow the QC in AC G-3600 and in the specific clean-up method.

10.2 Mandatory quality control to evaluate the GC system operation is found in AI G-8000.

10.2.1 The quality control check sample concentrate (AI G-8000) contains each single-component parameter of interest at the following concentrations (withing 5% of the stated value) in acetone: P,P' DDD, P,P' DDT, Endosulfan II, Endosulfan Sulfate and Endrin at 1.0 μg/mL; and the rest of the single component pesticides at 0.20 μg/mL. If this method is only to be used to analyze PCBs, technical Chlordane or Toxaphene, the QC check sample concentrate should contain the most representative multi-component parameter at a concentration of 5.0 μg/mL.

10.2.2. Table 3 indicates the EPA's calibration and QC acceptance criteria for this method. Table 4 gives the EPA's method accuracy and precision as functions of concentration for the analytes of interest. The contents of the Tables are used to evaluate the laboratory's ability to perform and generate acceptable data by this method.

10.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in AI G-8000).

10.3.1 If recovery is not within limits, the following are required:

a. Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

b. Recalculate the data and/or re-analyze the extract if any of the above checks reveal a problem.

c. Re-extract and re-analyze the sample if none of the above are a problem or flag the data as "estimated concentration."

10.3.2. The breakdown of DDT and endrin should be measured before samples are analyzed. Injector maintenance and re-calibration should be completed if the breakdown is greater than 20 % for either compound. If neither of these analytes is detected in the sample, then this breakdown is noted but does not invalidate the data.

10.3.3. Include an instrument blank followed by mid-concentration calibration standard after each group of 10 samples in the analysis sequence as a calibration check. The response factors for the mid-concentration calibration should be within 20 percent of the average values for the multi-concentration calibration. When this continuing calibration is out of this acceptance window, the laboratory should stop analyses, clean the injector and replace the septum. An instrument blank and the continuing calibration standard are analyzed again to determine if the system needs to be re-calibrated. Analysis may be continued if the response factor is within the 20 % value. Otherwise, the system must be re-calibrated.

10.3.4. Internal standards must be evaluated for acceptance. The measured height of the internal standard must be no more than 20 % different from the height from the mid- calibration. When the internal standard peak height is outside the limit, the problem must be corrected before any further analysis is done. Samples that fall outside the QC criteria must be re-analyzed.

10.4 GC/MS confirmation: Any compounds confirmed by two columns should also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory generated detection limits.

10.4.1 The GC/MS would normally require a minimum concentration of 10 ng/L in the final extract for each single-component compound.

10.4.2 The pesticide extract and associated blank should be analyzed by GC/MS as Method AM E-8270.

10.4.3 The confirmation may be from the GC/MS analysis of the base/neutral-acid extracts (sample and blank). However, if the compounds are not detected in the base/neutral-acid extract, even though the concentrations are high enough, a GC/MS analysis of the pesticide extract should be performed.

10.4.4 A QC reference sample of the compound must also be analyzed by GC/MS. The concentration of the QC reference standard must demonstrate the ability to confirm the pesticides/Aroclors identified by GC/ECD.

10.5 METHOD PERFORMANCE

10.5.1 The MDL concentrations listed in Table 1 were obtained using organic-free reagent water. The MDL actually achievable in a given analysis will vary depending on detector response characteristics, irreducible noise from instrument electronics and matrix effects. The single component pesticides along with aroclor 1242 are represented in this table.

10.5.2 Following this method, the obtainable accuracy and precision will be determined by the sample matrix, sample preparation technique, optional clean-up techniques, and the calibration procedures used. The supplied accuracy and precision for water analysis from the EPA are listed in Table 4.

11.0 REPORT

11.1 CALCULATIONS: [(μg/mL analyte/respose factor) x mL final volume x dilution factor] /amount extracted (in L for liquids)

11.2 PRECISION AND ACCURACY. See 10.5.2.

11.2.1 Units for reporting are μg/L (ppb).

11.2.2 Report all concentrations above the quantitation limits to 2 significant figures. Report values below the quantitation limit to 1 significant figure.

12.0 KEY WORDS

AM E-608, Arochlor, ECD, electron capture, EPA, Kuderna-Danish, KD, K-D, organochlorine, PCB, pesticide, polychlorinated biphenyls

13.0 REFERENCES

13.1 Code of Federal Regulations 40, Part 136, Appendix A, Method 608.

13.3 Organics Analysis - Multi-Media, Multi-Concentration, Document OLM 1.6, June 1991.

14.0 REVISION HISTORY

14.1 9/11/07 - Updated the codes to the referenced SOPs.

TABLES

TABLE 1
Weyerhaeuser's Annual Established Method Detection Limit (MDL) with retention times

ANALYTE	RT - DB1701	RT- DB608	μg/L 2/95 WATER DB1701	μg/L 2/95 WATER DB608
alpha-BHC	6.85	9.48	0.0008	0.0020
beta-BHC	8.28	13.23	0.0005	0.0019
delta-BHC	9.42	13.98	0.0016	0.0022
gamma-BHC	8.04	10.77	0.0006	0.0012
Heptachlor	9.03	11.40	0.0006	0.0017
Aldrin	10.13	12.28	0.0003	0.0025
Heptachlor_epoxide	11.90	14.53	0.0008	0.0018
Endosulfan_I	13.02	15.42	0.0004	0.0020
Dieldrin	14.04	16.58	0.0007	0.0021
4,4'-DDE	13.84	16.01	0.0006	0.0043
endrin	15.23	17.28	0.0007	0.0029
Endosulfan_II	15.84	18.82	0.0006	0.0043
4,4'-DDD	15.67	18.55	0.0007	0.0024
Endosulfan_sulfate	17.35	21.62	0.0008	0.033
4,4'-DDT	16.63	19.07	0.0011	0.0034
Methoxychlor	19.54	21.32	0.0036	0.0024
Endrin_ketone	19.90	23.48	0.0013	0.0028
Endrin_aldehyde	16.92	20.33	0.0020	0.0031
alpha-Chlordane	12.97	15.79	0.0004	0.0023
gamma-Chlordane	12.43	15.59	0.0004	0.0019
Chlordane (technical)	*	*	0.0047	0.0059
Toxaphene	*	*	0.10	0.11
Aroclor 1016	*	*	ND	ND
Aroclor 1221	*	*	ND	ND
Aroclor 1232	*	*	ND	ND
Aroclor 1242	*	*	0.016	0.012
Aroclor 1248	*	*	ND	ND
Aroclor 1254	*	*	ND	ND
Aroclor 1260	*	*	ND	ND

e = Multiple peak response
ND = not determined

TABLE 2
Low Concentration of the Individual Component Mixes

INDIVIDUAL MIX A	μg/mL
alpha-BHC	0.005
gamma-BHC	0.005
Heptachlor	0.010
Endosulfan_I	0.010
Dieldrin	0.010
endrin	0.010
4,4'-DDD	0.010
4,4'-DDT	0.010
Methoxychlor	0.050
INDIVIDUAL MIX B	μg/mL
Beta BHC	0.005
Delta BHC	0.005
Aldrin	0.005
Heptachlor Epoxide	0.005
alpha Chlordane	0.005
gamma Chlordane	0.005
4,4'-DDE	0.010
Endosulfan II	0.010
Endrin Aldehyde	0.010
Endosulfan Sulfate	0.010
Endrin Ketone	0.010
SEPARATE MULT- COMPONENT ANALYTES	μg/mL
Aroclor 1016/1260	0.100
Aroclor 1221	0.200
Aroclor 1232	0.100
Aroclor 1242	0.100
Aroclor 1254	0.100
Technical Grade Chlordane	0.050
Toxaphene	0.500

TABLE 3
EPA QC ACCEPTANCE CRITERIA FOR WATER ANALYSIS

Analyte	Test Conc. (μg/L)	limit for s (μg/L)	Range P,Ps (%)	Range of $\bar{x}$ (μg/L)
Aldrin	2.0	0.420	42 - 122	1.08 - 2.24
alpha BHC	2.0	0.480	37 - 134	0.98 - 2.44
beta BHC	2.0	0.640	17 - 147	0.78 - 2.60
gamma BHC	2.0	0.720	19 - 140	1.01 - 2.37
delta BHC	2.0	0.460	32 - 127	0.86 - 2.32
Technical Chlordane	50.0	10.0	45 - 119	27.6 - 54.3
DDE	2.0	2.80	31 - 141	4.80 - 12.6
DDD	10.0	0.55	30 - 145	1.08 - 2.60
DDT	10.0	3.60	25 - 160	4.60 - 13.7
Dieldrin	2.0	0.760	36 - 146	1.15 - 2.49
Endosulfan I	2.0	0.490	45 - 153	1.14 - 2.82
Endosulfan II	10.0	6.10	d - 202	2.20 - 17.1
Endosulfan Sulfate	10.0	2.70	26 - 144	3.80 - 13.2
Endrin	10.0	3.70	30 - 147	5.10 - 12.6
Heptachlor	2.0	0.040	34 - 111	0.86 - 2.00
Heptachlor Epoxide	2.0	0.410	37 - 142	1.13 - 2.63
Toxaphene	50.0	12.7	41 - 126	27.8 - 55.6
Aroclor 1016	50.0	10.0	50 - 114	30.5 - 51.5
Aroclor 1221	50.0	24.4	15 - 178	22.1 - 75.2
Aroclor 1232	50.0	17.9	10 - 215	14.0 - 98.5
Aroclor 1242	50.0	12.2	39 - 150	24.8 - 69.6
Aroclor 1248	50.0	15.9	38 - 158	29.0 - 70.2
Aroclor 1254	50.0	13.8	29 - 131	22.2 - 57.9
Aroclor 1260	50.0	10.4	8 - 127	18.7 - 54.9

s= Standard Deviation of four recovery measurements, in μg/L.
$\bar{x}$ = Average recovery for four recovery measurements, in μg/L.
P, Ps = Percent recovery measured
D = Detected; result must be greater than zero.

Criteria from 40 CFR Part 136 for Method 608. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4
EPA METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATIONS

Analyte	Accuracy, as recovery, x' (μg/L)	Single Analyst precision, s' (μg/L)	Overall precison, S' (μg/L)
Aldrin	0.81C+0.04	0.16x-0.04	0.20x-0.01
alpha BHC	0.84C+0.03	0.13x+0.04	0.23x+0.00
beta BHC	0.81C+0.07	0.22x+0.02	0.33x-0.95
gamma BHC	0.81C+0.07	0.18x+0.09	0.25x+0.03
delta BHC	0.82C-0.05	0.12x+0.06	0.22x+0.04
Technical Chlordane	0.82C-0.04	0.13x+0.13	0.18x+0.18
DDE	0.85C+0.14	0.20x-0.18	0.27x-0.14
DDD	0.84C+0.30	0.13x+0.06	0.28x-0.09
DDT	0.93C-0.13	0.17x+0.39	0.31x-0.21
Dieldrin	0.90C+0.02	0.12x+0.19	0.16x+0.16
Endosulfan I	0.97C+0.04	0.10x+0.07	0.18x+0.08
Endosulfan II	0.93C+0.34	0.41x-0.65	0.47x-0.20
Endosulfan Sulfate	0.89C-0.37	0.13x+0.33	0.24x+0.35
Endrin	0.89C-0.04	0.20x+0.25	0.24x+0.25
Heptachlor	0.69C+0.04	0.06x+0.13	0.16x+0.08
Heptachlor Epoxide	0.89C+0.10	0.18x+0.11	0.25x-0.08
Toxaphene	0.80C+1.74	0.09x+3.20	0.20x+0.22
Aroclor 1016	0.81C+0.50	0.13x+0.15	0.15x+0.45
Aroclor 1221	0.96C+0.65	0.29x-0.76	0.35x-0.62
Aroclor 1232	0.91C+10.79	0.21x-1.93	0.31x+3.50
Aroclor 1242	0.91C+10.79	0.21x-1.93	0.31x+3.50
Aroclor 1248	0.91C+10.79	0.21x-1.93	0.31x+3.50
Aroclor 1254	0.91C+10.79	0.21x-1.93	0.31x+3.50
Aroclor 1260	0.91C+10.79	0.21x-1.93	0.31x+3.50

x' = Expected recovery for one or more measurements of a sample containing concentration C, in μg/L.
s' = Expected single analyst standard deviation of measurements at an average concentration of x, in μg/L.
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of x, in μg/L.
C = True value for the concentation in μg/L.
x = Average recovery found for measurements of samples containing a concentration of C, in μg/L.

TABLE 5
WEYERHAEUSER DATA FOR PERFORMANCE EVALUATION OF
1 Liter of Water 4/95

Analyte	Amount spike μg/L	standard deviation μg/L on DB1701	standard deviation μg/L on DB608	% recovery DB1701	% recovery DB608
Aldrin	0.2	0.010	0.010	86%	89%
alpha-BHC	0.2	0.009	0.008	78%	81%
beta-BHC	0.2	0.014	0.017	98%	99%
gamma-BHC (Lindane)	0.2	0.010	0.010	77%	78%
delta-BHC	0.2	0.015	0.016	85%	88%
Chlordane	NA	NA	NA	NA	NA
4,4'-DDE	0.2	0.019	0.020	88%	100%
4,4'-DDD	1.0	0.11	0.16	90%	83%
4,4'-DDT	1.0	0.11	0.082	96%	79%
Dieldrin	0.2	0.015	0.015	91%	93%
Endosulfan I	0.6	0.010	0.009	98%	99%
Endosulfan II	0.7	0.065	0.056	94%	88%
Endosulfan sulfate	1.0	0.091	0.085	89%	84%
endrin	1.0	0.089	0.075	96%	83%
Heptachlor	0.2	0.011	0.014	87%	89%
Heptachlor epoxide	0.2	0.012	0.011	87%	88%
Methoxychlor	0.2	0.029	0.027	114%	120%
Toxaphene	NA	NA	NA	NA	NA
PCB-1016	NA	NA	NA	NA	NA
PCB-1221	NA	NA	NA	NA	NA
PCB-1232	NA	NA	NA	NA	NA
PCB-1242	5.0	0.11	0.036	90%	83%
PCB-1248	NA	NA	NA	NA	NA
PCB-1254	NA	NA	NA	NA	NA
PCB-1260	5.0	0.024	0.017	91%	90%

Data based on two sets of four extrations on millipore water
NA = not analyzed

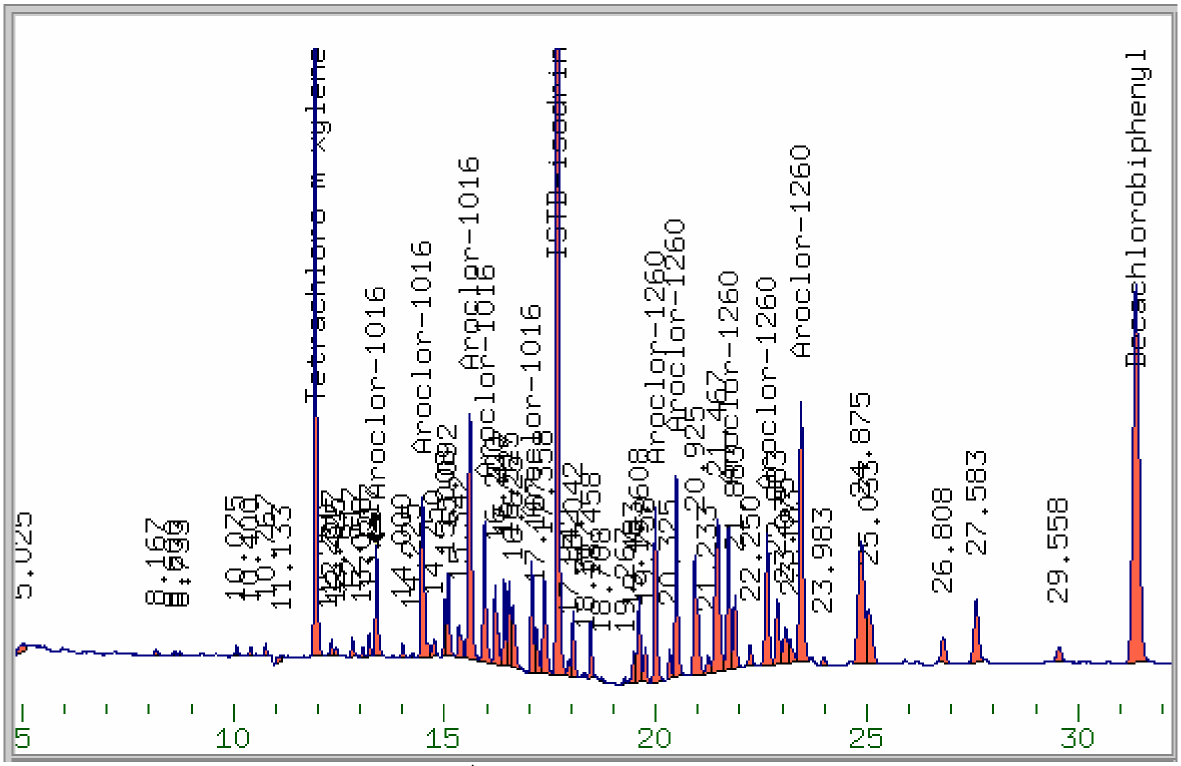

Figure 1: Aroclors 1016 and 1260 ↑

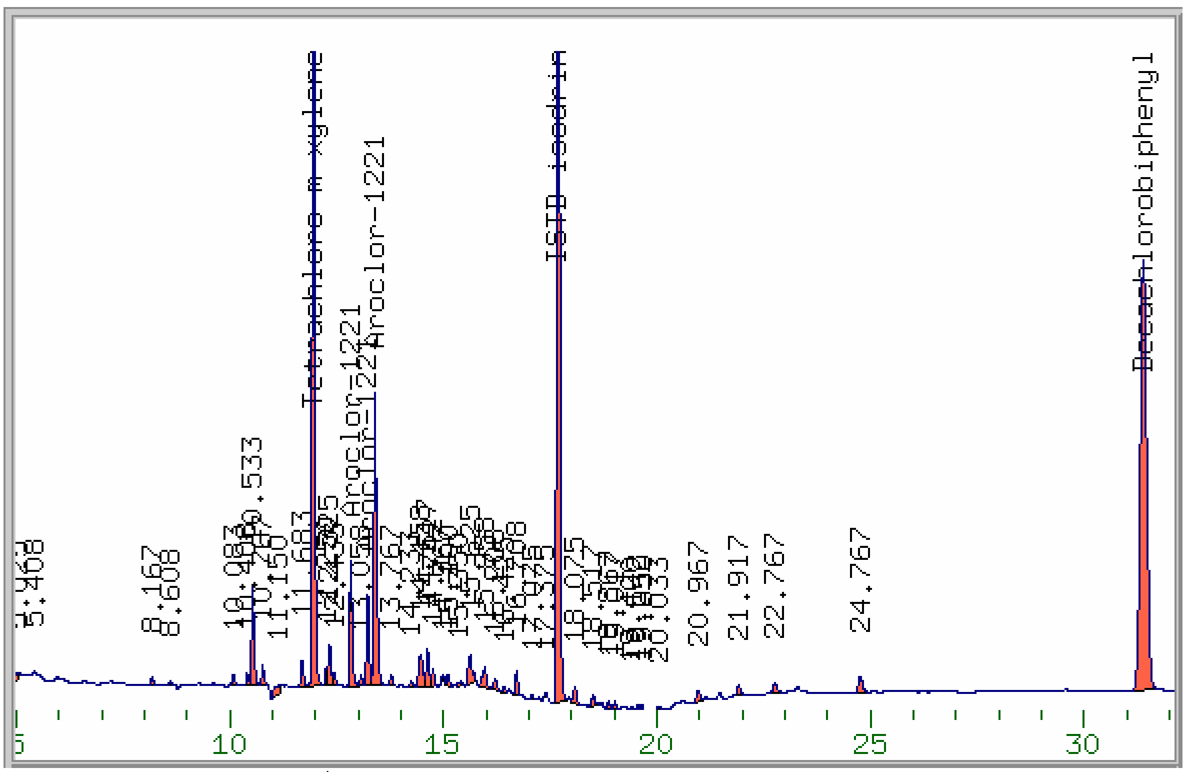

Figure 2: Aroclor 1221 ↑

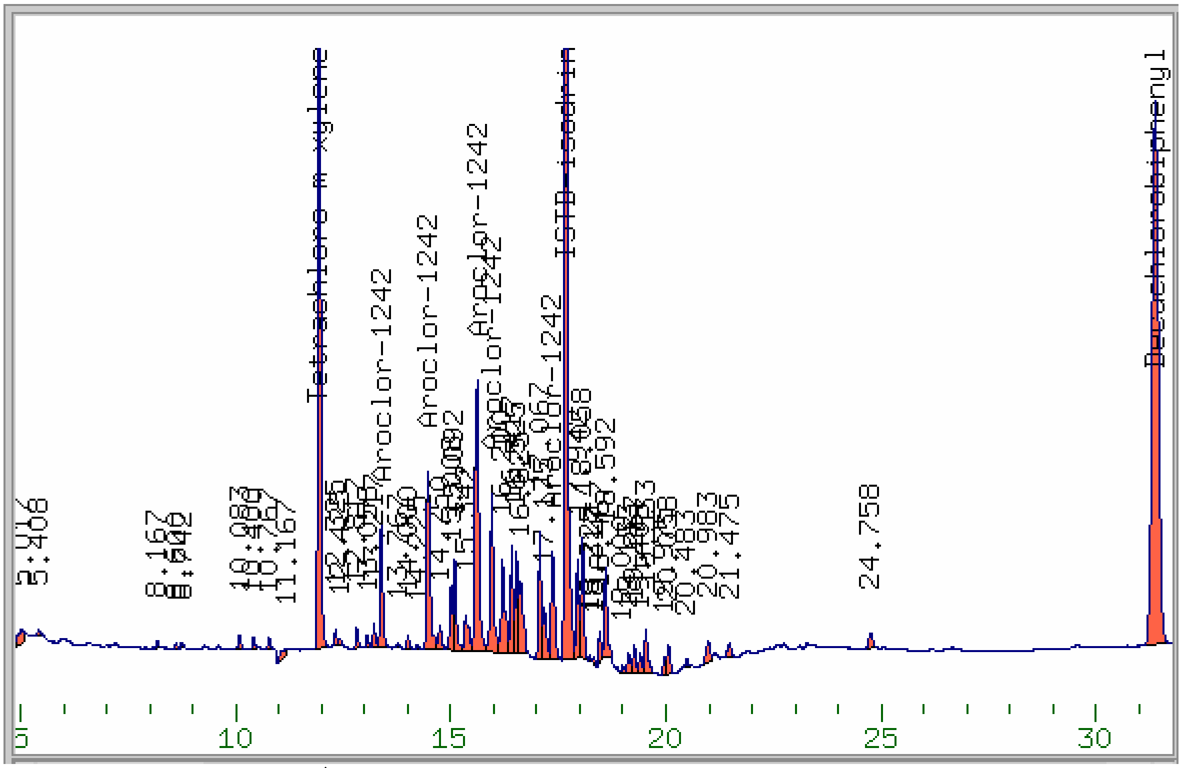

Figure 3: Aroclor 1232 ↑

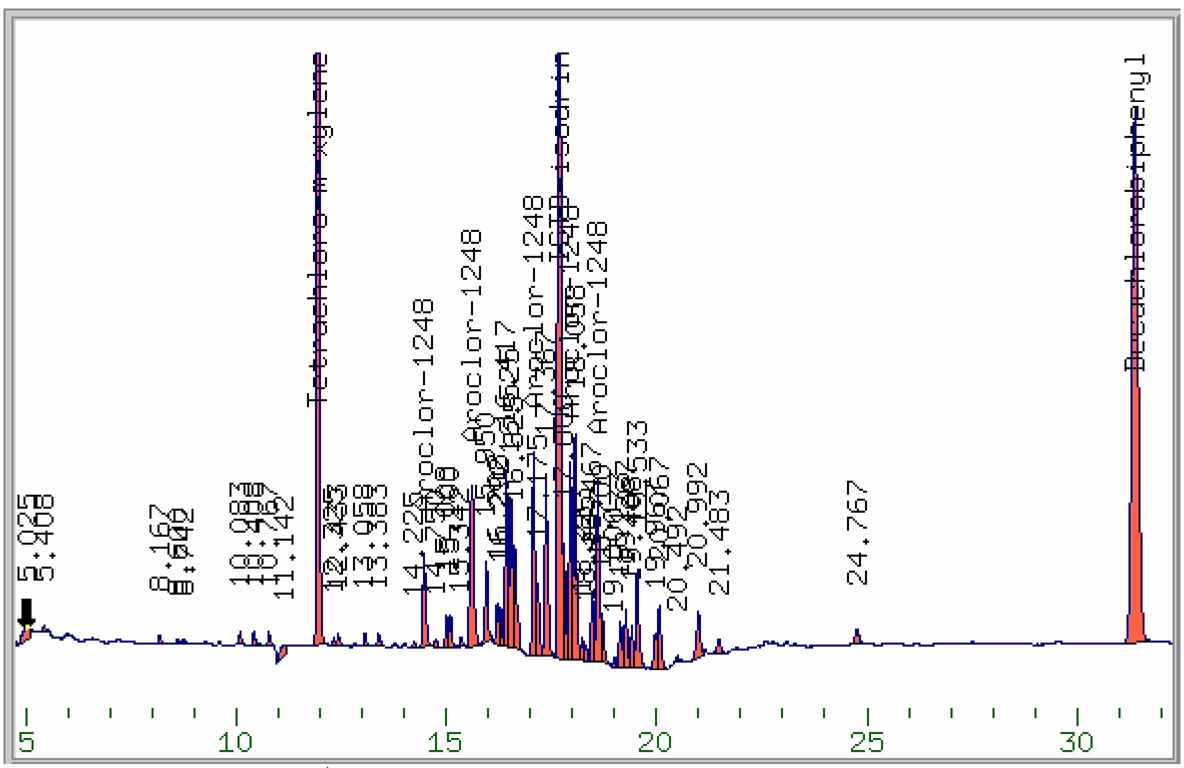

Figure 4: Aroclor 1242 ↑

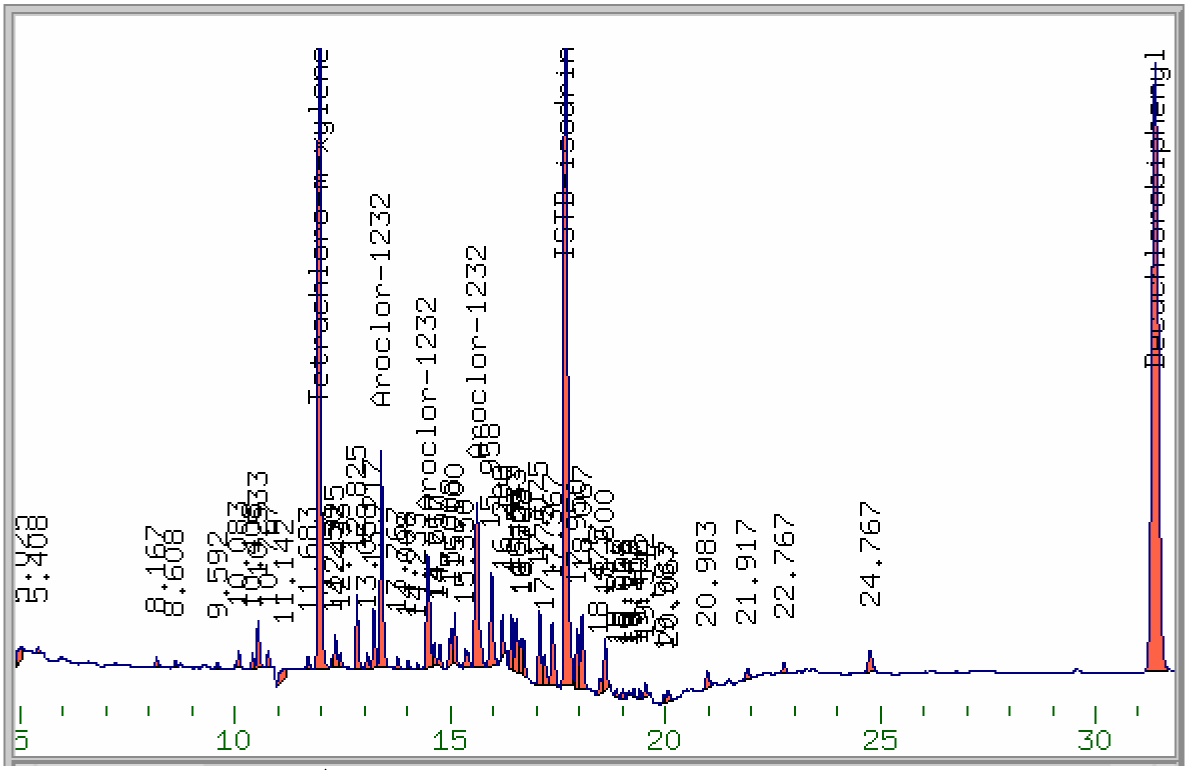

Figure 5: Aroclor 1248 ↑

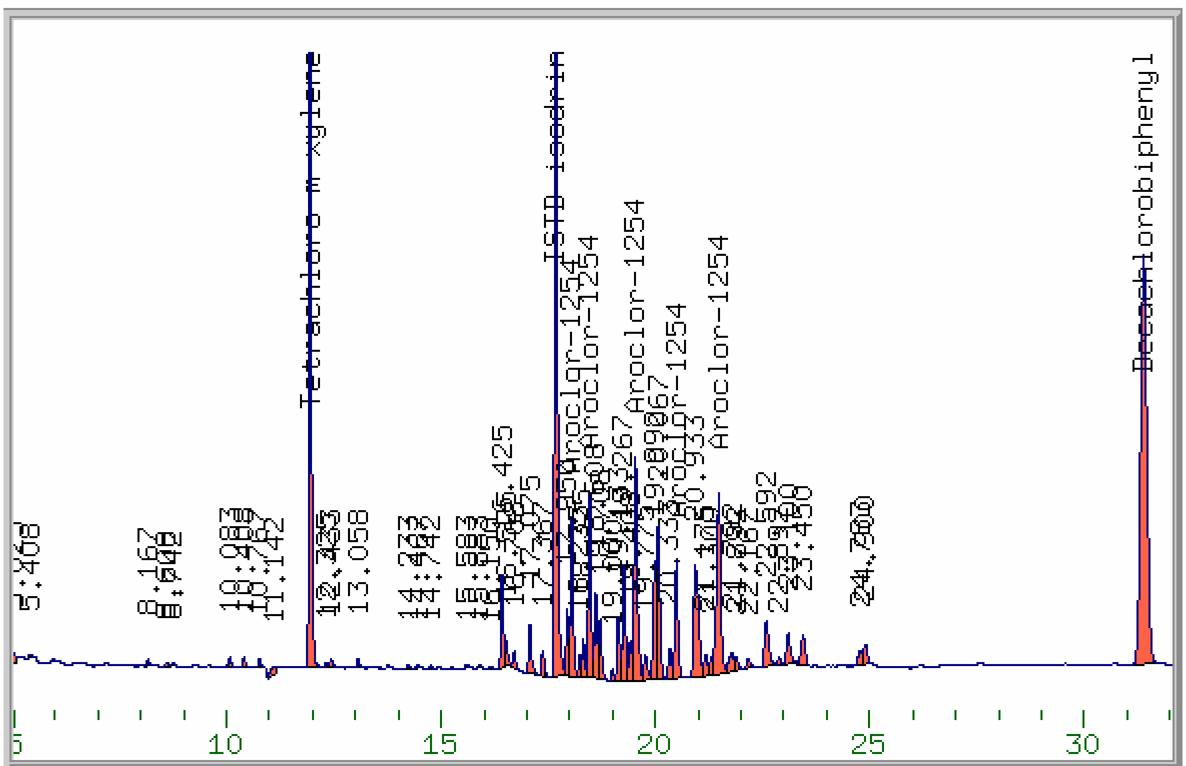

Figure 6: Aroclor 1254 ↑

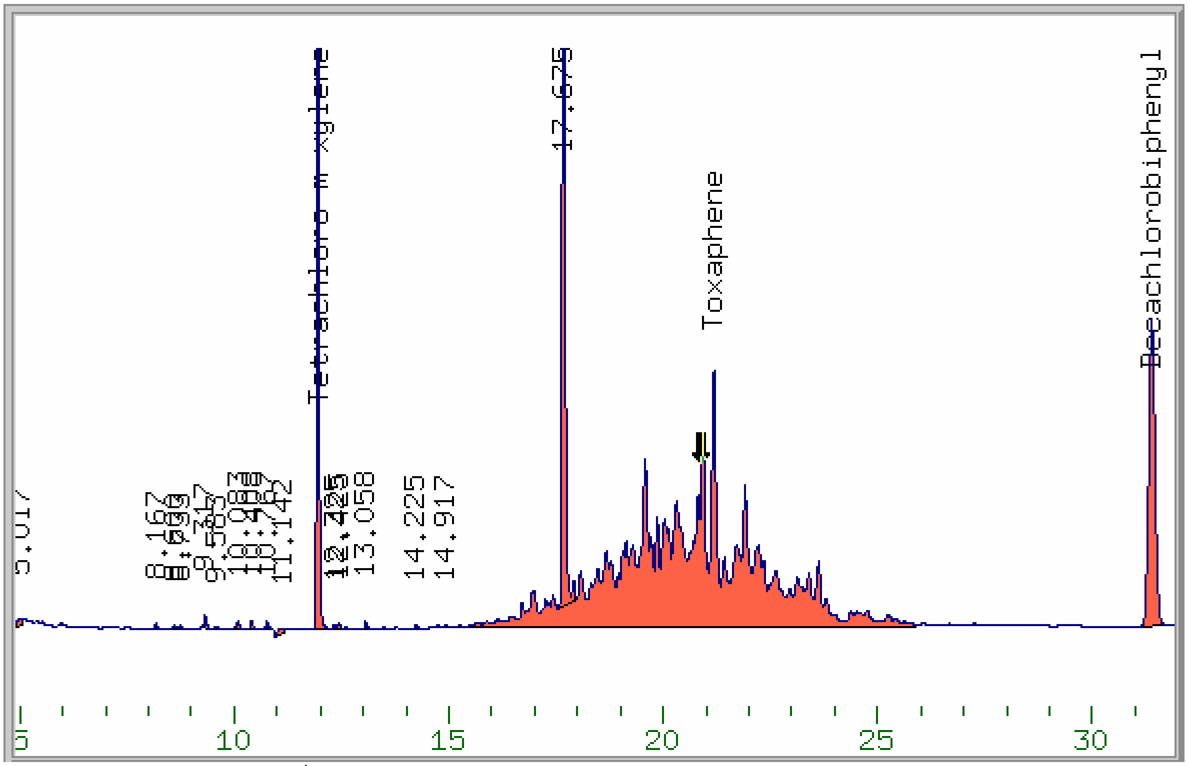

Figure 7: Toxaphene ↑

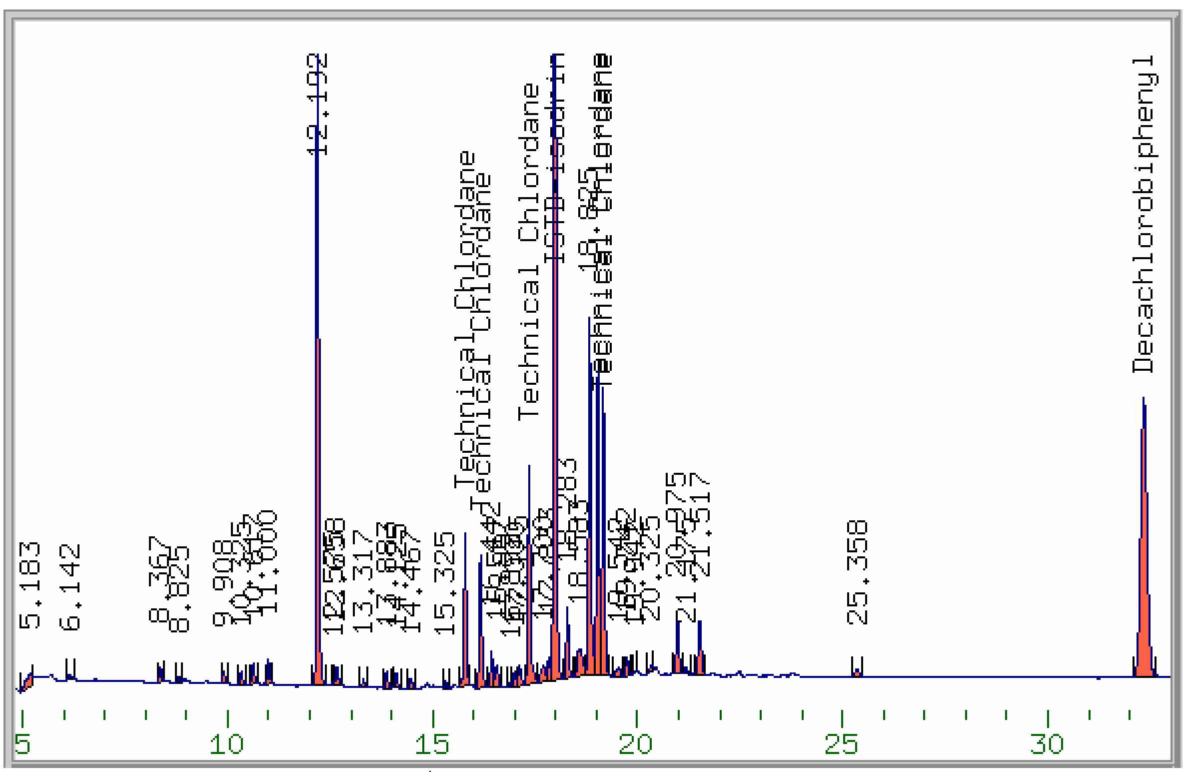

Figure 8: Technical Chlordane ↑

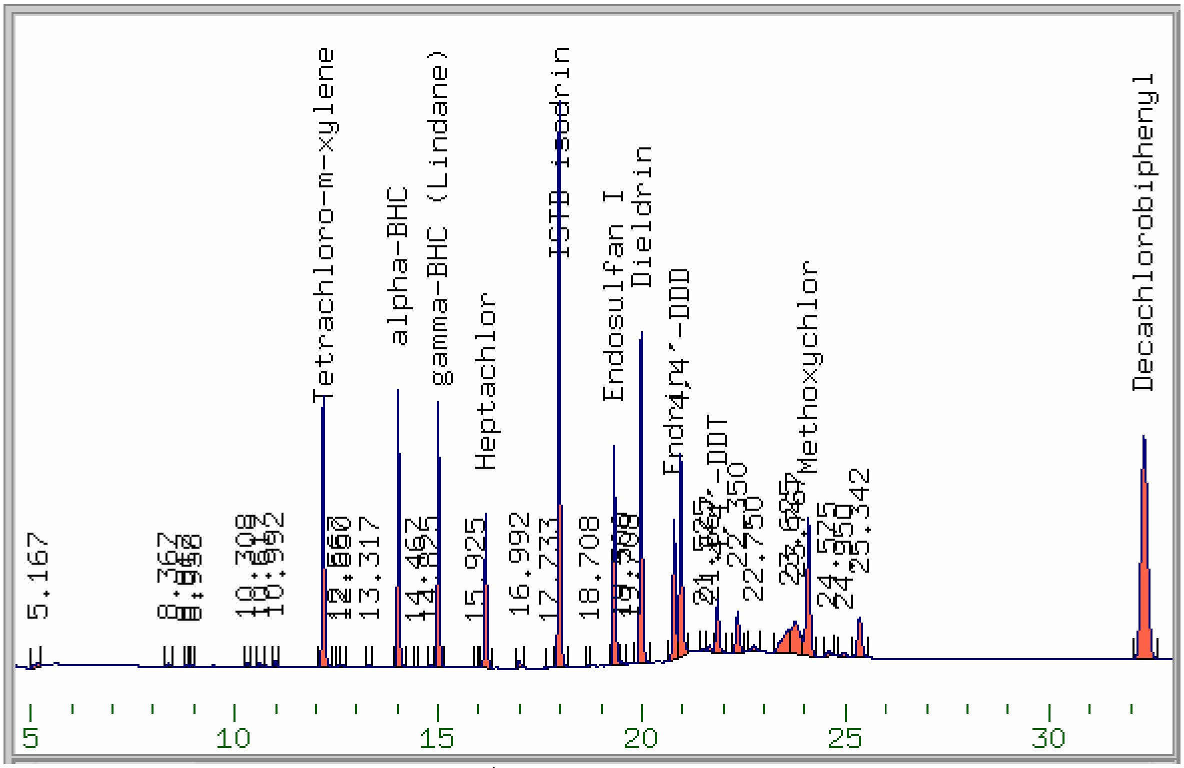

Figure 9: Individual Pesticide Mix A ↑

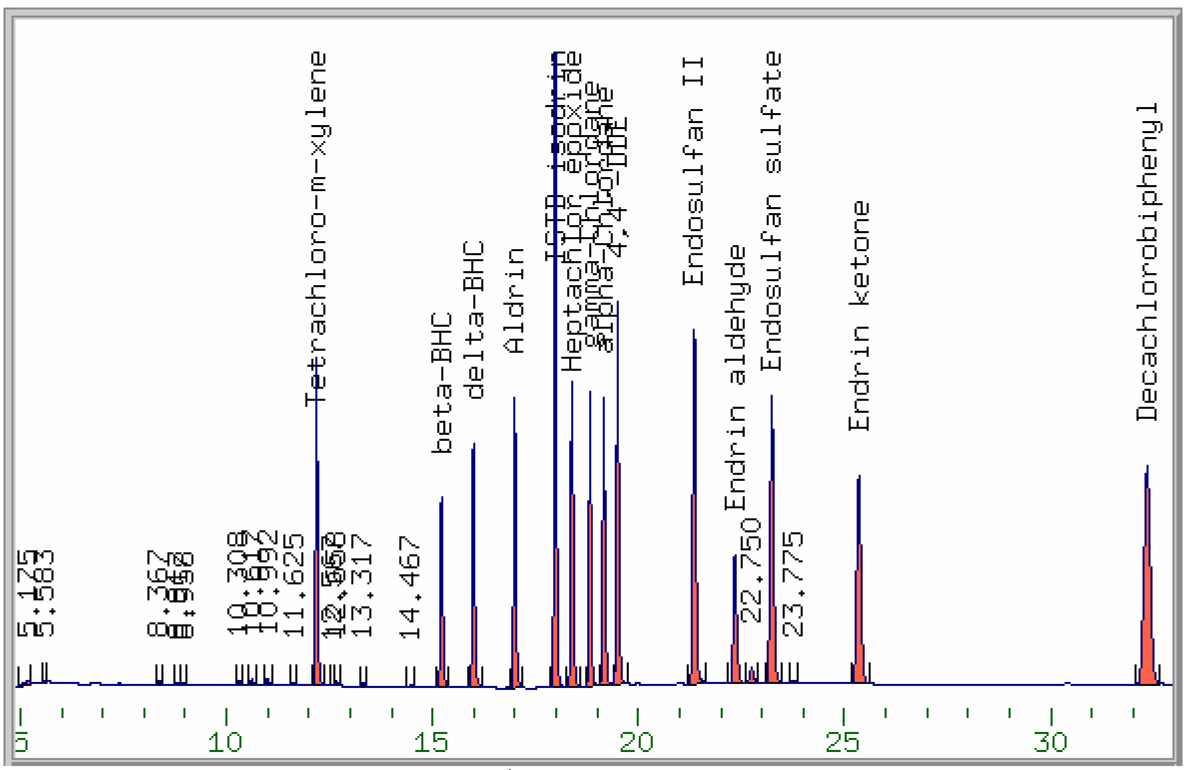

Figure 10: Individual Pesticide Mix B ↑

1.0 SCOPE

This method is applicable to the determination of suspended solids in pulp and paper effluents, wood products effluents, raw and treated water and natural waters.

Suspended solids are defined as those solids retained by a standard glass fiber filter.

This method is based upon EPA method 160.2. It replaces method AM1-160.2.

2.0 SUMMARY OF METHOD

A well-mixed sample is filtered through a standard glass fiber filter and the residue retained on the filter is dried to a constant weight at 104 ± 1°C.

3.0 INTERFERENCES

Non homogeneous materials, such as leaves, sticks, and large floating particles, should be excluded from the sample.

Some solids will decompose below the method required temperatures.

Biological organisms, such as algae and insects, are generally not considered to be part of the solids. Problems associated with these should be noted on the report, especially for regulatory monitoring. In some cases, method modifications may be needed to generate an estimate of the suspended solids.

Too much residue on the filter will entrap water and may require prolonged drying times. Clogging of the filter with residue will also prolong filtering time and retain small particles which would normally pass through the filter.

4.0 ESTIMATE OF ANALYTICAL TIME

An average sample will take 10 to 15 min to run. 10 normal samples may be run in 30 to 40 min. Samples with plugging, or high solids problems may take considerably longer, depending upon the nature of the sample.

5.0 SAMPLE SIZE REQUIRED

There is no fixed requirement for sample volume. Normal samples will take about 100 mL. Samples higher in solids may need considerably less. Samples very low in solids may require up to a liter or more; however, greater volumes decrease the accuracy of the test by increasing the amount of materials being washed from the filter. Normally volumes over 500 mL are not recommended.

Include single sample, plus amount needed for QC. This may include a desired amount, in case of need for re-running, or minimum.

6.0 SAMPLING, SAMPLE HANDLING, AND PRESERVATION

Samples should be collected in clean polyethylene or glass containers. Samples should be analyzed as soon as possible after collection, but can be held under refrigeration at < 4°C for seven days, if immediate analysis cannot be performed.

7.0 EQUIPMENT REQUIRED

7.1 Gelman membrane-style filter holder & membrane filter funnel.

7.2 4.7-cm glass fiber filter discs, without organic binder, Gelman type A/E.

7.3 Vacuum source.

7.4 Drying Oven.

7.5 Aluminum pans. (50-mm diameter)

7.6 Graduated cylinders, TC (to-contain) class B

7.7 Desiccator (with Drierite desiccant.)

7.8 Analytical balance capable of weighing to 0.1 mg.

7.9 Vacuum flask, 500-mL or 1-L.

8.0 PROCEDURE

8.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus. Apply vacuum and wash the disc with three successive 20 ± 2-mL volumes of water. This is to remove small loose fibers and wash away wet strength material from the filter. Allow each washing to completely pass through the filter before beginning the next. Continue suction to remove traces of water from filter disc. Release the vacuum. Remove filter disc from apparatus and transfer to a numbered aluminum pan.

8.2 Dry aluminum dish and glass fiber filter for at least one hour at 104 ± 1°C.

WARNING: Skin contact with hot surfaces may burn the skin.

8.3 A supply of filters may be prepared ahead of time and kept in the oven until needed. After drying, handle dish and filter with forceps or tongs only, never the fingers. Place in a desiccator for 20 ± 5 min and then weigh the filter and the pan. Weigh, to the nearest 0.1 mg, immediately before use.

8.4 Assemble membrane filter apparatus with glass filter in place and start suction. Apply a small amount of water to seat filter against the support.

DANGER: Damaged vacuum flasks can implode under high vacuum. Inspect flasks before use for visible signs of cracks, chips, or other signs of abuse. Do not use damaged or injured flasks.

NOTE: Glassware can become "bruised," or weakened by abuse, such as from impact. Discard any vacuum flasks if they have suffered any abuse.

NOTE: Flasks utilizing 'webbing,' tape, or plastic coating is encouraged so that any flying glass would be contained in event of an implosion. (The nature of the liquid being filtered may make this impractical.)

8.5 Shake the sample vigorously and rapidly transfer 100 mL to the graduated cylinder. Record volume to the nearest 1 mL if greater than 20 mL of sample is taken. Pour measured volume through the tared filter.

NOTE: If suspended matter is low, a larger volume may be filtered. With some samples, such as some pulp mill effluents, 100-mL aliquot causes filter plugging and prolonged filtration times. If filtration of 100 mL of sample is not accomplished within a reasonable time (three min), the sample volume should be reduced to allow for filtration within this time frame.

For NPDES, filter smaller increments of the sample and record the time necessary for filtering. Choose the proper sample volume to ensure that filtration is completed just short of the time a significant decrease in filtration rate occurs.

NOTE: For original volumes of less than 10 mL, dilute 10 ± 0.5 mL of the sample to 100 mL or more in volumetric flasks. Run the test on the diluted sample.

8.6 Rinse the graduated cylinder and filter holder three times with 10 ± 2-mL volumes of water. Allow the washing to completely pass through the filter before beginning the next.

8.7 Release the vacuum.

8.8 Remove the filter from the membrane filter assembly, being careful not to lose any of the sample, and place in the tared aluminum pan. Discard filtrate down the sink.

8.9 Dry 4 to 24 hr at 104 ± 1°C. Cool in a desiccator for 20 ± 5 min and weigh the pan and filter.

WARNING: Skin contact with hot surfaces may burn the skin.

8.10 Samples are dried overnight and historical data has shown that this is sufficient to reach a constant weight. If a shorter drying time is used or at client request, repeat step 8.9 to make sure there is less than 0.5 mg change of mass in the filter. Record the service request number for this information in the Laboratory Standard Recovery notebook.

8.11 Run one blank, a control, and one sample in duplicate in conformance with laboratory guidelines, with a minimum of one of each of these per batch or every 10 samples, whichever is more frequent. The blank is done without running any water through the filter except for the initial rinse.

The blank generally has a loss of 0.1 mg, which is <u>not</u> subtracted from the samples. If the blank gains mass or loses more than 0.2 mg on a 47 mm filter, the samples should be redone.

The controls shall meet the established QC requirements for that control sample. The manufacturer supplies acceptance limits with each lot of standard. Duplicates shall meet the QC requirements for that type of sample.

NOTE: The current control is NSI Standard Reference Material. The recovery limits are 85-115%.

9.0 QUALITY ASSURANCE

Quality assurance is addressed in part 8.11 above.

10.0 REPORT

10.1 Calculations:

Calculate suspended solids as follows:

$$\text{Suspended solids, mg/L} = \frac{(A - B)(1{,}000{,}000)}{C}$$

Where:

A = Mass of filter/pan and residue in g.
B = Mass of filter/pan in g.
C = Volume of sample filtered in mL.

10.2 Do not report more than 3 significant figures.

10.3 Results should be reported in mg/L.

10.4 The lower detectable amount of material is dependent upon the amount of the initial starting volume. The mass of residue used to calculate the detection limit is 1mg.

Example: (0.0010g) (1,000,000) ÷ 500mL = 2 mg/L
2 mg/L would be the detection limit for a 500-mL aliquot.

10.5 Precision and Accuracy

There is no way to determine the precision and accuracy for this method since it generates a method defined value. There is also no defined standard with which to make an objective determination of TSS recovery.

The precision of the determination varies directly with the concentration of suspended solids and degree of difficulty in obtaining a representative sample for analysis. Analysis of typical Weyerhaeuser wood products and pulp mill waste streams by WATS Laboratory showed a standard deviation of ± 1 mg/L (14 % - 11 replications) at 7 mg/L, ± 2 mg/L (4 % - 6 replicates) at 52 mg/L, and ± 3 mg/L (3% - 12 replications) at 100 mg/L.

The results of twenty 94.2 mg/L TSS standard run over a period of 7 months (Oct. 2006-April 2007) gave a recovery of 92.2 mg/L with a standard deviation of 2.1 mg/L.

11.0 KEY WORDS

glass fiber, filter, non-filterable solids, solids, suspended solids, total suspended solids, TSS, water, wastewater

12.0 REFERENCES

12.1 Standard Methods for the Examination of Water and Wastewater, 18th ed., p. 2-56, Method 2540D.

12.2 EPA Manual of Methods for Chemical Analysis of Water and Wastes, March 1983, p. 160.2.

12.3 "Precision of the TSS Test," Weyerhaeuser Technical Report by S. Vincent, February 1977.

12.4 ASTM method D5907.

13.0 REVISION HISTORY

13.1 7/13/07 8.9 – changed the drying time; 8.10 - changed wording to eliminate requirement to check constant weight; 8.11 – added information about QC requirements; 10.5 – Updated precision and accuracy

1.0 SCOPE

1.1 This method is applicable for the analysis of total and total soluble phosphorus in pulp and paper effluents, wood products effluents, raw and treated waters, and natural waters. Total phosphorus includes all of phosphorus present in the sample regardless of form, as measured by the persulfate digestion procedure.

1.2 This method is capable of measuring concentrations of phosphorus from 0.01 to 0.75 mg P/L. This range can be extended by diluting the sample.

1.3 This method replaces AM 1-365.3.

2.0 SUMMARY OF METHOD

Polyphosphates and organic phosphates are converted to orthophosphates by sulfuric acid/persulfate digestion. Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored heteropoly complex by ascorbic acid. The color is proportional to the phosphorus concentration present in the standard or sample.

NOTE: The heteropoly is not a true dissolved color, but is a fine precipitate.

3.0 INTERFERENCES

3.1 Arsenates react with the molybdate reagent to produce a blue color similar to that formed with phosphate. This can be removed by the addition of potassium iodide during the digestion stage.

3.2 Hexavalent chromium and nitrate interfere to give results about 3 % low at concentrations of 1.0 mg/L and 10-15 % low at concentrations of 10 mg/L.

3.3 Sulfide and silicate do not interfere in concentrations of 1.0 and 10.0 mg/L, respectively.

4.0 ESTIMATE OF ANALYTICAL TIME

For a single sample the time estimate is 1.5 hours. The best batch size is 15 samples and the time estimate is 6 hours for the digestion, color development, and calculation.

5.0 SAMPLE SIZE REQUIREMENT

250 mL of sample volume collected in a plastic bottle is needed to meet analysis and quality control requirements.

6.0 SAMPLING, SAMPLE HANDLING AND PRESERVATION

If immediate analysis is not possible, preserve the samples by acidifying to pH < 2 with 5 mL of 9 *N* H_2SO_4 per liter. Store at 4 ºC. Samples for regulatory use may be held in this manner for no longer than 28 days from sample collection.

7.0 EQUIPMENT REQUIRED

CAUTION: All glassware should be new and not have been used for other analyses. It should be washed separately from other glassware to avoid contamination. Care must be taken to avoid the use of phosphate soaps in the laboratory. See AP O-GlassClean.

7.1 Spectrophotometer with 1-cm and 5-cm quartz cells for measurements at 650 nm.

7.2 Filtration and centrifugation apparatus.

7.3 125-mL Phillips beaker.

7.4 Millipore filtration apparatus.

7.5 0.45-µm Millpore filter disc - 47-mm diameter.

7.6 Glass scoop that will deliver approximately 0.4 g.

8.0 REAGENTS REQUIRED

8.1 Ammonium molybdate-antimony potassium tartrate solution: In a 250-mL volumetric flask dissolve 2.0 ± 0.1 g of $(NH_4)_6 Mo_7O_{24}\bullet 4H_2O$ and 0.05 ± 0.005 g of $K(SbO)C_4H_4O_6.1/2\ H_2O$ in 100 - 200 mL of water. Dilute to volume with water. Mix well. This solution is stable for 6 months.

See WARNING under ammonium molybdate in the appendix.

See WARNING under antimony potassium tartrate in the appendix.

8.2 Ascorbic acid solution: In a 100-mL volumetric flask dissolve 6 ± 0.1 g ascorbic acid in 75 - 90 mL of water. Dilute to volume with water. Mix well. Make fresh daily.

See WARNING under ascorbic acid in the appendix.

8.3 Sulfuric acid, 11 *N*: In a 1000-mL volumetric flask slowly add 310 ± 1mL of conc H_2SO_4 to 550 - 650 mL of water while stirring constantly. Cool and dilute to 1000 mL. Mix well.

WARNING: SOLUTION WILL BECOME VERY HOT. THE FLASK SHOULD BE PLACED IN AN ICE BATH (WITHIN A HOOD) AND STIRRED CONSTANTLY. PROTECTIVE CLOTHING SUCH AS GLOVES, APRON, AND FACE SHIELD SHOULD BE WORN.

See DANGER under sulfuric acid in the appendix.

8.4 Sulfuric acid dilution solution: In a 500-mL volumetric flask add 10 ± 0.1mL of 11 *N* H_2SO_4 to approximately 350 - 450 mL of water. Dilute to volume with water. Mix well.

See DANGER under sulfuric acid in the appendix.

8.5 Ammonium Persulfate.

See WARNING under ammonium persulfate in the appendix.

8.6 Phosphorus stock solution, 50 mg P/L : In a 1000-mL volumetric flask dissolve 0.2195 g of pre-dried KH_2PO_4 (anhydrous) (105 ± 2 ºC for 1hour to overnight) in 800 – 900 mL of water. Dilute to volume with water. Mix well. This solution is stable for 6 months. 1 mL of this solution = 50 µg P.

See WARNING under potassium phosphate (monobasic) in the appendix.

8.7 Phosphorus standard solution, 2.5 mg P/L: Prepare fresh daily by pipeting 5 mL of phosphorus stock solution (8.6) into a 100 mL volumetric flask and dilute to volume with water. Mix well. 1 mL of this solution = 2.5 µg P.

See WARNING under potassium phosphate (monobasic) in the appendix.

9.0 PROCEDURE

9.1 Digestion

9.1.1 Transfer a maximum of 50 mL of sample, or a smaller aliquot, into a Phillips beaker and adjust the pH of the sample using a pH electrode to between pH 5 to 8.

9.1.2 If total soluble phosphorus is to be performed, filter the sample through a 45µm filter and transfer a maximum of 50 mL of sample, or a smaller aliquot, into a Phillips beaker and adjust the pH of the sample using a pH electrode to between pH 5 to 8.

9.1.3 If the sample is to be taken back to a final volume of 50 mL, add 1 mL of the 11 *N* H_2SO_4 to the flask and mix well. If the sample is to be taken back to a final volume of 25 mL, add 0.5 mL of the 11 N H_2SO_4 and mix well.

CAUTION: Improper acidity will retard or enhance color formation.

9.1.4 Add 0.4 g of ammonium persulfate (one level scoop) to the flask, mix and place on a hot plate to boil gently for approximately 30-40 min or until a final volume of 10 - 12 mL is reached. Alternately the samples can be heated in an autoclave at 121 ± 2ºC at 100-140 kPa (15-20 psi).

9.1.5 Filter samples through a 0.45µm filter and collect the filtrate in a 50-mL graduated test tube. Rinse the beaker and filter with several aliquots of water. Bring the sample to a final volume of 25 or 50 mL. Pour the sample back into the Phillips beaker and mix well. Rinse the tube and continue with the next sample.

9.1.6 Blanks, controls, and standards for the calibration curve must be carried through the digestion procedure.

9.1.7 The high level calibration curve should be prepared by diluting the following aliquots to a final volume of 50 mL using the same 50-mL graduated test tube used for the samples.

mL 2.5 mg/L Standard Solution	**Standard Concentration (mg/L)**
15	0.75
10	0.50
5.0	0.25
2.0	0.10
1.0	0.050
0	0

9.1.8 The low level calibration curve should be prepared by diluting the following aliquots to a final volume of 50 mL using the same 50-mL graduated test tube used for the samples.

mL 2.5 mg/L Standard Solution	**Standard Concentration (mg/L)**
5.0	0.25
2.0	0.10
1.0	0.050
0.50	0.025
0.20	0.010
0	0

9.1.9 Spikes and duplicates are run on every 10^{th} sample, or one per batch or service request, whichever is more frequent. ICV and ICB standards are run immediately after the calibration curve with CCV and CCB standards run after every 10 samples and at the end of the run.

9.2 Manual Spectrophotometric Determination

9.2.1 Pipet 10 mL of the digested sample and standards, or an aliquot to be diluted to 10 mL, into a 15-mL disposable test tube. Dilutions must be performed using the sulfuric acid dilution solution in section 8.4.

9.2.2 Add 0.8 mL of ammonium molybdate-antimony potassium tartrate solution, cap and mix.

9.2.3 Add 0.4 mL of ascorbic acid solution, cap and mix.

9.2.4 After 5 min, measure absorbance at 650 nm in a 1-cm cell with a spectrophotometer and determine the phosphorus concentration from the standard curve. The color is stable for 45 minutes to one hour. Concentrations in the range of 0.10 to 0.75 mg/L may be determined using the 1-cm cell. The linear calibration curve should have a correlation coefficient (r) of at least 0.995.

NOTE: Do not filter sample after color formation. The heteropoly is not a true dissolved color, but is a fine precipitate.

9.2.5 If samples are known to contain lower amounts of phosphorus, < 0.1 mg/L, pipet 25 mL of the digested sample into a 30-mL disposable beaker containing a stir bar.

9.2.6 Add 2 mL of ammonium molybdate-antimony potassium tartrate solution and mix.

9.2.7 Add 1 mL of ascorbic acid and mix.

9.2.8 Repeat step 9.2.4 above using a 5-cm cell. Concentrations in the range of 0.01 to 0.25 mg/L should be determined using the 5-cm cell. The linear calibration curve should have a correlation coefficient (r) of at least 0.995.

10.0 QUALITY CONTROL

Normally expected QC parameters are as follows:

10.1 Calibration curve – Coefficient of Correlation (r) 0.995

10.2	ICV and CCV recovery	100 ± 10%
10.3	ICB and CCB	< 0.01
10.4	Spike Recovery	100 ± 25%
10.5	Duplicate RPD	20%

11.0 REPORT

11.1 CALCULATION:

$$\text{P, mg/L} = \frac{(\text{mg/L P from curve})(\text{Final volume, mL})}{(\text{mL sample})}$$

11.2 Report the final value to two decimal places with no more than three significant figures. Values near the detection level should only have one significant figure.

11.3 Report results as total phosphorus (TP) or total soluble phosphorus (TSP) in mg/L.

11.4 PRECISION AND ACCURACY

From the most recent 15 runs, expected precision for the high level curve is 2.0 % RSD at a 10X dilution of the 3.50 mg/L standard and an expected accuracy of 95.1 ± 1.9 %.

From the most recent 14 runs, expected precision for the low level curve is 1.8 % RSD at a 50X dilution of the 3.50 mg/L standard and an expected accuracy of 95.3 ± 1.7%.

12.0 KEY WORDS

AM 1-365.3, AM E-365.3 TP, phosphorus, total soluble phosphorusAM 1-365.3, AM E-365.3 TP, phosphorus, total soluble phosphorus

13.0 REFERENCES

13.1 Methods for "Chemical Analysis of Water and Wastes," revised March 1983.

13.2 "Standard Methods for the Examination of Water and Waste Water," 18th Edition, 1992.

APPENDIX

Ascorbic acid

WARNING: Ascorbic acid is relatively non-hazardous in routine laboratory situations. It is not expected to present significant health risks to the workers who use it.
Avoid inhalation: May cause mild irritation to the respiratory tract.
Avoid eye and skin contact: May cause mild irritation.
Fire is possible at elevated temperatures or by contact with an ignition source.
OSHA Permissible Exposure Limit (PEL): 15 mg/m^3 total dust, 5 mg/m^3 respirable fraction for nuisance dusts
Aqueous solutions are rapidly oxidized by air.
Incompatibilities: Strong oxidizers and alkali hydroxides, alkalis, iron, copper, sodium salicylate, sodium nitrite, theobromine, and methenamine.

Ammonium molybdate

WARNING: Avoid inhalation: Ammonium molybdate is an irritant to mucous membranes and the upper respiratory system. Pungent taste in mouth and throat, coughing, labored breathing. Can be a route of absorption by the body with possible symptoms of sore throat, abdominal pain, nausea. May cause anemia, gout, headaches, weight loss, joint pain, and liver or kidney damage.
Avoid skin contact: Causes irritation to skin. Symptoms include redness, itching, and pain.
Avoid eye contact: causes irritation, redness, and pain.
It appears the chemical, physical, and toxicological properties have not been thoroughly investigated.
OSHA permissible exposure limit (PEL): 5 mg/m^3 for soluble molybdenum compounds as Mo, 15 mg/m^3 for insoluble molybdenum compounds as Mo.
Hazardous decomposition products: burning may produce ammonia, nitrogen oxides, and Mo metal fumes.
Incompatible with: alkali metals, strong oxidizing agents, and strong acids.

Ammonium persulfate

WARNING: Avoid breathing dust. Ammonium persulfate can cause irritation to the mucous membranes and respiratory tract. Symptoms may include sore throat, coughing, shortness of breath. Repeated or prolonged exposure may cause asthma.
Avoid skin contact. May cause irritation to skin. Symptoms include redness, burning sensation, and pain. May cause dermatitis, burns, and moderate skin necrosis. Persulfate allergy is not uncommon and manifest itself in the form of a skin rash.
Eye Contact can cause irritation, redness, and pain. May cause burns.
Ingestion can cause nausea, diarrhea, vomiting and sore throat.
Substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition. Contact with oxidizable substances may cause extremely violent combustion. Also may act as initiation source for dust or vapor explosions.
Incompatable with powdered metals, phosphorus, hydrides, organic matter, halogens, acids, strong alkalis, strong reducing agents, alcohols, organics, or other readily oxidizable materials.
Avoid heat and moisture.
Unstable. Gradually decomposes losing oxygen. Decomposes more rapidly at higher temperatures producing toxic and corrosive fumes including ammonia, nitrogen oxides and sulfur oxides. If in solution reacts violently with iron, powdered alumiinium and silver salts. The solution in water is a medium strong acid. Metals other than stainless steel are apt to cause decomposition of persulfate solutions.

Antimony potassium tartrate

WARNING: Avoid inhalation of antimony potassium tartrate dust. Toxic if inhaled. Symptoms of exposure: May cough, nausea, diraahea, metallic taste, salivation, skin rash, severe liver damage, death.
Avoid skin contact: May cause skin irritation.
Avoid eye contact: May cause eye irratation. May cause liver damage.
Avoid contact with acids (may yield SbH_3) and oxidizers (may be explosive with oxides of nitrogen and chlorine, and permanganate.)

Potassium phosphate (monobasic)

WARNING: Avoid inhalation off potassium phosphate dust: May cause mild irritation to the respiratory tract.
Avoid eye contact: May cause irritation, redness, and pain.
Avoid skin contact: Irritant due to its acidic nature. May cause inflammation and pain on prolonged contact, especially with moist skin.
Chronic Exposure from absorbance may sequester calcium and cause calcium phosphate deposits in the kidneys, however this is unlikely since phosphates are slowly and incompletely absorbed (when ingested), and seldom result in systemic effects. The toxicity of phosphates is because of their ability to sequester calcium.
OSHA Permissible Exposure Limit (PEL): 15 mg/m^3 total dust, 5 mg/m^3 respirable fraction for nuisance dusts.
Incompatible with moisture and strong oxidizing agents.

Sulfuric acid

DANGER: Degree of hazard depends upon concentration. Conc. acid mainly refers to those over 52 %. Handle with care. Wear safety goggles and a plastic apron. Use in a hood if mist or fumes generated. Conc. sulfuric acid is a strong, corrosive acid and can cause severe burns. Very carefully add acid to water with frequent or continuous stirring. Mix in a tub or stoppered sink. Upon dilution in water, the generation of heat could cause it to erupt and spatter over a large area. Proceed with caution.
Conc. sulfuric acid is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes and skin.
Inhalation of mist or heated fumes may result in spasm, inflammation and edema of the larynx and bronchi, chemical pneumonitis and pulmonary edema. Symptoms of exposure may include burning sensation or irritation of the nose and throat, coughing, wheezing, laryngitis, shortness of breath labored breathing, headache, nausea and vomiting.
Avoid skin contact. Conc. acid is extremely corrosive. Symptoms of redness, pain, and severe burn can occur. Circulatory collapse with clammy skin, weak and rapid pulse, shallow respirations, and scanty urine may follow skin contact or ingestion. Circulatory shock is often the immediate cause of death.
Avoid eye contact. Extremely corrosive. Sulfuric acid can cause severe irritation or burns and result in permanent damage. Contact can cause blurred vision, redness, pain and severe tissue burns. Strong concentrations will probably cause blindness.
Long-term exposure may cause erosion of teeth.
Sulfuric acid is an oxidizer and strong dehydrating agent. May cause ignition of finely divided organic materials on contact. Reacts with most metals to produce hydrogen gas, which can form an explosive mixture with air. Keep away from bases, carbides, chlorates, fulminates, nitrates, picrates, cyanides, alkali halides, zinc iodide, permanganates, hydrogen peroxide, azides, perchlorates, nitromethane, phosphorous, nitrites, halogens, metal acetylides, oxides and hydrides, metals (especially finely powdered ones) (yields hydrogen gas), strong oxidizing and reducing agents, water, and many other reactive substances.
Harmful if absorbed through skin.
Reaction products include hydrogen, from reaction with metals, or sulfur oxide fumes when heated.
Permissible exposure limit (PEL) is 1 mg/m^3.
Mist is a known carcinogen, depending on duration and level of exposure.

Polychlorinated Biphenyls Analysis by GC/ECD	
Process Owner (TS/PM/OM/LM) Randy Eatherton	Not valid without colored "Controlled" stamp (unless printing date appears) Expires August 31, 2010
Assignment Electronic only unless colored "Controlled" stamp is present	Reviewed June 20, 2003 by Christine Devine

1.0 SCOPE

1.1 Method 8082 (based on EPA's SW-846 method 8082, revision 0, December 1996) is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors ® in extracts from solid and liquid matrices. Analysis is employed with Megabore capillary columns in conjunction with electron capture detectors (ECD).

CAS #	ANALYTE
12674-11-2	Aroclor-1016
11104-28-2	Aroclor-1221
11141-16-5	Aroclor-1232
53469-21-9	Aroclor-1242
12672-29-6	Aroclor-1248
11097-69-1	Aroclor-1254
11096-82-5	Aroclor-1260

1.2 This capillary GC/ECD method allows the analyst to use 0.53-mm ID capillary columns (wide bore).

1.3 Table 1: Weyerhaeuser method detection limits (MDL) for Aroclor 1242, in water and soil/sediment matrices, for the wide-bore capillary column version of this method. The MDLs for the Aroclor analysis of a specific sample may differ from those listed in Tables 1 because they are dependent upon the nature of interferences in the sample matrix.

1.4 Aroclor identification is based on dual column/dual detector analysis. This method describes analytical conditions for a second gas chromatographic column that is used to confirm the measurements made with the primary column.

1.5 Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering"), which alters the peak patterns.

2.0 SUMMARY OF METHOD

2.1 A measured volume or mass of sample is extracted using the appropriate sample extraction technique specified in Methods AP E-3510, AP E-3520, AP E-3540, AP E-3550, and AP E-3580. The amount used is approximately 0.5 L for liquids, 2 g to 30 g for soils, 30 g to 150 g for sediments, 10 grams for pulp/paper and 0.1 grams for oil. Liquid samples are extracted with methylene chloride using a separatory funnel (AP E- 3510). Soil samples are extracted with methylene chloride using either Soxhlet extraction (AP E-3540) or Ultrasonic Extraction (AP E-

3550). **Sediment samples requiring a lower detection limit are extracted by either method with hexane.** For all soil/sediment and tissue samples, GPC (gel permeation chromatography) is optional but sulfuric acid clean up is mandatory. For all solid extracts, Florisil clean up is mandatory. After clean-up, the extract is analyzed by injecting a 1- to 2-μL sample into a gas chromatography with dual wide-bore fused silica capillary columns and dual electron capture detectors (GC/ECD).

2.2 The MDLs - achievable in routine analyses of complex samples using this method - will usually be dependent on the degree of interference associated with the presence of co-eluting compounds to which the ECD will respond. This interference will have more influence than on the inherent limitations in detector performance, or the irreducible noise associated with instrument electronics. If interferences prevent identification and qualification of the analytes within quality control (QC) limits at relevant concentrations, this method may also be performed on samples that have undergone clean up. If interferences prevent identification and qualification of the analytes within quality control (QC) limits at relevant concentrations, this method may also be performed on samples that have undergone clean up. AP E-3640, Gel-Permeation Clean up (GPC) and AP E-3665 (sulfuric acid clean up) are applicable for samples that contain high amounts of lipids, waxes, pulps, paper and other high molecular weight co-extractables. All soil, sediment, pulp, paper and oil samples undergo sulfuric acid clean up, with GPC clean up optional.

3.0 INTERFERENCES

3.1 Refer to Methods AP E-3550, AP E-3600, and AP E-8000.

3.2 Sources of interference in this method can be grouped into three broad categories: contaminated solvents, reagents, or sample processing hardware; contaminated GC carrier gas, parts, column or detector surfaces; and the presence of co-eluting compounds in the sample matrix to which the ECD will respond. Knowledge of good laboratory practices is assumed, including steps to be followed in routine testing and clean up of solvents, reagents and sample processing hardware, and instrument maintenance. The discussion that follows focuses on sources of interference associated with the sample matrix and compound classes that represent common sources of interference, particularly phthalate esters, organosulfur compounds, lipids, and waxes. Interferences co-extracted from the samples will vary considerably from waste to waste. While general clean-up techniques are referenced or provided as part of this method, unique samples may require additional clean-up approaches to achieve desired degree of discrimination and quantitation.

3.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. These materials may be removed prior to analysis using Gel Permeation Clean up - pesticide option (AP E-3640). Common flexible plastics contain varying amounts of phthalate esters that are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination can best minimize interferences from phthalate esters. Exhaustive clean up of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

3.4 The presence of elemental sulfur will result in large peaks that interfere with the detection of later eluting Aroclors. AP E-3660 is suggested for removal of sulfur, where mercury is used to remove sulfur.

Sulfur clean up is mandatory with sediment samples due to the high sulfur content.

DANGER: Mercury vapors are hazardous. Proper handling in the hood and proper disposal is required.

3.5 Wax, lipids other high molecular weight co-extractables can be removed by sulfuric acid clean up (AP E-3665) and by Gel-Permeation clean up (AP E-3640).

3.6 Pulp and paper samples extracted with methylene chloride result in small fibers being suspended, which must be removed with sulfuric acid clean up (AP E-3665).

3.7 All soil, sediment, oil and pulp/paper Aroclor extracts are subjected to Florisil cartridge clean-up (AP E-3620) to remove polar compounds.

3.8 Cross-contamination of glassware. High levels of Aroclors can easily contaminate low-level samples. Care must be exercised when handling samples that came from transformers or around transformers as these can contain % levels of Aroclors. If such samples are being analyzed, do not use Florisl clean up (contamination of the manifold will happen). Dilute the sample by 10,000 for analysis. All glassware that was used must be rinsed several times into a hazardous waste container. The glassware must be clean before it is sent to glass washing.

CAUTION: Do not oven dry glassware. Drying of glassware used for PCB analysis can increase contamination because PCBs are readily volatilized in the oven and can spread to other glassware.

4.0 ESTIMATE OF ANALYTICAL TIME

4.1 Oil samples require only dilution, so the time is less than ½ hour for a batch of 12. Pulp/paper samples require soxhlet extraction and multiple cleanups, requiring 4 man-hours per batch, 30 hours elapsed time per batch of 12. Water samples are dependent on emulsions formed during extraction. No emulsions require 2 hours prep time per batch of 6. Emulsions require 4 hours prep time per batch of 6. Soil samples with no fines would require 2 hours prep time per batch of 12. Samples containing fines, resulting in plugged up filter funnels, could add hours to the prep time.

5.0 AMOUNT OF SAMPLE REQUIRED

Soil samples require 200 grams; sediment require 500 grams; water requires 2 liters; oil requires 2 grams and pulp/paper samples require 30 grams per sample. This allows enough sample for matrix spike/matrix spike duplicate.

6.0 SAMPLING, SAMPLE HANDLING, AND PRESERVATION

6.1. Water samples must be extracted within 7 days from date of sampling. Soil/sediment samples must be extracted within 14 days from date of sampling. Water and soil/sediment samples are stored under refrigeration (4 ±2°C). Tissues, pulp, paper and oil samples have no defined holding time since the samples are stored in the freezer.

6.2 Extracts must be stored under refrigeration (4 ±2°C) and analyzed within 40 days of extraction.

7.0 EQUIPMENT REQUIRED

7.1 Glassware (see Methods AP E-3510, AP E-3520, AP E-3540, AP E-3550, AP E-3620, AP E-3640, and AP E-3660 for specifications).

7.2 Kuderna-Danish (K-D) or TurboVap© apparatus for concentration of initial extracts.

7.3 Gas chromatography analytical system complete with gas chromatography (HP5880) suitable for on-column and split/splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detector, and data system (Target). The columns are equipped with 5 meters of deactivated 0.32-mm fused silica guard columns.

7.3.1 Wide-bore columns.

7.3.4 Column 1 - 30 m x 0.53-mm ID fused silica capillary column chemically bonded (Rtx-CLPesticides,) 0.50-µm film thickness.

7.3.5 Column 2 - 30 m x 0.53-mm ID fused silica capillary column chemically bonded (Rtx-CLPesticides 2,) 0.42-µm film thickness.

7.3.6 Wide-bore columns are installed in 6.35-mm (1/4-inch) injectors with Siltek Drilled Uniliner (Restek #21055-214.5) deactivated liners designed specifically for use with these columns. The columns are connected to the 5-m guard column with a press fit Y-shaped 3-way fused silica union.

7.3.2 Alternate Column 1 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 % phenyl methylpolysiloxane (DB 608), 0.83-µm film thickness.

7.3.3 Alternate Column 2 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 % phenyl methylpolysiloxane (DB 1701), 1.0 µm film thickness.

8.0 REAGENTS

8.1 Pesticide grade, or equivalent, solvents and reagents shall be used in all tests, unless otherwise indicated. Reagent water shall be organic-free. All references to water in this method refer to Millipore water from lab 211S.

8.2 Solvents - as appropriate for AP E-3510, AP E-3520, AP E-3540, AP E-3550, AP E-3620, AP E-3640, or AP E-3660 - n-hexane, methylene chloride, acetone and iso-octane (2,2,4-trimethylpentane). Each lot of solvent should be determined to be phthalate free. All samples and standards must be in n-hexane or iso-octane prior to analysis.

DANGER: Acetone is highly flammable. It has a flash point of -20 °C (-4 °F) and poses a serious fire risk when heated, or exposed to flame or spark (this includes static electricity).
Avoid breathing vapors. Exposure can cause coughing, dullness, headache, dizziness, nausea, irritation to the eyes and respiratory tract, narcosis, and unconsciousness. Higher concentrations may cause damage to kidneys, liver, and central nervous system (depression). Chronic exposure during pregnancy may be harmful.
Avoid skin contact. Acetone is absorbed through the skin. Prolonged or repeated skin contact can cause severe irritation and dermatitis, because of the defatting action on skin. May cause redness, pain, drying and cracking of the skin. Toxicity of alcohol, and halogenated hydrocarbons may be increased.
Acetone can react vigorously with oxidizing materials. Avoid strong acids, strong alkalis, and halogens and halogen compounds.

DANGER: All manipulations involving hexane must be performed within a fume hood. n-Hexane is highly flammable. It has a flash point of -23 °C (-9 °F), has explosive limits in air in the range of 1 - 7 %, and poses a serious fire risk when heated, or exposed to flame or spark (this includes static electricity). n-Hexane can react vigorously with oxidizing materials.
Avoid breathing vapors. Exposure can cause dizziness, numbness of extremities, and intoxication. n-Hexane is a central nervous system depressant and neurotoxin. Acute exposure causes irritation, narcosis, and gastrointestinal tract irritation. Chronic inhalation causes peripheral neuropathy and can have neurotoxic effects.
Avoid skin contact. n-Hexane is absorbed through the skin. Prolonged or repeated skin contact can cause irritation and dermatitis, through defatting of skin.

WARNING: Avoid inhalation. Inhalation of iso-octane can cause mild mucous membrane irritation and central nervous system depression. Acute exposure causes irritation, narcosis, dizziness, nausea, incoordination, stupor, and unconsciousness, and death.
Avoid eye contact: Liquid and high vapor concentration can cause irritation.
Avoid skin contact: Prolonged or repeated skin contact can cause irritation and dermatitis through defatting of skin. Those individuals susceptible to dermatitis should avoid handling. Chronic exposure information is incomplete or unknown.
Avoid strong oxidizing agents, heat, sparks, open flame, open containers, and poor ventilation.
Hazardous decomposition products: incomplete combustion can generate carbon monoxide and other toxic vapors.
Flash point: -12 °C (tag closed cup)
Flammable limits in air % by volume: lower limit: 1.0, upper limit: 6.0
TLV 350 mg/m3 is the recommended 10-hr TWA for alkanes (c5-c8). There is presently no exposure limit established by OSHA.
Iso-octane should be protected from temperature extremes and direct sunlight. It should be stored in an acceptably protected and secure flammable liquid storage area.

DANGER: All manipulations involving methylene chloride must be performed within a fume hood or a sealed system to prevent venting into the laboratory. It is non-flammable.
Avoid breathing vapors. Exposure can cause anesthetic or narcotic effects, light-headedness, nausea, vomiting and headache. Excessive exposure may cause irritation to upper respiratory tract. Unconsciousness and death can result from extreme cases of over exposure. High levels may also cause cardiac arrhythmias (irregular heartbeats). Breathing vapors can elevate carboxyhemoglobin levels in the cardiovascular system thereby impairing the blood's ability to transport oxygen. Persons who smoke tobacco products will experience an intensified elevation of carboxyhemoglobin levels. Observations in animals include liver and kidney effects.
Delayed effects: exposure may aggravate symptoms of angina (chest pains). Liver and kidney damage may occur.
Avoid skin contact. Prolonged or repeated exposure may cause skin irritation, even a burn. Repeated contact may cause drying or flaking of skin. Can cause irritation and dermatitis.
Cancer information: Suspect carcinogen. Causes cancer in mice and benign tumors in rats.
Avoid direct sunlight and UV sources. High temperatures and open flame may produce phosgene.
Incompatibility with metals such as: aluminum powders, potassium, sodium, and zinc powder.
Avoid unintended contact with amines. Avoid contact with strong bases and strong oxidizers.
Avoid prolonged contact with or storage in aluminum or its alloys.
OSHA action level: 12.5 ppm. PEL is 25 ppm. (If you can smell it, the amount is too high.)

8.3 Stock standard solutions

WARNING: Many of the compounds used to make up mixed standards are extremely toxic. The practicality of providing hazard evaluation precludes supplying hazard warnings on each substance. Also, the interactive affect of the compounds make providing an overall evaluation impossible.

However, most are at very low concentrations. The standards are also handled in a manner such that the likelihood of contact is very small.
The greatest hazard is probably associated with the ability of the solvent used to carry the material through the skin.
There should be little health risks if handled in accordance with safe working practices. Consult the MSDS sheet if there is one for the material.

8.3.1 All standards are bought as premade solutions that have been tested by the manufacturer. These solutions are then diluted to the required concentration with hexane. The solutions are purchased from Accustandard, Restek, and Ultra. Spiking solutions are purchased from different manufacturers than the solutions used for standard curves (i.e., the initial calibration standards). All solutions are purchased with quality control paperwork for the given solutions. Standards are cross-checked by purchasing different standards from different manufacturers (i.e., when Aroclor 1260 is replaced, a different source is used for the next new Aroclor 1260).

8.3.2 Once the vials have been opened, transfer the stock standard solutions into bottles with Teflon-lined screw caps. Store at 4 ±2°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

8.3.3 Stock standard solutions must be replaced after 1 year (or before the manufacturer's expiration date), or sooner if comparison with check standards indicates a problem.

8.4 Calibration standards:

8.4.1 A standard containing a mixture of Aroclor 1260 and Aroclor 1016 will include many of the peaks represented in the other five Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing initial calibrations for each of the seven Aroclors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors.

8.4.2 Calibration standards, at a minimum of five concentrations are prepared through dilution of the stock standards with hexane. One of the concentrations should be at a concentration near, but above, the practical detection limit (PQL). The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. All calibration solutions must contain the injection standard.

8.4.3 Calibration solutions must be replaced after 1 year (or before the manufacturer's expiration date of the stock), or sooner, if comparison with check standards indicates a problem.

8.4.4 Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards have been used to demonstrate linearity of the detector, these single standards of the remaining five Aroclors are also used to determine the calibration factor for each Aroclor. The concentrations should correspond to the mid-point of the linear range of the detector (i.e., the same level as the mid-standard of the Aroclor 1260/1016 mixture).

8.5 Internal standards

The analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Isodrin is used as the internal standard. This internal standard is used to check the injection of the sample. All of the calibration standards, instrument blanks and samples have this added. The peak height must be within 80 to 120 % recovery for the injection to be deemed as a good injection. Poor injection indicates that the Teflon plug may need to be replaced or that the needle is partially plugged. A 10.0-uLspike (5000ng/μL of isodrin) is added to the GC vial containing 1.0 mL of the sample to be analyzed. Isodrin has been demonstrated not to interfere with the PCBs or the Aroclor pattern.

8.6 Surrogate standard: The analyst should monitor the performance of the extraction, clean-up (when used), and analytical system, and the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and water blank with pesticide surrogates. Because GC/ECD analyses are more subject to interference than GC/MS analysis, a secondary surrogate is to be used when sample interference is apparent. Decachlorobiphenyl is the primary surrogate. Proceed with corrective action when the surrogate is out of limits for a sample (re-analsysis to confirm that the injection was bad, checking the syringe needle and plunger, and checking the septum).

9.0 PROCEDURE

9.1 Extraction:

9.1.1 In general, water samples are extracted with methylene chloride as a solvent using a separatory funnel (AP E-3510). Soil/sediment samples are extracted with methylene chloride ultrasonic extraction (AP E-3550) procedures. Tissue, pulp and paper samples are extracted with methylene chloride soxhlet extraction (AP E-3540). Oil samples are diluted with hexane to 10-ml final volume (AP E-3580).

9.1.2 Spiked samples (Matrix Spikes) and spiked blanks (Lab Control Spikes) are used to verify the applicability of the chosen extraction technique to each new sample type. Each sample must be spiked with the compounds of interest to determine the percent recovery and the limit of detection for that sample.

9.1.2. a Each extraction batch of samples will have the following QC:

1. Matrix spike/Matrix spike duplicate of samples will be done at the rate of 10 % (1 set out of 10) for regulatory samples and 5 % (1 set out of 20) for all other samples.

2. All batches will include an LCS and a Method blank.

b. Spiking of water samples should be performed by adding appropriate amounts of Aroclor 1016/1260 mixture, dissolved in methanol, to the water sample immediately prior to extraction. After addition of the spike, mix the samples manually for 1 to 2 min. Typical spiking concentrations for water samples are 1.0 μg/L for samples in which Aroclors were not detected and 2 to 5 times the background concentration in those cases where Aroclors are present.

c. Spiking of soil, sediment and tissue samples should be performed by adding appropriate amounts of Aroclor 1016/1260 mixture, which are dissolved in methanol, to the solid sample aliquot. The solid sample should be wet prior to the addition of the spike (at least 20 % moisture) and should be mixed thoroughly with a metal spatula to homogenize the material. An appropriate amount (just enough to absorb the moisture) of sodium sulfate is added to the sample. This is thoroughly mixed. Allow the spike to equilibrate with the solid for 15-30 min. at room temperature prior to extraction. The sample is mixed to break up the solidified sodium sulfate to give the sample a granular/dry consistency. Additional sodium sulfate may need to be added to get this consistency. Proceed with the ultrasonic extraction (AP E-3550).

WARNING: Inhalation of sodium sulfate dust may cause mild irritation to the respiratory tract.
Eye contact may cause mild irritation and redness, or mechanical irritation.
Skin contact may cause mild irritation.

9.2 Clean up/Fractionation

9.2.1 If a sample is of biological origin, an oil, a soil/sediment sample, or contains high molecular weight materials, the use of sulfuric acid clean-up (AP E-3665) followed by Florisil cartridge clean up (AP E-3620) is employed.

9.2.2 If both PCBs and pesticides are to be measured in the sample, the sample is split prior to pesticide analysis. The PCB fraction sulfuric acid clean up will destroy some of the Organochlorine Pesticides.

9.2.3 Clean up by AP E-3620 unless the samples are known, or suspected to be, sampled from transformers.

9.2.4 Elemental sulfur, which may appear in sediments and industrial wastes, interferes with the electron capture gas chromatography of the Aroclors. Sulfur should be removed by the technique described in AP E-3660, Sulfur Clean up, using mercury.

9.3 Gas chromatography conditions (recommended):

Wide-bore columns:

Carrier gas (He) = 18 mL/min
Makeup gas (argon / 5 % methane) = 100 -150 mL/min
Injector temperature = 200 °C
Detector temperature = 300 °C
Initial temperature = 110 °C, hold 2.0 minute
Temperature program 1= 110 °C to 200°C at 4 °C/min
Temperature program 2= 200 °C to 270°C at 8 °C/min
Final temperature = 270 °C, hold 4.75 min.

9.4 Calibration:

9.4.1 Refer to AP E-8000 for proper calibration techniques. Table 2 is used for the lowest point on the calibration curve. If the laboratory is requested to use MDL, then Table 1 is used for the lowest point on the calibration curve.

9.4.2 The procedure for internal calibration is used unless there is interference from the sample. Refer to AP E-8000 for a description for this procedure.

9.4.3 The initial calibration consists of two parts:

a. A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. This five-level calibration curve of Aroclor 1016/1260 demonstrates the linearity of the detector and that the sample does not contain peaks that represent any one of the Aroclors.

b. Standards of the other five Aroclors are necessary for pattern recognition. These standards are also used to determine a single-point calibration factor for each Aroclor (assuming that the Aroclor 1016/1260 is linear).

9.5 Gas chromatographic analysis:

9.5.1 Refer to AP E-8000. Add 10.0 μL of internal standard (i.e. injection standard) to the sample extract prior to injection.

9.5.2 Follow AP E-8000 for instruction on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Analysis of a mid-concentration standard after each group of 10 samples is recommended (20 samples maximum if the samples are not regulatory samples).

9.5.3 Examples of GC/ECD chromatograms generated by instruments with wide-bore columns are presented in Figures 1 through 6.

9.5.4 The sample volume injected and the resulting peak sizes (in peak heights) are recorded via the chemstation software and transferred to the chemserver for processing via target software.

9.5.5 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted by the context in which the result is to be used.

9.5.6 If the peak response exceeds the working range of the system, dilute the extract and re-analyze.

9.5.7 Identification of mixtures is based on the characteristic "fingerprint" retention time and shape of the indicator peak(s). Quantitation is based on the height of the characteristic peaks as compared to the height of the corresponding calibration peak(s) of the same retention time and shape.

9.5.8 At least three peaks, preferably five, are used to quantitate the Aroclors. The peaks must be characteristic of the Aroclor in question. The peaks chosen are at least 25 % of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor (Aroclor 1232, 1242, and 1016 are so similar, this is not possible). For Aroclor 1016/1260 mixture, since there is no overlap of the patterns, five peaks from each pattern are used for quantitation.

9.5.9 Late-eluting peaks are generally the most stable in the environment, therefore when it is possible, later eluting peaks in the chromatogram are selected for quantitation, pattern recognition purposes.
In the case of oil samples, the later peaks may exhibit dampening of the response (probably from the background hydrocarbon interference with the ECD).

9.5.10 Identify compounds in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The retention time window used to make identifications is based upon measurements from multi-lab analysis (supplied by the EPA). Because of the stability of megabore columns, the window will never be greater than 0.07 min.

9.5.11 If compound identification or quantitation are precluded due to interference (e.g., broad, rounded peaks or ill-defined baseline are present) clean up or dilution of the extract is warranted. Running of instrument blanks followed by midpoint calibration checks are used to determine if the instruments integrity has been affected by the sample is necessary before further sample analysis can be continued. Refer to AM P-3600 for the procedures to be followed in sample clean up. If a sample is suspected of being high concentration or high background, multiple instrument blanks are added after the sample. These instrument blanks serve to demonstrate that there is no carryover into the next analyzed sample.

9.5.12 Each sample analysis must be bracketed by an acceptable initial or continuing calibration. When the acceptable criteria are not met, all samples must be re-analyzed under valid criteria with the following exception. If the standard analyzed after a bracketed set of samples exhibits a response for an analyte that is above the acceptance limit (i.e.; >15 %) and the analyte was not detected in the bracketed samples; then those samples do not need to be re-analyzed.

a. Verify calibration during each 12-hr shift of injection of an instrument blank followed by mid-concentration calibration of the Aroclor 1016/1260 mixture. This continuing calibration standard must also be injected after each group of 10 samples (20 samples maximum if the samples are not regulatory samples) in the analysis sequence as a calibration check. The response factors for the mid-concentration calibration should be within 15 % of the average values for the multi-concentration calibration.

$$\%\,\text{Difference} = \frac{\text{average response factor - response factor of CC}}{\text{average response factor}} \times 100$$

b. When this continuing calibration is out of this acceptance window (except if the samples preceding the continuing do not contain the target analytes and the response of the analytes in the continuing give a higher response than the standards), the laboratory should stop analyses, clean the injector and replace the septum. An instrument blank and the continuing calibration standard are analyzed again to determine if the system needs to be re-calibrated. Analysis may be continued if the response factor is within the 15 % value. Otherwise, the system must be recalibrated.

c. Use the continuing calibration standard to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. If the problem cannot be corrected (i.e., changing the septum or changing the gas does not correct the problem), the initial calibration must be rerun and all samples run previous to the bad continuing calibration must be rerun.

d. Internal standards must be evaluated for acceptance. The measured height of the internal standard must be no more than 20 % different from the height of the mid-calibration standard. When the internal standard peak height is outside the limit, the problem must be corrected before and further analysis is done. Samples that fall outside the QC criteria must be re-analyzed.

e. If compound identification or quantitation is precluded due to interference (i.e., broad, rounded peaks or ill-defined baselines are present), clean up of the extract or replacement of the capillary column or cleaning of the detector is warranted.

9.6 Qualitative analysis:

The qualitative analysis of PCB residues as Aroclors is accomplished be comparison of the sample chromatogram to that of the most similar Aroclor standard by pattern recognition. Overlaying the sample chromatogram on the standards is the most visually rewarding in choosing which Aroclor is most similar to that of the sample.

Tentative identification of an Aroclor must be confirmed using the second column.

9.7 Quantitation:

9.7.1 Five sets of response factors will be generated for Aroclor 1016/1260 mixture, each set consisting of the response factors from each of the five peaks chosen for this mixture. The single standards for each of the other Aroclors will generate at least three response factors, one for each peak.

9.7.2 The response factors from the initial calibration are used to evaluate the linearity of the initial calibration. This involves the calculation of the mean response, the standard deviation and the relative standard deviation (RSD) for each Aroclor peak. The calibration model chosen for the Aroclor 1016/1260 mixture must be applied to the other five Aroclors.

9.7.3 Due to the single injection, dual-column analysis scheme, it is not practical to designate one column as the primary, the other as a confirmation column. Since the calibration standards are analyzed on both columns, the results from both columns must meet the calibration acceptance criteria. If the retention times of the peaks on both columns fall within the retention time windows on the respective columns, then the target analyte identification has been confirmed.

9.7.4 The amount of the identified Aroclor is calculated from the individual response factors for each of the 3 to 5 characteristic peaks and the calibration model (linear or non-linear) established from the multi-point calibration peaks of the 1016/1260 mixture. A concentration is determined using each of the characteristic peaks and then those 3 to 5 concentrations are averaged to determine the concentration of the Aroclor.

9.7.5 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. If the purpose of the analysis is not regulatory compliance monitoring on the basis of Aroclor concentration, then it may be more appropriate to perform the analysis using the PCB congener approach (Weyerhaeuser is not equipped to do PCB congener analysis at this time and therefore has not been outlined in this method). If results in terms of Aroclors are required, then the quantitation as Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area. When quantitation is performed in this manner, the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

9.8 GC/MS confirmation: Any compounds confirmed by two columns should also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory generated detection limits.

9.8.1 The GC/MS would normally require a minimum concentration of 10 ng/μL in the final extract for each PCB congener. GC/MS confirmation may not be used when the concentrations are below 1 ng/μL

9.8.2 The pesticide extract and associated blank should be analyzed by GC/MS as AP E-8270.

9.8.3 The confirmation may be from the GC/MS analysis of the base/neutral-acid extracts (sample and blank) if the surrogates and the internal standards do not interfere and it is demonstrated that the target analytes are stable during acid/base partitioning. However, if the compounds are not detected in the base/neutral-acid extract even though the concentrations are high enough, a GC/MS analysis of the pesticide extract should be performed.

9.8.4 A QC reference sample of the compound must also be analyzed by GC/MS. The concentration of the QC reference standard must demonstrate the ability to confirm the pesticides identified by GC/ECD.

10.0 QUALITY CONTROL

10.1 Quality control to validate sample extraction is covered in AP E-3500 and in the extraction method utilized. If extract clean-up is performed, follow the QC in AP E-3600 and in the specific clean-up method.

10.2 Initial Demonstration of Proficiency - Mandatory quality control to evaluate the analyst and GC system operation is found in AP E-8000.

10.2.1 The quality control reference sample concentrate (AP E-8000) should contain the Aroclor 1016/1260 mix at 1 mg/L. A 1-mL volume of this concentrate spiked into 1 L of organic-free water will result in a sample concentration of 1 μg/L.

10.2.2 Instrument QC during analysis is documented above in Section 9.5.12.

10.2.3 Table 3 indicates the EPA's calibration and QC acceptance criteria for this method. Table 4 gives the EPA's method accuracy and precision as functions of concentration for the analytes of interest. The contents of the Tables are used to evaluate the laboratory's ability to perform and generate acceptable data by this method. Each analyst must demonstrate initial proficiency by generating data of acceptable accuracy and precision for target analysis in a clean matrix. New staff and significant changes in instrumentation must also repeat this initial proficiency demonstration.

10.3 Sample Quality Control for Preparation and Analysis – The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, a matrix spike, a duplicate, a laboratory control sample (LCS), and the addition of surrogates to each field sample and QC sample.

10.3.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pairs, spiked with Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for spiking.

10.3.2 Due to the infrequent analysis of Aroclors, in-house method performance criteria have been set to 60 to 120 for % recovery. Should Weyerhaeuser do a frequent analysis, the guidance found in Sec 8.0 of Method 8000 will be used to evaluate method performance and establish performance criteria.

10.3.3 Laboratory Control Sample (LCS) is included with each analytical batch. The LCS is a spiked clean sample (Millipore water for water extractions, pre-muffled sodium sulfate for soil/sediment extractions) with the target analytes of interest. This spike is the same as the Matrix spike. When the results of the matrix spike indicates a problem due to the sample matrix, the LCS results are used to validate the extraction method for that batch.

10.3.4 All samples and QC are spiked with surrogates. Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in AP E-8000). If recovery is not within limits, the following are required:

a. Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

b. Recalculate the data and/or re-analyze the extract if any of the above checks reveal a problem.

c. Re-extract and re-analyze the sample if none of the above are a problem or flag the data as "estimated concentration."

10.3.5 Whenever silica gel (3630) or Florisil (3620) clean-ups are used, the analyst must demonstrate that the fractionation scheme is reproducible. The LCS spike is used to characterize each batch. Recoveries must be in the range of 80 % - 120 %.

11.0 REPORT

11.1 Report all concentrations above the quantitation limits to 2 significant figures. Report values below the quantitation limit to 1 significant figure.

11.2 PRECISION AND ACCURACY

The accuracy and precision obtainable following this method will be determined by the sample matrix, sample preparation technique, optional clean-up techniques, and calibration procedures used. The supplied accuracy and precision for water analysis from the EPA are listed in Table 4. Table 5 shows Weyerhaeuser data for four matrix spikes for single component pesticides and four blank matrix spikes for each of the analyzed multi-component pesticides.

11.3 The MDL concentrations listed in Table 1 was obtained using organic-free reagent water and sandy loam soil. The MDL actually achievable in a given analysis will vary depending on detector response characteristics, irreducible noise from instrument electronics, and matrix effects.

12.0 KEY WORDS

AM E-8082, Aroclor, ECD, electron capture, EPA, Kuderna-dansih, KD, K-D, organochlorine, PCB, polychlorinated biphenyls

13.0 REFERENCES

13.1 U.S. Environmental Protection Agency, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846," 2nd Edition, June 11, 1991.

13.2 Organics Analysis - Multi-Media, Multi-Concentration, Document OLM 1.6, June 1991.

TABLE 1
Weyerhaeuser's Annual Established Method Detection Limit (MDL)
(1 mL final volume)

	µ/L	
ANALYTE	2/95 WATER DB1701	2/95 WATER DB608
Aroclor 1016	ND	ND
Aroclor 1221	ND	ND
Aroclor 1232	ND	ND
Aroclor 1242	0.016	0.012
Aroclor 1248	ND	ND
Aroclor 1254	ND	ND
Aroclor 1260	ND	ND

ND = not determined

TABLE 2
Low Concentration of the Individual Component Mixes

SEPARATE MULT- COMPONENT ANALYTES	µg/mL
Aroclor 1016/1260 Level 1	0.020
Aroclor 1016/1260 Level 2	0.040
Aroclor 1016/1260 Level 3	0.100
Aroclor 1016/1260 Level 4	0.200
Aroclor 1016/1260 Level 5	0.400
Aroclor 1221	0.200
Aroclor 1232	0.100
Aroclor 1242	0.100
Aroclor 1254	0.100

TABLE 3
EPA QC ACCEPTANCE CRITERIA FOR WATER ANALYSIS

Analyte	Test Conc. (µg/L)	limit for s (µg/L)	Range P,Ps (%)	Range of x (µg/L)
Aroclor 1016	50.0	10.0	50 - 114	30.5 - 51.5
Aroclor 1221	50.0	24.4	15 - 178	22.1 - 75.2
Aroclor 1232	50.0	17.9	10 - 215	14.0 - 98.5
Aroclor 1242	50.0	12.2	39 - 150	24.8 - 69.6
Aroclor 1248	50.0	15.9	38 - 158	29.0 - 70.2
Aroclor 1254	50.0	13.8	29 - 131	22.2 - 57.9
Aroclor 1260	50.0	10.4	8 - 127	18.7 - 54.9

s= Standard Deviation of four recovery measurements, in µg/L.
x = Average recovery for four recovery measurements, in µg/L
P, Ps = Percent recovery measured
D = Detected; result must be greater than zero.

Criteria from 40 CFR Part 136 for Method 608. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4
EPA METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATIONS

Analyte	Accuracy, as recovery, x' (µg/L)	Single Analyst precision, s' (µg/L)	Overall precision, S' (µg/L)
Aroclor 1016	0.81C+0.50	0.13x+0.15	0.15x+0.45
Aroclor 1221	0.96C+0.65	0.29x-0.76	0.35x-0.62
Aroclor 1232	0.91C+10.79	0.21x-1.93	0.31x+3.50
Aroclor 1242	0.91C+10.79	0.21x-1.93	0.31x+3.50
Aroclor 1248	0.91C+10.79	0.21x-1.93	0.31x+3.50
Aroclor 1254	0.91C+10.79	0.21x-1.93	0.31x+3.50
Aroclor 1260	0.91C+10.79	0.21x-1.93	0.31x+3.50

x' = Expected recovery for one or more measurements of a sample containing concentration C, in µg/L.
s' = Expected single analyst standard deviation of measurements at an average concentration of x, in µg/L.
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of x, in µg/L.
C = True value for the concentration in µg/L.
x = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

TABLE 5

WEYERHAEUSER DATA FOR PERFORMANCE EVALUATION OF 1 Liter of Water 4/95

Analyte	Amount spike µg/L	standard deviation µg/L on DB1701	standard deviation µg/L on DB608	% recovery DB1701	% recovery DB608
PCB-1016	NA	NA	NA	NA	NA
PCB-1221	NA	NA	NA	NA	NA
PCB-1232	NA	NA	NA	NA	NA
PCB-1242	5.0	0.11	0.036	90%	83%
PCB-1248	NA	NA	NA	NA	NA
PCB-1254	NA	NA	NA	NA	NA
PCB-1260	5.0	0.024	0.017	91%	90%

Data based on two sets of four extirpations on millipore water
NA = not analyzed

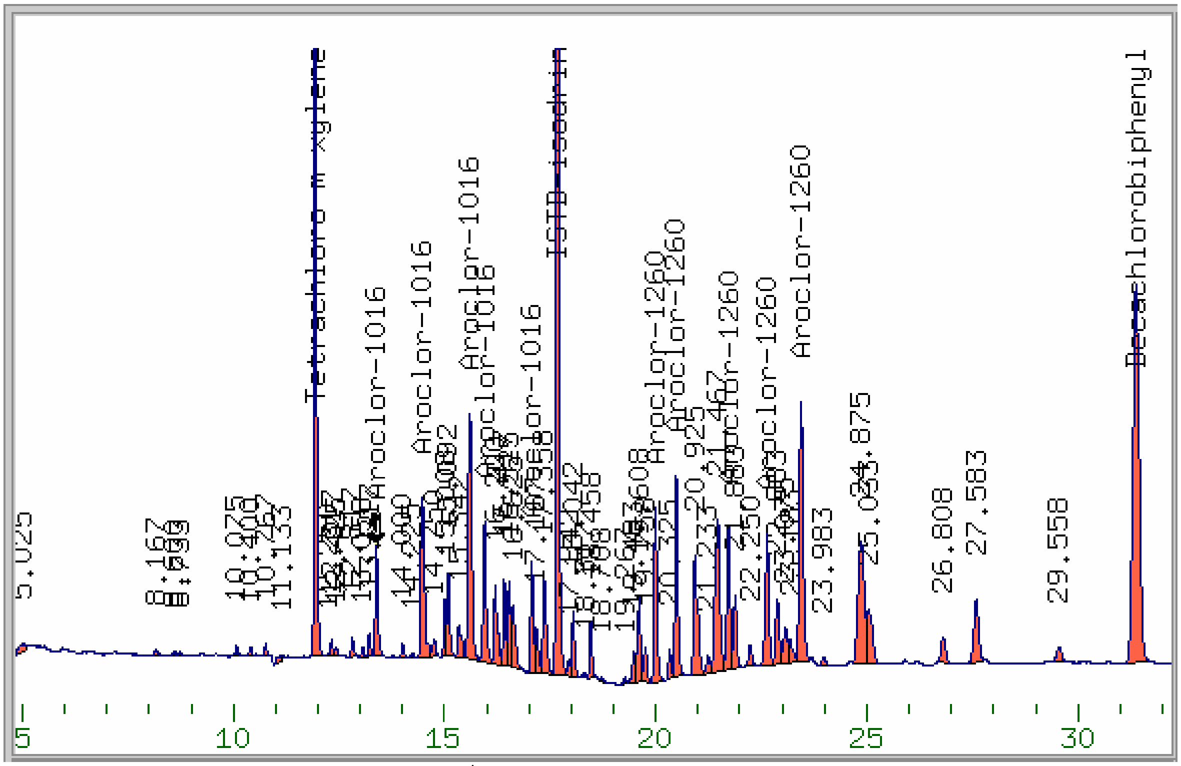

Figure 1: Aroclors 1016 and 1260 ↑

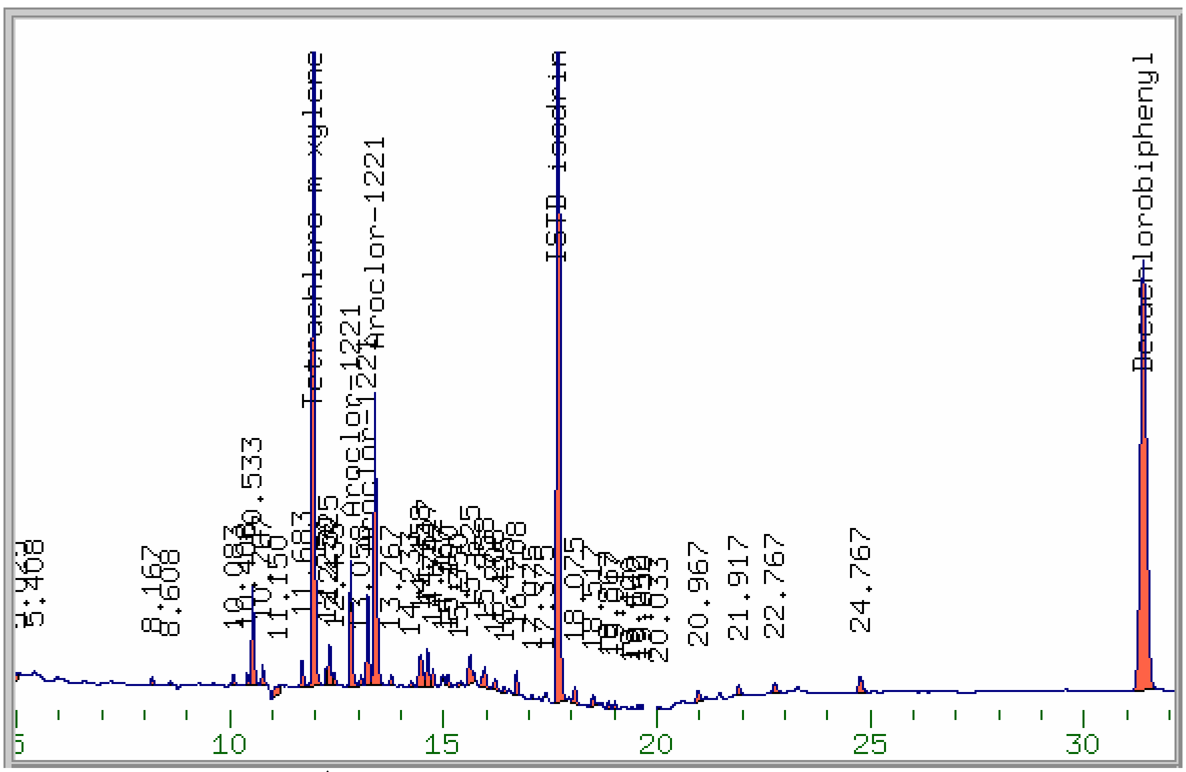

Figure 2: Aroclor 1221 ↑

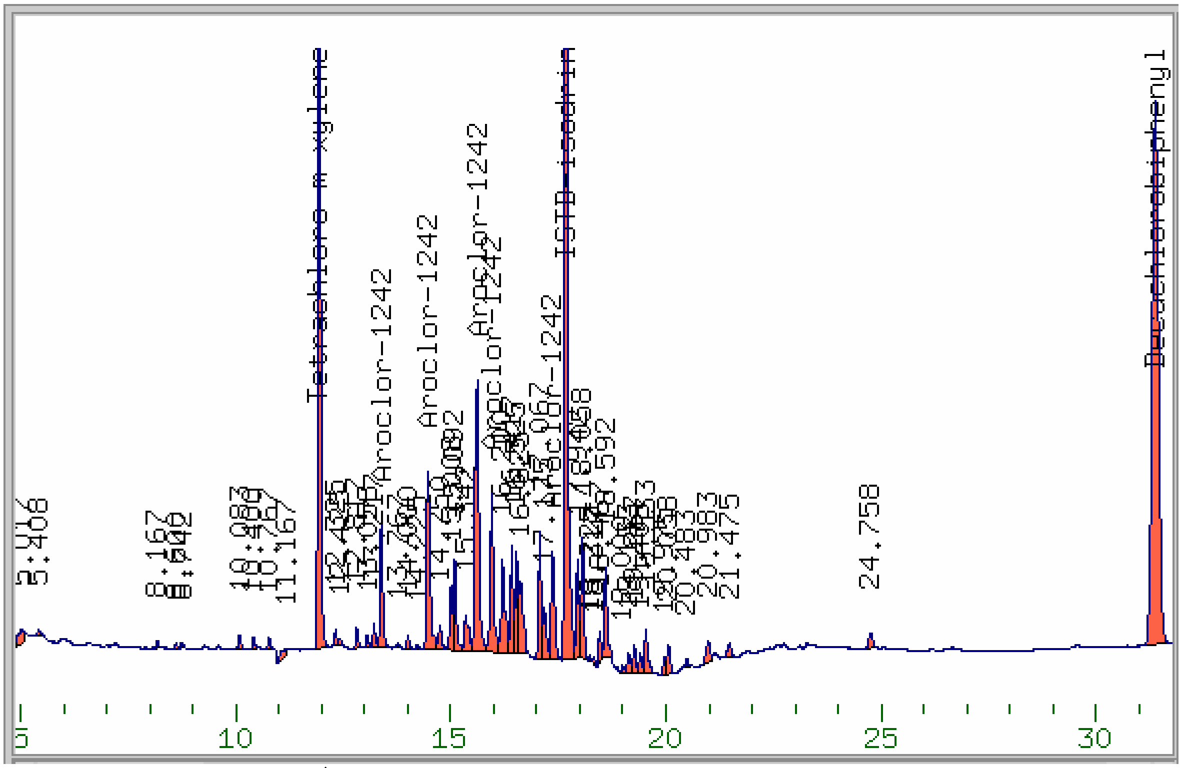

Figure 3: Aroclor 1232 ↑

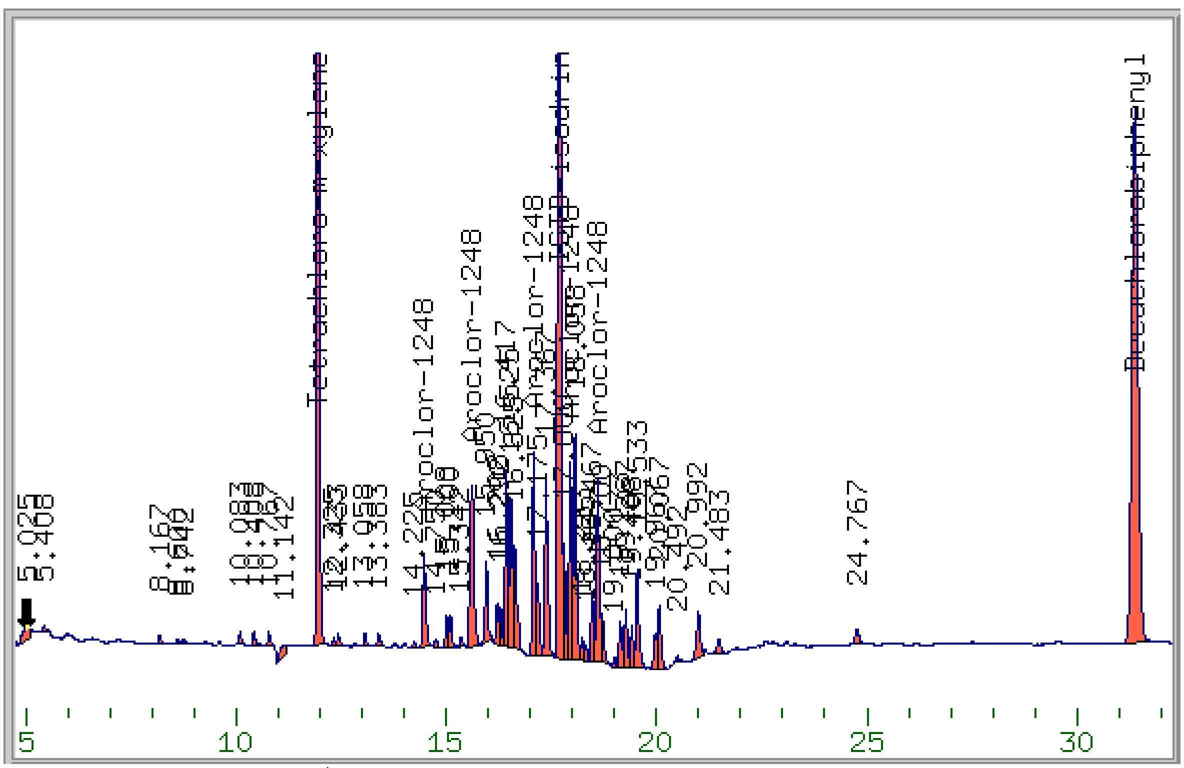

Figure 4: Aroclor 1242 ↑

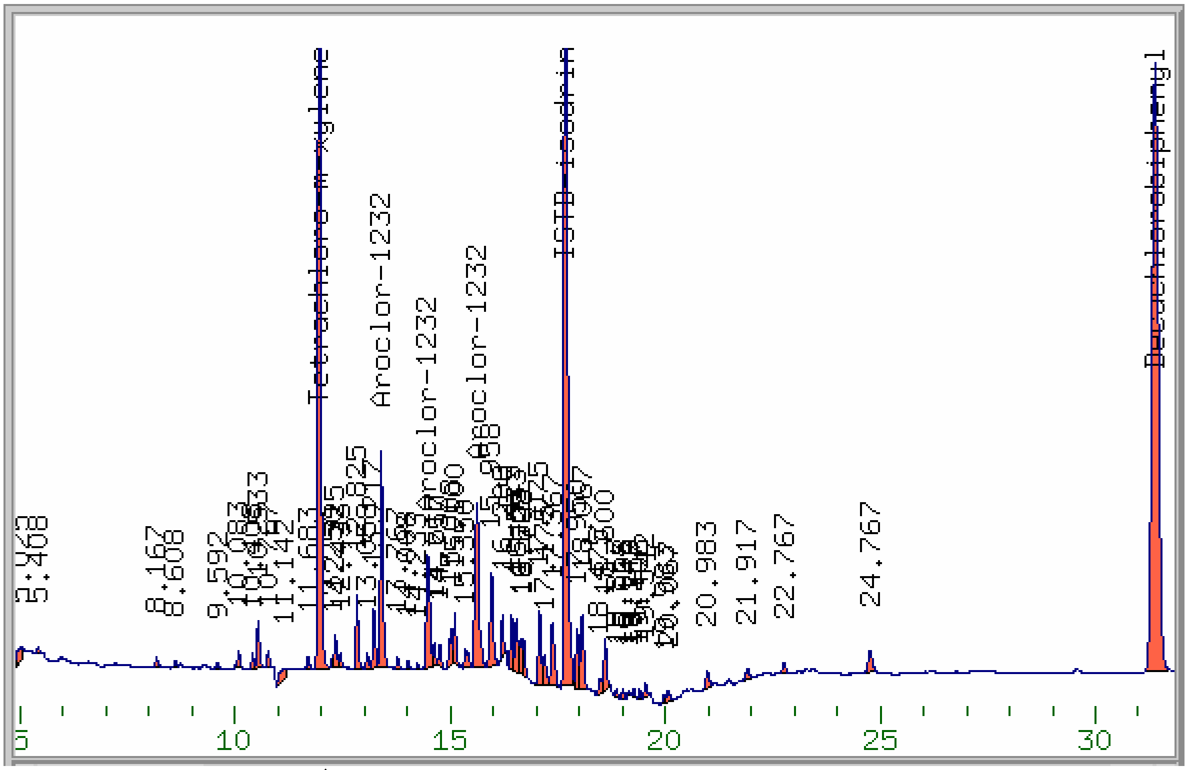

Figure 5: Aroclor 1248 ↑

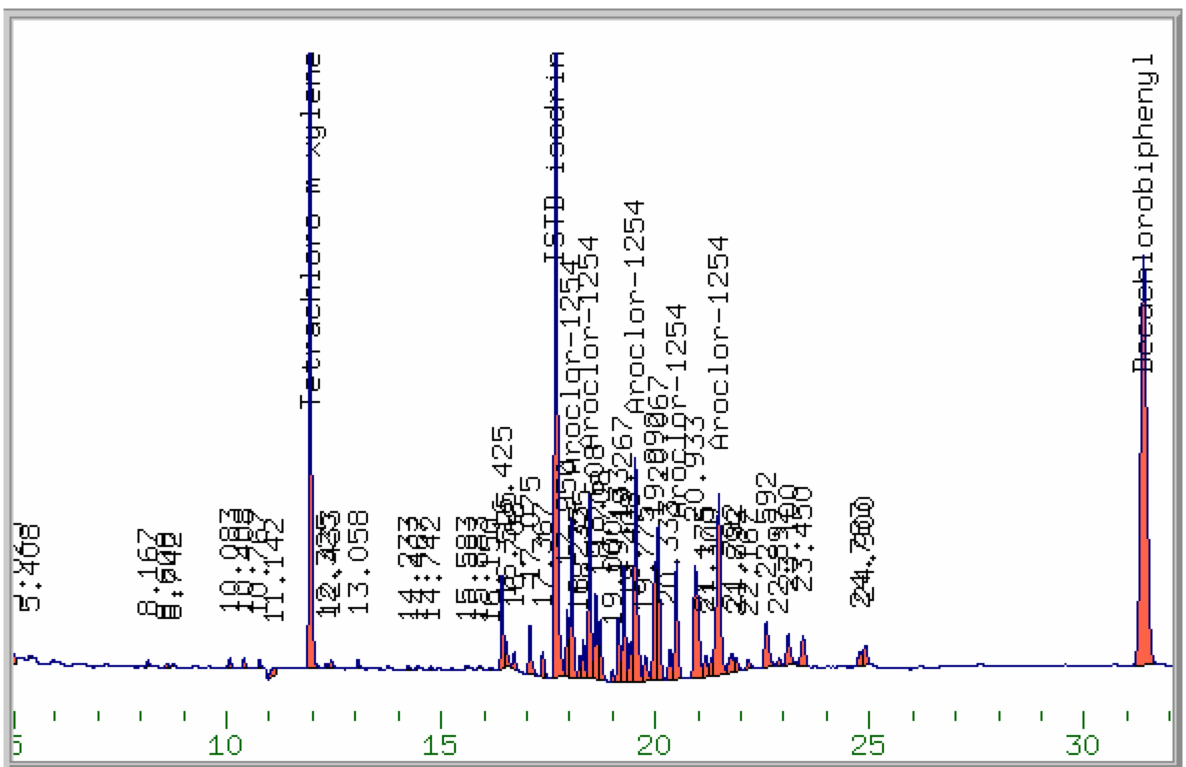

Figure 6: Aroclor 1254 ↑

1.0 SCOPE

1.1 This Standard Operating Procedure (SOP) contains the guidelines and protocols concerning daily balance, water, and temperature checks.

2.0 SUMMARY OF SOP

For each analytical laboratory, all balance, temperature, and water quality checks will be recorded daily in designated binders. The forms used for these records are controlled documents available on the Panagon document server through the A&T website. The forms and template files under Lab-general includes the Daily Check Log.

3.0 PROCEDURE

3.1 All balances in the laboratory will be checked daily with a standard mass (weight) and the results recorded on quarterly log sheets called Daily Check Log.

3.1.1 The weights used daily are Class S. These daily masses are verified annually against a certified set of Class S weight masses by the process owner or designee.

3.1.2 The weight used for the day is selected from the available weights and appropriate for the balance being checked.

3.1.3 The mass of the weight must be within the parameter listed for the mass of the balance being checked unless specifically stated otherwise in the appropriate method. (See Table I in attached appendix).

3.1.4 Any balance failing criteria will be flagged as not useable and appropriate laboratory personnel notified. This shall be noted on the Daily Check Log in the appropriate column for that month. It is the lab personnel's responsibility to check and verify a problem and obtain repair if necessary.

3.1.5 If the notified laboratory personnel do not respond with follow up action, a corrective action form shall be filled out and turned in to the QA advisor.

3.1.6 If several balances show a problem with a given weight, the supervisor will be contacted and the weight set will be recalibrated.

3.1.7 Once per quarter, each laboratory is required to do a Linearity Check on each balance using three different weights. These checks are noted on the bottom of each Daily Check Log. At the end of the quarter the Daily Check Log sheets are given to the process owner/designee. The process owner/designee will ensure accuracy, witness, sign and date the documents. The process owner will file away the log sheets in a three ring binder for that year.

3.2 The temperatures of all refrigerators, incubators, freezers, and ovens will be recorded on quarterly log sheets called Daily Check Log.

3.2.1 A calibrated thermometer will be kept within each refrigerator, incubation, freezer and oven used for storage of samples, extractions, and standards. Replacement thermometers will be obtained at the end of each calendar year from an ISO-approved vendor.

3.2.2 The true temperature must be within the tolerance listed in Table I in the attached appendix.

3.2.3 Any temperature controlled device (in See 3.2.1) failing criteria will be flagged as not useable and appropriate laboratory personnel notified. This notification shall be noted on the Daily Check Log in the appropriate column for that month. It is the laboratory personnel's responsibility to check and verify a problem and obtain repair if necessary.

a. Immediately notify appropriate laboratory personnel, Sample Management personnel and the Technical Specialist of any temperature-controlled unit outside of its criteria.

b. If the notified laboratory personnel does not respond with follow up action, a corrective action form shall be filled out and turned in to the QA advisor.

3.2.4 At the end of the quarter, the Daily Check Log sheets are given to the process owner/designee. The process owner/designee will witness, sign and date the documents to assure accuracy. The process owner will file away the log sheets in a three ring binder for that year.

3.3 The resistance of the Millipore Water Filtration systems will be checked and recorded on quarterly log sheets called Daily Check Log.

3.3.1 Water will run through the system for a minimum of 30 seconds before the resistance will be read on the built-in ohm meter.

3.3.2 The resistance shall exceed the control limit listed in Table I in the attached appendix.

3.3.3. Any system failing its criteria will be flagged as not useable and the appropriate laboratory personnel notified. This notification shall be noted on the daily check log sheet in the appropriate column for that month. It is the laboratory personnel's responsibility to maintain their system, check and verify a problem, and obtain repair if necessary.

3.3.4 If the notified laboratory personnel do not respond with follow up action, a corrective action form shall be filled out and turned in to the QA advisor.

3.3.5 At the end of the quarter, Daily Check Log sheets are given to the process owner/designee. The process owner/designee will witness, sign and date the documents to assure accuracy. The process owner will file away the log sheets in a three ring binder for that year.

3.4 The conductance of the distilled water system will be checked and recorded on the quarterly log sheets called Daily Check Log.

3.4.1 The conductance of freshly collected distilled water from the siphon tube will be read on the low level conductivity meter.

3.4.2 The conductance shall not exceed the control limit listed in Table I in the attached appendix.

3.4.3 Any system failing its criteria will be flagged as not useable and the appropriate laboratory personnel notified. This notification shall be noted on the Daily Check Log sheet in the appropriate column for that month. It is the laboratory personnel's responsibility to repair and maintain their system.

3.4.4 If the notified laboratory personnel do not respond with follow up action, a corrective action form shall be filled out by the above and turned in to the QA advisor.

3.4.5 At the end of the quarter, the Daily Check Log sheets are given to the process owner/designee. The process owner will file away the log sheets in a three ring binder for the year.

3.5 The Table in the attached appendix is reviewed annually and updated as necessary to account for changes in calibrations, requirements, etc. All updates are to be kept within this method file.

4.0 KEYWORDS

refrigerator, incubator, freezer, oven, balance, thermometer, Millipore, filtration, distilled water

5.0 REVISION HISTORY

5.1 2/21/07 – Updated section 3.1.1, 5, 7; 3.2.1, 4; 3.3.4; and 3.4.4.

Appendix
Table 1

Warning Limits for Class S Weight Balance Checks

Balance Range	0.1 g	0.5 g	1 g	2 g	5 g	10 g	20 g	50 g	100 g
1			1	2	5	10	20	50	100
			± 0	± 0	± 0	± 0	± 0	± 0	± 0
0.1		0.5	1.0	2.0	5.0	10.0	20.0	50.0	100.0
		± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.1	± 0.1	± 0.1
0.01	0.10	0.50	1.00	2.00	5.00	10.00	20.00	50.00	100.00
	± 0.00	± 0.00	± 0.00	± 0.00	± 0.00	± 0.01	± 0.01	± 0.01	± 0.01
0.001	0.099	0.500	1.000	2.000	5.000	10.000	20.000	50.000	99.999
	± 0.000	± 0.000	± 0.000	± 0.000	± 0.001	± 0.001	± 0.001	± 0.001	± 0.001
0.0001	0.0993	0.5000	1.0000	2.0000	5.0000	9.9998	19.9999	49.9997	99.9992
	± 0.0001	± 0.0001	± 0.0001	± 0.0001	± 0.0001	± 0.0001	± 0.0001	± 0.0002	± 0.0003
0.00001	99.31	499.97	1000.00	1999.98	4999.97	9999.84	19999.86	49999.68	99999.16
	± 0.03	± 0.03	± 0.03	± 0.06	± 0.06	± 0.08	± 0.08	± 0.12	± 0.25
0.000001	99.310	499.972	1000.000			9999.840			
	± 0.025	± 0.025	± 0.025			± 0.074			

	0.1 g	0.5 g	1 g	2 g	5 g	10 g	20 g	50 g	100 g
Troemner	-0.010	0.018	0.01	0.01	0.00	0.00	0.04	0.02	0.14
Fisher	0.7	0.01	-0.01	0.01	0.03	0.16	0.1	0.3	0.7

If balance check is out of range -
1 Clean, rezero and recheck weight
2 If still out of range -
Flag balance, flag data, notify that laboratory's personnel

The weights for ranges 0.00001 and 0.000001 are in mg.

Note:

Any 4-place or smaller balance used without a pedestal must meet limits for balance with 1 fewer place.

Control Limits for Sample and Standard Refrigerators

4 ± 2 Degrees C

Control Limits for BOD Incubators

20 ± 1 Degrees C

Control Limit for Freezers

< -15 Degrees C

If out of range, immediately notify Laboratory and Sample Recieving Personnel

Control Limits for Millipore Water Systems

Metals Lab	> 12 megaohm
Organics Lab	> 10 megaohm

Control Limits for Distilled Water System

Conventional Lab	< 1 microSeimens/cm

If out of range, flag outlet valve and immediately notify that Laboratory's personnel

Laboratory	Refrigerat	Freezers	Ovens	Incubators
212 S	R10		Precision	Freas 815 Hot Pack
212 N	R		Precision	
203 S	R		Oven	
225 S			Oven #1 Oven #2 Oven #3 Oven #4 Oven #5 Oven #6 Oven #7	
227 S	R 1 R 2	F 1		
211 S	R R R R R R	 F		
233 S	R R	F F		
Cold Room	R			

General Procedures for Performing Chromatographic Separations and Calibrations	
Process Owner (TS/PM/OM/LM) Randy Eatherton	Not valid without colored "Controlled" stamp (unless printing date appears) Expires August 31, 2010
Assignment	Reviewed by Christine Devine July 8, 2003 Reviewed by Christine Devine September 11, 2007
Electronic only unless colored "Controlled" stamp is present	

1.0 SCOPE AND APPLICATION

1.1 This procedure is not determinative, but instead provides guidance on analytical chromatography, describing resolution, calibration, and quality control requirements that are common to all SW-846 chromatographic procedures. AI G-8000 is to be applied in conjunction with the determinative chromatographic procedures.

1.2 Gas chromatography (GC) is a quantitative analytical technique useful for organic compounds capable of being volatilized without being decomposed or chemically re-arranged.

1.3 This procedure follows EPA method 8000B.

2.0 SUMMARY OF PROCEDURE

Each SW-846 organic analytical method provides a recommended technique for extraction, cleanup, and occasionally, derivatization of the samples to be analyzed. Before the prepared sample is introduced into the GC, a procedure for standardization must be followed to determine the recovery and the limits of detection for the analytes of interest. Following sample introduction into the GC, analysis proceeds with a comparison of sample values with standard values. Quantitative analysis is achieved through integration of peak area (for GC/MS) or measurement of peak height (for GC).

3.0 INTERFERENCES/CHROMATOGRAPHIC PERFORMANCE

3.1 Contamination by carry-over can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carry-over, the sample syringe or purging device must be rinsed out between samples with water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or of water to check for cross-contamination. For volatile samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide concentrations, it may be necessary to wash out the syringe, or purging device, with a detergent solution; rinse it with water; and then dry it in a 105 $\pm$ 5 °C oven between analyses.

3.2 In addition to carry-over of compounds from one sample to the next, the analysis of high concentration samples can lead to the contamination of the analytical instrument. This is particularly true to GC/MS and to GC/ECD. Eliminating this contamination can require significant time and effort in cleaning the instruments. This can be overcome by prescreening samples that are suspected or known to have high levels of organics.

3.3 One of the most important measures of chromatographic performance is resolution, the separation of chromatographic peaks. Baseline resolution of each target analyte from co-extracted materials is the goal of analytical chromatography. The ability of resolving individual compounds is generally the limiting factor for the number of analytes that can be measured using a single procedure. Methods utilizing mass spectrometry for detection are affected less by resolution problems because overlapping peaks may still be mass-resolved.

3.4 Elevated chromatographic baselines should be minimized or eliminated during these analyses. Baseline humps can be reduced or eliminated by appropriate sample clean-up, extraction, dilution or instrument maintenance.

3.5 Poor GC performance may be expected whenever a chromatographic system is contaminated with high boiling materials. Analysis should perform routine maintenance including replacement of septa, cleaning and/or replacing the injector liners, and removing a section of the column (or retention gap if used) at the inlet end.

Capillary columns are reliable and fairly rugged, but several rules-of-thumb are required to insure column life:

3.5.1 Columns should not have contact with the oven walls (this can cause hot spots) and can weaken the column coating due to friction.

3.5.2 Oxygen kills columns. Cool the oven before changing septa, doing maintenance of the injection port or changing of columns. Flush the system with carrier gas at least 15 min before increasing the oven temperature. Inspect the injector with a leak-detector-wand and keep track of carrier gas usage. High usage indicates a leak in the system.

3.5.3 The use of guard columns (retention gaps) can increase column life by minimizing the loss of resolution when cutting off the inlet side of the column.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. All systems are equipped with data systems.

This lab has the following GC systems for which this procedure may apply:

- 3 GC/MS systems for volatiles
- 2 GC/MS systems for semivolatiles (BNA's) and Resin Acids
- 1 GC/FID/NPD system with pyrolysis unit for fingerprinting.
- 1 GC/MS system for Dioxin
- 3 GC/ECD dual column/dual detector systems for pesticides, herbicides, chlorophenolics, chlorinated hydrocarbons
- 1 GC/FID system for TPH-D and 604/608 with dual detectors/dual columns
- 1 GC/FID system for Methanol 94.03 and 99.01
- 1 GC/FID/FPD/Purge& Trap system for TPH-G, Methanol, Sulfur and Organophospate compounds
- 2 GC/FID/FPD systems for Sulfur, Organophospate compounds and Methanol
- 1 GC/TCD detector for Gas compounds
- 1 NPD detector for Organonitrogen compounds

4.2 Gas chromatographic columns - See the specific determinative method. All analyses are done with either capillary or megabore columns.

4.2.1 Narrower columns have better resolution but lower capacity and increased retention times.

4.2.2 Longer columns can resolve more analytes, where resolution increases as a function of the square root of column length.

4.2.3 Increasing the film thickness increases column capacity, but also increases retention times.

4.2.4 The data system consists of each instrument being connected directly to a dedicated computer for data acquisition. For the GC/MS systems, the computer also controls the auto samplers. These computers are networked to a central UNIX system via LAN. Data reduction, reporting, and archiving are accomplished with TARGET and ENVISION software.

5.0 PROCEDURE

5.1 Extraction - Adhere to those procedures specified in the referring determinative method. General guidance on semivolatile extraction can be found in AC G-3500.

5.2 Clean up and separation - Adhere to those procedures specified in the referring determinative method. General guidance on cleanup procedures can be found in AC G-3600.

5.3 The recommended gas chromatographic columns and operating conditions for the instrument are specified in the referring determinative method.

5.4 Calibration - Establish gas chromatographic operating parameters equivalent to those indicated in the determinative method of interest. Prepare calibration standards using the procedures indicated in the determinative method of interest. Calibrate the chromatographic system using either the external standard technique or the internal standard technique.

5.4.1 External standard calibration procedure

a. For each analyte of interest, prepare calibration standards at a minimum of five concentrations by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with an appropriate solvent. The lowest of the external standards should be the method quantitation limit (based on a concentration with no dilution). The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. At least one of the calibration concentrations should correspond to a sample concentration at or below any regulatory or action limits associated with a target compound.

b. Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g., 1 - 5 µL on column, 5 mL with purge-and-trap). Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each analyte. Alternatively, for samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the Calibration Factor (CF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (% RSD) of the calibration factor is less than 20 % (this may vary according to different methods) over the working range, linearity through the origin can be assumed. In such cases, the average calibration factor can be used in place of a calibration curve.

$$\text{Calibration factor} = \frac{A_x}{C_f V_i}$$

where:

Ax	=	response for the analyte, units may be in area counts (for GC/MS) or peak height (for GC)
Cf	=	Concentration of analyte, unit is ng/µL

Vi = Volume of extract injected, µL. For purge-and-trap analysis, Vi is not applicable and therefore = 1.

NOTE: For multi-response pesticides/PCBs, at least three of the major peaks are calculated against a separate response factor for each of those peaks. The average of these calculated amounts are then used for quantitation, i.e., concentration = (average)(concentration of major peaks).

c. The working calibration curve or calibration factor must be verified on each working day of analysis by the injection of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary - every 12 hr of analysis or every 10 samples, depending on the method. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than ± 15 %, a new calibration curve must be prepared for that analyte.

$$\text{Percent Difference} = \frac{(R_1 - R_2) \times 100}{R_1}$$

where:
R1 = calibration factor from initial calibration
R2 = calibration factor from succeeding analysis

5.4.2 Internal standard calibration procedure

a. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard applicable to all samples can be suggested.

b. Prepare calibration standards at a minimum of five concentrations for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and dilute to volume with an appropriate solvent. The lowest of the standards should be the method quantitation limit (based on a concentration with no dilution). The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. At least one of the calibration concentrations should correspond to a sample concentration at or below any regulatory or action limits associated with a target compound.

c. Inject each calibration standard using the same introduction technique that will be applied to the actual samples, e.g., 1-5 µL on-column injection, 5 mL with purge-and-trap, etc. Tabulate the peak height or area responses against the concentration of each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s)(C_{is})/(A_{is})(C_s)(V_{inj})$$

where:
As = response for the analyte to be measured
Ais = response for the internal standard
Cis = concentration of the internal standard, ng/µL
Cs = concentration of the analyte to be measured, ng/µL

Vinj = Volume of extract injected in µL. For purge-and-trap analysis, Vinj is not applicable and therefore = 1.

If the RF value over the working range is constant (< 20 % RSD,) the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, As/Ais vs. RF

d. The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary (every 12 hr or every 10 samples, depending on the method). The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than ± 15 % (this may vary according to different methods), a new calibration curve must be prepared for that compound.

5.4.3 Retention time windows

Retention times produced from using megabore or capillary columns are very stable. During 72 hr of analysis, it is not unusual for retention time to drift less than 0.01 min. Because of this stability in retention time, a maximum retention time window of 0.10 min has been adapted for general GC analysis (Pesticides have set windows based on lab-pooled results) and 0.50 min for GC/MS analysis. (Semivolatiles and Volatiles use RRT.) For multi-response analytes (i.e., PCBS), the analyst should use the retention time window, but should primarily rely on pattern recognition, where the experience of the analyst weighs heavily in the interpretation of chromatograms. The retention time of the initial calibration standards is used for determining retention times during the sequence.

5.4.4 Gas chromatographic analysis

a. Introduction of organic compounds into the gas chromatograph varies depending on the volatility of the compound. Volatile organics are primarily introduced by purge-and-trap (EPA Method 5030). However, there are limited applications (in EPA Method 5030) where direct injection is acceptable. Use of EPA Method 3810 or 3820 as a screening technique for volatile organic analysis may be valuable with some sample matrices to prevent overloading and contamination of the GC systems. Semivolatile organics are introduced by direct injection.

b. The appropriate detector(s) is given in the specific method.

c. Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with mid-point continuing calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded. Sample sets are always bracketed with continuing calibration checks.

All instrument calibration and check standards must be preceded by an instrument blank, to demonstrate that there is no carry-over to affect calculations. Any highly contaminated samples must be followed with instrument blanks, to demonstrate that there is no cross contamination with following samples.

d. Direct Injection. Inject 2-5 ± 0.05 µL of the sample extract using the solvent flush technique, if the extract is manually injected. Smaller volumes (1.0 ± 0.05 µL) can be injected, and the solvent flush technique is not required, if automatic devices are employed. Record the volume injected to the nearest 0.05 μL and the resulting peak size in area units or peak height.

e. If the response exceeds the linear range of the system, dilute the extract and re-analyze. It is recommended that extract be diluted so that all peaks are on scale. Optimally, the diluted concentration would place the analyte concentration near the mid-point of the calibration range. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

f. If peak detection is prevented by the presence of interferences, further cleanup is required.

g. Examples of chromatograms for the compounds of interest are frequently available in the referring analytical method and commercial suppliers of capillary columns.

h. Calibrate the system immediately prior to conducting any analyses (see part 5.4). A mid-concentration standard must also be injected at intervals specified in the method and at the end of the analysis sequence. The calibration factor for each analyte to be quantitated, must not exceed a 15 % difference when compared to the initial calibration standards of the analysis sequence. When this criterion is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary before re-calibrating and proceeding with sample analysis. All samples that were injected after the standard exceeding the criteria must be re-injected, if the initial analysis indicated the presence of the specific target analytes that exceeded the criteria.

i. Use the absolute retention time for each analyte from part 5.4.3 as the midpoint of the window for that day. The daily retention time window equals the midpoint ± 0.10 min for general GC analysis and ± 0.50 min for GC/MS analysis - unless specified differently in the given method.

j. Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention-time window. Normally, confirmation is required on a second GC column, by GC/MS if concentration permits, or by other recognized confirmation techniques. Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses.

5.4.5 Suggested chromatography system maintenance. Corrective measures may require any one or more of the following remedial actions.

a. Capillary/Megabore columns - Clean and deactivate the glass injection-port insert or replace with a cleaned and deactivated insert. Break off the first few centimeters (up to 10 cm) of the injection port side of the column. If the column is using a retention gap/guard column, remove the first few centimeters, or replace the retention gap/guard column. Remove the column and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

b. Metal injector body - Usually, the split line needs flushing and deactivation. Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert (instruments with off-column injection or Grob). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

Cool the Injection Port (< 40 °C). Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone, methylene chloride, and then hexane; catching the rinseate in the beaker. If the problem is with the split line, disconnect the split line at the split solenoid, and connect a glass syringe to this end of the line. Flush with water, acetone, methylene chloride, and hexane. Sylon is not necessary.

ACETONE [67-64-1]

DANGER: Acetone is highly flammable. It has a flash point of -20 °C (-4 °F) and poses a serious fire risk when heated, or exposed to flame or spark (this includes static electricity).
Avoid breathing vapors. Exposure can cause coughing, dullness, headache, dizziness, nausea, irritation to the eyes and respiratory tract, narcosis, and unconsciousness. Higher concentrations may cause damage to kidneys, liver, and central nervous system (depression). Chronic exposure during pregnancy may be harmful.
Avoid skin contact. Acetone is absorbed through the skin. Prolonged or repeated skin contact can cause severe irritation and dermatitis, because of the defatting action on skin. May cause redness, pain, drying and cracking of the skin. Toxicity of alcohol, and halogentated hydrocarbons may be increased.
Acetone can react vigorously with oxidizing materials. Avoid strong acids, strong alkalis, and halogens and halogen compound.
ACGIH TWA: 500 ppm, 1,188 mg/m^3

Hexane [110-54-3]

DANGER: All manipulations involving hexane must be performed within a fume hood. Nitrile gloves are recommended. n-Hexane is highly flammable. It has a flash point of -23 °C (-9 °F), has explosive limits in air in the range of 1 - 7 %, and poses a serious fire risk when heated, or exposed to flame or spark (this includes static electricity). n-Hexane can react vigorously with oxidizing materials.
Avoid breathing vapors. Exposure can cause dizziness, numbness of extremities, and intoxication. n-Hexane is a central nervous system depressant and neurotoxin. Acute exposure causes irritation, narcosis, and gastrointestinal tract irritation. Chronic inhalation causes peripheral neuropathy can have neurotoxic effects.
Avoid skin contact. n-Hexane is absorbed through the skin. Prolonged or repeated skin contact can cause irritation and dermatitis, through defatting of skin.
No PEL given.

Methylene chloride [75-09-2]

DANGER: All manipulations involving methylene chloride must be performed within a fume hood or a sealed system to prevent venting into the laboratory. It is non-flammable. Wear laminated film or polyvinyl alcohol (PVA) gloves.
Avoid breathing vapors. Exposure can cause anesthetic or narcotic effects, light-headedness, nausea, vomiting and headache. Excessive exposure may cause irritation to upper respiratory tract. Unconsciousness and death can result from extreme cases of over exposure. High levels may also cause cardiac arrhythmias (irregular heartbeats). Breathing vapors can elevate carboxyhemoglobin levels in the cardiovascular system thereby impairing the blood's ability to transport oxygen. Persons who smoke tobacco products will experience an intensified elevation of carboxyhemoglobin levels. Observations in animals include liver and kidney effects.
Delayed effects: exposure may aggravate symptoms of angina (chest pains). Liver and kidney damage may occur.
Avoid skin contact. Prolonged or repeated exposure may cause skin irritation, even a burn. Repeated contact may cause drying or flaking of skin. Can cause irritation and dermatitis.
Cancer information: Suspect carcinogen. Causes cancer in mice and benign tumors in rats.
Avoid direct sunlight and UV sources. High temperatures and open flame may produce phosgene.

Incompatibility with metals such as: aluminum powders, potassium, sodium, and zinc powder. Avoid unintended contact with amines. Avoid contact with strong bases and strong oxidizers. Avoid prolonged contact with or storage in aluminum or its alloys.
OSHA action level: 12.5 ppm. PEL is 25 ppm. (If you can smell it, the amount is too high.)

c. Prepare a solution of deactivating agent (Sil-Prep) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, and hexane. Re-assemble the injector, bring the injector to temperature, and allow a good amount of helium flushing of the system before replacing the GC column.

DANGER: See **DANGER** under 'acetone' in part b. above.

Methanol, [67-56-1]

WARNING: All manipulations involving methanol should be performed within a fume hood. Wear nitrile gloves and a lab coat. Methanol is flammable and burns with a clear, almost invisible flame. It has a flash point of 12 °C, explosive limits in air in the range of 6 - 36 %, and poses a serious fire risk when heated, or exposed to flame or spark (this includes static electricity). Methanol can react vigorously with strong oxidizing materials. Avoid contact with strong acids, acid chlorides, acid anhydrides, and alkali metals.
Avoid breathing vapors. Initial symptoms may be only that of mild intoxication, but may become severe after 12 to 18 hours. Methanol can be irritating to mucous membranes and upper respiratory tract. Exposure can cause headache, muscle weakness, dizziness, nausea, vomiting, narcosis, respiratory failure, low blood pressure, gastrointestinal disturbances, convulsions, and may be fatal. Methanol is a central nervous system depressant and can cause kidney, liver (enlargement), eye (especially optic nerve) and heart damage.
Avoid skin contact. Methanol is absorbed through the skin. Prolonged or repeated skin contact can cause irritation and dermatitis.
Eye contact may cause irritation and/or temporary corneal damage.
Prolonged exposure to methanol has been known to cause fetal development abnormalities in pregnant rats.

US ACGIH TWA: 200 ppm; STEL: 250 ppm.

Toluene [108-88-3]

WARNING: All manipulations involving toluene must be performed within a fume hood. Wear PVA gloves. Toluene is highly flammable. It has a flash point of 4 °C, has explosive limits in air in the range of 1 - 7 %, and poses a serious fire risk when heated, or exposed to flame or spark (this includes static electricity).
Avoid breathing vapors. High concentrations are extremely destructive to tissues of the mucous membranes and upper respiratory tract (irritation), eyes and skin.
Symptoms of exposure may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, dizziness, dullness, narcosis, hallucinations, distorted perceptions, changes in motor activity, headache, nausea and vomiting, diarrhea, convulsions and unconsciousness. Exposure can cause lung irritation, chest pain, and edema, which may be fatal.
Chronic effects may cause nervous system disturbances. Inhalation studies on toluene have demonstrated the development of inflammatory and ulcerous lesions of the penis, prepuce and scrotum in animals.
Avoid skin contact. Toluene is absorbed through the skin. Prolonged or repeated skin contact can cause irritation and dermatitis, through defatting of skin.
Consumption of alcohol may increase toxic effects.

Eye contact can cause severe eye irritation and may cause temporary corneal damage.
Target organs: brain and coverings, (depression of) central nervous system, autonomic nervous system (parasympathomimetic), liver (damage), kidneys (damage), bladder and lungs.
Incompatible with strong oxidizing agents, nitric acid, sulfuric acid, chlorine.
No known PEL.

5.4.6 Calculations

a. External standard calibration - The concentration of each analyte in the sample may be determined by calculating the amount of standard purged or injected, from the peak response, using the calibration curve or the calibration factor determined in part 5.4.1. All injections in the lab are done via auto samplers and therefore all standards and samples are injected at a constant volume. Under no circumstances will samples be analyzed at different injection parameters from the standards associated with those samples. The concentration of a specific analyte is calculated as follows:

Aqueous samples

$$\text{Concentration}\left(\mu g/L\right) = \frac{(A_x)(V_{fv})(D)}{(C_f)(V_{inj})(V_s)}$$

where:

Ax	=	response for the analyte in the sample, units may be in area counts (for GC/MS) or peak height (for GC).
Vfv	=	final volume of total extract, µL. For purge-and-trap analysis, Vfv is not applicable and therefore = 1
D	=	dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless
Cf	=	Calibration factor of external standard, units in response/ng
Vinj	=	Volume of extract injected in µL. For purge-and-trap analysis, Vinj is not applicable and therefore = 1.
Vs	=	volume and sample extracted or purged, mL

Non aqueous samples

$$\text{Concentration}\left(\mu g/kg\right) = \frac{(A_x)(V_{fv})(D)(U)}{(C_f)(V_{inj})(W)}$$

where:

Ax	=	response for the analyte in the sample, units may be in area counts (for GC/MS) or peak height (for GC).
W	=	dry mass of sample extracted or purged, g. Wet mass will only be used upon request.
U	=	Correction factor for pesticide analysis, where GPC cleanup looses ½ of the sample, U is 2.
Cf	=	Calibration factor of external standard, units in response/ng
Vinj	=	Volume of extract injected in µL. For purge-and-trap analysis, Vinj is not applicable and therefore = 1.
Vs	=	volume and sample extracted or purged, mL

Ax, Vfv, D, Cf and Vinj have the same definition as for aqueous samples.

b. Internal standard calibration. For each analyte of interest, the concentration of that analyte in the sample is calculated as follows:

Aqueous samples

$$\text{Concentration}\,(\mu g/L) = \frac{\left[(A_x)\left[(C_{is})/A_{is}\right](V_{fv})(D)\right]}{(RF)(V_{inj})(V_s)}$$

where:

Ax	=	response for the analyte in the sample, units may be in area counts (for GC/MS) or peak height (for GC).
Ais	=	response of the internal standard, units same as Ax
Cis	=	amount of internal standard added to extract or volume purged, ng
D	=	dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless
Vfv	=	final volume of total extract, μL. For purge-and-trap analysis, Vfv is not applicable and therefore = 1
Cf	=	Calibration factor of external standard, units in response/ng
Vinj	=	Volume of extract injected in μL. For purge-and-trap analysis, Vinj is not applicable and therefore = 1.
Vs	=	volume and sample extracted or purged, mL
RF	=	response factor for analyte, units are dimensionless.

Non aqueous samples

$$\text{Concentration}\,(\mu g/kg) = \frac{\left[(A_x)\left((C_{is})/A_{is}\right)\right](V_{fv})(D)(U)}{(RF)(V_{inj})(W_s)}$$

where:

Ws	=	dry mass of sample extracted, g.
U	=	Correction factor for pesticide analysis, where GPC clean-up loses ½ of the sample, U is 2.

As, Cis, Vfv, D, Ais, RF, and Vini have the same definition as for aqueous samples.

6.0 QUALITY CONTROL

6.1 Refer to the specific determinative method for quality control procedures.

6.2 The experience of the analyst in performing gas chromatography is invaluable to the success of the methods.

6.2.1 Each day that analysis is performed, an instrument blank and the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are:

- Do the peaks look normal?
- Is the response obtained comparable to the response from previous calibrations?
- Are the instrument blanks clean?

Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., column changed,) re-calibration of the system must take place.

6.2.2 The performance of the entire analytical system should be checked daily, using data gathered from analyses of blanks, standards, and replicate samples. Significant peak tailing must be corrected. Tailing problems are generally traceable to active sites on the GC column or to the detector operation.

6.2.3 The precision between replicate analyses of standards and check samples should be evaluated. A properly operating system should perform with an average relative standard deviation of less than 10 % (this may vary according to different methods). Poor precision is generally traceable to pneumatic leaks, especially at the injection port, i.e., leaking septum or loose syringe plunger.

6.3 Summary of Required Instrument QC

6.3.1 The % RSDs vary by ≤ 20 % (this may vary according to different methods) when comparing calibration factors to determine if a five-point calibration curve is linear.

6.3.2 The % RSD limit is ± 15 % (this may vary according to different methods) difference when comparing daily response of a given analyte versus the initial response. If the limit is exceeded, a new standard curve must be prepared.

6.3.3 Part 5.4.3 indicates the establishment of retention time windows.

6.3.4 The % RSDs are ± 15 % (this may vary according to different methods) difference when comparing the initial response of a given analyte versus any succeeding standards analyzed during an analysis sequence.

6.3.5 All succeeding standards in an analysis sequence must fall within the daily retention-time window established by the first standard of the sequence.

6.4 Initial Demonstration of Proficiency. To establish the ability to generate data of acceptable bias and precision, the analyst must perform the following operations:

6.4.1 A Quality Control (QC) check sample concentrate is required containing each analyte of interest. The QC check sample concentrate may be prepared from pure standard materials, or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate must be made using stock standards prepared independently from those used for calibration.

The concentration of the QC check sample concentrate is highly dependent upon the analytes being investigated. Therefore, refer to AC G-3500, for the required concentration of the QC check sample concentrate.

6.4.2 Preparation of QC check sample: Refer to AP G-ORG STD.

6.4.3 Analyze replicate aliquots (at least four) of the well-mixed QC check sample by the same procedures used to analyze actual samples in each of the methods. For volatile organics, the preparation/analysis process is purge-and-trap/gas chromatography or direct injection/gas chromatography. For semivolatile and pesticide organics, the QC check samples must undergo solvent extraction (see AC G-3500) prior to chromatographic analysis.

6.4.4 Calculate the average recovery in μg/L, and the standard deviation of the recovery(s) in μg/L, for each analyte of interest using the four (or more) results.

6.4.5 For each analyte compare s and x with the corresponding acceptance criteria for precision and accuracy, respectively, given in the QC Acceptance Criteria Table at the end of each of the determinative methods. In the absence of method-specific acceptance criteria for the initial demonstration of proficiency, use the recoveries of 70 - 130 % as guidance in evaluating the results. If all analytes of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual analyte exceeds the precision limit or any individual falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in each of the QC Acceptance Criteria Tables present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

6.4.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to part 6.4.6.a or 6.4.6.b.

a. Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with part 6.2.1.

b. Beginning with part 6.2.1, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest.

6.5 Matrix Spike and Laboratory Control Samples

The laboratory procedures for documenting the effect of the matrix on method performance includes the analysis of at least one matrix spike, and either one matrix duplicate or one matrix spike duplicate per analytical batch, or at the rate of 5 %, whichever is greater.

In addition, a Laboratory Control Sample (LCS) is included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same mass or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. The rate of analysis of the LCS is one per analytical batch.

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

a. If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit.

b. If the concentration of a specific analyte in a water sample is not being checked against a limit specific to that analyte, the spike should be 2-10 times higher than the quantitation limit.

6.5.2. Analyze one unspiked and one spiked sample aliquot to determine percent recovery of each of the spiked compounds.

a. Volatile organics. Analyze one 5 ± 0.05-mL sample aliquot to determine the background concentration of each analyte. If necessary, prepare a new QC reference sample concentrate (part

6.4.2) appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 ± 0.1 µL of the QC reference sample concentrate and analyze it to determine the concentration after spiking of each analyte. Calculate each percent recovery (%R) as:

$$\%R = \frac{100(x_s - x_u)}{K}$$

where:

xs = measured value for spiked sample,
xu = measured value for unspiked sample,
K = known value of the spike in the sample.

b. Semivolatile organics. Analyze one sample aliquot (extract of 500-mL sample) to determine the background concentration of each analyte. Spike a second 500-mL sample aliquot with 0.25 ± 0.01 mL of the QC reference sample concentrate and analyze it to determine the concentration after spiking of each analyte. Calculate each percent recovery according to the calculation in part 6.5.2a. NOTE: There may be times where insufficient sample volume exists to use 500-mL for the spike. In such cases, use the remaining sample, record the volume in the extraction logbook, and use the value to calculate xs.

6.5.3 Compare the percent recovery (% R) for each analyte in a water sample with the corresponding criteria presented in the QC Acceptance Criteria Table found at the end of each of the determinative methods. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than the QC reference sample concentration (part 6.4.2), the analyst must use either the QC acceptance criteria presented in the tables, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) calculate accuracy (x') using the equation found in the Method Accuracy and Precision as a Function of Concentration Table (appears at the end of each determinative method), substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in the same Table, substituting x' for x; (3) calculate the range for recovery at the spike concentration as [(100x'/T) ± 2.44] x (100S'/T) %. Many methods do not contain acceptance criteria for LCS results. 70 - 130 % should used as interim acceptance criteria for recoveries of spiked analytes, until in-house LCS limits are developed. When in-house limits have been developed for matrix spike recoveries, the LCS results should fall within those limits.

6.5.4 If any individual % R falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed.

6.5.5 Compare the recovery data from the matrix spike with the LCS data (use the average recovery if a matrix spike and matrix spike duplicate were analyzed). If any individual percent recovery in the matrix spike (or matrix spike duplicate) falls outside the designated range for recovery, the analyst determines if there is a matrix effect or a laboratory performance problem. A matrix effect is indicated if the LCS data are within limits but the matrix spike data exceed the limits. The surrogate recovery data should also be used to evaluate the data. If any analyte in a water sample fails the acceptance criteria for recovery in part 6.5.3 and is determined not to be a matrix effect, a QC reference standard containing each analyte that failed must be prepared and re-analyzed.

6.6 Method Blanks

6.6.1 Method blanks are prepared at one method blank for each batch.

6.6.2 When samples that are extracted in the same batch are analyzed on separate instruments or on separate analytical shifts, the method blank associated with those samples must be analyzed on all the instruments used for sample analysis, and on all the analytical shifts.

6.6.3 The results of the method blank should be less than ½ of the quantitation limit. There is no blank subtraction from the reported results. The results for any analyte that is also found in the method blank at levels higher than ½ of the quantitation limit will be re-extracted.* If the holding time is exceeded with the re-extraction, then both the initial extraction and re-extraction will be reported in the data package.

*** See QA Plan for exceptions to this.**

6.7 Surrogate recoveries

6.7.1 It is necessary that surrogate recovery data be evaluated from individual samples versus surrogate recovery limits developed in the laboratory. The general considerations for developing in-house acceptance criteria for surrogate recoveries are described in part 6.8.3-6.8.4.

6.7.2 Surrogate recovery is calculated as:

$$\text{Recovery (\%)} = \frac{\text{Concentration found}}{\text{Concentration added}} \times 100$$

If the recovery is not within in-house surrogate recovery limits, the following procedures are necessary:

a. Examine the chromatograms for interfering peaks. If there appears to be interfering peaks, note this in the case narrative.

b. Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

c. If no problem is found, re-extract and re-analyze the sample.

d. If upon re-analysis, the recovery is again outside of recovery limits, flag the data as "estimated concentration". If the recovery is within the limits, report the re-analysis data. If the holding time for the method has expired prior to the re-analysis, provide both the original and the re-analysis results and note the holding time.

6.8 Generating performance criteria for matrix spike recoveries, surrogate recoveries, initial demonstration of proficiency, and laboratory control sample recoveries. (See QA Plan for exceptions to this. Note also 6.8.6.)

The laboratory is in the process of setting up of automated calculation of criteria for matrix spike recoveries, surrogate recoveries, and laboratory control sample (LCS) recoveries. Along with this will be the automated generation of control charts for laboratory control sample recoveries and method blank surrogate recoveries. At present, the recovery criteria for all GC and GC/MS methods are manually being generated, except in the case of AM E-608, -8081 and -8082, where infrequent analysis does not generate enough data for control charts. These methods that are done infrequently have limits derived from the SW-846 methods.

The procedure for the calculation of performance criteria is:

6.8.1 Calculate the average percent recovery and standard deviation for each of the matrix spike compounds after analysis of 20 matrix spike samples of the same matrix.*

*** See QA Plan for exceptions to this. Note also 6.8.6.**

6.8.2 Calculate the upper and lower control limit for each matrix spike or surrogate compound:

Upper Control Limit = x + 3s

Lower Control Limit = x - 3s

6.8.3 Calculate the upper and lower warning limit for each matrix spike or surrogate compound:

Upper Warning Limit = x - 2s

Lower Warning Limit = x - 2s

6.8.4 Any matrix spike or surrogate results outside of the control limits require corrective action by the laboratory, including but not limited to, the review of the sample results, inspection of the chromatographic system and re-analysis of the samples.

The warning limits should be used to guide internal evaluations of method performance, track the performance of individual analysts, and monitor the effects of change to the analytical procedures. Repeated results outside of the warning limits should result in corrective actions.

6.8.5 Once established, control limits and warning limits for matrix spike compounds should be updated after every 20 matrix spike samples of the same matrix* or at least quarterly. Control limits and warning limits for surrogates should be updated after every 20 field samples of the same matrix or at least quarterly. Trends should be tracked in both performance and in the control limits themselves.

*** See QA Plan for exceptions to this. Note also 6.8.6.**

6.8.6 For methods and matrices with very limited data (i.e., unusual matrices not analyzed often), interim limits are established using available data (i.e., the method QC criteria) or by analogy to similar methods or matrices.

6.8.7 Results used to develop acceptance criteria should meet all other QC criteria associated with the determinative method.

6.8.8 Because of the large variability of matrix types, the method blanks and LCS surrogate recoveries will be used to establish surrogate recoveries for those matrices with which they were extracted.

6.9 Additional quality assurance programs are practiced in the lab. As mentioned above, LCS are analyzed with every batch at the rate of at least 5 %. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer are used. The laboratory analyzes standard reference materials (through semi-annual APG round robins).

7.0 KEY WORDS

AP E-8000, aqueous, chromatography, EPA, gas chromatography, GC, QC, semi-volatiles, solids, SW-846, volatiles, water

8.0 REFERENCES

8.1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

8.2 U.S. EPA Manual, SW-846.

9.0 REVISION HISTORY

9.1 4/10/04 – Changed SOP code from AP E-8000.

9.2 9/11/07 – Updated codes for all referenced SOPs and updated safety information.

1.0 SCOPE

1.1 This document specifies the duties and responsibilities of the Sample Management Office (SMO) and those of the employees coming into contact with the samples.

1.2 SMO plays a critical role in the Unit's QA program through receipt, handling, documentation, and disposal of samples for Analysis and Testing.

1.3 This SOP only applies to samples submitted to the pulp (wet) lab, paper lab, and to the analytical laboratories. Microscopy has a separate procedure for the sample management process. See MP-SAMPLE RECEIVING.

2.0 SAMPLE SUBMITTAL PROCESS

The following forms are found on the A&T website under "Forms & Templates" in the SMO folder:

- Sample Receipt Form
- Sample Analysis Request & Chain of Custody Record
- Analytical Chemistry Service Request
- Pulp & Paper Service Request
- Microstructure Service Request

To submit a sample, the following forms are found on the A&T website under "Submit a Sample" to request the sample testing schedules:

- Analytical Chemistry Service Request Form
- Pulp & Paper Service Request
- Microstructure Service Request

See section 4.0 below for more information regarding how to locate the necessary forms.

3.0 REAGENTS REQUIRED

3.1 HNO_3 (1+1) with water. Add 250 mL of conc. acid to 250 mL of water and mix. Need not be extremely accurate.

NOTE: For safety and purity reasons, this should be made up by metals laboratory personnel, not SMO personnel.

Nitric acid (concentrated), HNO_3, CAS# 7697-37-2

DANGER: Handle with extreme care. Wear safety glasses, lab coat, vinyl gloves and use in a hood. Conc. nitric acid is a strong, corrosive acid and liquid and vapor can cause severe burns. Carefully add acid to water with frequent or continuous stirring. Mix in a tub or stoppered sink. Upon dilution in water, the generation of heat could cause it to erupt and spatter over a large area. Proceed with caution.

- Harmful if inhaled and may cause delayed lung injury. If inhaled, can cause severe irritation or burns of mucous membranes and respiratory system, resulting in coughing, difficult breathing, chest pains, pneumonia, pulmonary edema, lung inflammation, unconsciousness, and may be fatal. Can cause severe ulceration.
- Skin contact can cause severe irritation, redness, pain, and severe skin burns. Concentrated acid causes deep ulcers and stain skin a yellow or yellow-brown color.
- Eye contact can cause severe irritation or burns and result in permanent damage.
- Nitric acid is a strong oxidizer. Contact with combustible materials, flammable materials - such as wood and solvents - or powdered metals can cause fire or explosion. Reacts with most metals to produce hydrogen gas, which can form an explosive mixture with air. Keep away from strong bases, carbides, carbonates, charcoal, (hydrogen) sulfides, cyanides, combustible materials, combustible organics or organic materials, turpentine, strong reducing agents, most common metals, carbides, ammonium hydroxide, water, and alcohols.
- Certain mixtures with benzene, 1,2-dichloroethane, or dichloromethane may be detonatable.
- Reaction products include highly toxic and dangerous fumes of reddish oxides of nitrogen having the equivalent affects as those noted above.
- Long-term exposure to concentrated vapors may cause erosion of teeth.
- Short-term exposure limit (STEL) is 10 mg/m^3 (4 ppm) and permissible exposure limit (PEL) is 5 mg/m^3 (2 ppm.)

4.0 PROCEDURE

SMO is responsible for the general cleanliness of the sample storage and receiving areas. A clean and orderly storage area is necessary for the integrity of the samples. Important records can be lost if paperwork is not kept organized.

4.1 Location of forms to submit a sample

Go to A&T web site

Click on "Submit a form". Under Service Request forms, choose from the following: Pulp and Paper, Microstructure, Sample Analysis & Testing Request with a chain of Custody form or Sample Analysis & Testing Request without a chain of custody.

4.2 Receiving Samples

Sample Management Office (SMO) receives samples through a variety of methods.

4.2.1 Samples are brought directly into SMO by the client. If no one is present in SMO, the client should consult with one of the Project Managers (PM) about his sample request.

4.2.2 Samples are shipped and/or mailed to the Technology Center via various methods.

a. Samples are accepted by our receiving personnel and delivered to the SMO. (At times, SMO will come down and retrieve samples from the receiving dock.)

b. On occasion, samples will be dropped off in the south lobby area. The receptionist will then contact SMO to pick-up the samples.

NOTE: Although section 4.1.2.b is still listed as a viable method for sample drop off, it is strongly discouraged due to safety reasons.

4.2.3 <u>Samples are brought in to SMO by the analyst.</u>

a. Samples are sent or given directly to the analyst by the client.

b. On occasion, samples are created by an analyst in collaboration with a client.

4.2.4 <u>Samples are delivered to the Technology Center during off-hours</u>.

Security handles samples as per their SOP.

a. Samples received in coolers are placed in the basement cold storage G01/G02 and security sends a voice mail message to the SMO personnel.

b. Samples not received in coolers (not to be kept chilled) are placed in the receiving area and delivered to SMO at the start of the following business day.

4.3 Project Manager Role

When samples arrive, the SMO staff calls a Project Manager (PM). The PM is determined by the client/job type received.

4.4 Unpack and evaluate the samples.

The following is a list of procedures performed in the sample check-in process. See AQ S-SampleSplitting if needed. (Section 4.4.1.j)

4.4.1 Sample handling.

THE INTEGRITY OF ALL SAMPLES SHALL BE MAINTAINED WHILE IN LABORATORY CUSTODY. FOR EXAMPLE, IF SAMPLES REQUIRE 4°C, THEY WILL BE MAINTAINED AT 4°C DURING ANY HANDLING PROCESSES (except when warming them for sub-sampling).

SAMPLES WILL BE APPROPRIATELY PROTECTED FROM CROSS-CONTAMINATION. FOR EXAMPLE, THE VOAs OR HI-RES SAMPLES WILL BE ISOLATED TO KEEP FROM POTENTIALLY CONTAMINATING OTHER SAMPLES.

a. For samples received chilled or in coolers, the SMO staff uses the Sample Receipt Form found on the A&T website under “Forms & Templates” in the SMO folder. This form is used to record, date and time samples are received, pH conditions, temperature of cooler/temperature blank and custody seal conditions, etc.

b. When temperatures are in question (i.e. no ice present or blue ice totally melted), a probe is used to check temperatures. The probes are stored in the cabinet under sample fume hood 216-4.

If there are no coolant blanks, place the probe in the cooler next to a sample bottles for the most accurate ambient temperature. Make a note on the sample receipt form how the temperatures were measured (coolant blank, water, ambient air).

c. Unpack samples and check for breakage, missing samples and correct identification, etc.

NOTE: TOTALLY UNKNOWN SAMPLES, OR SAMPLES KNOWN OR SUSPECTED TO BE HAZARDOUS, ARE TO BE OPENED AND INSPECTED IN A LABORATORY HOOD ONLY.

Broken sample containers, irregular preservation and improper paperwork are noted on a nonconformance form as per OQ CORRACT. The assigned PM is contacted so a course of action can be taken such as the following:

- Contacting clients so more samples can be submitted
- Reducing the number of tests requested by the clients
- Contacting clients regarding future packing of samples

If anything is unclear, special or requires immediate handling about a client's request, the SMO personnel will contact the assigned PM or the appropriate analysts for assistance.

d. The SMO personnel (who unload coolers, boxes, etc.) will verify that samples and accompanying paperwork match. The SMO personnel will promptly sign all of the chain of custody forms.

When there is no client paperwork, the SMO personnel contact the project managers to see if they have any knowledge of the work that was received. When project managers have no knowledge of samples received, the SMO personnel will then look on the package for sender information (i.e. mill, company or name on the package) so that the SMO personnel or project managers can contact the sender to find out what kind of analyses are required.

All paperwork that accompanies the incoming samples is kept together and becomes part of the original SR package.

e. Determine if the samples received are within holding times.

Holding Time	Action
No Issues	Process normally
Exceeded	Contact PM, laboratories affected and complete a nonconformance f
Short	Contact PM and laboratories affected immediately

f. Determine if the samples are properly preserved.

1. Using the Sample Receipt form, confirm which samples have a pH preservation requirement and require a pH measurement to be taken. Retrieve the pH test strips (these are located in both hoods ((216-3 & 216-4)) in the SMO area.

i. To take a pH of a sample, pour a small amount of the sample into a disposable 50-mL polypropylene beaker. Dip the pH strip into the liquid.

ii. Pour excess sample down the sink with the water running and the dip sticks in the trash.

2. Most samples needing their pH checked should be preserved to a pH < 2. Samples requiring more H_2SO_4, or HNO_3 (if not designated as low level metals), may be preserved by SMO personnel or taken to the lab for preservation.

CAUTION: Be aware that an unpreserved bottle (for metals analysis) may be for silicon testing and does not require preservation. See chain of custody and/or other testing information before adding any preservatives to such sample containers.

DANGER: Handle with extreme care. Nitric acid is a strong, corrosive mineral acid. Use all appropriate safety apparel and proceed with caution. See 'DANGER' under 3.1.

3. Cyanide pH should be > 12. If the cyanide sample has not been preserved and appears to have an improper pH, take the sample to the Lab 212 SLM and have a chemist preserve it to a pH >12 by adding 2 mL of 10N NaOH per liter of sample.

4. Use lead acetate strips to check for presence of sulfide in liquid samples where cyanide is requested. If sulfide is present in the sample, it will be indicated by a darkening of the test strip or a dark precipitate on the test strip due to PbS (lead sulfide) precipitating out with color (black). Record pH and sulfide information on Sample Receipt Form (Section 4.4.1.a).

5. Check other preservation required as specified, such as RCl_2 (residual chlorine), as necessary for N. Carolina regulatory samples.

g. Add any needed preservative in accordance with proper analytical protocol as stated in 40 CFR 136.3, Table II. See a copy of Table II in the appendix of this document.

h. Preservation is done immediately upon receipt in the lab and recorded on Sample Receipt Form.

i. If initial attempts to add preservative do not achieve the desired effect, contact an analyst to see about adding a more concentrated preservative. Total volume of preservative should not dilute the sample by more than 1 % (10 mL/L).

j. Evaluate whether there is sufficient sample to run the requested tests. If there is not, or if there is doubt, consult AQ S-SampleSplitting and/or contact the PM. Should testing proceed when there is insufficient sample, a nonconformance memo will be filled out.

k. If the samples are in an unusual or abnormal state, such as lack of proper preservative for testing (i.e. H_2SO_4 rather than HNO_3), the PM is notified and a determination is made on how to proceed. This may require a note on the sample log-in sheet under "*Comments*" or a nonconformance form may need to be completed.

4.4.2 Determine if paperwork matches samples. If not, then the PM is informed and a nonconformance memo will be filled out.

4.4.3 Evaluating Service Request (SR) needs:

a. Determine if an 'upcoming request' was created. Look in the "UPCOMING" notebook for copy.

If:	
Yes	Contact appropriate PM that samples have arrived. Proceed with log-in following detail on upcoming.
No	Contact appropriate PM for analysis details. These details would include:

	•who the client is •client location and phone number •correct project number for charging •correct tests and corresponding test codes •special instructions regarding these samples •reference SR number •confirmation of a committed turnaround time •lab doing the work

b. When there is an upcoming notice for a particular job and the samples that are received do not match the initial notice (i.e., expect 41 samples, receive only 7 in current shipment), make a copy of the upcoming notice. This copy goes with the new SR being created. Write on the original copy of the upcoming notice the number of the SR created for the work received and place the upcoming notice back into the notebook for future samples to be received for that same job.

c. Determine if there is a reference Service Request (SR).

1. A reference SR number is noted on the upcoming notice by the PM if we've done previous work for that client/project.

2. If a referenced SR number is not noted on the upcoming notice, open 'A&T SR Search' from the main screen of Laboratory Information System (LIMS).

3. A LIMS search is based on several criteria.
   i. Mill site, such as "Columbus".
   ii. Client, such as "Mike White".

4. The search is much quicker using only the upper part of the LIMS page. (Most searches will give the information required when using the upper part of the page.) Entering a test or test schedule (shown on the lower half of the page) will be much broader and take longer.

4.4.4 When the list of SRs comes up on the LIMS screen, the most recent SR is at the top (this is not true when searching the committed database). If the information being searched for is not found in the active database, try searching under the committed database. Active/committed SR's can be opened and printed by clicking on the database header in LIMS & toggling between 'Toggle act/com'.

NOTE: SRs are moved into the committed database after an SR has been closed for 120 days.

4.5 Enter sample/requested information/documentation into LIMS

After all questions are answered and issues are resolved, the SMO personnel are ready to enter the information into the Laboratory Information Management System (LIMS) and create a unique Service Request (SR) for that particular sample set. This document (SOP) does not cover the detail of sample entry into the LIMS. See LIMS notebook located in the SMO area for LIMS entry instruction.

NOTE: SR numbers are assigned in sequential order by the computer. The SR number is a 6 digit number, with the first 2 digits designating the year, e.g., 2007 becomes 07-, and the last 4 for the sequential SR in that year, allowing up to 9999 SR's in a given year. The 4985th SR of 2007 would be 07-4985. See section 4.5.2 for labeling information.

If a sample is deleted, the LIMS does not allow that particular ID number to be reused. Not all sample ID's will be sequential.

4.5.1 After all information is entered into the LIMS and the SR is complete, print one full SR copy. Print one single copy of the front page of the SR and mark F in upper right corner. The F copy is placed in the SR file at the back of the SR and accompanying paperwork for archival filing after reporting. Scan the client paperwork into LIMS. Place all paperwork for SR in the appropriate folder.

Folder Color	Folder Contents
Green	'Permit' in title
Red	"outside" SRs
Yellow	Analytical

NOTE: No folder is made for the Cellulose Properties samples. All work is scanned into an electronic copy. However, if the Cellulose Properties SR has one or more tests for Analytical Chemistry, a yellow folder will be made and stored as in 4.5.1

Place file folder in rack next to SR printer. Notify appropriate PM electronically when SR's are ready for reviewing.

4.5.2 The PM will come to SMO and pick up SR folders. The PM will review the SR's either in SMO or at their desk to evaluate whether all aspects of the SR are in agreement with both the laboratory and the client. If no changes are required, then the PM 'releases' the SR to the laboratories (with scanned attachments) via a shared e-mail file. This puts the SR in the LIMS system so the laboratories are able to enter their data.

4.5.3 IR LAB: SMO will print a full copy of the SR, scan the client paperwork and create a folder. This folder is reviewed by a SMO technician who did not enter the SR. After review, corrections or changes, the SR is sent electronically to the IR specialist for review and released to the labs. The SR folder is placed behind the purple folder labeled Mary Beth at the back of the SR rack which is located next to the scanner. The IR specialist will either pick up the SR folder to place in the SR file cabinet drawer or SMO personnel will take it out to the drawer.

4.5.4 When the PM 'releases' the SR, it is seen in the exchange file. The SR number shows up followed by numbers. Each number represents an area of the lab. Some areas are broken down further by specialty and these show up with a letter, i.e. 4p indicates group 4 or Conventionals and the pulp area of that lab. The list below shows the number of each lab and it is the lab number that is used when sending the SR electronically. When a group opens the exchange file, they need only look for SRs with their own group number attached. Remember that all attachments are with the lab copy.

0 Project Management/QC
1 Chromatography
2 IR/Voa/Dioxin, with i (IR), v (VOA) or d (dioxin)
3 Elemental
4 Conventional, with *w* (waters) or *p (pulp)*
6 Physical Test Lab (Paper Lab)
7 Pulp Lab (Wet Lab)
8 Containerboard Lab
9 Microscopy

Changes can be made and/or samples can be added to an SR until it is authorized (final closing).

NOTE: Archiving of completed SRs is a function of the Administrative personnel.

Exemptions

MICROSTRUCTURE:

SMO will print a full copy of the SR and scan the client paperwork as directed above. This SR is reviewed by a SMO technician who did not enter the SR. After review, corrections or changes, the SR is sent electronically to microstructure for review and released to the labs. The complete SR is put in WOW box (micro will print their own copies). The client paperwork goes in a purple folder labeled Ron which is at the back of the SR rack next to the SR scanner. The micro PM either prints this paperwork at his desk, while SMO retains the original paperwork until the file folder gets too full. At that time, SMO will discard the oldest sets of paperwork and continue to rotate paperwork in and out of that folder. Samples for Microstructure are usually delivered directly to that lab area. The procedure follows MP-SAMPLE RECEIVING.

CFTP (formerly PPTS):

SMO will print a full copy of the SR and scan the client paperwork as directed above. The SR is reviewed by a SMO technician who did not enter the SR. After review, corrections or changes, the SR is sent electronically to CFTP OM/PM for review and released to the labs. The complete SR is put in WOW box (CFTP will print their own copies). The client paperwork goes in a purple folder labeled Rick which is at the back of the SR rack next to the scanner. The CFTP OM/PM also prints this paperwork at his desk, while SMO retains the original paperwork until the file folder gets too full. At that time, SMO will discard the oldest sets of paperwork and continue to rotate paperwork in and out of that folder.

4.7 Label Samples

4.7.1 Each sample is assigned a unique lab code number. This is done through the process of logging the samples into the computer on a given SR. The lab code numbers are assigned sequentially by the computer. When new samples are "created" (such as by combining samples together), lab code numbers will be created for these as well. An SR can contain up to 999 samples.

NOTE: Generally, for work internal to the company, containers known to hold split samples from one identical source, are given the same number, being differentiated by bottle type/preservation.

Each sample number contains the 6 digit SR number, which is the two digit year, then a "–" (dash) followed by the next sequential SR number, another dash, and the first sample number, starting with 001. Each additional sample is assigned the next sequential number (e.g. 002,003, etc.). See NOTE in section 4.6.1 for more information.

Example: 00-1925-001, 00-1925-002, etc

4.7.3 Print sample labels. This is done through the LIMS. If available from the client, the label also contains the sample date and time.

4.7.4 Attach labels to each sample container. When affixing the sample number label, take care not to cover the sample detail information on the sample container such as sample ID, date/time/preservative. Also take care not to damage samples with the label in cases where there is no container, such as with pulp sheets. In this case, attach the sample label by using a paper clip or stapling.

NOTE: See SMO staff for when to staple and when to use paper clips. Frequently, samples for the Wet Lab are taken directly to the Wet Lab by the client. (See section 4.8.12.)

4.7.5 All pulp samples going to the Paper Laboratories or to the 20 % room need to have sample labels paper clipped directly to the samples. DO NOT USE STAPLES. Ensure that sample label backing is intact so that nothing "sticky" adheres to the sample. For pulp samples requiring metals analysis, wear cotton gloves while handling samples, place samples in plastic bags and ensure no metal is touching the pulps. For pulp samples requiring Conventionals testing, wear cotton gloves while handling samples, place samples in plastic bag. For IR samples, place in envelopes. Do not staple, put in plastic or use paperclips.

4.8 Storing Samples

4.8.1 SMO personnel stores samples appropriately to maintain the integrity of the samples and the safety of the lab. Samples generating hazardous fumes require placement in a hood. Samples that will deteriorate are refrigerated or frozen. Light sensitive samples are kept in the dark.

4.8.2 There is one 65 m^3 (2,300 ft^3) walk-in cooler in the SMO area. Refrigerated samples go directly to this location after initial check-in. This refrigeration unit is large enough to accommodate a large number of sample containers. There is one 0.6 m^3 freezer (located in lab 227 SLM) for frozen samples. Non-perishable samples are kept in cupboards, shelves, and drawers in the SMO area.

4.8.3 After the Service Request is generated, label the samples and assign a storage location. (See section 4.7 - Label Samples.)

4.8.4 For each SR, complete a Sample Log Sheet. This sheet is placed in the Sample Log Book for samples processed through the SMO. There is one book for Analytical Chemistry and another for the Wet Lab, Paper Lab, & Microscopy labs. The SR is created by SMO for Microstructure, but samples do not usually come through the SMO. The Sample Log Sheet page is designed to track the location and status of samples that come into the lab. For Analytical Chemistry, each SR is assigned a separate page. Enter the SR number, the initials of the person handling the samples, the date you are placing samples in the location, the inclusive sample numbers, number of containers (bottles and bottle type (i.e.- 2X1L MET), plastic bag, envelope, etc.) and the location to which the samples are assigned.

4.8.5 For Wet Lab, Paper Lab, & Microstructure (when necessary), a modified sheet in a separate book is used in the SMO. One SR per line is used. In addition to the SR, enter the initials of the person who placed the samples in a given location, the inclusive sample numbers, the date samples are processed, and the location to which the samples are assigned.

4.8.6 For most of the routine work done for Analytical Chemistry, samples will be assigned to storage locations in the SMO and the laboratory personnel will check out samples from the SMO area. Preserved samples (in particular, those for metals) that can be stored at room temperature should be placed in cupboards C1 or C2. Liquors, caustics, acids, and samples other than waters that are held at room temperature are placed in C3. Secondary containment (plastic 'tubs') is used for all liquors, caustics, and acids. Care should be taken to store samples from each service request together and not to mix samples from more than one SR in the secondary containment 'tub.'

WARNING: Do not store caustics and acids from the same SR together in the same tub. Accidental spills may react violently and burn or otherwise injure personnel.

4.8.7 Use the following codes to designate location in SMO:

216V: where 216 = SMO walk-in cooler and V = assigned shelf number.
D-#: where D = drawer and # =drawer number.
C-#-S: where C = cabinet, # = cabinet number, and S = shelf letter.
S-#: where S = shelf and # = shelf number.

4.8.8 EXEMPTION: VOA lab. Place all samples for volatiles analysis directly in the refrigerator located in the volatiles lab (223 SLM). This location is noted as the lab number then V-1 (223-V-1). Round Robin samples (usually small ampoules) are placed upright in a small beaker and stored in the VOA lab freezer (223 F-1).

4.8.9 When samples are picked up by the lab before being assigned a SMO location, they are noted as lab number followed by P/U (pick-up). If lab 212 SLM picks up samples directly from SMO the location is noted as 212 P/U which indicates that samples were picked up by someone from lab 212. This could be used by any lab location. On occasion, samples may be assigned to other locations. Apply an appropriate description, e.g., "northeast hood in 211," "Eatherton-233," or "G01-'S#.'" Use 'R' when designating refrigerators in lab rooms, e.g., R226N for the refrigerator in NLM 226, and 'F' for freezers. For large projects, samples may need to be kept in the cold room downstairs (G01 or G02).

4.8.10 Analysts shall sign samples out when taking them and sign them back in when they are returned. The log also contains a brief description of any sample modification or preparation, including any sub-sampling.

a. Employees taking samples will log the sample location (not the lab that the employee works in) to which the sample will be taken. At times, more than one lab will be working on the same sample and oral communication takes place regarding the current location of the sample. At the end of the shift, one of these employees logs the sample's location in the Sample Log Book sheet.

b. In the case of sample extractions requiring further analytical work, the extractives will be logged on the Sample Log sheet as to the location in SMO and with the appropriate comments as to the sample preparation performed. For example, a TCLP sample may be prepared in the Metals Lab. This sample will require further analysis in the Chromatography lab. The Metals personnel will return the TCLP sample to SMO, log its location and notify the Chromatography lab of the samples readiness and location. If the Metals personnel puts the samples in the Chromatography lab in order to be helpful, the Metals personnel must still log the location of the sample in the SMO Sample Log sheet.

4.8.11 Samples that are completely used during analysis, (except for O & G), or are returned to the client by analysts, should be noted on the sample log sheet by that analyst with the appropriate 'Disposal' and 'Comment' code noted at the bottom of the Sample Log sheet.

4.8.12 Samples for the Wet Lab are taken to Lab 105 in the high bay. Most are placed in the 50%- RH conditioning room, 105C. Room 105C has boxes and shelves noted for sample drop off. There is a clipboard in 105C where the SMO staff records the delivered samples. The information on the clipboard includes the SR#, the location of the samples and the date that the samples are delivered to the lab. Wet samples are stored in the lab refrigerator, located in lab 105 and are noted on the clipboard sheet.

4.8.13 Most samples for the Paper Lab are placed by the paper lab personnel in the 20% conditioning room overnight. The 20% conditioning room is at the north end of the west corridor on the second floor. There is a clipboard in the 20 % conditioning room where the storage location is noted. The information on the clipboard includes the SR#, the shelf location, and the date samples were delivered to that room. If samples are clipped to wire, the location is wire. Samples for the Paper Lab are picked up daily by paper lab personnel and taken to the appropriate locations.

4.8.14 If the sample for Paper Lab requires optical testing (opacity, scattering, brightness) and is a light-sensitive product, such as newsprint, the sample should be placed (if not so received) in black plastic to prevent discoloring.

4.9 **Disposing of Samples**

4.9.1 Unless otherwise requested, the SMO holds samples that have been assigned to Analytical Chemistry for one month after closing an SR. Samples assigned to Wet Lab or Paper Lab are disposed of or returned to the client by the staff in those areas and never returned to the SMO, unless requested.

4.9.2 Final disposition could be sewering water samples, returning sample to the client, or passing appropriate samples to the Chemical Management unit.

4.9.3 Properly dispose of samples as per the disposal procedure in the appendix of the Chemical Hygiene Plan.

NOTE: If unsure of sample type or disposal method needed, see Chemical Hygiene Officer.

4.9.4 If samples were returned to the client, the return is entered into LIMS. Click on SR+Samples, then click on enter disposal to SR. Type in SR number that needs to be returned. Where it says "actual disposal", choose R for return, where it says "disposal date", enter the date that the sample was returned it to the client.

4.9.5 Upon completion of work, the sample log page is removed, updated as needed and filed in a separate notebook in numerical order. These records will be treated in the same manner as Archived Service Requests (ASR) for storage purposes. (See OQ DOCTRL.)

5.0 QUALITY ASSURANCE

5.1 The refrigerators and freezers are checked daily by assigned personnel from the lab per AQ O-DLYCHK. Refrigerators are kept in the range of 4 ± 2 °C and freezers at <-15 °C. If abnormal conditions are discovered, they are noted in the temperature logbook and the SMO is notified. SMO then takes appropriate action to correct the situation. This may include replacing a thermometer, notifying the project manager, calling (x4200) to initiate repairs, and/or transferring samples to other locations. Lab personnel also make notice of unusual situations in their daily use of the refrigerators.

5.2 Nonconformances include, but are not limited to:

- Broken sample containers
- Irregular preservation or lack of proper preservative
- No COC (Chain of Custody) or improper paperwork
- Insufficient sample
- Received sample temperatures warm
- Id’s don’t match customer lists

6.0 KEY WORDS

OP S-SMO, OP S-SAMPSPLIT, sample disposal, Sample Receipt Form, Sample Log sheet, sample submission, sample management, sample management office, SMO, Chain of Custody (COC), Analytical Chemistry Service Request Form, Pulp & Paper Service Request Form

7.0 REVISION HISTORY

7.1 05 SEPT 2006: Complete revision and update of SMO processes.

7.2 01 FEB 2007: Updated document to reflect changes in Weyerhaeuser structure – PPTS is now known as CFTP.

7.3 28 FEB 2007: Added safety note to section 4.1.2, added information to section 4.4.1.d, changed SOP identification.

7.4 13 JUL 2007: Added references to the appropriate departmental SOPs, corrected typo and numbering errors, corrected section 4.5.1 and added sections a and b to 4.8.10. Also added section 4.8.11 and the appendix.

Appendix

40 CFR136.3

Table II—Required Containers, Preservation Techniques, and Holding Times

Parameter No./name	**Container**[1]	**Preservation**[2,3]	**Maximum holding time**[4]
Table IA—Bacterial Tests:			
1–5. Coliform, total, fecal, and *E. coli*	PA, G	Cool, <10 °C, 0.0008% Na2S2O3[5]	6 hours.[22,23]
6. Fecal streptococci	PA, G	Cool, <10 °C, 0.0008% Na2S2O3[5]	6 hours.[22]
7. Enterococci	PA, G	Cool, <10 °C, 0.0008% Na2S2O3[5]	6 hours.[22]
8. Salmonella	PA, G	Cool, <10 °C, 0.0008% Na2S2O3[5]	6 hours.[22]
Table IA—Aquatic Toxicity Tests:			
9–11. Toxicity, acute and chronic	P, FP, G	Cool, ≤6 °C[16]	36 hours.
Table IB—Inorganic Tests:			
1. Acidity	P, FP, G	Cool, ≤6 °C[18]	14 days.
2. Alkalinity	P, FP, G	Cool, ≤6 °C[18]	14 days.
4. Ammonia	P, FP, G	Cool, ≤6 °C[18], H2SO4 to pH<2	28 days.
9. Biochemical oxygen demand	P, FP, G	Cool, ≤6 °C[18]	48 hours.
10. Boron	P, FP, or Quartz	HNO3 to pH<2	6 months.
11. Bromide	P, FP, G	None required	28 days.
14. Biochemical oxygen demand, carbonaceous	P, FP G	Cool, ≤6 °C[18]	48 hours.
15. Chemical oxygen demand	P, FP, G	Cool, ≤6 °C[18], H2SO4 to pH<2	28 days.
16. Chloride	P, FP, G	None required	28 days.
17. Chlorine, total residual	P, G	None required	Analyze within 15 minutes.
21. Color	P, FP, G	Cool, ≤6 °C[18]	48 hours.
23–24. Cyanide, total or available (or CATC)	P, FP, G	Cool, ≤6 °C[18], NaOH to pH>12[6], reducing agent[5]	14 days.
25. Fluoride	P	None required	28 days.
27. Hardness	P, FP, G	HNO3 or H2SO4 to pH<2	6 months.
28. Hydrogen ion (pH)	P, FP, G	None required	Analyze within 15 minutes.
31, 43. Kjeldahl and organic N	P, FP, G	Cool, ≤6 °C[18], H2SO4 to pH<2	28 days.
Table IB—Metals:[7]			
18. Chromium VI	P, FP, G	Cool, ≤6 °C[18], pH = 9.3–9.7[20]	28 days.
35. Mercury (CVAA)	P, FP, G	HNO3 to pH<2	28 days.
35. Mercury (CVAFS)	FP, G; and FP-lined cap[17]	5 mL/L 12N HCl or 5 mL/L BrCl[17]	90 days.[17]
3, 5–8, 12, 13, 19, 20, 22, 26, 29, 30, 32–34, 36, 37, 45, 47, 51, 52, 58–60, 62, 63, 70–72, 74, 75	P, FP, G	HNO3 to pH<2, or at least 24 hours prior to analysis[19]	6 months.
Metals, except boron, chromium VI, and mercury			
38. Nitrate	P, FP, G	Cool, ≤6 °C[18]	48 hours.
39. Nitrate-nitrite	P, FP, G	Cool, ≤6 °C[18], H2SO4 to pH<2	28 days.
40. Nitrite	P, FP, G	Cool, ≤6 °C[18]	48 hours.

Parameter No./name	Container[1]	Preservation[2,3]	Maximum holding time[4]
41. Oil and grease	G	Cool to ≤6 °C[18], HCl or H_2SO_4 to pH<2	28 days.
42. Organic Carbon	P, FP, G	Cool to ≤6 °C[18], HCl, H_2SO_4, or H_3PO_4 to pH<2	28 days.
44. Orthophosphate	P, FP, G	Cool, ≤6 °C[18]	Filter within 15 minutes; Analyze within 48 hours.
46. Oxygen, Dissolved Probe	G, Bottle and top	None required	Analyze within 15 minutes.
47. Winkler	G, Bottle and top	Fix on site and store in dark	8 hours.
48. Phenols	G	Cool, ≤6 °C[18], H_2SO_4 to pH<2	28 days.
49. Phosphorous (elemental)	G	Cool, ≤6 °C[18]	48 hours.
50. Phosphorous, total	P, FP, G	Cool, ≤6 °C[18], H_2SO_4 to pH<2	28 days.
53. Residue, total	P, FP, G	Cool, ≤6 °C[18]	7 days.
54. Residue, Filterable	P, FP, G	Cool, ≤6 °C[18]	7 days.
55. Residue, Nonfilterable (TSS)	P, FP, G	Cool, ≤6 °C[18]	7 days.
56. Residue, Settleable	P, FP, G	Cool, ≤6 °C[18]	48 hours.
57. Residue, Volatile	P, FP, G	Cool, ≤6 °C[18]	7 days.
61. Silica	P or Quartz	Cool, ≤6 °C[18]	28 days.
64. Specific conductance	P, FP, G	Cool, ≤6 °C[18]	28 days.
65. Sulfate	P, FP, G	Cool, ≤6 °C[18]	28 days.
66. Sulfide	P, FP, G	Cool, ≤6 °C[18], add zinc acetate plus sodium hydroxide to pH>9	7 days.
67. Sulfite	P, FP, G	None required	Analyze within 15 minutes.
68. Surfactants	P, FP, G	Cool, ≤6 °C[18]	48 hours.
69. Temperature	P, FP, G	None required	Analyze.
73. Turbidity	P, FP, G	Cool, ≤6 °C[18]	48 hours.
Table IC—Organic Tests[8]			
13, 18–20, 22, 24–28, 34–37, 39–43, 45–47, 56, 76, 104, 105, 108–111, 113. Purgeable Halocarbons	G, FP-lined septum	Cool, ≤6 °C[18], 0.008% $Na_2S_2O_3$[5]	14 days.
6, 57, 106. Purgeable aromatic hydrocarbons	G, FP-lined septum	Cool, ≤6 °C[18], 0.008% $Na_2S_2O_3$[5], HCl to pH 2[9]	14 days.[9]
3, 4. Acrolein and acrylonitrile	G, FP-lined septum	Cool, ≤6 °C[18], 0.008% $Na_2S_2O_3$[5], pH to 4–5[10]	14 days.[10]
23, 30, 44, 49, 53, 77, 80, 81, 98, 100, 112. Phenols[11]	G, FP-lined cap	Cool, ≤6 °C[18], 0.008% $Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction.
7, 38. Benzidines[11,12]	G, FP-lined cap	Cool, ≤6 °C[18], 0.008% $Na_2S_2O_3$[5]	7 days until extraction.[13]
14, 17, 48, 50–52. Phthalate esters[11]	G, FP-lined cap	Cool, ≤6 °C[18]	7 days until extraction, 40 days after extraction.
82–84. Nitrosamines[11,14]	G, FP-lined cap	Cool, ≤6 °C[18], store in dark, 0.008% $Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction.
88–94. PCBs[11]	G, FP-lined cap	Cool, ≤6 °C[18]	1 year until extraction, 1 year after extraction.
54, 55, 75, 79. Nitroaromatics and isophorone[11]	G, FP-lined cap	Cool, ≤6 °C[18], store in dark, 0.008% $Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction.
1, 2, 5, 8–12, 32, 33, 58, 59, 74, 78, 99, 101. Polynuclear aromatic hydrocarbons[11]	G, FP-lined cap	Cool, ≤6 °C[18], store in dark, 0.008% $Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction.

Parameter No./name	Container[1]	Preservation[2,3]	Maximum holding time[4]
15, 16, 21, 31, 87. Haloethers[11]	G, FP-lined cap	Cool, ≤6 ℃[18], 0.008% $Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction.
29, 35–37, 63–65, 107. Chlorinated hydrocarbons[11]	G, FP-lined cap	Cool, ≤6 ℃[18]	7 days until extraction, 40 days after extraction.
60–62, 66–72, 85, 86, 95–97, 102, 103. CDDs/CDFs[11]			
Aqueous Samples: Field and Lab Preservation	G	Cool, ≤6 ℃[18], 0.008% $Na_2S_2O_3$[5], pH<9	1 year.
Solids and Mixed-Phase Samples: Field Preservation	G	Cool, ≤6 ℃[18]	7 days.
Tissue Samples: Field Preservation	G	Cool, ≤6 ℃[18]	24 hours.
Solids, Mixed-Phase, and Tissue Samples: Lab Preservation	G	Freeze, ≤−10 ℃	1 year.
Table ID—Pesticides Tests:			
1–70. Pesticides[11]	G, FP-lined cap	Cool, ≤6 ℃[18], pH 5–9[15]	7 days until extraction, 40 days after extraction.
Table IE—Radiological Tests:			
1–5. Alpha, beta, and radium	P, FP, G	HNO_3 to pH<2	6 months.
Table IH—Bacterial Tests:			
1. *E. coli*	PA, G	Cool, <10 ℃, 0.0008% $Na_2S_2O_3$[5]	6 hours.[22]
2. Enterococci	PA, G	Cool, <10 ℃, 0.0008% $Na_2S_2O_3$[5]	6 hours.[22]
Table IH—Protozoan Tests:			
8. Cryptosporidium	LDPE; field filtration	0–8 ℃	96 hours.[21]
9. Giardia	LDPE; field filtration	0–8 ℃	96 hours.[21]

[1]“P” is polyethylene; “FP” is fluoropolymer (polytetrafluoroethylene (PTFE; Teflon&supreg;), or other fluoropolymer, unless stated otherwise in this Table II; “G” is glass; “PA” is any plastic that is made of a sterlizable material (polypropylene or other autoclavable plastic); “LDPE” is low density polyethylene.

[2]Except where noted in this Table II and the method for the parameter, preserve each grab sample within 15 minutes of collection. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), refrigerate the sample at ≤6 ℃ during collection unless specified otherwise in this Table II or in the method(s). For a composite sample to be split into separate aliquots for preservation and/or analysis, maintain the sample at ≤6 ℃, unless specified otherwise in this Table II or in the method(s), until collection, splitting, and preservation is completed. Add the preservative to the sample container prior to sample collection when the preservative will not compromise the integrity of a grab sample, a composite sample, or an aliquot split from a composite sample; otherwise, preserve the grab sample, composite sample, or aliquot split from a composite sample within 15 minutes of collection. If a composite measurement is required but a composite sample would compromise sample integrity, individual grab samples must be collected at prescribed time intervals (e.g., 4 samples over the course of a day, at 6-hour intervals). Grab samples must be analyzed separately and the concentrations averaged. Alternatively, grab samples may be collected in the field and composited in the laboratory if the compositing procedure produces results equivalent to results produced by arithmetic averaging of the results of analysis of individual grab samples. For examples of laboratory compositing procedures, see EPA Method 1664A (oil and grease) and the procedures at 40 CFR 141.34(f)(14)(iv) and (v) (volatile organics).

[3]When any sample is to be shipped by common carrier or sent via the U.S. Postal Service, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

[4]Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before the start of analysis and still be considered valid (e.g., samples analyzed for fecal coliforms may be held up to 6 hours prior to commencing analysis). Samples may be held for longer periods only if the permittee or monitoring laboratory has data on file to show that, for the specific types of samples under study, the analytes are stable for the longer time, and has received a variance from the Regional Administrator under §136.3(e). For a grab sample, the holding time begins at the time of collection. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), the holding time begins at the time of the end of collection of the composite sample. For a set of grab samples composited in the field or laboratory, the holding time begins at the time of collection of the last grab sample in the set. Some samples may not be stable for the maximum time period given in the table. A permittee or monitoring laboratory is obligated to hold the sample for a shorter time if it knows that a shorter time is necessary to maintain sample stability. See §136.3(e) for details. The date and time of collection of an individual grab sample is the date and time at which the sample is collected. For a set of grab samples to be composited, and that are all collected on the same calendar date, the date of collection is the date on which the samples are collected. For a set of grab samples to be composited, and that are collected across two calendar dates, the date of collection is the dates of the two days; e.g., November 14–15. For a composite sample collected automatically on a given date, the date of collection is the date on which the sample is collected. For a composite sample collected automatically, and that is collected across two calendar dates, the date of collection is the dates of the two days; e.g., November 14–15.

[5]Add a reducing agent only if an oxidant (e.g., chlorine) is present. Reducing agents shown to be effective are sodium thiosulfate (Na2S2O3), ascorbic acid, sodium arsenite (NaAsO2), or sodium borohydride (NaBH4). However, some of these agents have been shown to produce a positive or negative cyanide bias, depending on other substances in the sample and the analytical method used. Therefore, do not add an excess of reducing agent. Methods recommending ascorbic acid (e.g., EPA Method 335.4) specify adding ascorbic acid crystals, 0.1–0.6 g, until a drop of sample produces no color on potassium iodide (KI) starch paper, then adding 0.06 g (60 mg) for each liter of sample volume. If NaBH4 or NaAsO2 is used, 25 mg/L NaBH4 or 100 mg/L NaAsO2 will reduce more than 50 mg/L of chlorine (see method "Kelada-01" and/or Standard Method 4500–$CN^-$for more information). After adding reducing agent, test the sample using KI paper, a test strip (e.g. for chlorine, SenSafe™Total Chlorine Water Check 480010) moistened with acetate buffer solution (see Standard Method 4500–Cl.C.3e), or a chlorine/oxidant test method (e.g., EPA Method 330.4 or 330.5), to make sure all oxidant is removed. If oxidant remains, add more reducing agent. Whatever agent is used, it should be tested to assure that cyanide results are not affected adversely.

[6]Sample collection and preservation: Collect a volume of sample appropriate to the analytical method in a bottle of the material specified. If the sample can be analyzed within 48 hours and sulfide is not present, adjust the pH to > 12 with sodium hydroxide solution (e.g., 5% w/v), refrigerate as specified, and analyze within 48 hours. Otherwise, to extend the holding time to 14 days and mitigate interferences, treat the sample immediately using any or all of the following techniques, as necessary, followed by adjustment of the sample pH to > 12 and refrigeration as specified. There may be interferences that are not mitigated by approved procedures. Any procedure for removal or suppression of an interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide. Particulate cyanide (e.g., ferric ferrocyanide) or a strong cyanide complex (e.g., cobalt cyanide) are more accurately measured if the laboratory holds the sample at room temperature and pH > 12 for a minimum of 4 hours prior to analysis, and performs UV digestion or dissolution under alkaline (pH=12) conditions, if necessary.

(1) Sulfur: To remove elemental sulfur (S8), filter the sample immediately. If the filtration time will exceed 15 minutes, use a larger filter or a method that requires a smaller sample volume (e.g., EPA Method 335.4 or Lachat Method 01). Adjust the pH of the filtrate to > 12 with NaOH, refrigerate the filter and filtrate, and ship or transport to the laboratory. In the laboratory, extract the filter with 100 mL of 5% NaOH solution for a minimum of 2 hours. Filter the extract and discard the solids. Combine the 5% NaOH-extracted filtrate with the initial filtrate, lower the pH to approximately 12 with concentrated hydrochloric or sulfuric acid, and analyze the combined filtrate. Because the detection limit for cyanide will be increased by dilution by the filtrate from the solids, test the sample with and without the solids procedure if a low detection limit for cyanide is necessary. Do not use the solids procedure if a higher cyanide concentration is obtained without it. Alternatively, analyze the filtrates from the sample and the solids separately, add the amounts determined (in µg or mg), and divide by the original sample volume to obtain the cyanide concentration.

(2) Sulfide: If the sample contains sulfide as determined by lead acetate paper, or if sulfide is known or suspected to be present, immediately conduct one of the volatilization treatments or the precipitation treatment as follows: Volatilization—Headspace expelling. In a fume hood or well-ventilated area, transfer 0.75 liter of sample to a 4.4 L collapsible container (e.g., Cubitainer™). Acidify with concentrated hydrochloric acid to pH < 2. Cap the container and shake vigorously for 30 seconds. Remove the cap and expel the headspace into the fume hood or open area by collapsing the container without expelling the sample. Refill the headspace by expanding the container. Repeat expelling a total of five headspace volumes. Adjust the pH to > 12, refrigerate, and ship or transport to the laboratory. Scaling to a smaller or larger sample volume must maintain the air to sample volume ratio. A larger volume of air will result in too great a loss of cyanide (> 10%). Dynamic stripping: In a fume hood or well-ventilated area, transfer 0.75 liter of sample to a container of the material specified and acidify with concentrated hydrochloric acid to pH < 2. Using a calibrated air sampling pump or flowmeter, purge the acidified sample into the fume hood or open area through a fritted glass aerator at a flow rate of 2.25 L/min for 4 minutes. Adjust the pH to > 12, refrigerate, and ship or transport to the laboratory. Scaling to a smaller or larger sample volume must maintain the air to sample volume ratio. A larger volume of air will result in too great a loss of cyanide (> 10%). Precipitation: If the sample contains particulate matter that would be removed by filtration, filter the sample prior to treatment to assure that cyanide associated with the particulate matter is included in the measurement. Ship or transport the filter to the laboratory. In the laboratory, extract the filter with 100 mL of 5% NaOH solution for a minimum of 2 hours. Filter the

extract and discard the solids. Combine the 5% NaOH-extracted filtrate with the initial filtrate, lower the pH to approximately 12 with concentrated hydrochloric or sulfuric acid, and analyze the combined filtrate. Because the detection limit for cyanide will be increased by dilution by the filtrate from the solids, test the sample with and without the solids procedure if a low detection limit for cyanide is necessary. Do not use the solids procedure if a higher cyanide concentration is obtained without it. Alternatively, analyze the filtrates from the sample and the solids separately, add the amounts determined (in µg or mg), and divide by the original sample volume to obtain the cyanide concentration. For removal of sulfide by precipitation, raise the pH of the sample to > 12 with NaOH solution, then add approximately 1 mg of powdered cadmium chloride for each mL of sample. For example, add approximately 500 mg to a 500-mL sample. Cap and shake the container to mix. Allow the precipitate to settle and test the sample with lead acetate paper. If necessary, add cadmium chloride but avoid adding an excess. Finally, filter through 0.45 micron filter. Cool the sample as specified and ship or transport the filtrate and filter to the laboratory. In the laboratory, extract the filter with 100 mL of 5% NaOH solution for a minimum of 2 hours. Filter the extract and discard the solids. Combine the 5% NaOH-extracted filtrate with the initial filtrate, lower the pH to approximately 12 with concentrated hydrochloric or sulfuric acid, and analyze the combined filtrate. Because the detection limit for cyanide will be increased by dilution by the filtrate from the solids, test the sample with and without the solids procedure if a low detection limit for cyanide is necessary. Do not use the solids procedure if a higher cyanide concentration is obtained without it. Alternatively, analyze the filtrates from the sample and the solids separately, add the amounts determined (in µg or mg), and divide by the original sample volume to obtain the cyanide concentration. If a ligand-exchange method is used (e.g., ASTM D6888), it may be necessary to increase the ligand-exchange reagent to offset any excess of cadmium chloride.

(3) Sulfite, thiosulfate, or thiocyanate: If sulfite, thiosulfate, or thiocyanate is known or suspected to be present, use UV digestion with a glass coil (Method Kelada-01) or ligand exchange (Method OIA–1677) to preclude cyanide loss or positive interference.

(4) Aldehyde: If formaldehyde, acetaldehyde, or another water-soluble aldehyde is known or suspected to be present, treat the sample with 20 mL of 3.5% ethylenediamine solution per liter of sample.

(5) Carbonate: Carbonate interference is evidenced by noticeable effervescence upon acidification in the distillation flask, a reduction in the pH of the absorber solution, and incomplete cyanide spike recovery. When significant carbonate is present, adjust the pH to ≥12 using calcium hydroxide instead of sodium hydroxide. Allow the precipitate to settle and decant or filter the sample prior to analysis (also see Standard Method 4500–CN.B.3.d).

(6) Chlorine, hypochlorite, or other oxidant: Treat a sample known or suspected to contain chlorine, hypochlorite, or other oxidant as directed in footnote 5.

[7]For dissolved metals, filter grab samples within 15 minutes of collection and before adding preservatives. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), filter the sample within 15 minutes after completion of collection and before adding preservatives. If it is known or suspected that dissolved sample integrity will be compromised during collection of a composite sample collected automatically over time (e.g., by interchange of a metal between dissolved and suspended forms), collect and filter grab samples to be composited (footnote 2) in place of a composite sample collected automatically.

[8]Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

[9]If the sample is not adjusted to pH 2, then the sample must be analyzed within seven days of sampling.

[10]The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.

[11]When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity (i.e., use all necessary preservatives and hold for the shortest time listed). When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to ≤6 °C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6–9; samples preserved in this manner may be held for seven days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (regarding the requirement for thiosulfate reduction), and footnotes 12, 13 (regarding the analysis of benzidine).

[12]If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0 ± 0.2 to prevent rearrangement to benzidine.

[13]Extracts may be stored up to 30 days at < 0 °C.

[14]For the analysis of diphenylnitrosamine, add 0.008% Na2S2O3 and adjust pH to 7–10 with NaOH within 24 hours of sampling.

[15]The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% Na2S2O3.

[16]Sufficient ice should be placed with the samples in the shipping container to ensure that ice is still present when the samples arrive at the laboratory. However, even if ice is present when the samples arrive, it is necessary to immediately measure the

temperature of the samples and confirm that the preservation temperature maximum has not been exceeded. In the isolated cases where it can be documented that this holding temperature cannot be met, the permittee can be given the option of on-site testing or can request a variance. The request for a variance should include supportive data which show that the toxicity of the effluent samples is not reduced because of the increased holding temperature.

[17]Samples collected for the determination of trace level mercury (<100 ng/L) using EPA Method 1631 must be collected in tightly-capped fluoropolymer or glass bottles and preserved with BrCl or HCl solution within 48 hours of sample collection. The time to preservation may be extended to 28 days if a sample is oxidized in the sample bottle. A sample collected for dissolved trace level mercury should be filtered in the laboratory within 24 hours of the time of collection. However, if circumstances preclude overnight shipment, the sample should be filtered in a designated clean area in the field in accordance with procedures given in Method 1669. If sample integrity will not be maintained by shipment to and filtration in the laboratory, the sample must be filtered in a designated clean area in the field within the time period necessary to maintain sample integrity. A sample that has been collected for determination of total or dissolved trace level mercury must be analyzed within 90 days of sample collection.

[18]Aqueous samples must be preserved at ≤6 °C, and should not be frozen unless data demonstrating that sample freezing does not adversely impact sample integrity is maintained on file and accepted as valid by the regulatory authority. Also, for purposes of NPDES monitoring, the specification of “≤ °C” is used in place of the “4 °C” and “< 4 °C” sample temperature requirements listed in some methods. It is not necessary to measure the sample temperature to three significant figures (1/100th of 1 degree); rather, three significant figures are specified so that rounding down to 6 °C may not be used to meet the ≤6 °C requirement. The preservation temperature does not apply to samples that are analyzed immediately (less than 15 minutes).

[19]An aqueous sample may be collected and shipped without acid preservation. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. If the sample must be analyzed within 24 hours of collection, add the acid immediately (see footnote 2). Soil and sediment samples do not need to be preserved with acid. The allowances in this footnote supersede the preservation and holding time requirements in the approved metals methods.

[20]To achieve the 28-day holding time, use the ammonium sulfate buffer solution specified in EPA Method 218.6. The allowance in this footnote supersedes preservation and holding time requirements in the approved hexavalent chromium methods, unless this supersession would compromise the measurement, in which case requirements in the method must be followed.

[21]Holding time is calculated from time of sample collection to elution for samples shipped to the laboratory in bulk and calculated from the time of sample filtration to elution for samples filtered in the field.

[22]Samples analysis should begin immediately, preferably within 2 hours of collection. The maximum transport time to the laboratory is 6 hours, and samples should be processed within 2 hours of receipt at the laboratory.

[23]For fecal coliform samples for sewage sludge (biosolids) only, the holding time is extended to 24 hours for the following sample types using either EPA Method 1680 (LTB–EC) or 1681 (A–1): Class A composted, Class B aerobically digested, and Class B anaerobically digested.

[38 FR 28758, Oct. 16, 1973]