Standard Operating Procedure for:

ANALYSIS OF CHLORINATED PESTICIDES, PYRETHROIDS, TRACERS, AND PCBs IN WATER SAMPLES USING SOLID PHASE EXTRACTION AND GC/MS/MS

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1.0 SCOPE AND APPLICATION

This method is applicable to the determination of selected organochlorine pesticides, pyrethroids, some environmental tracers and PCB aroclors in water as listed in Tables 1A and 1B. Method Detection Limits and Practical Quantitation Limits yielded by this method are also provided in Tables 1A and 1B.

1.1 The preparation part of this method is based on EPA 3535A (ref 15.6). Since EPA 3535A is a guidance method rather than a specific protocol this procedure also incorporates some elements of USGS-Method-O-1126-95. The analytical part is based on EPA 8270E (ref 15.1) Laboratory Information Management System (LIMS) tests: W-PCL-TQ-R, and W-PCB-TQ-R. it also covers TCLP/SPLP samples under tests TCLP-CL-TQ, SPLP-CL-TQ and SPLP-PCBTQ.

1.2 This Standard Operation Procedure is restricted to use by an analyst experienced in the use of an Agilent 7010 GC/MS/MS system, and in the use of appropriate computer programs. The minimum qualifications required:

- B.S. in Chemistry or Biochemistry with minimum one year of professional chemical or biochemical experience
- Knowledge of principles and practice of gas chromatography/mass spectrometry
- Ability to perform basic laboratory mathematics
- Knowledge of the Masshunter GC/MS/MS software and DEP LIMS.

2.0 SUMMARY OF THE METHOD

2.1. General description.
Water samples are extracted using C-18 solid phase extraction (as per EPA 3535A with some elements of USGS-Method-O-1126-95). The extracts are analyzed using an Agilent 7010 GC/MS/MS system. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of the characteristic MRM transitions. Quantitative analysis is performed using an internal standard technique. In addition to tests specified in 1.1 the prep method described here is also used for test W-CT-CI-R (see ref 15.16 for analysis).

2.2 Agilent Masshunter Optimizer.
Agilent Masshunter Optimizer software (ref. 15.6) is used to perform MRM optimization to find most suitable transitions for target analytes for GC analysis. The Optimizer is a version of the Agilent acquisition software. An individual standard of a pesticide is prepared at a suitable concentration and used for the MRM study. In fully automated mode the software runs a full scan analysis and picks precursor ions, follows with a SIM mode analysis to determine the product ions and then finally performs the MRM optimization for all the transitions for collision energies. Since the final result can be a very large table summarizing all the transitions arranged by abundance, for practical purposes the procedure is usually done stepwise to select the most promising precursor ions for further study to save on time and limit the amount of data generated. Once the final MRM table is obtained several of the most abundant transitions are further tested for possible interferences from the instrument background and to get an estimation of the MDL. Typically, the most abundant transition is used as a quantifier and the second one as a qualifier. The transitions are also tested for interferences from real environmental samples. Once all these steps are completed, the MDL validation is performed.

2.3 Preparation method modifications as compared to EPA 3535A:

2.3.1 The samples' pH is adjusted to 3.0 as opposed to neutral. pH 3.0 improves recoveries of some analytes with no negative effects on other.

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2.3.2 The Kuderna-Danish (k-D) concentration technique is eliminated entirely. The sample extracts go straight to N-Evap for volume reduction.

2.3.4 Final volume 0.25 ml rather than "around" 100 ul). 100 ul is hard to measure with the existing test tubes; Greater sensitivity of Agilent 7010 GC/MS/MS allows for higher final volumes, which also mean less matrix injected on the instruments (less maintenance and less interferences).

2.3.5 Sample volume 500 ml rather than 1 L. 1L sample volumes are notoriously difficult to aspire through SPE cartridges, even if pre-filtered. Due to increased sensitivity of Agilent 7010 GC/MS/MS sample volume reduction was feasible.

2.4 Modifications to analytical method as EPA 8270E:

The analysis uses analyte protectants (Ethoxyglycerin, Gulonolactone and Sorbitol). Those compounds are injected using the sandwich technique at 25,000ppm/2500ppm/5000ppm respectively. Analyte protectants are necessary to suppress matrix induced response enhancement effects. The 7010 GC/MS/MS seem to be especially sensitive to those kinds of effects.

The degradation /tailing factor mix is run at lower concentration (5 ppm instead of 50 ppm) to reduce carry-over effects with DDT-p,p'. Only pentachlorophenol peak is used to determine the tailing factors. Benzidine peak is not detected in the presence of the analyte protectants. Since the absence of Benzidine peak does not have any bearing on the analysis of the target analytes it is considered inconsequential for the purpose of this analysis.

The method uses different internal standards and a different surrogate that suggested in EPA 8270E due to their closer similarity to the target analytes.

3.0 INTERFERENCES

Raw GC/MS/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. To reduce carryover, rinse the syringe several times with solvent between samples. It may be necessary to analyze one or more solvent blanks between samples and even change out the syringe in extreme cases.

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must routinely demonstrate to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by rinsing with DI water. The glassware should then be drained dry and heated in a muffle furnace at 550 °C for 8 hours. Some thermally stable materials may not be eliminated by this treatment.

Solvent rinses with acetone and pesticide quality hexane may supplement the muffle furnace heating. Volumetric glassware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil. The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required or irradiation with UV light. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the sample characteristics.

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4.0 DEFINITIONS

ACCURACY: The closeness of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random component and of a common systematic error (or bias) component.

BATCH: A group of samples, which behave similarly with respect to the sampling or the testing procedures being employed, that are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

BIAS: The deviation due to matrix effects of the measured value (Xs - Xu) from a known spiked amount. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike). Thus, the bias (B) due to matrix effects based on a matrix spike is calculated as:

$$B = (Xs - Xu) - K$$

where:
Xs = measured value for spiked sample,
Xu = measured value for unspiked sample, and
K = known value of the spike in the sample.

Using the following equation yields the percent recovery (%R).

$$\%R = 100 (Xs - Xu) / K$$

PRACTICAL QUANTITATION LIMIT (PQL): The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The PQL is generally 3 to 5 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the PQL concentration is selected as the lowest non-zero standard in the calibration curve. Sample PQLs are highly matrix dependent.

FIELD DUPLICATES: Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.

INTERNAL STANDARD: A pure compound added to a sample extract in known amounts and used to calibrate concentration measurements of other compounds that are sample components. The internal standard must be a compound that is not a sample component.

LABORATORY FORTIFIED BLANK/LABORATORY CONTROL SAMPLE (LFB/LCS): A known matrix material spiked with compound(s) representative of the target analytes. The LFB is analyzed exactly the same way as other samples. This is used to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

MATRIX: The component or substrate (e.g., surface water, drinking water) which contains the analyte of interest.

MATRIX SPIKE: An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.

MATRIX SPIKE DUPLICATES: A second aliquot of the same sample used for matrix spike spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

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METHOD BLANK: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank must be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process. For a method blank to be acceptable for use with the accompanying samples, the concentration in the blank of any analyte of concern shall not be higher than the method detection limit.

METHOD DETECTION LIMIT (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte. For operational purposes, when it is necessary to determine the MDL in the matrix, the MDL should be determined by multiplying the appropriate one-sided 99% t-statistic by the standard deviation obtained from a minimum of seven analyses of a matrix spike containing the analyte of interest at a concentration one to five times the estimated MDL.

ORGANIC-FREE REAGENT WATER: All references to water in the method refer to water in which interference is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free de-ionized water.

PRECISION: The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate analyses. These samples should contain concentrations of analyte above the MDL and involve the use of matrix spikes or laboratory fortified blanks. The estimates of precision are based on the relative percent difference (RPD).

$$RPD = 100 [2 (X1 - X2) / (X1 + X2)]$$

where X1 and X2 are the two measurements

INITIAL CALIBRATION VERIFICATION (ICV): A standard solution from a source, other than normal calibration standards, that is certified and traceable. These standards are used to check the accuracy of a calibration curve immediately after the calibration standards are run.

CONTINOUS CALIBRATION VERIFICATION (CCV): A standard solution from a source that is certified and traceable. These standards are used to check the accuracy of a calibration curve.

SPIKE SOLUTION (SS): A solution of method analytes of known concentrations that is used to fortify an aliquot of laboratory reagent water or sample matrix.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards, which cover the working range of the instrument. Standards should be prepared at the frequency specified in section six (6) of this SOP. The calibration standards should be prepared using the same type of solvent as the final sample preparation solvent.

SURROGATE: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Surrogates are used to monitor the preparation and are added to each field and QC sample prior to extraction.

5.0 APPARATUS AND EQUIPMENT

5.1 Apparatus.
Agilent 7010 GC/MS/MS with High Sensitivity Source, or equivalent is recommended. The instrument must be temperature programmable with an injector port designed for cold splitless injection. A Multi-Mode Inlet (MMI) may be used if available. The GC, GC Automatic Sampler and MSD operating parameters are summarized in Appendix 1. The analytical column is an HP-5MS UI or equivalent, fused

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silica capillary, 20 m x 0.25 mm x 0.25 um or similar column with Ultimate Union placed after the initial 5 m of the column (5m-15m mid-column backflash configuration).

5.2 Data system
A computer system is interfaced to the GC/MS/MS that allows the continuous acquisition and storage on machine-readable media of all chromatographic measurements obtained throughout the duration of the chromatographic run sequence program.

This system currently uses the Masshunter software from Agilent Technologies Inc. For reporting data, the system currently uses DEP LIMS.

5.3 Gases
Helium, UPC Grade or higher, is used as the carrier and collision cell gas. The helium is passed through an oxygen and a hydrocarbon filters before it enters the GC.

6.0 REAGENTS AND CHEMICALS

6.1 Solvents

Methylene Chloride, Fisher Scientific, Pesticide, HPLC or OPTIMA grade.
Isooctane, Fisher Scientific, Pesticide, HPLC or OPTIMA grade.
Acetone, Fisher Scientific, Pesticides, HPLC or Optima grade.
Hydrochloric acid, Fisher Scientific.

6.2 Standards
For description of standard preparations see APPENDICES 2 and 3

6.3 Stock and Intermediate Standards

6.3.1 Custom made stock standards and/or neat standards for individual analytes are purchased from commercial suppliers. Their concentrations are recorded in the standard preparation tracker (part of LIMS). Two different sources of stock standards are normally purchased from two different suppliers; if not available then two different lots are purchased from one supplier.

6.3.2 Intermediate standard solutions are mixtures of individual standards used to prepare working standards. They are prepared in our lab from stock standards by mixing / diluting with isooctane or acetone. They can also be purchased from a certified manufacturer (ISO 9000 or EPA certified). The concentrations of the components in the intermediate standard are typically in the low mg/L (ppm) range. Intermediate standards are replaced once per year. New standard is checked vs. a second source (QC Standard), after diluting it to one of the working standard levels. The typical criterion of acceptance is +/- 10% difference. All standard preparations and verifications have to be recorded in the Standard Preparation Tracker located in DEP LIMS. A list containing all working standards used in the analysis with their serial numbers must be part of analysis documentation folder.

6.4 Working Standard Solutions (Calibration standards)

Working standard solutions are a series of diluted individual or mixed standards in isooctane. They are used for calibration and are prepared by diluting intermediate standard solutions. The internal standard mixtures listed below are added to every working standard at 100 µg/L.

Internal Standard Mixture for CL analytes and PCBs:

Trifluralin-d14
Alpha-BHC-d6

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2,5-Dichlorobiphenyl-2',3',4',5',6'-d5 (DCB-d5)
2,3,5,6-Tetrachlorobiphenyl-2',3',4',5',6'-d5 (TCB-d5)
2,3,3',4,4'5-Hexachlorobiphenyl-2',6,6'-d3 (HCB-d3)
DDT-p,p'-d8
Dicofol-d8
Octachloronaphthalene

The concentrations for each analyte in the working (calibration) standards are listed in Table 2 for chlorinated pesticides. The second source/ICV standard is prepared at a midpoint level.

6.5 Spiking Solution

These solutions are used when fortifying sample matrix spikes or lab fortified blanks at extraction. These fortified samples are used to verify the accuracy and precision of the sample preparation and analysis.

Spike solutions are prepared by diluting stock or intermediate standards with acetone.

Freshly prepared spike solutions are checked vs. valid working standards. The acceptance criterion is ± 20% difference.

6.6 Initial Calibration Verification (ICV). A standard solution from a source, other than normal calibration standards, that is certified and traceable. These standards are used to check the accuracy of a calibration curve immediately after the calibration standards are run. The acceptance criterion is ± 30%.

6.7 Continuous Calibration Verification (CCV). A mid-level calibration standard solution from a source that is certified and traceable. These standards are used to check the accuracy of a calibration curve on daily bases.

6.7.1 The acceptance criterion is ± 20% difference.

6.7.2 The Analyst must ensure that the instrument response is checked with the corresponding CCV before running samples and then in 12 hrs intervals.

6.8 Analyte protectants.

The use of analyte protectants was proposed by Anastassiades et al. (ref 15-3 and 15-4) and it has become an established practice for pesticides analysis in food products analysis, using triple quad GC/MS/MS technology. Matrix induced response enhancements make exact quantitation problematic, especially for some analytes. Analyte protectants are generally very polar organic compounds injected at very high concentrations along with every standard and sample in the analytical run sequence.

Due to their polarity, they are thought to deactivate all the active sites in the system, and, due to their very high concentration, they render all the other matrices in the samples basically insignificant. In effect all the samples and standards injected into the GC/MS/MS system have effectively the same matrix – the analyte protectants – and therefore matrix induced response differences are greatly reduced. This method uses a mixture of three specific analyte protectant compounds: Ethoxyglycerin, Gulonolactone and Sorbitol at 25000 ppm, 2500 ppm and 5000 ppm respectively.

Due to solubility considerations the working solution is prepared in MeOH containing 5% of DI water. It is injected along with every standard and sample using a "sandwich injection" technique. 0.4 uL of the above analyte protectants mixture is injected, which corresponds to 5.0 ug, 0.5 ug and 1 ug of the corresponding analyte protectants on column. 10% glacial acetic acid in MeOH is used in the second layer (middle) of the three layer "sandwich". The presence of the trace amounts of acetic acid during the injection reduces the decomposition of Dicofol and Chlorothalonil in the inlet.

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7.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples must be collected in glass containers with Teflon-lined screw caps. All samples and sample extracts must be refrigerated at 6 degrees C or less from time of collection until extraction.

All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction. If the water samples are to be analyzed for aldrin and residual chlorine is present, then add 80 mg of Sodium Thiosulfate per 1 L of sample and mix well. If chlorine is present , the sample results for aldrin need to be qualified and commented.

8.0 SAMPLE PREPARATION PROCEDURE

8.1 Prep method summary
The water samples are filtered using glass-fiber filters with 0.7 um pore diameter to remove suspended particulate matter. The pH of water samples is adjusted to 3.0 with Hydrochloric acid and the samples are pumped through 500 mg C-18 SPE columns, preconditioned with DI water at pH=2.5. The SPE columns are dried using a gentle stream nitrogen to remove residual water. The absorbed pesticides/PCBs are then eluted from the columns by using methylene chloride. 25 ul of 1000 ppb internal standards mix is then added and the eluent is further evaporated using gentle stream of nitrogen followed by solvent exchange to iso-octane. The final volume is 0.25 ml.

8.2 Background contamination
Extreme care has to be exercised by all the laboratory staff involved in preparation and analysis to limit background contamination due to very low detection limits achievable with the Agilent 7010 GC/MS/MS systems. DI water should be used to perform both method blanks and Laboratory Fortified Blanks due to low level pesticide contamination usually found in both tap water and well water.

8.3 Glassware and consummables

General use organic preparations glassware and supplies are listed in SOP GC-002-2 (ref 15.15).
JTBaker or similar vacuum manifold with Luer lock connectors and stopcocks and 75 mL reservoir tubes.
Restek 3 mL, 500 mg C-18 cartridges, cat no: 24050 or Restek 6 mL, 1000 mg C-18 cartridges, cat no: 28963 or Agilent 500 mg, 3 mL Bond Elute C-18 cartridges cat no: 12102028 or Agilent 1 g, 6 mL Bond Elute C-18 cartridges cat no: 12256001.
Empore Filter-aid 400, 3M Corporation, Fisher cat: 14-378-6

8.4 SPE extraction procedure

8.4.1 Pre-filter the samples using 0.7 um glass-fiber filter to remove particulate matter. The filtration is necessary to avoid clogging of the SPE cartridges. The entire 0.5 mL bottle of sample should be filtered at this stage into pre-weighted 600 mL glass beaker. Weigh the bottle with the sample and without to determine sample volume. In some, rare cases, it may be necessary to extract smaller volume of sample (i.e. 50 ml). This typically happens when very high positives are expected in the sample and there is a possibility of loses during the extraction step due to limited SPE column's capacity. **Occasionally, samples maybe be received in one-liter bottles due to sampling mistake. In such cases the 1L samples are shaken/stirred vigorously and half of the volume is discarded in accordance with the waste disposal procedures. The remainder is treated like a regular 500 mL sample and processed accordingly.**

8.4.2 SPE column pre-cleaning: pre-clean the 500 mg C-18 SPE columns by rinsing with 2x3 ml of methylene chloride. The columns should be installed on the SPE vacuum manifold. Allow the solvent to drain by gravity, until the solvent level is slightly above the sorbent; proceed to 8.4.4.

8.4.3 SPE column conditioning: Immediately before sample extraction, add 2x3 ml of methanol to the SPE column and allow the methanol to partially drain through the column by gravity. Conditioning is needed to

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solvate the C-18 phase attached to silica particles in the SPE column. Condition the SPE column for at least 10 min with methanol. The conditioning ensures maximum interaction of the C-18 phase with the sample. **Note: do not allow the columns to go dry once conditioning has started. Maintain levels of fluids by adding additional fluid or by closing Luer lock fittings.**

8.4.4 SPE column equilibration: replace the methanol in the SPE column with DI water at pH=3.0 to equilibrate the column with the sample matrix. Add 2x3 ml of DI water at pH=3.0 and allow the water and methanol to partially drain through the column by gravity or slight vacuum. About five minutes is required for each volume of water and methanol to drip through the column. Do not allow the sorbent to dry.

8.4.5 Adjust the pH of the sample in the beaker to pH=3.0 with 1M hydrochloric acid. For DI water it takes about 0.5 mL of acid. For "real world" matrices 0.5 mL may not be enough, and more acid may need to be added to reach the pH of 3.0. In such cases add additional acid dropwise, while constantly mixing, until the pH of 3.0 is achieved.

8.4.6 Pre-dissolve 50 ul of 200 ppb chlorinated surrogates spike (for all blanks and samples) in 10 mL of acetone per sample/blank. Add 45 ul of isooctane. Larger volume of pre-diluted spikes may be prepared base on the anticipated number of samples/QC samples in the extraction batch. Add 10 ml of the pre-diluted spikes to each sample and blank. For Laboratory fortified Blanks and Matrix Spikes pre-dissolve 50 ul of 200 ppb chlorinated surrogates spike as well as 80 ul of 20/160 ppb chlorinated pesticides spike (W-PSCL-spk) and/or and add to each LFB/MS. These should be called LFB_1, LFB_2, MS_1 and MS_2. For tests W-CT-CI-R and W-PCB-TQ-R a separate sets of matrix spikes/LFBs needs to be extracted. Along with surrogates, use 25 ul of a mixed Chlordane/Toxaphene spike (1000/6000 respectively) and. 50 ul of 200 ppb W-PCB Aroclors spike in 10 mL of acetone and add to each LFB/MS. These should be called LFB_3, LFB_4, M_3 and M_4. If no samples in the batch are scheduled for W-CT-CI-R then PCB aroclors can be spiked together with Chlorinated pesticides in the first set of LFBs/MSs. Additionally, W-CT-CI-R requires a PQL spike to be extracted. Use 25 ul of 4x dil Chlordane/Toxaphene spike to prepare the PQL spike QC sample. 45 ul of isooctane only needs to be added if none of the spike solutions contains isooctane. Mix the samples in the beakers thoroughly. Acetone serves as conditioner for the sample; pre-diluting the spikes and addition of isooctane greatly improves the recoveries for some analytes poorly soluble in water.

8.4.7 Sample extraction: Attach 75 ml reservoir tubes to the SPE columns using Luer connectors. Pour the sample to the upper container and make sure that the entire system is under vacuum. Depending on the sample it may take even several hours to filter a 500 ml sample. Glass wool or other filtration aid maybe used to facilitate this step.

8.4.8 SPE column drying: Dry the SPE columns by using slight vacuum. Do not dry the columns for excessive periods of time. Some low boiling pesticides might evaporate with longer drying times, resulting in low recoveries.

8.4.9 Elution of target analytes: Label 15 ml, pre-calibrated to 250 ul, culture tubes with sample identifications and place in a holding rack. Place the dried SPE columns in the appropriate culture tubes. The open end of the SPE column rests on the edge of the culture tube, keeping the male Luer end of the SPE column raised a few centimeters above the bottom of the culture tube. Add small amount of glasswool to the SPE column to remove residual water. Add 3 ml of acetone to the SPE column and allow to soak for 10 min. Rinse the sample bottle, the filter paper through which the sample was filtered, and then the beaker, the filtration flask, the glass stir rod, and the reservoir tube with methylene chloride. A small amount of Na_2SO_4 may be added to the filtration flask. Once the initial volume of acetone has almost drained, add that methylene chloride aliquot to SPE column and allow the solvent to drain by slight vacuum into the culture tube. Collect about 15 ml total volume of extract. Transfer dry eluent to another culture tube and add 25 ul of 1000 ppb chlorinated internal standard solution to each culture tube. **Note:** Rinsing the entire sample pathway with methylene chloride ensures that the whole sample is extracted and also improves recoveries for some target analytes that tend to adsorb on glass surfaces and /or precipitated matter collected on the filter.

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8.4.10 Evaporation of solvent/solvent exchange: Setup a Nitrogen Evaporator (N-Evap™) by turning on nitrogen-gas, heater (30 °C bath temperature), and attaching clean needles. Blow down to 0.25 ml, vortexing several times during initial blow down to remove any residual water. Solvent exchange to isooctane three times. Do not use iso-octane stored in plastic squeeze bottles. It tends to produce high background signal for Dieldrin in the method blanks. Submit 0.25 ml in isooctane for analysis. Small amount of Na_2SO_4 may be added to the culture tubes, if excessive amounts of water are still present.

8.4.11 Some samples with large amounts of suspended matter may require unreasonably long time to filter through the SPE cartridge so more than one cartridge per sample may have to be used. In such cases, it is permissible, based on analyst's judgment, to use larger, 1 g SPE cartridges instead. All the solvent volumes described above for pre-cleaning (8.4.4), conditioning (8.4.5), and equilibrating the cartridge (8.4.6) have to be doubled. The solvent volumes used for elution (8.4.9) have to be doubled as well and the eluate has to be collected in two 15 mL tubes. Those two tubes are then combined during the solvent evaporation stage (8.4.10). If 1 g cartridges are used for any of the samples in the batch then one of the two method blanks has to be prepared with a 1 g cartridge. The pertinent information, including lot # for the 1g cartridges used must be entered in the electronic preparation worksheet.

8.4.12 Each sample preparation must be recorded by the preparation team in the electronic Prep Worksheet Manager module of LIMS. For chlorinated pesticides extractions using SPE technique there is a ready- made, partially prefilled template in LIMS. The template name is identical with LIMS prep ID: 3535A (GC). For exact instructions how to fill an electronic prep worksheet please refer to SOP GC-002-2 (ref 15.15).

9.0 GENERAL DESCRIPTION OF GC/MS/MS ANALYSIS

9.1 GC/MS/MS Maintenance and Tuning

9.1.1 DFTPP tune, recommended for single quad GC/MS systems by EPA 8270E, is not applicable to triple quadrupole systems including Agilent 7010 GC/MS/MS. Instead, the instrument is tuned according to manufacturer's tuning instructions using PFTBA autotune. The PFTBA autotune has to be performed each time after major maintenance is performed, including source cleaning, source parts replacement, filament replacement and EMV horn replacement. It may also be performed whenever deemed necessary by the chemist. If the autotune criteria are not met repeat the autotune. If still failing, run the autotune from the default values. If that fails, the ion source may have to be cleaned. Additionally, a daily tune check, is performed.

9.1.2 Initial checking and maintenance of the instrument consists mainly of the following steps.

9.1.2.1 Check the vacuum operation and periodically run an air/water leak test. The air/water leak check is now included in the autotune and tune check procedures, so it is performed anyway every time the instrument is tuned or the tune check is run.

9.1.2.2. Before each run perform a daily tune check of the GC/MS/MS system. The report is saved and printed automatically, and it should be placed in the sequence reports folder.

9.1.2.3. Replace the injector liner (Agilent 2 mm dimpled liner part no: 5190-2297) is recommended for cold splitless injection), cut 1-3 inch of the column after running contaminated samples or encountering unusually heavy matrix. Occasional trimming of the column is still necessary even if backflush technology is used.

9.1.2.4. Run an Instrument Blank and look for instrument contamination.

9.1.2.5. In case the instrument is contaminated raise the furnace temperature to 260 ºC and leave it overnight.

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9.1.2.6. To perform maintenance of the MMI inlet replace the liner and septum and clean the inside of the inlet body with cotton swabs soaked with methanol acetone and isooctane. **Do not use a harsh brush to clean the inside of the inlet body!** To complete the MMI inlet cleaning perform an inlet bake out procedure. Set the inlet mode to split (split ratio 200:1) and let the gas flow for a couple of minutes. Then raise the inlet temperature to 330 ºC and the oven temperature to 300 ºC. Bake for 1-2 hrs. It is beneficial and recommended to bake the ion source at 350 ºC at the same time.

9.1.2.7. The autosampler syringe has to be frequently and thoroughly cleaned to avoid injection repeatability problems. A dirty plunger will cause reproducibility problems, bad injections occurring randomly, and poor peak shapes and calibration problems. Replacing the syringe on regular, frequent basis is highly recommended.

9.1.2.8. Re-check for instrument contamination and if needed repeat the procedure until the instrument is contamination free.

9.1.2.9. Following column trimming and/or replacement the retention times in the dMRM acquisition method may need to be adjusted. For that purpose, a high-level calibration standard needs to be run for each method. The data file for that single run is then added to the most recent Masshunter Quant batch file and quantitated (quantitate single sample option is strongly preferred here). Peak assignments for each analyte, internal standard and surrogate need to be verified carefully. The beginning and the end of each acquisition window (visible in quant) should be assessed, and adjustments should be made if deemed necessary. When done, the entire batch is saved under different name indicating RT adjustment. In some, extreme cases, it is desirable to adjust the retention times in the quant method and save the quant method under different name, again indicating RT adjustment. That, RT adjusted quant method, can then be used (copied) to process the next batch of samples. In order to adjust the acquisition times in the dMRM method the single run data file with RTs verified above is used. In the MS acquisition screen go to Method/Update RTs, browse to the quant file to be used and hit “update”. Even with the retention times correctly assigned in Quant, the automated adjustment in the dMRM method is, occasionally, error prone, The software may confuse some closely eluting, isomeric or chemically very similar compounds assigning the same RT to both, Therefore, the RT assignments in the acquisition method must be carefully verified.

Certain isomeric/chemically similar analytes tend to be confused by the quant software. Therefore, the RT assignments in the acquisition method must be very carefully verified. Special attention needs to be paid to the following compounds: all BHCs, especially Beta and Gamma-BHC, Gamma-Chlordane and Alpha-Chlordane, Dieldrin and Endrin, Similarly, PCB peaks get easily confused by the software. If in doubt, refer to the peak assignments in this SOP.

9.2 GC/MS/MS System Initial Calibration

9.2.1. Analyze the calibration standards at the following levels listed in Tables 2A and 2B. At each level, the internal standards should be present at 100 µg/L. The linearity of the calibration curve is defined by an RSD that is less than or equal to 20% of the Response Factors of the calibration curve, or by a correlation coefficient R^2 not smaller than 0.99. If a higher order curve is to be used the correlation coefficient R^2 has to be at least 0.99. When new calibration is inspected linear fit is usually tried first, followed by average response factor (%RSD) which is equivalent to weighted linear forced through origin), then followed by quadratic fit and finally higher order curves. Do not use the “include” option for the origin. “Ignore origin” should be used preferentially though forcing through origin may have to be used under some circumstances. When calibration curve fit is selected in the Masshunter software the % calibration drift has to be monitored in order to have all the calibration levels within 70-130% of the expected value. Special care has to be taken to carefully fit the curves at the lower end of the calibration range where the vast majority of problems occur. All calibration curves should be weighted curves (1/x or 1/x2); do not use equal weighing. It is permissible to remove individual analyte calibration levels from either the lowest and/or highest levels of the curve (the PQL may have to be adjusted). Removal of interior levels is forbidden. An entire single standard calibration level may be removed from the interior of the curve whenever the standard was not correctly injected, or a wrong standard was injected. If more than 10% of the total number of analytes fail the calibration fit criteria or more than 20% of analytes fail the %

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calibration drift criteria, then the instrument system must be corrected. Some possible problems include standard mixture degradation, injection port inlet contamination, analytical column contamination, and active sites in the column or chromatographic system.

9.2.2. For chlorinated pesticides the approximate retention times, the primary MRM transitions and confirmatory, secondary transitions are given along with dMRM acquisition time windows in Table 1A. For PCB aroclors, the corresponding data is compiled in table 1B. The primary and secondary ions should all be present, and the relative intensities should agree within absolute ±30% of the reference mass spectrum after background subtraction is performed. In cases where the qualifier has higher intensity than quantifier ions, relative ±30% is used.

9.2.3 The initial calibration curve is always immediately checked with the second source initial calibration verification standard (ICV). The acceptance criterion is ±30%. If the Initial Calibration is not run with the batch, the CCV acceptance criterium is +/- 20% (see 9.3.2)

9.3 Daily GC/MS/MS Performance and Calibration Check

The initial calibration curve and instrument performance must be verified on each day of analysis by the measurement of one or more check standards.

Degradation/tailing factor check (required by EPA 8270E)
A modified GC/MS tuning standard is used to perform this task. The standard contains 5 mg/l each of DDT-p,p' and Pentachlorophenol. Benzidine, which is also recommended by method 8270E, is usually not detectable in the presence of analyte protectants. Since the absence of benzidine peak in the chromatograms has no bearing on the chromatographic behavior of the target analytes and surrogates, only pentachlorophenol is used for the tailing factor determination. The degradation check/tailing factor standard is run at the beginning of the analytical run sequence to verify injection port inertness and GC column performance. A full scan version of the acquisition method is used for this purpose. Degradation of DDT to DDD and DDE should not exceed 20%.

The percent breakdown calculation is performed using the following formula (EPA method 8081B)

%Dec. DDT = Sum Peak Area (DDE + DDD) / Sum Peak Area (DDE + DDD + DDT) × 100%

The following are the Relative Retention Times for DDD-p,p' and DDE-p,p' (relative to DDT-p,p'):

DDE-p,p' RRT = 0.880
DDD-p,p' RRT = 0.945

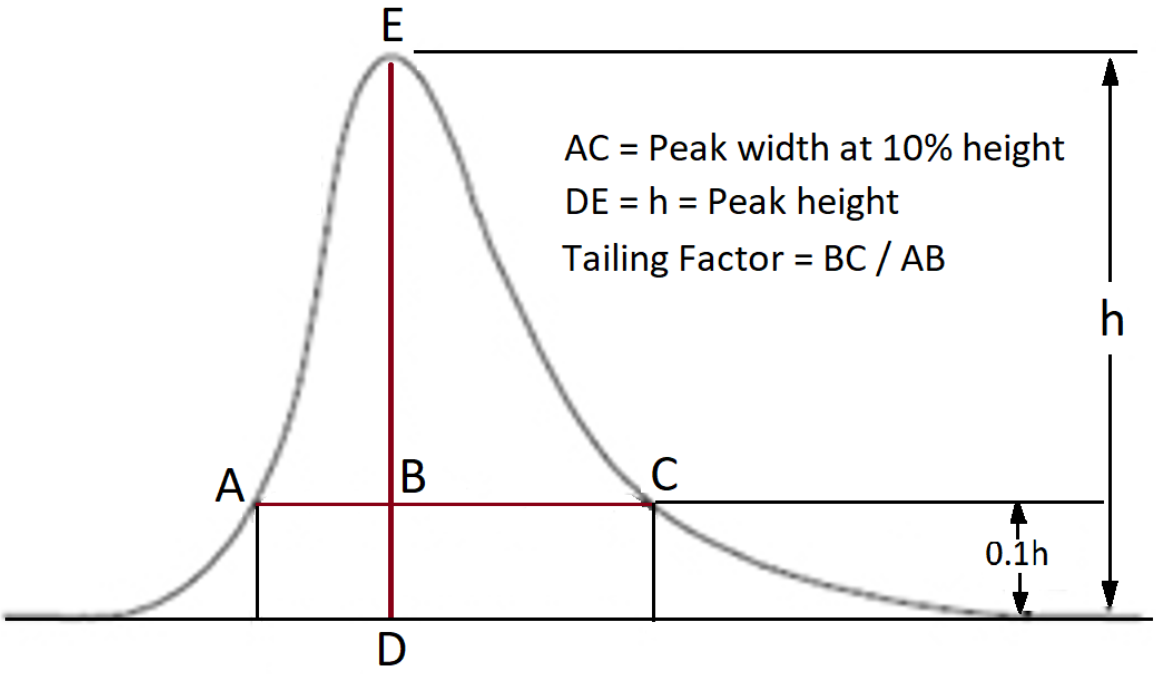
Usually, it is necessary to perform spectral deconvolution of the chromatograms to remove the analyte protectants "hump" and obtain correct integration values and clean spectra for target analytes. Deconvolution for GC/MS data is the process of computationally separating co-eluting components and creating a pure spectrum for each component. Specifically, for each observed EIC that results from two or more components, deconvolution calculates the contribution of each component to EIC.

The tailing factor for pentachlorophenol should not be higher than 2 according to the following equation:

Tailing Factor = BC / AB

Where the peak is defined as follows: AC is the width at 10% height; DE is the height of peak and B is the height at 10% of DE. This equation compares the width of the back half of the peak to the width of the front half of the peak at 10% of the height. If DDT-p,p' degradation and or tailing factors are excessive the injection port maintenance has to be performed until proper chromatographic performance is restored.

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9.3.2 Analyze midpoint level standards as continuing calibration check (CCV) standards. These calibration check standards must be analyzed at the start of each run and at 12-hour intervals thereafter. The acceptance criteria for all components are 80-120% recovery. If multiple CCV failures are observed corrective action must be taken prior to the analysis of samples. When compounds fail, they may still be reported as non-detects (with a "J" qualifier) if it can be demonstrated that there was adequate sensitivity to detect the compounds at the applicable quantitation limit. For situations when the failed compound is present, the concentrations in the affected samples must be reported as estimated.

9.3.3 Calibration verification standard must also meet the following criteria:

9.3.3.1 Minimum response factors: The minimum RF of the most common target analytes must be within 50% of the original calibration.

9.3.3.2 Internal standard responses: the peak area for each of the internal standards may not change beyond the factor of two (-50% to +100%) from that of the average internal standard response of all the levels in the most recent initial calibration.

9.3.3.3 Internal standards retention times- the retention times of the internal standards in the calibration verification standard must not drift by more than 30 seconds from that of the mid-point standard level of the most recent initial calibration.

9.3.3.4 If any of the requirements mentioned in 9.3.3 are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, active sites in the column or chromatographic system, and a contaminated MS source.

9.4 GC/MS/MS Sample Analysis.

Quantitative analysis of all analytes is accomplished by the internal standard calibration method. All target component positives found have to be quantified using at least a five-point calibration curve (for linear fit),

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at least six points for quadratic and at least seven points for higher order curves. Each sample extract MUST contain 100 µg/L of each internal standard. Any extract that is determined, in initial analysis, to contain high concentrations of any of the target analytes should be diluted as deemed necessary. **The concentration of internal standard must remain at 100 µg/L when diluting samples by adding additional internal standard to the extract.**

9.5 Analysis Run Sequence.
Due to different acquisition methods two separate analytical runs are required to analyze for both chlorinated pesticides and PCB aroclors (refer to 9.6 for PCB aroclors analysis). The analyst will set up an analysis run sequence by placing the GC vials containing the sample extracts and standards on the autosampler tray in the following order or similar:

isooctane (to clean the system)
degradation/performance check
Instrument Blank W-PSCL-ISTD (containing internal standards at 100 ug/L)
pesticides calibration set (when initial calibration is run, levels 1-8)
W-PSCL ICV L-4 initial calibration verification check (when initial calibration is run)
W-PSCL CCV L-4 continuing calibration check
Instrument Blank (containing internal standards at 100 ug/L)*
Or extraction blank (method blank)
laboratory fortified blank (LFB)
laboratory fortified blank duplicate
sample matrix spike,
sample matrix spike duplicate
samples (for up to 12 hours, including QC samples)
CCV continuing calibration check
Instrument Blank (containing internal standards at 100 ug/L)*
samples (up to 12 hours)

* If a CCV is directly followed by the method blank, then the instrument blank is not needed.

Print a hard copy of the run sequence and place it in the final data folder.

Data Processing using the Masshunter software.

9.5.1 Using the Masshunter Qual software examine the degradation/performance check sample. Calculate DDT decomposition and the tailing factor for pentachlorophenol.

9.5.2 Examine the quantitation reports soon after the samples have been analyzed. Check all of the calibration check standards analyzed during the run sequence and ensure that they met the minimum criteria given above.

9.5.3 The concentration reported for an identified hit in the sample extract, expressed in ug/L, is quantitated using the initial calibration curve. However, the analyst must ensure that all identification criteria are fulfilled, and the peak area integration was correctly done. If not, the integration has to be re-done by choosing a new set of integration parameters or by manual integration (see SOP CM-018.1 for lab manual integration, ref 15.12).

9.5.4 If the response for any of the compounds exceeds the calibration curve, the extract must be diluted so that the response will be within the limits of the curve, and then reanalyzed. Make sure when performing dilutions to use isooctane spiked with the appropriate levels of internal standard so that their response will be the same in the dilution as it was in the original extract.

9.5.5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after data acquisition. If the retention time for any internal standard changes by more than 0.05 minutes from the last calibration, then the chromatographic system must be evaluated for

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either a) chromatographic matrix induced shift or inspected for malfunctions (such as leaks) and corrections must be made. The m/z abundances for all of the internal standards must be within a factor of two (50% to 200%) from the abundance in the daily calibration standard check. Corrective action is indicated if the m/z abundance is outside of these limits. If the holding time for a sample has expired and the internal standard areas are out of the acceptance range, then the final report must be commented upon and any positives detected must be qualified with a "J" to indicate that the result is an estimate.

9.5.6 Analysis of surrogates.

9.5.6.1 The analyst should monitor the performance of the extraction, cleanup, analytical system, and effectiveness of the method by spiking each sample, QC samples and Method Blanks with PSCL surrogate spike solution currently containing Decachlorobiphenyl and Tetrachloro-m-xylene at 200 ug/L. The surrogate compounds are expected to be found at 40 µg/L in all the sample extracts, Blanks, LFBs, and Matrix Spikes.

9.5.6.2 To determine the acceptance accuracy limits for a surrogate the following procedure should be used (ref 15.5): (1) for each sample analyzed, calculate the percent recovery of each surrogate in the sample, (2) once a minimum of twenty samples of the same matrix has been analyzed, calculate the average percent recovery (p), and standard deviation of the percent recoveries (s), for each of the surrogates, (3) for a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard as follows:

Upper Control Limit (UCL) = p + ts
Lower Control Limit (LCL) = p – ts
Where “t” stands for Student’s coefficient for 99% confidence level for n-1 degrees of freedom (n = number of measurements). “p” stands for average recovery, and “s” stands for standard deviation.

The control limits are supposed to be checked and updated once per year if enough measurements have been conducted.

9.5.6.3 If a surrogate recovery fails, and there is a reasonable suspicion that instrument related factors may be responsible, the sample maybe re-analyzed and the rerun reported if passing. If the surrogate recovery fails again, and the recovery is biased low, the sample has to be re-extracted and re-analyzed. If the sample exceeded the holding time for extraction, and the recovery is biased high, a re-extraction is not required, and the reported hits have to be qualified as estimated (J), An automatic comment will be generated by LIMS.

9.5.7 Analysis of matrix spikes and LFBs

Check the Matrix Spike and Lab Fortified Blank recoveries. They must be within the current acceptance ranges. A comment must be added to the final report explaining any deviation from the routine limits whenever the spikes or surrogates are out of range. Matrix spikes and LFBs recovery and precision limits should be calculated based on available in-house data once enough data points are collected. See ref 15.8, chapter 5.3 for details.. LFB and matrix spikes recovery limits are calculated independently; the limits for LFBs may then be applied to both LFBs and matrix spikes. In case LFB failures are observed the LFBs may be rerun and reanalyzed. All the associated samples that have positives (above PQL) for the analytes failing in the LFBs must be re-run and reanalyzed as well. Similarly, if the number of matrix spikes failures is deemed excessive matrix spikes (along with the background sample) may be rerun and reanalyzed. See ref 15.8, chapter 5.3 for details on disposition of QC failures.

9.5.8 Blank contamination

9.5.8.1 Instrument Blanks. In the event a positive identification is found in both the sample(s) and the instrument blank, the instrument must be cleaned and the sample(s) rerun/reanalyzed.

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9.5.8.2 Method Blanks. In the event a positive identification is found in both the sample(s) and the extraction blank then the unexpired sample has to be re-extracted and reanalyzed. If samples passed the holding time, the results will be reported with a "V" qualifier up to ten times the amount found in the blank. The re-extraction is not necessary when the analytes in question are non-detects in the samples or whenever the values found in the samples are >10x the value detected in the method blank(s).

9.5.8.3 Field Blanks. In the event a positive identification is found in a field blank, but method blank(s) pass, all field blank detections above PQL generally need to be confirmed by re-extraction. If the field blank detections are below PQL, then the re-extraction is not necessary in the following cases:
The same analyte is not found in the associated samples (samples in the same job),
The same analyte is found in the associated samples at levels at least 10 times the value in the field blank.
It is always prudent, and strongly recommended that the extracts are rerun, and positives confirmed before sending samples for re-extraction.

9.5.8.4 Equipment Blanks. The rules for field blanks are generally also applicable to equipment blanks. One needs to remember that samples associated with equipment blanks may be soil samples. Such association must be clear if the rule is to be applied.

9.5.9 Continuing Calibration

9.5.9.1 After initial calibration, the GC/MS/MS response is checked immediately by running an Initial Calibration Verification standard (ICV) and then, on a continuing basis every 12hrs, by using a continuing calibration check (CCV), middle range pesticides standard. Criterion of acceptance for continuing calibration check is +/-20 % of initial calibration. If a CCV fails, all the samples run after this standard, have to be re-run for all positive hits found at concentrations higher than PQL level. If the samples have exceeded the analysis holding time, then all hits must be flagged as estimated.

9.5.9.2 If CCVs do not meet method requirements but the associated analytical results are below the detection limit or below the quantifiable threshold (PQL) and no systematic failure is observed (i.e., the failure is deduced to be due to a statistical outlier in a multi-component analysis where results from other CCV components and LFB results do not indicate a systematic bias in the analysis or detector response), an appropriate test comment and result qualifier (J) shall be provided to indicate the CCVs are outside control limits. However, when a systematic or system failure is detected or the affected analytical data are above the quantifiable threshold, the analysis shall be re-run if possible. If re-analysis is not an option, the analytical results shall be qualified as estimates (see ref 15.8 for more details).

9.6. Quantitation of positives.
Positives are quantified based on their peak area. The concentration reported for an identified hit in the sample extract, expressed in ug/L, is based on calibration curve of the initial calibration. The Masshunter software used to process data will do the interpolation for the sample extract. However, the analyst must ensure that all identification criteria are fulfilled, and the peak area integration was correctly done. If not, the integration has to be corrected by choosing a new set of integration parameters or by manual integration (for manual integration procedure see ref 15.12). Only the extract concentrations are calculated by the processing software. The final analyte concentrations in sample are calculated in the QC Manager during the data upload process software. This is done as follows:

C_{sample} (ng/L) = (Cx) × ($V_{extract}$) × (DF)/(V_{sample}) for water samples

where:

C_X: The concentration, in ug/L, of the analyte in the sample extract determined by the processing software.

$V_{extract}$: The volume of the extract, in mls (usually 0.25) recorded in the preparation report.

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DF: The dilution of the sample extract recorded in the dilution report.

V_{sample} -This is the volume of the water sample taken in extraction, expressed in mLs (usually 500 mL).

Analysis of PCB Aroclors using GC/MS/MS.

9.6.1 The acquisition method for PCB Aroclors (AR-W_dMRM_yymmdd) contains, in one single acquisition segment, 21 individual PCB transitions along with transitions for internal standards (three deuterated PCB congeners are used) and transitions for surrogates Tetrachloro-m-xylene. and Decachloribiphenyl. The list of PCB transitions includes, at least, one for each level of chlorination plus a number of other transitions prominent in specific Aroclors. The use of single acquisition window for all PCB aroclors ensures that the entire PCB pattern can be recreated by summing up all the different ions. All the individual transitions used in the acquisition method are listed in Appendix 1B. The individual PCB transitions listed in the acquisition method each reconstruct parts of the Aroclors pattern, over certain RT spans; they will each show as clusters of PCB peaks at different RTs in different parts of the chromatogram. Those peaks would, usually, be common for two or more individual Aroclors. Therefore, a correlation between the acquisition ions and the analytical Aroclor peaks is not straightforward. The typical Aroclor analytical peaks with their quantifier and qualifier ions are listed in Table 1B. Analyst will select 5 analytical peaks for each Aroclor that cover the entire RT range and include major ions for that particular PCB aroclor.

9.6.2 Identification of PCB Aroclor pattern is accomplished by visual comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made by the analyst whether that standard is truly representative of the PCBs in the sample. Individual Aroclor standards are run for PCBs 1221, 1232, 1242, 1248, 1254 along with PCB 1016/1260 mixture (also referred to as PCB-1060). The visual comparison is accomplished in Qualitative Software by extracting the relevant chromatograms in the EIC-MRM mode. Once the identification is made the relevant chromatograms are printed out and included with the documentation. Refer to appendix **5** for PCB Aroclor patterns and analytical peaks.

Although this SOP is based on EPA method 8270E the quantitation algorithm of the PCBs Aroclors analysis essentially follows EPA method 8082A (Polychlorinated Biphenyls (PCBs) by Gas Chromatography) (ref 15.14). Method 8270E (ref 15.1) states in paragraph 11.7.5 that quantitation of multicomponent compounds such as Aroclors is beyond its scope and refers to GC/ECD methods (i.e.; 8082).

9.6.4 The analytical run sequence for the PCB Aroclors analysis includes a full seven points calibration for PCB 1016/1260 mix along with single standards for the five, remaining individual Aroclors, for pattern identification purposes. During the days after the initial calibration and PCB patterns are run, it is sufficient to run only PCB-1060 CCV-L3, provided that no retention time changes occurred (no column cutting!). If the CCV fails or other factors occur (such as ion source cleaning, column cutting or replacement) the entire initial calibration has to be run again. If no PCBs are identified in the sample, non- detects are reported. Positive hits for PCB 1016 and 1260 can also be reported, provided their concentrations do not exceed the calibration range. If any of the remaining Aroclor is identified, the samples must be rerun along with a full calibration for that particular Aroclor.

9.6.5 Once the Aroclor pattern has been identified the quantitation of Aroclors is accomplished by using 5-major peaks characteristic for each individual Aroclor (see table 1B). For the best results those peaks should be evenly spread over the entire Aroclor pattern. A separate calibration curve is built for each of the individual analytical peaks. The concentration for the total Aroclor is then assigned to each analytical peak. The amount of the Aroclor is calculated using the individual calibration factors for each of the 5 analytical peaks and the calibration model established (linear or non-linear) from the multi-point calibration. Different calibration models may be used for each selected peak. The concentrations obtained for those five analytical peaks are then, finally, averaged to determine the concentration of that Aroclor.

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9.6.6 Weathering of PCBs in the environment and changes resulting from waste treatment processes may significantly alter the PCB patterns. Averaging of five, carefully chosen, analytical peaks provides for some ability to overcome weathering effects and still obtain acceptable quantitation results. To accomplish that, it is essential not to attempt to" reverse match" the analytical peaks used for calibration to those identified in the degraded sample pattern. Instead, the individual concentrations calculated for the analytical peaks are summed up and still divided by five, even if some peaks are missing in the sample.

9.6.7 In some cases it may be advisable to use the total area approach to calculate the concentration in a weathered Aroclor sample. Great care must be exercised, however, to ensure that no interfering compounds elute in the same portion of the chromatogram.

9.6.8 Additional PCB aroclor standard called PCB-1268 maybe be run in some cases, especially when there is a reasonable suspicion that PCB congeners higher than those commonly found in PCB-1260 are present in the sample. PCB-1268 is not currently a target analyte in S-PCB-TQ test. However, the presence of PCB-1268 pattern indicates the presence of Decachlorobiphenyl (PCB-209, a component of PCB-1268 pattern) in the sample. Since Decachlorobiphenyl is used as a surrogate, such samples will typically have that surrogate failing high. It is therefore not necessary to report Decachlorobiphenyl surrogate in such samples.

9.6.9 In case when two overlapping PCB aroclors are present in the sample, it is permissible to select different peaks for quantitation. This includes situations when an estimate of the Total Aroclor concentration is requested by the client.

10.0 REPORTING AND DOCUMENTATION

10.1 When analysis is complete, generate a .txt file in the Masshunter software for all the reported samples, QC samples and CCVs. The QC Manager is then used to download the final sample results into the Laboratory Information Management System (LIMS). If a sample has been diluted, then make sure that the information was entered properly into the QC Manager. The following convention should be used in QC calculator:

CLW_CCV, WPCB-1060 (or other)CCV
SURWCL_1234567 for surrogate in sample. SURWPCB code is applied for PCBs.

10.2 The QC manager will convert the data from ug/L to ng/L (LIMS reporting units, water samples only; not applicable for soils and tissues) and also it will add MDLs for all analytes not included in the text file (non-detects). The converter will also average the PCB aroclors result and report the average as the corresponding aroclor.

10.3 Add the appropriate qualifiers and comments to the sample data in the QC Manager after performing a complete review of the sample data and QC data. Follow DEP SOP GC-001 (ref 15-8) for details of data review and reporting. See DEP SOP LB-027, (ref 15-7) for guidelines for qualifying data when quality control results are outside established control limits and re-analysis is not a viable or desired option. Definitions of the available qualifying codes are listed in DEP SOP LB-027

10.4 All quantitation reports for samples and QC should be placed in a results folder labeled with the job number, the sample numbers, and the type of analysis.

10.5 Enter the results for each sample in the analysis results form. Print out QC results from the QC Manager. Include a copy of dilutions page if any. Also include a printout of sample positives from the data review (a scrollable report) and file it in the data folder.

10.6 Submit the result folder to the GC pesticides section supervisor. The supervisor will review results and then authorize the sample. The supervisor will then file the folders in the GC-pesticides filing cabinets.

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11.0 QUALITY CONTROL

11.1 See DEP SOP GC-001, (ref 15.8) for detailed information on quality control, definitions and interferences. See DEP SOP LB-027, Standard Operating Procedure for Reporting Qualified Data (ref 15.7) for guidelines for qualifying data when quality control results are outside established control limits and re-analysis is not a viable or desired option.

11.2 All data generated by a chemistry analyst are subjected to supervisory review and authorization. The supervisor is assessing the validity of data generated by assuring that all QA/QC criteria are met by checking the following review/authorization checklist:

- Check sample preparation report
- procedure
- surrogate and spiking solutions
- preparation holding time
- Check project log-in folder for special requests
- Check initial calibration for linearity and fit
- Check continuing calibration check standards
- Check surrogate recoveries
- Check accuracy and precision for LFB and Matrix Spikes
- Check internal standard recoveries
- Check retention time drift
- Check for blanks contamination
- Check for positives:
- Proper integration of the peaks (baseline)
- Retention time confirmation
- Amount confirmation
- If response is within the calibration range
- Calculations
- Qualifiers
- Proper identification of Aroclor patterns
- Check information in the MassHunter Report Header:
- SOP #
- Instrument ID
- Analyst name
- Evaluate the data against any field information
- Check field preservation record
- Check LIMS report:
- Preparation and analysis dates
- MDLs
- Amounts reported for positives
- Qualifiers
- Comments

12.0 DATA ARCHIVAL

All raw data are retained in electronic or hard copy format. All paper formats are maintained either in the laboratory office or in a State of Florida warehouse for at least ten years. Electronic chromatographic raw data are archived by analysis file ID and instrument ID on dual CDs by the Laboratory Support Section.

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The valid data files (tune, ICALS, CCVs, QC and sample data files) are moved soon after collection from the hard disk of the instrument computers to the network drive \\TLHLAB3\GC\BACKUP_GC_MSD-3 (or MSD-4). Raw data files on the hard disk of each instrument may be deleted after 3 to 4 months or whenever they are no longer needed. This process is now automated with backup executable files that run automatically every 24 hrs.

Upload files are generated by a macro and stored automatically (.txt files) into \\TLHLAB3\GC\UPLOAD_GC_TQ-1 (or TQ2, or TQ3 or TQ4). They are then converted in QC Manager for reporting in LIMS.

13.0 DETERMINATION OF METHOD DETECTION LIMITS

13.1 The MDLs were established using procedures given in EPA Chapter 40 Part 136, Appendix B of the Federal Register (ref 15.13). Also refer to Reference 15.9 and 15.10**.**

13.2 At least seven replicate samples are analyzed near the MDL. The MDL is the concentration of analyte at which there is analyte present with 99% confidence. The validation exercise is split into at least three extraction batches performed on three separate days. The samples are run in all the instruments that are considered identical for the purpose of this analysis. Along with the spikes an equal number of blanks is extracted.

13.3 The results of the spikes and blanks analysis are tabulated, and the statistical calculations are performed electronically to establish or update the MDLs and PQLs for each analyte and matrix. The MDL results calculated based on the blanks and spikes data are compared and the MDL is set at the higher value (at least).

13.4 MDLs for PCB Aroclors are determined for PCB -1016 and PCB-1260. The higher of the two numbers is then applied to all seven PCB Aroclors.

13.5 MDLs are verified quarterly and recalculated annually. At least one spike is run in each instrument per quarter in which samples are analyzed. The spike is prepared at concentration between MDL and PQL and it is also considered a PQL verification. The PQL acceptance criteria are specified in the QCM limits tables for each analyte and are typically up to 20% wider than the corresponding LFB recovery limits The MDLs are recalculated annually (at least) based on the last 24 months of data. Both spikes and blanks are used in calculations. If the calculated MDL is within a factor of 2 of the current MDL, the current MDL may be kept unchanged. Otherwise, the MDL has to be changed to the new calculated value. MDL/PQL verification spikes are reported to LIMS as QC type SRM. The LIMS statistics module is used for the annual re-calculation of MDLs.

14.0 SAFETY/HAZARDOUS WASTE MANAGEMENT

See SOP OG-001, Safety and Waste Management Practices in the Organic Analysis Groups (Volatile, Semi-Volatile and Pesticide Laboratories) (ref 15.11) for specific details on safety and hazardous waste management.

15.0 REFERENCES

15.1 Test Methods for Evaluating Solid Wastes, Third Edition, SW-846 Update VI, Method 8270E, Semi-volatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS). Revision 6, June 2018.

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15.3 Anastassiades, M., Mastovska, K., Lehotay, S..J., "Evaluation of analyte protectants to improve gas chromatographic analysis of pesticides" Journal of Chromatography A, 1015 (2003) 163-184.

15.4 Mastovska, K., Lehotay, S.J., Anastassiades, M., "Combination of analyte protectants to overcome matrix effects in routine GC analysis of pesticides residues in food matrices" anal. Chem. **2005**, 77, 8129-8137.

15.5 EPA 8000D Determinative Chromatographic Separation; Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, SW 846; 3rd Edition, Update -5, revision 4, July, 2014.

15.6 EPA method 3535A, Revision 1, 2007

15.7 DEP SOP LB-027. Reporting Qualified Data and Correcting Quality Control Problems.

15.8 DEP SOP GC-001. Quality Assurance/Quality Control and Data Review/Authorization in the GC Pesticides Laboratory.

15.9 DEP SOP LB-007. Procedure and Policy for Demonstration of Capability for Methods, Instruments and Laboratory Staff.

15.10 DEP SOP LB-031. Method Detection Limit Verification.

15.11 DEP SOP OG-001. Safety and Waste Management Practices in the Organic Analysis Groups (Volatile, Semi-Volatile and Pesticide Laboratories).

15.12 DEP SOP CM-018-1 Laboratory Policy Regarding Manual Chromatographic Peak Integration.

15.13 Code of Federal Regulations, Title 40, Part 136, Appendix B.

15.14 Test Methods for Evaluating Solid Wastes, Third Edition, SW-846, Method 8082A, Polychlorinated Biphenyls (PCBs) By Gas Chromatography

15.15 DEP SOP GC-002-2. Extraction of Pesticides and Polychlorinated Biphenyls (PCBs) from Water, Wastes, Soil/Sediment, and Filters for Subsequent Analysis by GC/MS Techniques.

15.16 DEP SOP GC-034-1. Analysis of Chlordane and Toxaphene using GC/MS with Negative Chemical Ionization.

15.17 Agilent Masshunter Optimizer software. Agilent Masshunter Workstation Optimization Tools B.10.00 (10.0.706.2). 11/05/2020.

15.18 Wylie, P., Meng, Chin-Kai, "A Method for the Trace Analysis of 175 Pesticides Using Agilent Triple Quadrupole GC/MS/MS" Agilent Technologies Application Note.

15.19 Mastovska, K. "Rugged GC/MS/MS Pesticide Residue Analysis Fulfilling the USDA Pesticide Data Program (PDP) Requirements." Agilent Technologies Application Note

15.20 Foch, I., Ciceri, E., Huebschmann, H., "Fast GC-MS/MS for High Throughput Pesticides Analysis" Thermo Fisher Scientific Application Note 52027

15.21 Walker, D., "Analyzing PCB Aroclors by Agilent's 7000B GCMS tandem quadrupole Mass Spectrometer" Agilent presentation.

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TABLES

TABLE 1A: Quantifier and qualifier Ions, Internal standard associations, MDLs, PQLs and approximate RTs for Chlorinated Pesticides included in LIMS test W-PCL-SQ-R **LIMS reporting units are ng/L.**

Analyte	Approx. Retention Time min)	Associated internal standard	Quantifier transition	Qualifier transition	MDL ug/L in extract	PQL ug/L in extract	MDL ng/L in sample	PQL ng/L in sample
Tetrachloro-m-xylene surrogate	6.34	DCB-d5	206.9 - 136.0	226.9 - 192.1				
Decachlorobiphenyl surrogate	16.21	HCB-d3	497.6 - 427.9	362.7 - 292.9				
Dichlobenil	4.67	DCB-d5	171.0 - 100.0	171.0 - 136.1	0.50	2.50	0.25	1.2
Ethalfluralin	6.55	Trifluralin-d14	276.0 - 202.0	316.0 - 276.0	0.30	1.5	0.15	0.75
Trifluralin	6.68	Trifluralin-d14	306.1 - 264.0	306.1 - 160.0	0.40	2.0	0.20	1.0
Alpha-BHC	6.98	Alpha-BHC-d6	181.0 - 145.0	181.0 - 109.0	0.20	1.0	0.10	0.50
Hexachlorobenzene	7.08	DCB-d5	283.7 - 213.9	283.7 - 248.8	2.0	10	1.0	5.0
Beta-BHC	7.41	Alpha-BHC-d6	181.0 - 145.0	181.0 - 109.0	0.20	1.0	0.10	0.50
Gamma-BHC	7.51	Alpha-BHC-d6	181.0 - 145.0	181.0 - 109.0	0.25	1.25	0.13	0.67
Delta-BHC	7.93	Alpha-BHC-d6	181.0 - 145.0	181.0 - 109.0	0.80	4.0	0.40	2.0
Chlorothalonil	8.02	TCB-d5	265.9 - 230.9	265.9 - 133.0	7.2	36	3.6	18
Heptachlor	8.80	TCB-d5	271.9 - 236.8	271.9 - 234.8	0.40	2.0	0.20	1.0
Aldrin	9.47	TCB-d5	254.9 - 220.0	260.9 - 190.9	1.3	6.5	0.65	3.2
Dacthal	9.72	TCB-d5	300.8 - 222.9	300.8 - 257.8	0.30	1.5	0.15	0.75
MGK-264*	9.95, 10.18	TCB-d5	164.1 - 80.1	164.1 - 98.1	0.40	2.0	0.20	1.0
Heptachlor Epoxide	10.27	TCB-d5	352.9 - 262.8	352.9 - 81.9	0.50	2.5	0.25	1.3
Oxychlordane	10.29	TCB-d5	387.0-263.0	187-151	0.60	3.0	0.30	1.5
Methoprene	10.68	TCB-d5	153-111	107-91	1.5	7.5	0.75	3.8
Prallethrin	10.83	TCB-d5	168.1 - 123.1	153.1 - 90.9	4.0	20	2.0	10
Gamma-Chlordane	10.76	TCB-d5	271.7 - 236.9	372.9 - 263.9	0.40	2.0	0.20	1.0
Triclosan Methyl	11.01	TCB-d5	301.8 - 251.9	301.8 - 189.0	0.30	1.5	0.15	0.75
Endosulfan I	11.02	TCB-d5	240.9 - 205.9	240.9 - 136	0.80	4.0	0.40	2.0
Alpha-Chlordane	11.08	TCB-d5	271.7 - 236.9	372.9 - 263.9	0.40	2.0	0.20	1.0
Trans-Nonachlor	11.19	TCB-d5	408.7 - 299.8	408.7 - 372.7	0.40	2.0	0.20	1.0
DDE-p,p’	11.56	TCB-d5	246.0 - 176.1	246.0 - 175.1	0.40	2.0	0.20	1.0
Dieldrin	11.56	TCB-d5	277.0 - 240.8	260.9 - 190.9	0.80	4.0	0.40	2.0
Endrin	12.02	HCB-d3	281.0 - 245.0	262.7 - 191.1	1.80	9.0	0.90	4.5
Endosulfan II	12.22	HCB-d3	241.0 - 206.0	206.9 - 172.1	1.80	9.0	0.90	4.5
DDD-p,p’	12.45	HCB-d3	235.0 - 165.1	235.0 - 199.1	0.50	2.5	0.25	1.3

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Analyte	Approx. Retention Time min)	Associated internal standard	Quantifier transition	Qualifier transition	MDL ug/L in extract	PQL ug/L in extract	MDL ng/L in sample	PQL ng/L in sample
Cis-Nonachlor	12.51	HCB-d3	408.7 - 299.8	408.7 - 372.7	0.40	2.0	0.20	1.0
Endrin Aldehyde	12.63	HCB-d3	344.8 - 280.9	344.8 - 244.9	1.5	7.5	0.75	3.3
Kepone	12.77	HCB-d3	355.0 - 320.0	355.0 - 285.0	27	135	14	68
Carbophenothion	13.02	HCB-d3	341.9 - 157.0	343.9 - 158.9	1.8	9.0	0.90	4.5
Endosulfan Sulfate	13.14	HCB-d3	271.7 - 236.8	271.9 - 116.9	0.60	3.0	0.30	1.5
DDT-p,p’	13.24	DDT-p,p’-d8	235.0 - 165.1	235.0 - 199.1	1.6	8.0	0.80	4.0
Piperonyl Butoxide	13.78	HCB-d3	176.1 - 103.1	176.1 - 117.1	0.30	1.5	0.15	0.75
Endrin Ketone	14.00	HCB-d3	316.9 - 280.9	316.9 - 101.1	0.80	4.0	0.40	2.0
Bifenthrin	14.23	HCB-d3	181.1 - 165.1	181.1 - 166.1	1.0	5.0	0.50	2.5
Tetramethrin	14.23	HCB-d3	164.1 - 107.1	164.1 - 135.1	1.5	7.5	0.75	3.3
Methoxychlor	14.25	DDT-p,p’-d8	227.1 - 169.1	227.1 - 141.1	0.60	3.0	0.30	1.5
Dicofol	14.25	Dicofol-d8	251.0 - 139.0	253.0 - 141.0	2.50	12.5	1.3	6.3
Fenpropathrin	14.30	HCb-d3	265.0 - 210.0	181.1 - 127.1	0.50	2.5	0.25	1.3
Phenothrin	14.54	HCB-d3	183.1 - 153.1	183.1 - 168.1	1.8	9.0	0.90	4.5
Mirex	14.69	HCB-d3	271.9 - 236.9	271.9 - 234.8	0.70	3.5	0.35	1.8
Lambda-Cyhalothrin**	14.86	HCB-d3	181.1 - 152.1	208.0 - 181.0	1.5	7.5	0.75	3.3
Permethrin**	15.26	HCB-d3	183.1 - 153.1	183.1 - 168.1	3.2	16	1.6	8.0
Beta-Cyfluthrin**	15.76	HCB-d3	226.1 - 206.1	163.0 - 127.1	2.5	12.5	1.3	6.3
Cypermethrin**	15.90	HCB-d3	163.0 - 127.1	180.9 - 152.1	3.0	15	1.5	7.5
Esfenvalerate	16.72	HCB-d3	167.1 - 125.1	225.0 - 119.0	1.5	7.5	0.75	3.8
Tau-Fluvalinate **	16.75	HCB-d3	250.0 - 55.0	252.0 - 55.0	0.50	2.5	0.25	1.3
Deltamethrin	17.23	HCB-d3	253.0 - 172.0	253.0 - 93.0	2.5	12.5	1.3	6.3
Trifluralin-d14	6.62	Internal Std.	315.0 - 267.1	266.9 - 163.1				
DCB-d5	6.66	Internal Std.	226.9 - 157.1	226.9 - 192.1				
Alpha-BHC-d6	6.93	Internal Std.	223.8 - 187.0	223.8 - 150.0				
TCB-d5	9.39	Internal Std.	296.8 - 225.0	296.8 - 234.8				
DDT-p,p’-d8	13.21	Internal Std.	243.0 - 172.6	243.0 - 206.1				
Dicofol-d8	14.22	Internal Std.	142.9 - 115.1	142.9 - 78.0				
HCB-d3	14.20	Internal Std.	362.7 - 362.7	362.7 - 292.9				
Octachloronaphthalene	16.20	Internal Sd.	354.9 - 267.0	354.9 - 251.0				

***-Summary peak quantitation used due to two peaks**
****- sum-all integration used due to closely eluting isomers**
PQL=5xMDL for all analytes except chlorothalonil PQL=6xMDL.
All analytes are associated to both surrogates.

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TABLE 1B: Internal standard associations, RTs, quantifier and qualifier transitions for analytical peaks, as well as MDLs and PQLs for PCB Aroclors included in LIMS test W-PCB-TQ-R. **LIMS reporting units are ng/L**

Analyte	Approximate Retention Time (min)	Internal standard	Quantifier transition	Qualifier transition	MDL ug/L	MDL ng/L	PQL ug/L	PQL ng/L
					extract	sample	extract	sample
Tetrachloro-m-xylene surrogate	6.38	DCB-d5	206.9 - 136.0	206.9 - 171.9				
Decachlorobiphenyl surrogate	16.27	HCB-d3	497.6 - 427.9	497.6 - 462.7				
PCB-1016					4.0	2.0	20	10
PCB-1016_1	6.37	DCB-d5	220.0 - 152.0	222.0 - 187.1				
PCB-1016_2	7.69	DCB-d5	220.0 - 152.0	222.0 - 187.1				
PCB-1016_3	8.08	TCB-d5	255.8 - 185.9	258.0 - 186.0				
PCB-1016_4	8.78	TCB-d5	255.8 - 185.9	258.0 - 186.0				
PCB-1016_5	9.68	TCB-d5	291.9 - 222.0	291.9 - 220.1				
PCB-1221					4.0	2.0	20	10
PCB-1221_1	5.47	DCB-d5	188.0 - 152.0	N/A				
PCB-1221_2	5.99	DCB-d5	188.0 - 152.0	N/A				
PCB-1221_3	6.30	TCB-d5	222.0 - 152.0	222.0 - 187.1				
PCB-1221_4	7.60	TCB-d5	222.0 - 152.0	222.0 - 187.1				
PCB-1221_5	7.70	TCB-d5	222.0 - 152.0	222.0 - 187.1				
PCB-1232					4.0	2.0	20	10
PCB-1232_1	6.30	DCB-d5	222.0 - 152.0	222.0 - 187.1				
PCB-1232_2	6.94	DCB-d5	222.0 - 152.0	222.0 - 187.1				
PCB-1232_3	8.00	TCB-d5	255.8 - 185.9	258.0 - 186.0				
PCB-1232_4	8.70	TCB-d5	255.8 - 185.9	258.0 - 186.0				
PCB-1232_5	9.59	TCB-d5	291.9 - 222.0	291.9 - 220.1				
PCB-1242					4.0	2.0	20	10
PCB-1242_1	6.30	DCB-d5	222.0 - 152.0	222.0 - 187.1				
PCB-1242_2	6.94	DCB-d5	222.0 - 152.0	222.0 - 187.1				
PCB-1242_3	8.00	TCB-d5	255.8 - 185.9	258.0 - 186.0				
PCB-1242_4	8.69	TCB-d5	255.8 - 185.9	258.0 - 186.0				
PCB-1242_5	8.84	TCB-d5	255.8 - 185.9	258.0 - 186.0				
PCB-1248					4.0	2.0	20	10
PCB-1248_1	7.99	DCB-d5	255.8 - 185.9	258.0 - 186.0				
PCB-1248_2	8.69	DCB-d5	255.8 - 185.9	258.0 - 186.0				
PCB-1248_3	9.59	TCB-d5	291.9 - 222.0	291.9 - 220.1				
PCB-1248_4	10.39	TCB-d5	291.9 - 222.0	291.9 - 220.1				
PCB-1248_5	10.46	TCB-d5	291.9 - 222.0	291.9 - 220.1				
PCB-1254					4.0	2.0	20	10

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Analyte	Approximate Retention Time (min)	Internal standard	Quantifier transition	Qualifier transition	MDL ug/L	MDL ng/L	PQL ug/L	PQL ng/L
PCB-1254_1	9.59	TCB-d5	291.9 - 222.0	291.9 - 220.1				
PCB-1254_2	10.39	TCB-d5	291.9 - 222.0	291.9 - 220.1				
PCB-1254_3	11.72	HCB-d5	325.9 - 255.9	325.9 - 253.9				
PCB-1254_4	12.27	HCB-d5	325.9 - 255.9	325.9 - 253.9				
PCB-1254_5	13.34	HCB-d3	359.8 - 289.9	359.8 - 324.9				
PCB-1260					4.0	2.0	20	10
PCB-1260_1	12.33	TCB-d5	359.8 - 289.9	359.8 - 324.9				
PCB-1260_2	12.85	TCB-d5	359.8 - 289.9	359.8 - 324.9				
PCB-1260_3	13.77	HCB-d3	393.8 - 323.9	393.8 - 358.7				
PCB-1260_4	14.13	HCB-d3	393.8 - 323.9	393.8 - 358.7				
PCB-1260_5	14.47	HCB-d3	393.8 - 323.9	393.8 - 358.7				
DCB-d5	6.68	Internal Std.	226.9 - 157.1	226.9 - 192.1				
TCB-d5	9.40	Internal Std.	296.8 - 225.0	296.8 - 262.0				
HCB-d3	14.42	Internal Std.	362.7 - 362.7	362.7 - 292.9				

The same MDL is applied to all PCB Aroclors.
All analytes are associated to both surrogates.

Table 2A: Analyte concentrations in calibration standards and ICV for Chlorinated pesticides (ug/L) (Test ID W-PCL-TQ-R). The expected spike concentrations in LFBs/MSs are equal to 6.4/12.8/25.6/51.2/ ug/L (in extract)

	L8	L7	L6	L5 CCV	L4	L3	L-2	L-1	ICV
W-PSCL	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
Aldrin	400	200	100	40	20	12	4	2	40
Alpha-BHC	200	100	50	20	10	6	2	1	20
Alpha-Chlordane	200	100	50	20	10	6	2	1	20
Beta-BHC	200	100	50	20	10	6	2	1	20
Beta-Cyfluthrin	800	400	200	80	40	24	8	4	80
Bifenthrin	200	100	50	20	10	6	2	1	20
Carbophenothion	800	400	200	80	40	24	8	4	80
Chlorothalonil	800	400	200	80	40	24	8	4	80
Cis-Nonachlor	200	100	50	20	10	6	2	1	20
Cypermethrin	800	400	200	80	40	24	8	4	80
Dacthal	200	100	50	20	10	6	2	1	20
DDD-p,p'	200	100	50	20	10	6	2	1	20
DDE-p,p'	200	100	50	20	10	6	2	1	20
DDT-p,p'	400	200	100	40	20	12	4	2	40
Delta-BHC	800	400	200	80	40	24	8	4	80

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	L8	L7	L6	L5 CCV	L4	L3	L-2	L-1	ICV
W-PSCL	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
Deltamethrin	800	400	200	80	40	24	8	4	80
Dichlobenil	200	100	50	20	10	6	2	1	20
Dicofol	800	400	200	80	40	24	8	4	80
Dieldrin	800	400	200	80	40	24	8	4	80
Endosulfan I	800	400	200	80	40	24	8	4	80
Endosulfan II	800	400	200	80	40	24	8	4	80
Endosulfan Sulfate	400	200	100	40	20	12	4	2	40
Endrin	800	400	200	80	40	24	8	4	80
Endrin Aldehyde	800	400	200	80	40	24	8	4	80
Endrin Ketone	800	400	200	80	40	24	8	4	80
Esfenvalerate	800	400	200	80	40	24	8	4	80
Ethalfluralin	200	100	50	20	10	6	2	1	20
Fenpropathrin	200	100	50	20	10	6	2	1	20
Gamma-BHC	200	100	50	20	10	6	2	1	20
Gamma-Chlordane	200	100	50	20	10	6	2	1	20
Heptachlor	200	100	50	20	10	6	2	1	20
Heptachlor Epoxide	200	100	50	20	10	6	2	1	20
Hexachlorobenzene	800	400	200	80	40	24	8	4	80
Kepone	1600	800	400	160	80	48	16	8	160
Lambda-Cyhallothrin	800	400	200	80	40	24	8	4	80
Methoprene	800	400	200	80	40	24	8	4	80
Methoxychlor	200	100	50	20	10	6	2	1	20
MGK-264	200	100	50	20	10	6	2	1	20
Mirex	800	200	100	40	20	12	4	2	40
Oxychlordane	200	100	50	20	10	6	2	1	20
Permethrin	800	400	200	80	40	24	8	4	80
Phenothrin	800	400	200	80	40	24	8	4	80
Piperonil Butoxide	200	100	50	20	10	6	2	1	20
Prallethrin	800	400	200	80	40	24	8	4	80
Tau-Fluvalinate	400	200	100	40	20	12	4	2	40
Tetramethrin	800	400	200	80	40	24	8	4	80
Trans-Nonachlor	200	100	50	20	10	6	2	1	20
Triclosan Methyl	200	100	50	20	10	6	2	1	20
Trifluralin	800	200	100	40	20	12	4	2	40
Tetrachloro-m-xylene	200	100	50	20	10	6	2	1	
DCB	200	100	50	20	10	6	2	1	

Table 2B Analyte concentrations in calibration standards and /QCS/ICV for PCB Aroclors (ug/L) (Test ID W-PCB-TQ-R). The expected spike concentrations in LFBs/MSs are equal to 40 ug/L (in extract)

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	L7	L6	L5	L4	L3/CCV	L2	L1	ICV/L3
AROCLORS	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
Tetrachloro-m-xylene	100	75	50	25	10	5	1	10
PCB-1016	1000	750	500	250	100	50	10	100
PCB-1221	1000	750	500	250	100	50	10	100
PCB-1232	1000	750	500	250	100	50	10	100
PCB-1242	1000	750	500	250	100	50	10	100
PCB-1248	1000	750	500	250	100	50	10	100
PCB-1254	1000	750	500	250	100	50	10	100
PCB-1260	1000	750	500	250	100	50	10	100
Decachlorobiphenyl	100	75	50	25	10	5	1	10

.

TABLE 3: QC MEASUREMENTS AND ACCEPTACE CRITERIA

QC MEASUREMENT	ACCEPTANCE CRITERION	CORRECTIVE ACTION
LFB, Matrix Spike recoveries and precision: W-PCL-TQ-R	Statistical limits as per QC limits tables	Reanalyze/Re-extract/Flag
LFB, Matrix spikes recoveries and precision W-PCB-TQ-R	Statistical limits as per QCM limits tables. For PCBs other than 1060, recoveries 50-120%, precision ,30%	Reanalyze/Re-extract/Flag
ICV	± 30%	Reanalyze/Flag
CCV	± 20%	Re-run and recalibrate/Flag
Surrogate recoveries for W-PCL-TQ-R	Tetrachloro-m-xylene 29-95%, Decachlorobiphenyl 26-115%,	Reanalyze/Re-extract/Flag
Surrogate recoveries for W-PCB-TQ-R	Tetrachloro-m-xylene 30-101% Decachlorobiphenyl 37-129%	Reanalyze/Re-extract/Flag
Linearity criterion	20% RSD; 0.99 R^2	Use appropriate cal fit / Re-run/ Recalibrate
Internal Std. recovery	-50% to+200%	Reanalyze/recalibrate/flag
% cal drift	± 30% of expected value	Change fit/ recalibrate/flag
Instrument performance check	< 20% DDT degradation, tailing factor more than 2.0 for pentachlorophenol.	Perform instrument maintenance, rerun the performance check sample.
Method Blank	<MDL	Rerun/re-extract; qualify samples with "V" if up to 10X the value in method blank.

Statistical recovery limits for LFB/MS and surrogates recoveries are typically based on QC Manager statistics for the last two to five calendar years (if available). The limits are recalculated at least annually.The results of statistical calculations are saved at FLDEP1\DEAR\LABS\LAB5\CHEMISTRY\ORGANIC\QC LIMITS STATS. The statistical recovery limits are then uploaded into QC Manager limits tables. The initial QC limits are replaced with statistical ones whenever enough data points are accumulated. For more details refer to ref 15.8 chapter 5.3.

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APPENDICES

APPENDIX 1A
GC/MS/MS dMRM acquisition method for Chlorinated pesticides, pyrethroids and environmental tracers. (ref 15.17)

Method File	C:\MassHunter\GCMS\1\methods\WCL_dMRM_210311.M\qqqacqmethod.xml
Tune File	atunes.eihs.tune.xml
Ion Source	EI
Source Temp. (°C)	300
Electron Energy Mode	Use tune setting
Fixed Electron Energy (eV)	
Stop Mode	By Chromatograph Time
Stop Time (min)	1
Solvent Delay (min)	4
Use Gain	Yes
EM Saver	
Auto Baseline Subtract	Yes
Advanced Filtering	Yes

Time filter type: off		
Row	**Time (min)**	**Peak Width (sec)**

Index	Start Time (min)	Scan Type	Electron Energy (eV)	Data Stored	Delta EMV (V)	Gain
1	4.00	dMRM		X		10

Time Events:

Time Segments:

Compound Name	ISTD ?	Precursor ion	MS1 res	Product ion	MS2 res	RT	Left Delta RT	Right Delta RT	Dwell (ms)	CE (V)
Dichlobenil		171	Unit	136.1	Wide	4.62	0.40	0.30	134.7	15
Dichlobenil		171	Unit	100	Wide	4.62	0.40	0.30	134.7	25
Tetrachloro-m-xylene		206.9	Unit	171.9	Wide	6.34	0.30	0.30	58.7	27
Tetrachloro-m-xylene		206.9	Unit	136	Wide	6.34	0.30	0.30	58.7	20
Ethalfluralin		316	Unit	276	Wide	6.57	0.30	0.30	32.2	11
Ethalfluralin		276	Unit	202	Wide	6.57	0.30	0.30	32.2	18
Trifluralin-d14	X	315	Unit	267.1	Wide	6.63	0.30	0.30	25.8	7
Trifluralin-d14	X	266.9	Unit	163.1	Wide	6.63	0.30	0.30	25.8	17

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Time Filter Table:

Total MRMs	136
Minimum Concurrent MRMs	2
Maximum Concurrent MRMs	23
Min Dwell (group average)	12.6
Max Dwell (group average)	134.7
Estimated Cycle Time	270.8027

DMRM Statistics:

Compound Table:

Compound Name	ISTD ?	Precursor ion	MS1 res	Product ion	MS2 res	RT	Left Delta RT	Right Delta RT	Dwell (ms)	CE (V)
DCB-d5	X	226.9	Unit	192.1	Wide	6.69	0.30	0.30	23.2	12
DCB-d5	X	226.9	Unit	157.1	Wide	6.69	0.30	0.30	23.2	28
Trifluralin		306.1	Unit	264	Wide	6.70	0.30	0.30	24.4	5
Trifluralin		306.1	Unit	160	Wide	6.70	0.30	0.30	24.4	30
alpha-BHC-d6	X	223.8	Unit	187	Wide	6.93	0.30	0.30	25.3	8
alpha-BHC-d6	X	223.8	Unit	150	Wide	6.93	0.30	0.30	25.3	23
Alpha-BHC		181	Unit	145	Wide	6.99	0.30	0.30	26.7	15
Alpha-BHC		181	Unit	109	Wide	6.99	0.30	0.30	26.7	30
Hexachlorobenzene		283.7	Unit	248.8	Wide	7.11	0.30	0.30	30	23
Hexachlorobenzene		283.7	Unit	213.9	Wide	7.11	0.30	0.30	30	35
Beta-BHC		181	Unit	145	Wide	7.43	0.30	0.30	44.4	15
Beta-BHC		181	Unit	109	Wide	7.43	0.30	0.30	44.4	30
Gamma-BHC		181	Unit	145	Wide	7.53	0.30	0.30	46.6	15
Gamma-BHC		181	Unit	109	Wide	7.53	0.30	0.30	46.6	30
Delta-BHC		181	Unit	145	Wide	7.95	0.30	0.30	51.8	15
Delta-BHC		181	Unit	109	Wide	7.95	0.30	0.30	51.8	30
Chlorothalonil		265.9	Unit	230.9	Wide	8.04	0.30	0.30	81.9	20
Chlorothalonil		265.9	Unit	133	Wide	8.04	0.30	0.30	81.9	40
Heptachlor		271.9	Unit	236.8	Wide	8.83	0.30	0.30	134.7	25
Heptachlor		271.9	Unit	234.8	Wide	8.83	0.30	0.30	134.7	14
TCB-d5	X	296.8	Unit	262	Wide	9.49	0.30	0.30	30.9	12
TCB-d5	X	296.8	Unit	225	Wide	9.49	0.30	0.30	30.9	28
Aldrin		262.9	Unit	192.9	Wide	9.50	0.30	0.30	30.9	40
Aldrin		262.9	Unit	190.9	Wide	9.50	0.30	0.30	30.9	40
Aldrin		260.9	Unit	190.9	Wide	9.50	0.30	0.30	30.9	40
Aldrin		254.9	Unit	220	Wide	9.50	0.30	0.30	30.9	35
Dacthal		300.8	Unit	257.8	Wide	9.76	0.30	0.30	28.3	25
Dacthal		300.8	Unit	222.9	Wide	9.76	0.30	0.30	28.3	30
MGK-264 1		164.1	Unit	98.1	Wide	9.99	0.40	0.30	27.1	15
MGK-264 1		164.1	Unit	80.1	Wide	9.99	0.40	0.30	27.1	30

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Compound Name	ISTD ?	Precursor ion	MS1 res	Product ion	MS2 res	RT	Left Delta RT	Right Delta RT	Dwell (ms)	CE (V)
Oxychlordane		387	Unit	263	Wide	10.17	0.40	0.30	26.8	14
Oxychlordane		187	Unit	151	Wide	10.17	0.40	0.30	26.8	4
Oxychlordane		185	Unit	149	Wide	10.17	0.40	0.30	26.8	4
MGK-264 2		164.1	Unit	98.1	Wide	10.22	0.40	0.30	25.8	15
MGK-264 2		164.1	Unit	80.1	Wide	10.22	0.40	0.30	25.8	30
Heptachlor Epoxide		352.9	Unit	281.9	Wide	10.32	0.30	0.30	25.8	16
Heptachlor Epoxide		352.9	Unit	262.8	Wide	10.32	0.30	0.30	25.8	15
Methoprene		153	Unit	111	Wide	10.57	0.30	0.30	26.1	5
Methoprene		107	Unit	91	Wide	10.57	0.30	0.30	26.1	10
Gamma-Chlordane		372.9	Unit	263.9	Wide	10.81	0.30	0.30	24.7	20
Gamma-Chlordane		271.7	Unit	236.9	Wide	10.81	0.30	0.30	24.7	12
Prallethrin		168.1	Unit	123.1	Wide	10.87	0.40	0.40	23.9	8
Prallethrin		153.1	Unit	107.1	Wide	10.87	0.40	0.40	23.9	13
Prallethrin		153.1	Unit	90.9	Wide	10.87	0.40	0.40	23.9	26
Alpha-Chlordane		372.9	Unit	263.9	Wide	11.03	0.30	0.30	20	20
Alpha-Chlordane		271.7	Unit	236.9	Wide	11.03	0.30	0.30	20	12
Triclosan Methyl		301.8	Unit	251.9	Wide	11.05	0.40	0.30	20.9	20
Triclosan Methyl		301.8	Unit	189	Wide	11.05	0.40	0.30	20.9	42
Endosulfan I		339	Unit	267	Wide	11.14	0.30	0.30	19.3	2
Endosulfan I		240.9	Unit	205.9	Wide	11.14	0.30	0.30	19.3	15
Endosulfan I		240.9	Unit	136	Wide	11.14	0.30	0.30	19.3	40
Endosulfan I		206.8	Unit	172	Wide	11.14	0.30	0.30	19.3	13
Trans-Nonachlor		408.7	Unit	372.7	Wide	11.23	0.30	0.30	21.8	10
Trans-Nonachlor		408.7	Unit	299.8	Wide	11.23	0.30	0.30	21.8	19
DDE-p,p'		246	Unit	176.1	Wide	11.60	0.30	0.30	28.2	40
DDE-p,p'		246	Unit	175.1	Wide	11.60	0.30	0.30	28.2	40
Dieldrin		277	Unit	240.8	Wide	11.60	0.30	0.30	28.2	5
Dieldrin		262.9	Unit	192.9	Wide	11.60	0.30	0.30	28.2	40
Dieldrin		262.9	Unit	190.9	Wide	11.60	0.30	0.30	28.2	40
Dieldrin		260.9	Unit	190.9	Wide	11.60	0.30	0.30	28.2	35
Endrin		281	Unit	245	Wide	12.06	0.30	0.30	47.8	7
Endrin		262.8	Unit	192.8	Wide	12.06	0.30	0.30	47.8	30
Endrin		262.7	Unit	191.1	Wide	12.06	0.30	0.30	47.8	40
Endosulfan II		241	Unit	206	Wide	12.26	0.30	0.30	37.3	15
Endosulfan II		206.9	Unit	172.1	Wide	12.26	0.30	0.30	37.3	14
DDD-p,p'		235	Unit	199.1	Wide	12.49	0.30	0.30	32.8	20
DDD-p,p'		235	Unit	165.1	Wide	12.49	0.30	0.30	32.8	25
Cis-Nonachlor		408.7	Unit	372.7	Wide	12.55	0.30	0.30	32.1	10
Cis-Nonachlor		408.7	Unit	299.8	Wide	12.55	0.30	0.30	32.1	19
Endrin Aldehyde		344.8	Unit	280.9	Wide	12.68	0.30	0.30	30.4	6
Endrin Aldehyde		344.8	Unit	244.9	Wide	12.68	0.30	0.30	30.4	10
Kepone		355	Unit	320	Wide	12.83	0.30	0.50	26.3	30

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Compound Name	ISTD ?	Precursor ion	MS1 res	Product ion	MS2 res	RT	Left Delta RT	Right Delta RT	Dwell (ms)	CE (V)
Kepone		355	Unit	285	Wide	12.83	0.30	0.50	26.3	35
Carbophenothion		343.9	Unit	158.9	Wide	13.06	0.30	0.30	24.3	13
Carbophenothion		341.9	Unit	157	Wide	13.06	0.30	0.30	24.3	13
Endosulfan Sulfate		387	Unit	253	Wide	13.19	0.30	0.30	18.4	10
Endosulfan Sulfate		271.9	Unit	116.9	Wide	13.19	0.30	0.30	18.4	40
Endosulfan Sulfate		271.7	Unit	236.8	Wide	13.19	0.30	0.30	18.4	12
Endosulfan Sulfate		269.7	Unit	234.9	Wide	13.19	0.30	0.30	18.4	12
DDT-D8	X	243.03	Unit	206.14	Wide	13.23	0.30	0.30	17.7	15
DDT-D8	X	243.03	Unit	172.6	Wide	13.23	0.30	0.30	17.7	20
DDT-p,p'		235	Unit	199.1	Wide	13.28	0.30	0.30	17.9	20
DDT-p,p'		235	Unit	165.1	Wide	13.28	0.30	0.30	17.9	30
Piperonyl Butoxide		176.1	Unit	117.1	Wide	13.80	0.40	0.30	19.6	25
Piperonyl Butoxide		176.1	Unit	103.1	Wide	13.80	0.40	0.30	19.6	30
Endrin Ketone		316.9	Unit	280.9	Wide	14.04	0.30	0.30	16.7	7
Endrin Ketone		316.9	Unit	101.1	Wide	14.04	0.30	0.30	16.7	14
Tetramethrin		164.1	Unit	135.1	Wide	14.15	1.00	1.00	17.2	15
Tetramethrin		164.1	Unit	107.1	Wide	14.15	1.00	1.00	17.2	15
Tetramethrin		164.1	Unit	77	Wide	14.15	1.00	1.00	17.2	30
HCB-d3	X	362.7	Unit	362.7	Wide	14.22	0.30	0.30	14.1	5
HCB-d3	X	362.7	Unit	292.9	Wide	14.22	0.30	0.30	14.1	32
Dicofol-d8		142.9	Unit	115.1	Wide	14.24	0.30	0.30	13.1	15
Dicofol-d8		142.9	Unit	78	Wide	14.24	0.30	0.30	13.1	34
Bifenthrin		181.1	Unit	166.1	Wide	14.26	0.30	0.30	12.6	13
Bifenthrin		181.1	Unit	165.1	Wide	14.26	0.30	0.30	12.6	33
Dicofol		253	Unit	141	Wide	14.28	0.30	0.30	12.6	15
Dicofol		251	Unit	139	Wide	14.28	0.30	0.30	12.6	15
Fenpropathrin		265	Unit	210	Wide	14.29	1.00	1.00	18.9	15
Fenpropathrin		181.1	Unit	152.1	Wide	14.29	1.00	1.00	18.9	30
Fenpropathrin		181.1	Unit	127.1	Wide	14.29	1.00	1.00	18.9	35
Fenpropathrin		181	Unit	126	Wide	14.29	1.00	1.00	18.9	30
Methoxychlor		227.1	Unit	169.1	Wide	14.29	0.30	0.30	13.2	30
Methoxychlor		227.1	Unit	141.1	Wide	14.29	0.30	0.30	13.2	40
Phenothrin		183.1	Unit	168.1	Wide	14.51	0.40	0.40	13.3	15
Phenothrin		183.1	Unit	153.1	Wide	14.51	0.40	0.40	13.3	15
Mirex		271.9	Unit	236.9	Wide	14.74	0.30	0.30	16.1	15
Mirex		271.9	Unit	234.8	Wide	14.74	0.30	0.30	16.1	14
Lambda-Cyhalothrin		208	Unit	181	Wide	14.78	0.40	0.40	18.1	7
Lambda-Cyhalothrin		181.1	Unit	152.1	Wide	14.78	0.40	0.40	18.1	30
Permethrin		183.1	Unit	168.1	Wide	15.39	0.40	0.40	49.5	15
Permethrin		183.1	Unit	153.1	Wide	15.39	0.40	0.40	49.5	15
Beta-Cyfluthrin		226.1	Unit	206.1	Wide	15.74	0.40	0.40	41.4	15
Beta-Cyfluthrin		163	Unit	127.1	Wide	15.74	0.40	0.40	41.4	5

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Compound Name	ISTD ?	Precursor ion	MS1 res	Product ion	MS2 res	RT	Left Delta RT	Right Delta RT	Dwell (ms)	CE (V)
Octachloronaphthalene		354.9	Unit	267	Wide	15.93	0.40	0.40	35.6	15
Octachloronaphthalene		354.9	Unit	251	Wide	15.93	0.40	0.40	35.6	40
Cypermethrin		208.9	Unit	169.2	Wide	15.95	0.40	0.40	36	11
Cypermethrin		180.9	Unit	152.1	Wide	15.95	0.40	0.40	36	23
Cypermethrin		163	Unit	127.1	Wide	15.95	0.40	0.40	36	6
Decachlorobiphenyl		497.6	Unit	462.7	Wide	16.27	0.30	0.30	37.3	15
Decachlorobiphenyl		497.6	Unit	427.9	Wide	16.27	0.30	0.30	37.3	20
Tau-Fluvalinate		252	Unit	55	Wide	16.75	0.40	0.30	44.6	15
Tau-Fluvalinate		250	Unit	55	Wide	16.75	0.40	0.30	44.6	15
Esfenvalerate		225	Unit	119	Wide	16.76	0.40	0.30	46.7	18
Esfenvalerate		167.1	Unit	125.1	Wide	16.76	0.40	0.30	46.7	12
Deltamethrin		253	Unit	172	Wide	17.26	0.40	0.30	45.5	5
Deltamethrin		253	Unit	93	Wide	17.26	0.40	0.30	45.5	20
Deltamethrin		181.1	Unit	152.1	Wide	17.26	0.40	0.30	45.5	25

INSTRUMENT CONTROL PARAMETERS: GC_TQ-2

C:\MassHunter\GCMS\1\methods\WCL_dMRM_210311.M
Tue Mar 16 08:13:52 2021

Control Information

Sample Inlet : GC
Injection Source : GC ALS
Injection Location: Front
Mass Spectrometer : Enabled

No Sample Prep method has been assigned to this method.

GC
GC Summary
Run Time 21.9 min
Post Run Time 0 min

Oven Temperature
Setpoint On
(Initial) 50 °C
Hold Time 1.5 min
Post Run 280 °C
Program
#1 Rate 55 °C/min
#1 Value 160 °C

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#1 Hold Time	**0 min**
#2 Rate	**8 °C/min**
#2 Value	**240 °C**
#2 Hold Time	**0 min**
#3 Rate	**50 °C/min**
#3 Value	**280 °C**
#3 Hold Time	**0 min**
#4 Rate	**100 °C/min**
#4 Value	**290 °C**
#4 Hold Time	**7.5 min**

Equilibration Time	**0.5 min**
Max Temperature	**325 °C**
Maximum Temperature Override	**Disabled**
Slow Fan	**Disabled**

ALS
Front Injector

Syringe Size	**10 µL**
Injection Volume	**1 µL**
Solvent A Washes (PreInj)	**5**
Solvent A Washes (PostInj)	**15**
Solvent A Volume	**8 µL**
Solvent B Washes (PreInj)	**5**
Solvent B Washes (PostInj)	**15**
Solvent B Volume	**8 µL**
Sample Washes	**1**
Sample Wash Volume	**4 µL**
Sample Pumps	**7**
Dwell Time (PreInj)	**0 min**
Dwell Time (PostInj)	**0 min**
Solvent Wash Draw Speed	**300 µL/min**
Solvent Wash Dispense Speed	**3000 µL/min**
Sample Wash Draw Speed	**300 µL/min**
Sample Wash Dispense Speed	**3000 µL/min**
Injection Dispense Speed	**6000 µL/min**
Viscosity Delay	**7 sec**
Sample Depth	**Disabled**
Injection Type	**3-layer Sandwich (L1,L2,L3)**
L1 Airgap	**0 µL**
L2 Volume	**0.2 µL**
L2 Airgap	**0 µL**
L3 Volume	**0.4 µL**
L3 Airgap	**0 µL**
Solvent Wash Mode	**A-A6,B-B4**

Sample Overlap

Mode	**Prepare sample after end of GC run 2 min**

ALS Errors	**Pause for user interaction**

Front MM Inlet He
Front MM Inlet He Temperature

Setpoint	**On**
(Initial)	**70 °C**

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Hold Time	**0.35 min**
Program	
#1 Rate	**900 °C/min**
#1 Value	**280 °C**
#1 Hold Time	**14 min**
#2 Rate	**900 °C/min**
#2 Value	**300 °C**
#2 Hold Time	**0 min**

Mode	**Pulsed Splitless**
Pressure	**On 2.3728 psi**
Total Flow	**On 53.8 mL/min**
Septum Purge Flow	**On 3 mL/min**
Septum Purge Flow Mode	**Standard**
Gas Saver	**Off**
Injection Pulse Pressure	**30 psi Until 1.4 min**
Purge Flow to Split Vent	**50 mL/min at 1.5 min**
Cryo	**On**
Cryo Type	**N2**
Fast Cooldown	**Off**
Cryo Use Temperature	**150 °C**
Timeout Detection	**Off**
Fault Detection	**Off**
Liner	**A Liner has not been selected.**

Back SS Inlet He	
Excluded from Readiness	*****Excluded from Affecting GC's Readiness State*****
Mode	**Splitless**
Heater	**Off**
Pressure	**Off**
Total Flow	**Off**
Septum Purge Flow	**On 2 mL/min**
Septum Purge Flow Mode	**Standard**
Purge Flow to Split Vent	**60 mL/min at 2 min**
Liner	**A Liner has not been selected.**

Thermal Aux 2 (MSD Transfer Line)	
Temperature	
Setpoint	**On**
(Initial)	**300 °C**

Column	
Column #1	
Flow	
Setpoint	**On**
(Initial)	**0.8 mL/min**
Hold Time	**17.5 min**
Post Run	**-4.3283 mL/min**
Program	
#1 Rate	**100 mL/min per min**
#1 Value	**-2.5 mL/min**
#1 Hold Time	**1.5 min**
#2 Rate	**100 mL/min per min**
#2 Value	**-5 mL/min**

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#2 Hold Time **0 min**

Column Information **Agilent 19091S-431UI: 2197.57912**
HP-5MS UI
Temperature Range **-60 °C—325 °C (325 °C)**
Dimensions **5 m x 250 µm x 0.25 µm**
In **Front MM Inlet He**
Out **Aux EPC 6**
(Initial) **50 °C**
Pressure **2.3728 psi**
Flow **0.8 mL/min**
Average Velocity **27.06 cm/sec**
Holdup Time **0.30796 min**
Control Mode **Ramped Flow**

Column #2
Flow
Setpoint **On**
(Initial) **0.9 mL/min**
Hold Time **19.03 min**
Post Run **0.98996 mL/min**
Program
#1 Rate **100 mL/min per min**
#1 Value **2.4 mL/min**
#1 Hold Time **0 min**

Column Information **Agilent 19091S-431: 2**
HP-5MS UI
Temperature Range **-60 °C—325 °C (325 °C)**
Dimensions **15 m x 250 µm x 0.25 µm**
In **Aux EPC 6 He**
Out **MSD**
(Initial) **50 °C**
Pressure **0.29568 psi**
Flow **0.9 mL/min**
Average Velocity **48.896 cm/sec**
Holdup Time **0.51129 min**
Control Mode **Ramped Flow**

Column Outlet Pressure **0 psi**

Aux EPC 4,5,6
Aux EPC 4 N2
Pressure
Setpoint **Off**
(Initial) **2.6149 psi**
Post Run **0 psi**

Excluded from Readiness *****Excluded from Affecting GC's Readiness State*****

Aux EPC 5 N2
Pressure
Setpoint **Off**
(Initial) **10 psi**

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Post Run **0 psi**

Excluded from Readiness *****Excluded from Affecting GC's Readiness State*****

Aux EPC 6 He
Excluded from Readiness *****Excluded from Affecting GC's Readiness State*****
Aux EPC 6 He **Supplies Column 2**

Collision Cell EPC
Quench Gas He **On 2.25 mL/min**
Collision Gas N2 **On 1.5 mL/min**

Signals
Signal #1: Test Plot
Description **Test Plot**
Save **Off**
Data Rate **50 Hz**
Dual Injection Assignment **Front Sample**

Signal #2: Test Plot
Description **Test Plot**
Save **Off**
Data Rate **50 Hz**
Dual Injection Assignment **Front Sample**

Signal #3: Test Plot
Description **Test Plot**
Save **Off**
Data Rate **50 Hz**
Dual Injection Assignment **Back Sample**

Signal #4: Test Plot
Description **Test Plot**
Save **Off**
Data Rate **50 Hz**
Dual Injection Assignment **Back Sample**

END OF INSTRUMENT CONTROL PARAMETERS

APPENDIX 1B

GC/MS/MS ACQUISITION METHOD FOR PCB AROCLORS (ref 15.21)

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Method File	C:\MassHunter\GCMS\1\methods\AR-W_dMRM_201201.M\qqqacqmethod.xml
Tune File	atunes.eihs.tune.xml
Ion Source	EI
Source Temp. (°C)	300
Electron Energy Mode	Use tune setting
Fixed Electron Energy (eV)	
Stop Mode	By Chromatograph Time
Stop Time (min)	1
Solvent Delay (min)	3.70000004768372
Use Gain	Yes
EM Saver	
Auto Baseline Subtract	Yes
Advanced Filtering	No

Time filter type: off

Row	Time (min)	Peak Width (sec)

Index	Start Time (min)	Scan Type	Electron Energy (eV)	Data Stored	Delta EMV (V)	Gain
1	3.70	dMRM		X		10

Time Events:

Time Segments:

Time Filter Table:

Total MRMs	28
Minimum Concurrent MRMs	1
Maximum Concurrent MRMs	13
Min Dwell (group average)	23.2
Max Dwell (group average)	77.9
Estimated Cycle Time	286.5936

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DMRM Statistics:
Triple Quadrupole Acquisition Method - MS Parameters Report

Compound Name	ISTD ?	Precursor ion	MS1 res	Product ion	MS2 res	RT	Left Delta RT	Right Delta RT	Dwell (ms)	CE (V)
Monochlorobiphenyl-2		153.9	Unit	115.2	Wide	4.45	0.20	3.50	77.9	22
Monochlorobiphenyl		188	Unit	152	Wide	5.55	0.50	2.00	54.4	25
Tetrachloro-m-xylene		206.9	Unit	171.9	Wide	6.40	0.50	0.50	47.3	27
Tetrachloro-m-xylene		206.9	Unit	136	Wide	6.40	0.50	0.50	47.3	20
Dichlorobiphenyl		222	Unit	152	Wide	6.45	0.50	6.00	31.6	25
Dichlorobiphenyl-2		222	Unit	187.1	Wide	6.45	0.50	6.00	31.6	9
Dichlorobiphenyl-3		219.8	Unit	149.7	Wide	6.45	0.50	6.00	31.6	26
DCB-d5	X	226.9	Unit	192.1	Wide	6.73	0.50	0.50	32.1	12
DCB-d5	X	226.9	Unit	157.1	Wide	6.73	0.50	0.50	32.1	28
Tetrachlorobiphenyl		291.9	Unit	222	Wide	7.45	0.50	8.00	27.9	25
Tetrachlorobiphenyl-2		291.9	Unit	220.1	Wide	7.45	0.50	8.00	27.9	22
Trichlorobiphenyl		258	Unit	186	Wide	7.45	0.50	6.00	29.2	25
Trichlorobiphenyl-2		255.8	Unit	185.9	Wide	7.45	0.50	6.00	29.2	21
TCB-d5	X	296.8	Unit	262	Wide	9.43	0.50	1.00	27	12
TCB-d5	X	296.8	Unit	225	Wide	9.43	0.50	1.00	27	28
Pentachlorobiphenyl		325.9	Unit	255.9	Wide	10.05	0.50	7.00	26.4	25
Pentachlorobiphenyl-2		325.9	Unit	291	Wide	10.05	0.50	7.00	26.4	10
Pentachlorobiphenyl-3		325.9	Unit	253.9	Wide	10.05	0.50	7.00	26.4	18
Hexachlorobiphenyl		359.8	Unit	289.9	Wide	11.75	0.50	5.50	31.5	25
Hexachlorobiphenyl-2		359.8	Unit	324.9	Wide	11.75	0.50	5.50	31.5	11
Heptachlorobiphenyl		393.8	Unit	323.9	Wide	13.15	0.50	4.00	28.5	25
Heptachlorobiphenyl-2		393.8	Unit	358.7	Wide	13.15	0.50	4.00	28.5	12
HCB-d3	X	362.7	Unit	362.7	Wide	14.23	0.50	0.50	23.2	5
HCB-d3	X	362.7	Unit	292.9	Wide	14.23	0.50	0.50	23.2	32
Octachlorobiphenyl		427.8	Unit	357.8	Wide	14.25	0.50	3.00	34.3	25
Nonachlorobiphenyl		461.7	Unit	391.8	Wide	14.75	0.50	3.00	67.1	25
Decachlorobiphenyl		497.6	Unit	462.7	Wide	16.28	0.50	0.50	25.2	15
Decachlorobiphenyl		497.6	Unit	427.9	Wide	16.28	0.50	0.50	25.2	20

Compound Table:
Triple Quadrupole Acquisition Method - MS Parameters Report

INSTRUMENT CONTROL PARAMETERS: GC_TQ-1

C:\MassHunter\GCMS\1\methods\AR-W_dMRM_201201.M
Tue Dec 01 08:05:22 2020

Control Information
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Sample Inlet : GC
Injection Source : GC ALS
Injection Location: Front
Mass Spectrometer : Enabled

No Sample Prep method has been assigned to this method.

GC
GC Summary

Run Time	21.4 min
Post Run Time	0 min

Oven
Temperature

Setpoint	On
(Initial)	50 °C
Hold Time	1.5 min
Post Run	280 °C

Program

#1 Rate	55 °C/min
#1 Value	160 °C
#1 Hold Time	0 min
#2 Rate	8 °C/min
#2 Value	240 °C
#2 Hold Time	0 min
#3 Rate	50 °C/min
#3 Value	280 °C
#3 Hold Time	0 min
#4 Rate	100 °C/min
#4 Value	290 °C
#4 Hold Time	7 min

Equilibration Time	0.5 min
Max Temperature	325 °C
Maximum Temperature Override	Disabled
Slow Fan	Disabled

ALS
Front Injector

Syringe Size	10 µL
Injection Volume	1 µL
Solvent A Washes (PreInj)	5
Solvent A Washes (PostInj)	15
Solvent A Volume	8 µL
Solvent B Washes (PreInj)	5
Solvent B Washes (PostInj)	15
Solvent B Volume	8 µL
Sample Washes	1
Sample Wash Volume	4 µL
Sample Pumps	7
Dwell Time (PreInj)	0 min
Dwell Time (PostInj)	0 min
Solvent Wash Draw Speed	300 µL/min

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Solvent Wash Dispense Speed	3000 µL/min
Sample Wash Draw Speed	300 µL/min
Sample Wash Dispense Speed	3000 µL/min
Injection Dispense Speed	6000 µL/min
Viscosity Delay	7 sec
Sample Depth	Disabled
Injection Type	3-layer Sandwich (L1,L2,L3)
L1 Airgap	0 µL
L2 Volume	0.2 µL
L2 Airgap	0 µL
L3 Volume	0.4 µL
L3 Airgap	0 µL
Solvent Wash Mode	A-A6,B-B4

Sample Overlap Mode	Prepare sample after end of GC run 5 min

ALS Errors	Pause for user interaction

Front MM Inlet He

Front MM Inlet He Temperature	
Setpoint	On
(Initial)	70 °C
Hold Time	0.35 min
Program	
#1 Rate	900 °C/min
#1 Value	280 °C
#1 Hold Time	14 min
#2 Rate	900 °C/min
#2 Value	300 °C
#2 Hold Time	0 min

Mode	Pulsed Splitless
Pressure	On 2.3728 psi
Total Flow	On 53.8 mL/min
Septum Purge Flow	On 3 mL/min
Septum Purge Flow Mode	Standard
Gas Saver	Off
Injection Pulse Pressure	30 psi Until 1.4 min
Purge Flow to Split Vent	50 mL/min at 1.5 min
Cryo	On
Cryo Type	N2
Fast Cooldown	Off
Cryo Use Temperature	150 °C
Timeout Detection	Off
Fault Detection	Off
Liner	A Liner has not been selected.

Back SS Inlet He

Excluded from Readiness	***Excluded from Affecting GC's Readiness State***
Mode	Splitless
Heater	Off
Pressure	On 1 psi
Total Flow	On 5.25 mL/min
Septum Purge Flow	On 2 mL/min

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Septum Purge Flow Mode	Standard
Purge Flow to Split Vent	60 mL/min at 2 min
Liner	A Liner has not been selected.

Thermal Aux 2 (MSD Transfer Line)

Temperature	
Setpoint	On
(Initial)	300 °C

Column

Column #1	
Flow	
Setpoint	On
(Initial)	0.8 mL/min
Hold Time	17 min
Post Run	-4.3283 mL/min
Program	
#1 Rate	100 mL/min per min
#1 Value	-2.5 mL/min
#1 Hold Time	1.5 min
#2 Rate	100 mL/min per min
#2 Value	-5 mL/min
#2 Hold Time	0 min

Column Information	Agilent 19091S-431UI: 2197.57912
HP-5MS UI	
Temperature Range	-60 °C—325 °C (325 °C)
Dimensions	5 m x 250 µm x 0.25 µm
In	Front MM Inlet He
Out	Aux EPC 4
(Initial)	50 °C
Pressure	2.3728 psi
Flow	0.8 mL/min
Average Velocity	27.06 cm/sec
Holdup Time	0.30796 min
Control Mode	Ramped Flow

Column #2	
Flow	
Setpoint	On
(Initial)	0.9 mL/min
Hold Time	18.53 min
Post Run	0.98996 mL/min
Program	
#1 Rate	100 mL/min per min
#1 Value	2.4 mL/min
#1 Hold Time	0 min

Column Information	Agilent 19091S-431: 2
HP-5MS UI	
Temperature Range	-60 °C—325 °C (325 °C)
Dimensions	15 m x 250 µm x 0.25 µm
In	Aux EPC 4 He

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Out	MSD
(Initial)	50 °C
Pressure	0.29568 psi
Flow	0.9 mL/min
Average Velocity	48.896 cm/sec
Holdup Time	0.51129 min
Control Mode	Ramped Flow

Column Outlet Pressure	0 psi

Aux EPC 4,5,6	
Aux EPC 4 He	
Excluded from Readiness	***Excluded from Affecting GC's Readiness State***
Aux EPC 4 He	Supplies Column 2

Aux EPC 5 N2	
Pressure	
Setpoint	Off
(Initial)	10 psi
Post Run	0 psi

Excluded from Readiness	***Excluded from Affecting GC's Readiness State***

Aux EPC 6 N2	
Pressure	
Setpoint	Off
(Initial)	0.29568 psi
Post Run	0 psi

Excluded from Readiness	***Excluded from Affecting GC's Readiness State***

Collision Cell EPC		
Quench Gas He	On	2.25 mL/min
Collision Gas N2	On	1.5 mL/min

Signals

Signal #1: Test Plot	
Description	Test Plot
Save	Off
Data Rate	50 Hz
Dual Injection Assignment	Front Sample

Signal #2: Test Plot	
Description	Test Plot
Save	Off
Data Rate	50 Hz
Dual Injection Assignment	Front Sample

Signal #3: Test Plot	
Description	Test Plot
Save	Off
Data Rate	50 Hz
Dual Injection Assignment	Back Sample

Signal #4: Test Plot

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Description	Test Plot
Save	Off
Data Rate	50 Hz
Dual Injection Assignment	Back Sample

END OF INSTRUMENT CONTROL PARAMETERS

APPENDIX 2: Standard Preparation Procedure

Stock solutions usually come in 1ml glass vials. Take the vials out of the freezer at least 30min before preparation. Open vials and transfer the entire solution into 1mL GC vials (using Pasteur pipettes). Record the transfer date and keep the vial label.

The Intermediate Standard is prepared by diluting the Stock solution. The Working Level Standards are prepared by diluting the Intermediate Standard.

All standard preparations are recorded in the Standard/Reagent Preparation Tracker. In order to prepare fresh standards, go to LIMS-Technical-Standard/Reagent Preparation Tracker. Select GC from the pull down list. Hit “Reports” and then “History”. When prompted enter the standard tracking number for the standard you are going to replace. Examine the “History Tree”. An example of a “History Tree” is shown below:

History of Serial# 76827

76827- PSCL_TQ ICV L6
- 76812-PSCL_TQ_ ICV INT
  - 75889-ECD A
  - 75885-ECD B STOCK
- 76629-CL_MS_ISTD_ lOO_ PPM
  - 76628-CL_MS_ISTD_STOCK
    - 68086-CL_ MS_ ISTD_STOCK
      - 68083-A-BHC-D6 NEAT
      - 68082-DDT-DB
      - 66960-HCB-D3 NEAT
      - 66959-TCB-DS NEAT
      - 66958-DCB-DS NEAT

In order to get exact information on how the standard was prepared look at “history data sheets” that will show exact information on standards preparations.
Additionally, standards preparations are tabulated in excel files “STANDARDS-PREP-yyyy-mm-dd” located at \\FLDEP1\DEAR\LABS\LAB5\Chemistry\organic\GC-MDL-STD-SPK.
Before preparing new standards consult with the GC group supervisor whether any changes to standards preparation procedures should be made. Those may include different prepared volumes, concentrations, new, additional concentration levels, etc.

All freshly prepared standards need to be entered in the Standard Preparation Tracker.

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APPENDIX 3

ANALYTE PROTECTANTS

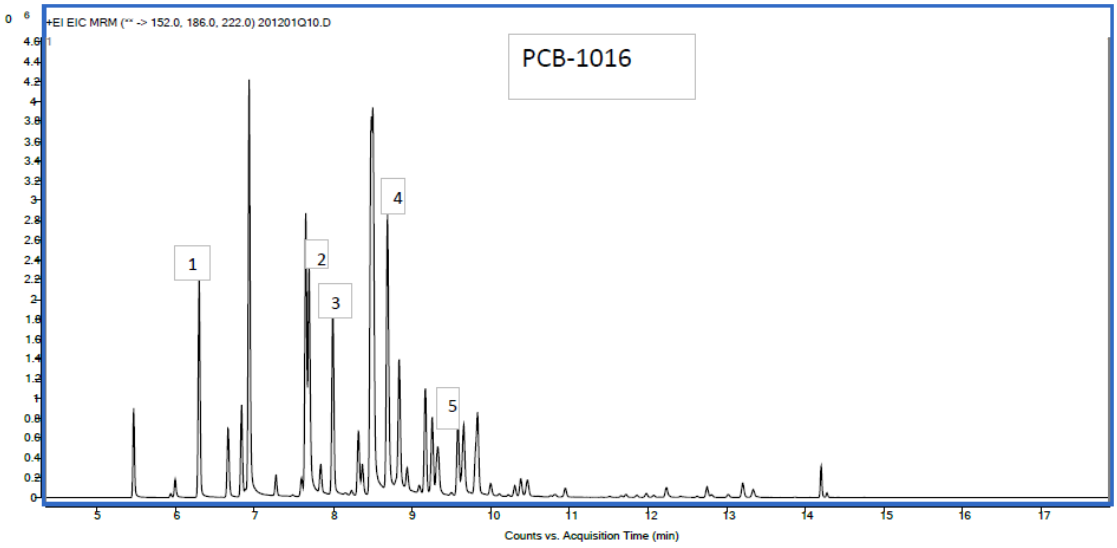
Follow the instructions in appendix 2 to re-prepare analytes protectants solutions.

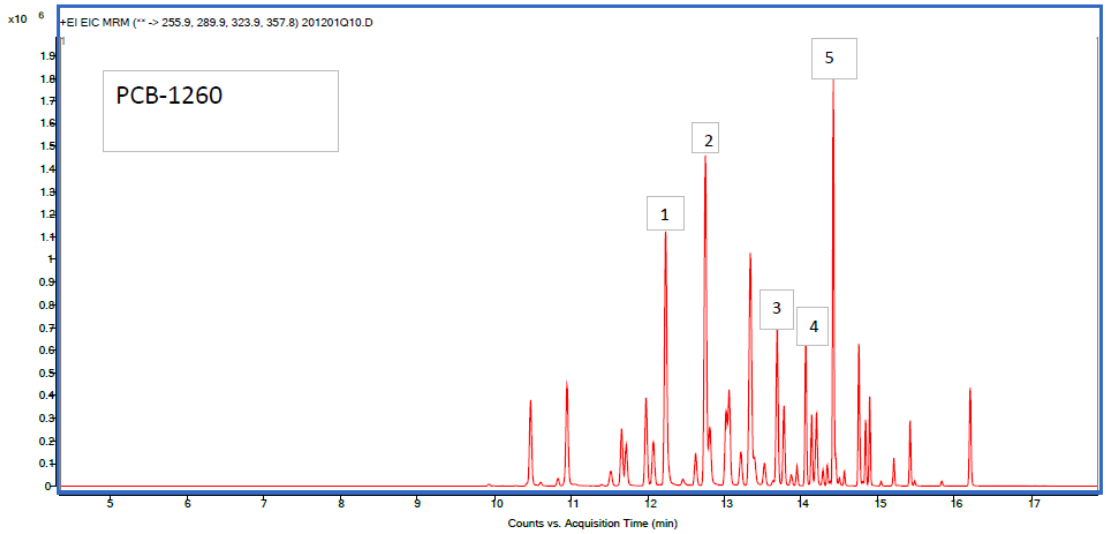
Notes:

Neat D-sorbitol is hygroscopic and should be stored in a desiccator. D-Sorbitol and, especially, gulonolactone are difficult to dissolve in MeOH. To achieve complete dissolution of these components, 1 – 3 hours of hot sonication and repeated vigorous shaking (vortexing) may be needed. To avoid extensive sonication, required quantities of analyte protectants may be initially dissolved in 5 mL of water. The resulting solution may then be brought up to the final volume of 100 mL by adding methanol. The resulting solution is saturated with gulonolactone and therefore should be kept at room temperature to avoid excessive precipitation. Some precipitation, however, appears to be unavoidable.

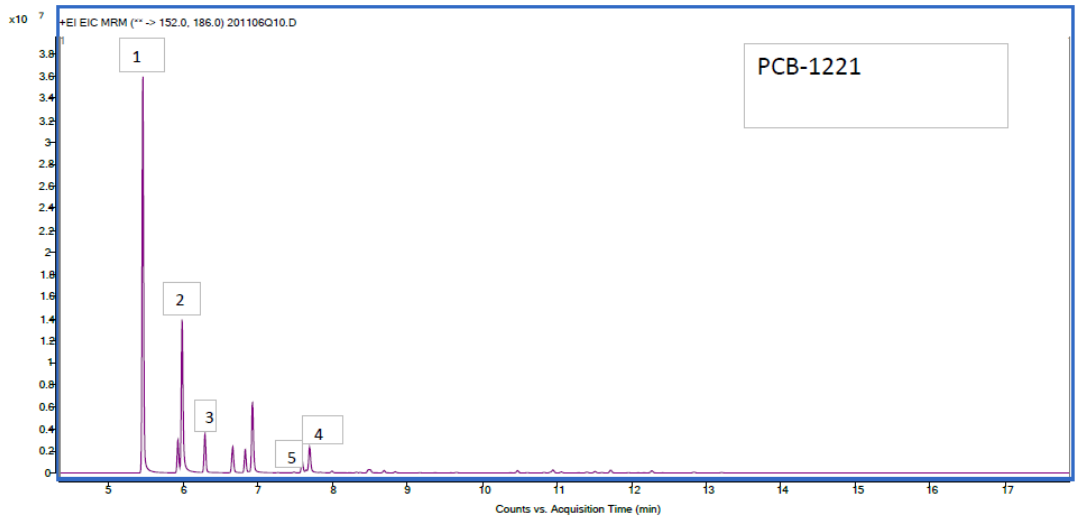
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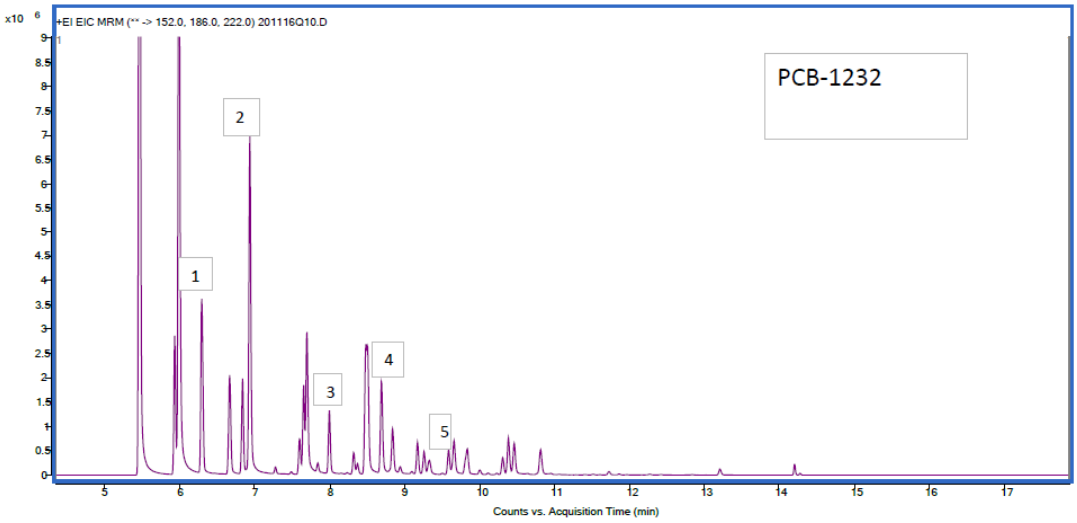
APPENDIX 4: PCB aroclor patterns and analytical peaks as extracted with the corresponding EIC "extract *PCB name*" method in Masshunter Qual.



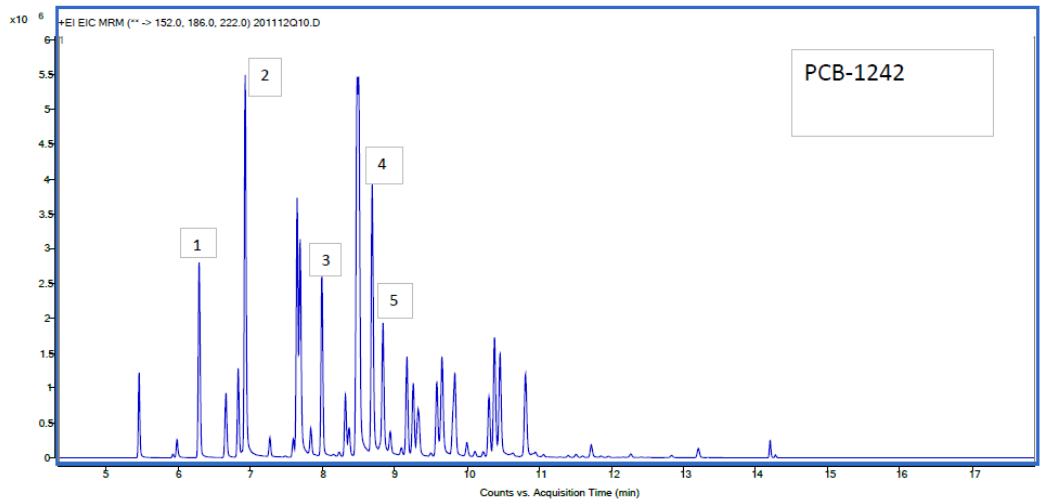


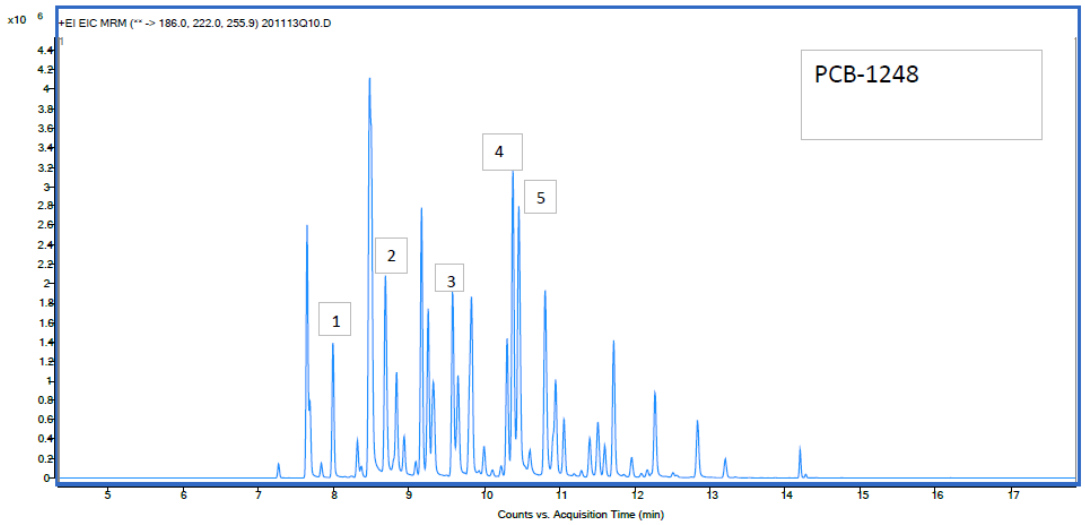
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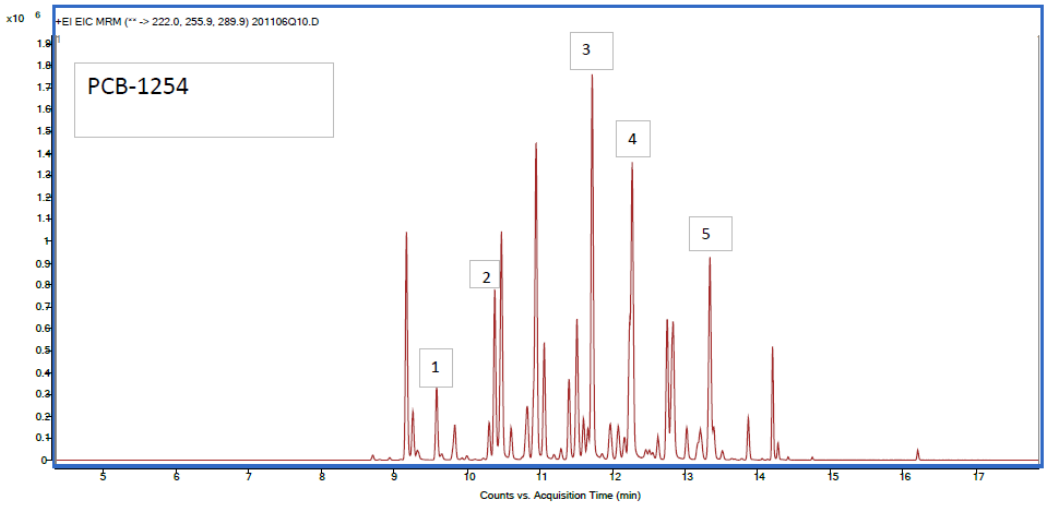


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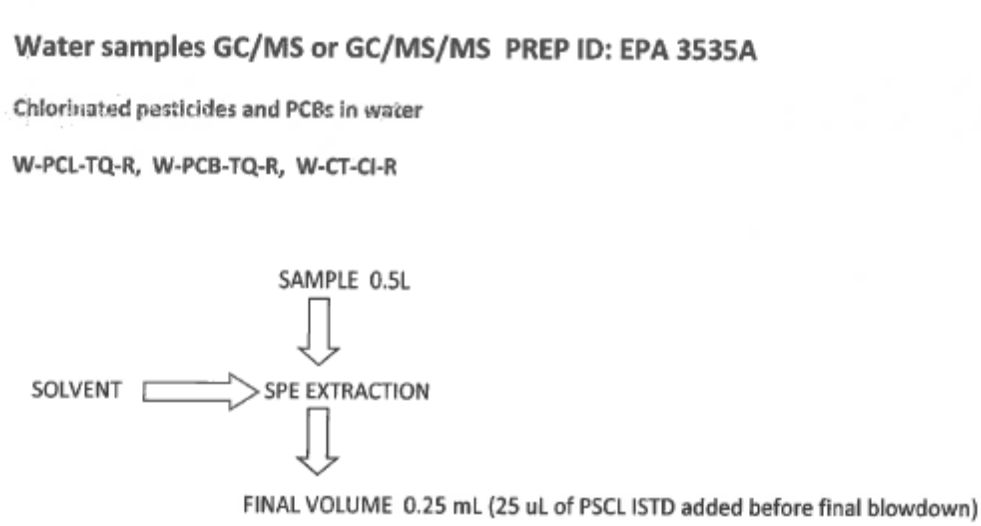




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Appendix 5 preparation flowchart



Appendix of significant changes.

01/11/2016	Addition of PCB aroclors analysis.
07/14/2016	Addition of tests W-DIELDRIN and W-CT-CI-R to the preparation procedure. Include origin prohibited for calibration fits. Ignore origin preferred. Updates to the preparation procedure.
11/08/2016	Updated chapter 8.4 – SPE Procedure.
01/13/2017	Updated chapter 8.4 – the SPE procedure; updated PCB Aroclors analysis – chapter 9.6; updated QC acceptance criteria, Table 3

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01/09/2018	Updated table 1A for new internal standards. Updated QC limits. Added preparation flowchart.
01/11/2019	Updated QC limits, MDLs and standard concentrations.
02/11/2019	Updated calibration procedure, spiking volumes and concentrations. Added TCLP/SPLP tests. Added five new analytes to the method: Ethalfluralin, Hexachlorobenzene, Trans-Nonachlor, Cis-Nonachlor and Bifenthrin.
05/30/2019	Updated the method to 8270E.
02/11/2020	Added new analytes to the W-PCL-SQ-R test: Dacthal, Phenothrin, Prallethrin, Lambda-Cyhalothrin, Beta-Cyfluthrin. Update MDLs and QC limits. Updated MDL verifications chapter. Updated concentration levels in table 2A. Updated appendix 1, acquisition method for Chlorinated pesticides.
06/17/2020	Prep method changed to EPA 3535A; prep procedure modified. Method USGS-O-1126-95 removed for analysis. Added section 9.1.2.9 describing Rt adjustment procedure for SIM acquisition method. Updated data archival for the use of automated backups. More detail added for the analysis of surrogates, matrix spikes and LFBs.
07/24/2020	Addition of Deltamethrin. Updated table 6. Updated PCB aroclors acquisition method. Updated some MDLs due to recent annual recalculations.
09/09/2020	Addition of 8 new analytes. Updated standard concentrations to reflect recent changes.
01/07/2021	W-PCB-SQ-R replaced with W-PCB-TQ-R. Appendix 6 – “preparation flowcharts’ updated. Preparation procedure updated to include 1 g SPE cartridges for difficult to filter samples. Coefficient of correlation R^2 minimum requirement >0.99. Updated QC limits for W-PCL-SQ-R.
03/31/2021	Minor editorial changes as per CERP audit recommendation of 02/26/2021. Added performance check and method blank to table 3. Added graphical depiction of tailing factor determination in chapter 9.3.1. Section 13.5 updated with PQL verification criteria. Section 15.1 updated. Replacement of W-PCL-SQ-R (single quad) test with W-PCL-TQ-R (triple quad) test throughout the text. Tables 1A, 2A, 3 and appendix 1A updated.
09/07/2021	Addition of oxychlordane and methoprene to test W-PCL-TQ-R. MDLs updated. Cal L-1 for W-PCL-TQ-R updated, QC limits for W-PCB-TQ-R updated to statistical limits.
01/13/2022	Updated spiking volumes for W-CT-CI-R and other parts of the sample preparation procedure. Updated spiking procedure. Updated QC limits. Updated MDLs due to annual recalculations.
02/28/2022	Re-extraction rules for field blanks added. Statistical limits calculations updated. Preparation procedure re-edited for pH adjustment.
04/07/2022	Calibration standards concentrations for some analytes updated due to recent changes. pH of the extraction process adjusted to 3.0.
05/12/2022	Clarified the language in the SOP to specifically indicate that GC/MS/MS technique is used. Added chapter 2.2 describing Agilent Masshunter Optimized software. Additional references added. Surrogate associations clarified.
07/14/2022	Updated MDL/PQL for mirex and surrogate recovery limits.
02/17/2023	Clarification of re-extraction rules in case of MBLK contamination. MDL/PQL for chlorothalonil updated. Calibration standards concentrations updated.
07/11/2023	Updated MDLs/PQLs and surrogate recovery limits.

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01/10/2024	Updated ICV concentrations in Table 2A. Rule regarding positives in the equipment blanks added to chapter 9.5.8. Rule regarding positives in the field blanks modified.

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