Standard Operating Procedure for:

ANALYSIS OF CHLORINATED PESTICIDES AND PCBs IN WATER SAMPLES USING SOLID PHASE EXTRACTION AND GC/MS-SIM

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1. SCOPE AND APPLICATION

This method is applicable to the determination of selected organochlorine pesticides in water as listed in Table 1. Method Detection Limits and Practical Quantitation Limits yielded by this method are also provided in Table 1.

1.1 The preparation part of this method is based on EPA 3535A (ref 15.18). 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-SQ-R, and W-PCB-SQ-R. it also covers TCLP/SPLP samples under tests TCLP-CL-SQ, SPLP-CL-SQ and SPLP-PCBSQ.

1.2 This Standard Operation Procedure is restricted to use by an analyst experienced in the use of an Agilent 5977A GC/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 software and DEP LIMS.

2. SUMMARY OF THE METHOD

2.1. General description.

Water samples are extracted using C-18 solid phase extraction (as per USGS-Method-O-1126-95) and analyzed using GC/MS with selected –ion monitoring (SIM mode). The extracts are analyzed using an Agilent 5977A GC/MS/ system. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of the characteristic SIM ions. 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 tests: W-DIELDRIN (see ref 15.16 for analysis) and W-CT-CI-R (see ref 15.17 for analysis).

2.2 Preparation method modifications as compared to EPA 3535A:

2.2.1 The samples' pH is adjusted to 2 as opposed to neutral. pH 2 improves recoveries of some anaytes with no negative effects on other.

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

2.2.3 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 5977A allows for higher final volumes, which also mean less matrix injected on the instruments (less maintenance and less interferences).

2.2.4 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 5977 GC/MS sample volume reduction was feasible.

2.3 Modifications to analytical method as EPA 8270E:

2.3.1 DFTPP tune/tune check (EPA 8270E only) is not used. As allowed by the method 8270E, manufacturer's recommendations regarding instrument tuning are followed. High sensitivity autotune is performed before each run using "e-tune" file. The Extractor Ion Source was not designed to tune to DFTPP due to different fragmentation patterns resulting in generally higher abundance of higher mass fragments.

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2.3.2 The analysis uses analyte protectants (Ethoxyglycerin, Gulonolactone and Sorbitol). Those compounds are injected using the sandwich technique at 12,500ppm/1250ppm/2500ppm respectively. Analyte protectants are necessary to suppress matrix induced response enhancement effects. The Agilent 5977 GC/MS system with Extractor Ion Source seems to be especially sensitive to those kinds of effects.

2.3.3 The degradation /tailing factor mix (EPA 8270E only) 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.

2.3.4 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. INTERFERENCES

3.1. Raw GC/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.

3.2. 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.

3.3 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.

4. DEFINITIONS

4.1 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.

4.2 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.

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4.3 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).

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

4.4 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.

4.5 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.

4.6 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.

4.7 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.

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

4.9 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.

4.10 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.

4.11 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

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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.

4.12 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.

4.13 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.

4.14 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

4.15 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.

4.16 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.

4.17 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.

4.18 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.

4.19 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. APPARATUS AND EQUIPMENT

5.1 Apparatus.

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Agilent 5977A GC/MS system with an extractor ion source or equivalent instrumentation. Extractor source on Agilent 5977A is necessary to achieve the detection limits as described in this SOP. 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 silica capillary, 30 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-25m mid-column backflash configuration).

5.2 Data system

5.2.1 A computer system is interfaced to the GC/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.

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

5.3 Gases

5.3.1 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. REAGENTS AND CHEMICALS

6.1. Solvents

6.1.1. Methylene Chloride, Fisher Scientific, Pesticide, HPLC or OPTIMA grade.

6.1.2. Isooctane, Fisher Scientific, Pesticide, HPLC or OPTIMA grade.

6.1.3. Acetone, Fisher Scientific, Pesticides, HPLC or Optima grade.

6.1.4. Hydrochloric acid, Fisher Scientific.

6.2. Standards

6.2.1. 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

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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)

6.4.1. 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
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

6.4.2. 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

6.5.1. 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.

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

6.5.3. 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.

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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. Similar to Agilent 7000 series GC/MS/MS system the single quad Agilent 5977C GC/MS instruments are also quite sensitive to matrix induced response enhancements which makes 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 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 12500 ppm, 1250 ppm and 2500 ppm respectively. Please note that this formulation (named APs 5977) is two times diluted as compared to the formulation used in this laboratory for GC/MS triple quad analysis. Due to solubility considerations the working solution is prepared in MeOH. 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.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1. Samples must be collected in glass containers with Teflon-lined screw caps.

7.2. All samples and sample extracts must be refrigerated at 6 degrees C or less from time of collection until extraction.

7.3. 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.

8. SAMPLE PREPARATION PROCEDURE

8.1. PREP METHOD SUMMARY. The water samples are filtered at the collection site using glass-fiber filters with 0.7 um pore diameter to remove suspended particulate matter. The pH of water samples is adjusted to 2 with Hydrochloric acid and the filtered water samples are pumped through 500 mg C-18 SPE columns, preconditioned with DI water at pH=2. 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. 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 5977A GC/MS system. 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:

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8.3.1. General use organic preparations glassware and supplies are listed in SOP GC-002-2 (ref 15.15).
8.3.2. JTBaker or similar vacuum manifold
8.3.3. Luer lock connectors and stopcocks
8.3.4. 75 mL reservoir tubes.
8.3.5. Restek 3 mL, 500 mg C-18 cartridges, cat no: 24050
8.3.6. Empore Filter-aid 400, 3M Corporation, Fisher cat: 14-378-6

8.4. SPE 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.

8.4.2 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 75 ul of 200/1000 ppb chlorinated pesticides spike and/or 50 ul of 2000 ppb PCB Aroclors spike in 10 mL of acetone and add to each LFB/MS. If test W-CT-CI-R and W-DIELDRIN are scheduled, then separate sets of matrix spikes/LFBs needs to be extracted. Use 40 ul of a mixed Chlordane/Toxaphene spike (1000/6000 respectively) and 75 ul of DLD spike. Additionally, W-CT-CI-R requires a PQL spike to be extracted. Use 10 ul of the aforementioned 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.
8.4.3 Adjust the pH of the sample in the beaker to pH=2 with 1M hydrochloric acid.

8.4.4 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.

8.4.5 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 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.**

8.4.6 SPE column equilibration: replace the methanol in the SPE column with DI water at pH=2 to equilibrate the column with the sample matrix. Add 2x3 ml of DI water at pH=2 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.

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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

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 (for W-DIELDRIN test). 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 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. GENERAL DESCRIPTION OF GC/MS-SIM ANALYSIS

9.1. GC/MS Maintenance and Tuning

9.1.1 DFTPP tune recommended by EPA 8270E is not applicable for Agilent 5977A GC/MS with the Extractor Ion Source. Instead, , this SOP modifies the method to follow manufacturer's tuning instructions, which, in this case, is PFTBA autotune. Therefore, PFTBA autotune is performed before each run to fulfill the requirements of both methods.

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

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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 procedure, so it is performed anyway every time the instrument is tuned.

9.1.2.2 Before each run perform the EI high sensitivity autotune of the GC/MS system and save the current settings in the autotune file. The report is printed automatically, and it should be placed in the autotune reports log. 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.

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 ^{o}C and leave it overnight.

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 ^{o}C and the oven temperature to 300 ^{o}C. Bake for 1-2 hrs. It is beneficial and recommended to bake the ion source at 350 ^{o}C 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 SIM 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.

Certain isomeric/chemically similar analytes tend to be confused by the quant software. Therefore, the RT assignments in the acquisition method

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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 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 not smaller than 0.995. If a higher order curve is to be used the correlation coefficient has to be at least 0.995. 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 % 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. Each time the column length is trimmed due to contamination or a new column is installed the retention times for each compound have to be determined from the scan mode or special SIM methods with no time segments. The SIM mode time segments (acquisition windows) have to be then adjusted accordingly. A mid-level standard should be then run to confirm that all the peaks are fully within the acquisition windows. Both the analysis end of the method (Masshunter) as well as the data-gathering end of the method (Acquisition) must be adjusted. Alternatively, RT locking procedure can be used to keep the retention times unchanged after the column is trimmed. Approximate retention times, the primary quantitation ions and confirmatory, secondary ions are given along with SIM acquisition time segments start/stop times in Table 1. The primary and secondary ions should all be present, and the relative intensities should agree within ±30% (absolute, RCRA tests) of the reference mass spectrum after background subtraction is performed.

9.2.3 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 Performance and Calibration Check

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

9.3.1 Degradation/tailing factor check (required by EPA 8270D)
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.

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.

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:

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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-SIM Sample Analysis.

9.4.1 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), 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.**

9.4.2 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 (containing internal standards at 100 ug/L)
- pesticides calibration set (when initial calibration is run, levels 3-10)
- PSCL ICV L-6 initial calibration verification check (when initial calibration is run)
- PSCL CCV L-6 continuing calibration check
- Instrument Blank (containing internal standards at 100 ug/L)*
- 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)*

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- samples (up to 12 hours)

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

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

9.5 Data Processing using the Masshunter software.

9.5.1 Using the 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 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 thirty 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)

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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 n-1 degrees of freedom (n = number of measurements).

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 recoveries should be calculated based on available in-house data once enough data points are collected. The limits are established as in 9.5.6.2. 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 failure is deemed excessive matrix spikes (along with the background sample) may be rerun and reanalyzed.

9.5.8 Blank contamination

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.
In the event a positive identification is found in both the sample(s) and the extraction blank then the 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.

9.5.9 Continuing Calibration

9.5.9.1 After initial calibration, the GC/MS response is checked immediately by running an Initial Calibration Verification standard (ICV) and then, on a continuing basis every 12 hrs, 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

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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 15.6 for more details).

9.5.10. 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 fullfilled 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 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.

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).

9.6 Analysis of PCB Aroclors using GC/MS-SIM.

9.6.1 The acquisition method for PCB Aroclors (PCB_SIM_yymmdd) contains, in one single acquisition segment, 22 individual PCB ions along with ions for internal standards (three deuterated PCB congeners are used) and surrogate Tetrachloro-m-xylene. Three additional ions for the second surrogate decachlorobiphenyl are included in the second acquisition window. The list of PCB ions includes, at least, one ion for each level of chlorination plus a number of other ions 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

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up all the different ions. All the individual ions used in the acquisition method are listed in Appendix 1B. The individual PCB ions 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-SIM 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.

9.6.3 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 8270D (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 six points calibration for PCB 1016/1260 mix along with single standards for the five, remaining individual Aroclors, for pattern identification purposes. Single standards for those other Aroclors do not need to be run daily, as long as no RT changes occurred since the last time those Aroclors were run. 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.

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

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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 In cases where pattern recognition is problematic due to sample properties like weathering or matrix interferences it may be advisable to use independent techniques for Aroclor identification/confirmation. Those techniques include GC/MS/MS and GC-ECD.

10 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:

PSCL_CCV, PCB-1060 (or other) CCV
SURPSCL_CCV, or SURRPCB-1060_CCV for surrogate in CCV
SURWCL_1234567 for surrogate in sample. The same code is applied whether Chlorinated pesticides or PCBs are analyzed.

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 OG-003-Data Review/Authorization Checklist (ref 15-6) for details of data review and reporting. 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. 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.

11 QUALITY CONTROL

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11.1 See DEP SOP GC-001, Quality Assurance/Quality Control in the GC Pesticides Laboratory (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 DATA ARCHIVAL

12.1 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 warehouse for at least ten years. Electronic

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chromatographic raw data are archived by analysis file ID and instrument ID on dual CDs by the Laboratory Support Section.

12.2 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_MSD-3(or MSD-4). They are then converted in QC Manager for reporting in LIMS.

13. 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 15.3). 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 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.

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14. 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. 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, February 2017.

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15.2 USGS-Method-O-1126-95." Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of Pesticides in Water by C-18 Solid-Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry with Selected Ion Monitoring". Denver, Colorado 1995.

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 DEP SOP OG-003. Data Review/Authorization Checklist

15.7 DEP SOP LB-027. Standard Operating Procedure for Reporting Qualified Data.

15.8 DEP SOP GC-001. Quality Assurance/Quality Control in the GC Pesticides Laboratory

15.9 Florida Department of Environmental Protection, Standard Operating Procedure LB-007 *Procedure and Policy for Method and Instrument Validation.*

15.10 Florida Department of Environmental Protection, Standard Operating Procedure LB-031 *Limit of Detection 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, PUFs and Filters for Subsequent Analysis by GC or GC/MS Techniques.

15.16 DEP SOP GC-033-1. Analysis of Pesticides and PCBs in Water, Soil and Tissue Samples Using GC/MS/MS.

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

15.18 EPA method 3535A, Revision 1, 2007

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16. 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	Quant. ion	Qual. ions	MDL ug/L in extract	PQL ug/L in extract	MDL ng/L in sample	PQL ng/L in sample
Tetrachloro-m-xylene surrogate	7.747	DCB-d5	242.0	209.0 244.0				
Decachlorobiphenyl surrogate	18.843	HCB-d3	498.0	428.0 214.0				
Ethalfluralin	7.85	Trifluralin-d14	276.0	292.0 316.0	6.0	24	3.0	12
Trifluralin	8.101	Trifluralin-d14	264.0	306.0 290.0	5.0	20	2.5	10
Alpha-BHC	8.524	Alpha-BHC-d6	183.0	217.0 219.0	4.0	16	2.0	8.0
Hexachlorobenzene	8.67	DCB-d5	284.0	249.0 286.0	4.0	16	2.0	8.0
Beta-BHC	9.063	Alpha-BHC-d6	219.0	221.0 254.0	20	80	10	40
Gamma-BHC	9.209	Alpha-BHC-d6	219.0	183.0 217.0	16	64	8.0	32
Delta-BHC	9.706	Alpha-BHC-d6	183.0	219.0 217.0	16	64	8.0	32
Chlorothalonil	9.820	TCB-d5	266.0	264.0 268.0	4.0	16	2.0	8.0
Heptachlor	10.817	TCB-d5	337.0	339.0 372.0	3.0	12	1.5	6.0
Aldrin	11.635	TCB-d5	293.0	291.0 265.0	8.0	32	2.0	8.0
Dacthal	11.90	TCB-d5	301.0	299.0 303.0	2.0	8.0	1.0	4.0
Heptachlor Epoxide	12.591	TCB-d5	353.0	351.0 263.0	4.0	16	2.0	8.0
Prallethrin	13.10	TCB-d5	123.1	153.1 168.1	60	240	30	120
Gamma-Chlordane	13.174	TCB-d5	373.0	375.0 377.0	2.0	8.0	1.0	4.0
Endosulfan I	13.478	TCB-d5	277.0	337.0 339.0	8.0	32	4.0	16
Alpha-Chlordane	13.543	TCB-d5	373.0	375.0 377.0	2.0	8.0	1.0	4.0

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Trans-Nonachlor	13.65	TCB-d5	408.8	271.8 299.9	2.0	8.0	1.0	4.0
DDE-p,p’	14.055	TCB-d5	246.0	318.0 316.0	12	48	6.0	24
Dieldrin	14.123	TCB-d5	380.0	263.0 279.0	8.0	32	4.0	16
Endrin	14.661	TCB-d5	263.0	265.0 261.0	4.0	16	2.0	8.0
Endosulfan II	14.892	TCB-d5	337.0	339.0 277.0	8.0	32	4.0	16
DDD-p,p’	15.101	TCB-d5	235.0	237.0 212.0	12	48	6.0	24
Cis-Nonachlor	15.22	TCB-d5	408.8	271.8 299.9	2.0	8.0	1.0	4.0
Endrin Aldehyde	15.366	TCB-d5	345.0	349.0 347.0	4.0	16	2.0	8.0
Carbophenothion	15.757	TCB-d5	342.0	344.0 296.0	20	80	10	40
Endosulfan Sulfate	15.922	HCB-d3	272.0	274 276	4.0	16	2.0	8.0
DDT-p,p’	15.983	DDT-p,p’-d8	235.0	237.0 318.0	14	56	7.0	28
Endrin Ketone	16.695	HCB-d3	317.0	319.0 345.0	4.0	16	2.0	8.0
Bifenthrin	16.79	HCB-d3	181.1	165.1 166.1	8.0	32	4.0	16
Methoxychlor	16.872	DDT-p,p’-d8	227.0	228.0 212.0	8.0	32	4.0	16
Dicofol	16.885	Dicofol-d8	139.0	251.0 141.0	60	240	30	120
Phenothrin	17.10	HCB-d3	183.1	123.2 124.1	60	240	30	120
Mirex	17.400	HCB-d3	272.0	274.0 237.0	4.0	16	2.0	8.0
Lambda-Cyhallothrin	17.45	HCB-d3	181.1	197.1 209.1	30	120	15	60
Permethrin	17.952	HCB-d3	183.0	184.0 165.0	20	80	10	40
Beta-Cyfluthrin	18.3	HCB-d3	206.1	163.0 165.0	30	120	15	60
Cypermethrin	18.428	HCB-d3	181.0	163.0 165.0	40	160	20	80

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Trifluralin-d14	7.92	Internal Standard	315.0	251.0 267.0				
DCB-d5	8.141	Internal standard	227.0	157.0 229.0				
Alpha-BHC-d6	8.450	Internal standard	226.0	224.0 222.0				
TCB-d5	11.498	Internal standard	297.0	225.0 295.0				
DDT-p,p'-d8	15.933	Internal standard	243.0	245.0 173.0				
Dicofol-d8	16.81	Internal Standard	143	115.0 259.1				
HCB-d3	16.833	Internal standard	363.0	365.0 293.0				
Octachloronaphthalene	18.74	Internal standard	403.8	331.8 401.8				

TABLE 1B: Internal standard associations, MDLs, PQLs and approximate RTs for typical analytical PCB Aroclors included in LIMS test and W-PCB-SQ-R. **LIMS reporting units are ng/L**

Analyte	**Approximate Retention Time (min)**	**Associated internal standard**	**RRT**	**Quant ion**	**Qual ions**	**MDL ug/L**	**PQL ug/L**	**MDL ng/L**	**PQL ng/L**
						extract	extract	sample	sample
Tetrachloro-m-xylene surrogate	7.67	DCB-d5	0.95	244	242, 246				
Decachlorobiphenyl surrogate	18.75	HCB-d3	1.12	498	496, 500				
PCB-1016						65	260	33	130
PCB-1016_1	7.62	DCB-d5	0.94	224	152, 188				
PCB-1016_2	8.42	DCB-d5	1.04	224	152, 186				
PCB-1016_3	9.72	DCB-d5	1.20	256	258, 186				
PCB-1016_4	10.57	TCB-d5	0.93	256	258, 186				
PCB-1016_5	11.63	TCB-d5	1.02	292	290, 294				
PCB-1221						65	260	33	130
PCB-1221_1	6.57	DCB-d5	0.81	188	152, 190				
PCB-1221_2	7.23	DCB-d5	0.90	188	152, 190				
PCB-1221_3	7.62	DCB-d5	0.94	152	188, 224				
PCB-1221_4	8.09	DCB-d5	1.00	224	152, 186				
PCB-1221_5	8.42	DCB-d5	1.04	224	152, 186				
PCB-1232						65	260	33	130
PCB-1232_1	7.63	DCB-d5	0.95	224	152, 188				

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PCB-1232_2	8.43	DCB-d5	1.04	224	152, 186				
PCB-1232_3	9.72	DCB-d5	1.20	256	258, 186				
PCB-1232_4	10.57	TCB-d5	0.93	256	258, 186				
PCB-1232_5	11.23	TCB-d5	0.99	292	290, 294				
PCB-1242						65	260	33	130
PCB-1242_1	7.62	DCB-d5	0.94	224	152, 188				
PCB-1242_2	9.72	DCB-d5	1.20	256	258, 186				
PCB-1242_3	10.56	TCB-d5	0.93	256	258, 186				
PCB-1242_4	11.62	TCB-d5	1.02	292	290, 294				
PCB-1242_5	12.57	TCB-d5	1.10	292	290, 294				
PCB-1248						65	260	33	130
PCB-1248_1	9.73	DCB-d5	1.21	256	258, 186				
PCB-1248_2	10.55	TCB-d5	0.93	256	258, 186				
PCB-1248_3	11.12	TCB-d5	0.98	292	290, 294				
PCB-1248_4	12.56	TCB-d5	1.10	292	290, 294				
PCB-1248_5	14.12	TCB-d5	1.05	326	324, 2256				
PCB-1254						65	260	33	130
PCB-1254_1	11.12	TCB-d5	0.98	292	290, 294				
PCB-1254_2	12.67	TCB-d5	1.11	326	324, 256				
PCB-1254_3	14.13	TCB-d5	1.24	326	324, 256				
PCB-1254_4	14.77	HCB-d3	0.88	326	324, 256				
PCB-1254_5	15.97	HCB-d3	0.95	360	362, 290				
PCB-1260						65	260	33	130
PCB-1260_1	14.73	HCB-d3	0.88	360	362, 290				
PCB-1260_2	15.33	HCB-d3	0.91	360	362, 290				
PCB-1260_3	15.97	HCB-d3	0.95	368	362, 290				
PCB-1260_4	16.62	HCB-d3	0.99	394	396, 324				
PCB-1260_5	16.98	HCB-d3	1.01	394	396, 324				
DCB-d5	8.07	Internal standard		227	157, 229				
TCB-d5	11.39	Internal standard		297	258, 186				
HCB-d3	16.77	Internal standard		363	365, 293				

The same MDL is applied to all PCB Aroclors.

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Table 2A: Analyte concentrations in calibration standards and /QCS/ICV for Chlorinated pesticides (ug/L) (Test ID W-PCL-SQ-R). The expected spike concentrations in LFBs/MSs are equal to 60/300 ug/L (in extract)

	L10	L9	L8	L7	L6/ccv	L5	L4	L3	ICV/QCS
PSCL	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	L6 ppb
Aldrin	600	400	200	100	50	20	10	6	50
Alpha-BHC	600	400	200	100	50	20	10	6	50
Alpha-Chlordane	600	400	200	100	50	20	10	6	50
Beta-BHC	600	400	200	100	50	20	10	6	50
Beta-Cyfluthrin	3000	2000	1000	500	250	100	50	30	250
Bifenthrin	600	400	200	100	50	20	10	6	50
Carbophenothion	600	400	200	100	50	20	10	6	50
Chlorothalonil	600	400	200	100	50	20	10	6	50
Cis-Nonachlor	600	400	200	100	50	20	10	6	50
Cypermethrin	3000	2000	1000	500	250	100	50	30	250
Dacthal	600	400	200	100	50	20	10	6	50
DDD-p,p'	600	400	200	100	50	20	10	6	50
DDE-p,p'	600	400	200	100	50	20	10	6	50
DDT-p,p'	600	400	200	100	50	20	10	6	50
Delta-BHC	600	400	200	100	50	20	10	6	50
Deltamethrin	3000	2000	1000	500	250	100	50	30	250
Dicofol	3000	2000	1000	500	250	100	50	30	250
Dieldrin	600	400	200	100	50	20	10	6	50
Endosulfan I	600	400	200	100	50	20	10	6	50
Endosulfan II	600	400	200	100	50	20	10	6	50
Endosulfan Sulfate	600	400	200	100	50	20	10	6	50
Endrin	600	400	200	100	50	20	10	6	50
Endrin Aldehyde	600	400	200	100	50	20	10	6	50
Endrin Ketone	600	400	200	100	50	20	10	6	50
Ethalfluralin	600	400	200	100	50	20	10	6	50
Gamma-BHC	600	400	200	100	50	20	10	6	50
Gamma-Chlordane	600	400	200	100	50	20	10	6	50
Heptachlor	600	400	200	100	50	20	10	6	50
Heptachlor Epoxide	600	400	200	100	50	20	10	6	50
Hexachlorobenzene	600	400	200	100	50	20	10	6	50
Lambda-Cyhallothrin	3000	2000	1000	500	250	100	50	30	250
Methoxychlor	600	400	200	100	50	20	10	6	50
Mirex	600	400	200	100	50	20	10	6	50
Permethrin	3000	2000	1000	500	250	100	50	30	250
Phenothrin	3000	2000	1000	500	250	100	50	30	250
Prallethrin	3000	2000	1000	500	250	100	50	30	250
Trans-Nonachlor	600	400	200	100	50	20	10	6	50
Trifluralin	600	400	200	100	50	20	10	6	50
Tetrachloro-m-xylene	600	400	200	100	50	20	10	6	50
DCB	600	400	200	100	50	20	10	6	50

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Table 2B Analyte concentrations in calibration standards and /QCS/ICV for PCB Aroclors (ug/L) (Test ID W-PCB-SQ and W-PCB-SQ-R). The expected spike concentrations in LFBs/MSs are equal to 500 ug/L (in extract) .

AROCLORS	L-6	L-5	L-4	L-3	L-2	L-1	ICV L-4
Tetrachloro-m-xylene	100	75	50	25	12.5	7.5	50
PCB-1016	1000	750	500	250	125	75	500
PCB-1221	1000	750	500	250	125	75	500
PCB-1232	1000	750	500	250	125	75	500
PCB-1242	1000	750	500	250	125	75	500
PCB-1248	1000	750	500	250	125	75	500
PCB-1254	1000	750	500	250	125	75	500
PCB-1260	1000	750	500	250	125	75	500
Decachlorobiphenyl	100	75	50	25	12.5	7.5	50

TABLE 3: QC MEASUREMENTS AND ACCEPTACE CRITERIA

#	QC MEASUREMENT	ACCEPTANCE CRITERION	CORRECTIVE ACTION
1	LFB, Matrix Spike precision	≤ 30%	Reanalyze/Re-extract/Flag
2	LFB, recoveries: W-PCL-SQ-R, W-PCL-SQ	LFB statistical limits, 50-150% for Phenothrin, Dacthal, Lambda-Cyhalohrin, Beta-Cyfluthrin, 40-140% for Prallethrin,	Reanalyze/Re-extract/Flag
	Matrix Spike recoveries	Matrix spikes statistical limits, 50-150% for Phenothrin, Dacthal, Lambda-Cyhallohrin, Beta-Cyfluthrin, 40-140% for Prallethrin	
	LFB recoveries: W-PCB-SQ-R, W-PCB-SQ	LFB statistical limits for PCB-1060; 50-120% for PCBs other than 1060	
3	Matrix Spike – recoveries: W-PCB-SQ-R, W-PCB-SQ	Matrix spikes statistical limits for PCB-1060; 50-120% for PCBs other than 1060	Reanalyze/Re-extract/Flag
3	ICV	± 30%	Reanalyze/Flag
4	CCV	± 20%	Re-run and recalibrate/Flag
5	Surrogate recovery	Tetrachloro-m-xylene 34-106%, 34-90% for PCBs Decachlorobiphenyl 44-112%, 42-104% for PCBs	Reanalyze/Re-extract/Flag
6	Linearity criterion	20% RSD; 0.995 CC	Use appropriate cal fit / Re-run/ Recalibrate
7	Internal Std. recovery	50-200%	Reanalyze/recalibrate/flag
8	% cal drift	± 30% of expected value	Change fit/weighing/recalibrate/flag

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Statistical recovery limits for LFB/MS and surrogates recoveries are typically based on QC Manager statistics for the last two 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 entered into QC Manager limits tables. The initial QC limits are replaced with statistical ones whenever enough data points are accumulated. At least 20 points are required, but it is preferable to wait for about 50 points or more. If enough data points is available for LFBs but not for matrix spikes then LFB statistical limits may be applicable for both categories on temporary basis.

17. APPENDICES

APPENDIX 1

GC/MS Acquisition Method – Method: PSCL_SIM_yymmdd

INSTRUMENT CONTROL PARAMETERS: GC_MSD-3

C:\MassHunter\GCMS\1\methods\PSCL_SIM_200615.M
Mon Jun 15 09:01:40 2020

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	**23.543 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	**7 °C/min**
#2 Value	**245 °C**
#2 Hold Time	**0 min**
#3 Rate	**50 °C/min**
#3 Value	**310 °C**
#3 Hold Time	**6.6 min**

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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) 3
Solvent A Washes (PostInj) 15
Solvent A Volume 8 µL
Solvent B Washes (PreInj) 3
Solvent B Washes (PostInj) 15
Solvent B Volume 8 µL
Sample Washes 1
Sample Wash Volume 4 µL
Sample Pumps 3
Dwell Time (PreInj) 0 min
Dwell Time (PostInj) 0 min
Solvent Wash Draw Speed 300 µL/min
Solvent Wash Dispense Speed 6000 µL/min
Sample Wash Draw Speed 50 µL/min
Sample Wash Dispense Speed 6000 µL/min
Injection Dispense Speed 6000 µL/min
Viscosity Delay 7 sec
Sample Depth Disabled
Injection Type Reversed 3-Layer (L3,L2,L1)
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 3 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 17 min
#2 Rate 900 °C/min
#2 Value 310 °C
#2 Hold Time 0 min

Mode Pulsed Splitless

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Pressure **On 9.6147 psi**
Total Flow **On 54.1 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 **Off**
Cryo Type **N2**
Liner **Agilent 5190-2293: 900 µL (Splitless, single taper, ultra inert)**

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 **Agilent 5190-3167: 900 µL (Splitless, single taper, ultra inert)**

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

Column
Column #1
Flow
Setpoint **Off**
(Initial) **1.1 mL/min**
Hold Time **19.5 min**
Post Run **-4.3283 mL/min**
Program
#1 Rate **100 mL/min per min**
#1 Value **-2.5 mL/min**
#1 Hold Time **2.5 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 **0 °C—325 °C (325 °C)**
Dimensions **5 m x 250 µm x 0.25 µm**
Column lock **Unlocked**
In **Front MM Inlet He**
Out **Aux EPC 3**
(Initial) **50 °C**
Pressure **9.6147 psi**
Flow **1.1 mL/min**
Average Velocity **25.587 cm/sec**
Holdup Time **0.32569 min**

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Control Mode **Ramped Flow**

Column #2
Flow
Setpoint **Off**
(Initial) **1.2 mL/min**
Hold Time **22.036 min**
Post Run **0.21034 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-433UI-25m**
HP-5ms Ultra Inert
Temperature Range **-60 °C—325 °C (350 °C)**
Dimensions **25 m x 250 µm x 0.25 µm**
Column lock **Unlocked**
In **Aux EPC 3 He**
Out **MSD**
(Initial) **50 °C**
Pressure **7.6522 psi**
Flow **1.2 mL/min**
Average Velocity **43.734 cm/sec**
Holdup Time **0.95274 min**
Control Mode **Ramped Flow**

Column Outlet Pressure **0 psi**

Aux EPC 1,2,3
Aux EPC 1 N2
Pressure
Setpoint **Off**
(Initial) **10 psi**
Post Run **0 psi**

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

Aux EPC 2 N2
Pressure
Setpoint **Off**
(Initial) **10 psi**
Post Run **0 psi**

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

Aux EPC 3 He
Excluded from Readiness *****Excluded from Affecting GC's Readiness State*****
Aux EPC 3 He **Supplies Column 2**

Signals
Signal #1: Test Plot
Description **Test Plot**
Save **Off**

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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 Back 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

MS Information
-- ----------

General Information
------- ----------

Acquisition Mode : SIM
Solvent Delay (minutes) : 7
Tune file : C:\MassHunter\GCMS\1\5977\etune.u
EM Setting mode Gain : 5.000000

Number of SIM Groups : 17
Run Time (if MS only) : 23.54 minutes

[SIM Parameters]
Group 1 Group ID : 1
Resolution : 0
Group Start Time : 7
Number of Ions : 15
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(157.00,20) (209.00,20) (227.00,20)
(229.00,20) (242.00,20) (244.00,20)
(251.10,20) (264.00,20) (267.10,20)
(276.00,20) (290.00,20) (292.00,20)
(306.00,20) (315.10,20) (316.00,20)

Group 2 Group ID : 2
Resolution : 0
Group Start Time : 8.3

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Number of Ions : 9
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(183.00,35) (217.00,35) (219.00,35)
(222.00,35) (224.00,35) (226.00,35)
(249.00,35) (284.00,35) (286.00,35)

Group 3 Group ID : 3
Resolution : 0
Group Start Time : 8.9
Number of Ions : 8
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(183.00,37) (217.00,37) (219.00,37)
(221.00,37) (236.90,37) (249.00,37)
(249.90,37) (254.00,37)
Group 4 Group ID : 4
Resolution : 0
Group Start Time : 9.5
Number of Ions : 6
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(183.00,50) (217.00,50) (219.00,50)
(264.00,50) (266.00,50) (268.00,50)

Group 5 Group ID : 5
Resolution : 0
Group Start Time : 10.5
Number of Ions : 3
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(337.00,100) (339.00,100) (372.00,100)

Group 6 Group ID : 6
Resolution : 0
Group Start Time : 11.4
Number of Ions : 6
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(225.00,50) (265.00,50) (291.00,50)
(293.00,50) (295.00,50) (297.00,50)

Group 7 Group ID : 7
Resolution : 0
Group Start Time : 11.8
Number of Ions : 3
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(299.00,100) (301.00,100) (303.00,100)

Group 8 Group ID : 8
Resolution : 0
Group Start Time : 12.3
Number of Ions : 3
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)

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(263.00,100) (351.00,100) (353.00,100)

Group 9 Group ID : 9
Resolution : 0
Group Start Time : 12.9
Number of Ions : 12
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(123.10,25) (153.10,25) (168.10,25)
(271.80,25) (277.00,25) (299.90,25)
(337.00,25) (339.00,25) (373.00,25)
(375.00,25) (377.00,25) (408.80,25)

Group 10 Group ID : 10
Resolution : 0
Group Start Time : 13.9
Number of Ions : 7
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(246.00,45) (263.00,45) (277.00,45)
(279.00,45) (316.00,45) (318.00,45)
(380.00,45)
Group 11 Group ID : 11
Resolution : 0
Group Start Time : 14.35
Number of Ions : 15
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(212.00,20) (235.00,20) (236.90,20)
(237.00,20) (261.00,20) (263.00,20)
(265.00,20) (271.80,20) (277.00,20)
(337.00,20) (339.00,20) (345.00,20)
(347.00,20) (349.00,20) (408.80,20)

Group 12 Group ID : 12
Resolution : 0
Group Start Time : 15.6
Number of Ions : 12
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(173.00,25) (235.00,25) (237.00,25)
(243.00,25) (245.00,25) (272.00,25)
(274.00,25) (276.00,25) (296.00,25)
(318.00,25) (342.00,25) (344.00,25)

Group 13 Group ID : 13
Resolution : 0
Group Start Time : 16.5
Number of Ions : 21
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(115.00,14) (123.20,14) (124.20,14)
(139.00,14) (141.00,14) (143.00,14)
(165.10,14) (166.10,14) (181.10,14)
(183.10,14) (212.00,14) (227.00,14)
(228.00,14) (251.00,14) (259.10,14)

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(293.00,14) (317.00,14) (319.00,14)
(345.00,14) (363.00,14) (365.00,14)

Group 14 Group ID : 14
Resolution : 0
Group Start Time : 17.35
Number of Ions : 6
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(181.10,50) (197.10,50) (209.10,50)
(237.00,50) (272.00,50) (274.00,50)

Group 15 Group ID : 15
Resolution : 0
Group Start Time : 17.7
Number of Ions : 3
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(165.00,100) (183.00,100) (184.00,100)

Group 16 Group ID : 16
Resolution : 0
Group Start Time : 18.2
Number of Ions : 10
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(163.00,30) (165.00,30) (181.00,30)
(206.10,30) (214.00,30) (331.80,30)
(401.80,30) (403.80,30) (428.00,30)
(498.00,30)
Group 17 Group ID : 17
Resolution : 0
Group Start Time : 19.4
Number of Ions : 3
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(181.10,100) (251.00,100) (255.00,100)

[MSZones]

MS Source : 300 C maximum 350 C
MS Quad : 150 C maximum 200 C

Timed Events
----- ------
Number Events= 1

[Timed MS Detector Table Entries]

Time (min) State (MS On/off)
19.90 off

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END OF MS ACQUISITION PARAMETERS

TUNE PARAMETERS for SN: US1418M201

Trace Ion Detection is ON.

34.593 : EMISSION
70.007 : ENERGY
1.300 : REPELLER
80.939 : IONFOCUS
20.181 : ENTRANCE_LENS
1700.787 : EMVOLTS
1700.8 : Actual EMV
0.28 : GAIN FACTOR
1416.000 : AMUGAIN
121.625 : AMUOFFSET
2.000 : FILAMENT
1.000 : DCPOLARITY
9.077 : ENTLENSOFFSET
8.502 : Ion_Body
1.204 : EXTLENS
-466.000 : MASSGAIN
-36.000 : MASSOFFSET

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

APPENDIX 1B

GC/MS ACQUISITION METHOD FOR PCB AROCLORS

MS Information
-- -----------

General Information
------- -----------

Acquisistion Mode : SIM
Solvent Delay (minutes) : 6.00
Tune file : D:\MassHunter\GCMS\1\5977\etune.u
EM Setting mode Gain : 5.000000

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Number of SIM Groups : 2
Run Time (if MS only) : 650 minutes

[SIM Parameters]
Group 1 Group ID : 1
Resolution : 0
Group Start Time : 6.00
Number of Ions : 33
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(152.00,9) (157.00,9) (186.00,9)
(188.00,9) (190.00,9) (224.00,9)
(225.00,9) (227.00,9) (229.00,9)
(242.00,9) (244.00,9) (246.00,9)
(256.00,9) (258.00,9) (260.00,9)
(288.00,9) (290.00,9) (292.00,9)
(293.00,9) (294.00,9) (297.00,9)
(322.00,9) (324.00,9) (326.00,9)
(360.00,9) (362.00,9) (363.00,9)
(365.00,9) (392.00,9) (394.00,9)
(396.00,9) (426.00,9) (460.00,9)

Group 2 Group ID : 2
Resolution : 0
Group Start Time : 18.40
Number of Ions : 3
Ions
Dwell In Group :(Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(496.00,100) (498.00,100) (500.00,100)

[MSZones]

MS Source : 300 C maximum 350 C
MS Quad : 150 C maximum 200 C

Timed Events
----- ------
Number Events= 1

[Timed MS Detector Table Entries]

Time (min) State (MS On/off)
19.53 off

END OF MS ACQUISTION PARAMETERS

TUNE PARAMETERS for SN: US1418M201

Trace Ion Detection is ON.

EMISSION : 34.593
ENERGY : 70.007
REPELLER : 4.979

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IONFOCUS : 89.822
ENTRANCE_LE : 12.582
EMVOLTS : 1382.348
Actual EMV : 1615.6
GAIN FACTOR : 5.33
AMUGAIN : 1417.000
AMUOFFSET : 120.625
FILAMENT : 1.000
DCPOLARITY : 1.000
ENTLENSOFFS : 12.689
MASSGAIN : -468.000
MASSOFFSET : -37.000

END OF TUNE PARAMETERS

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

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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.

APPENDIX 3

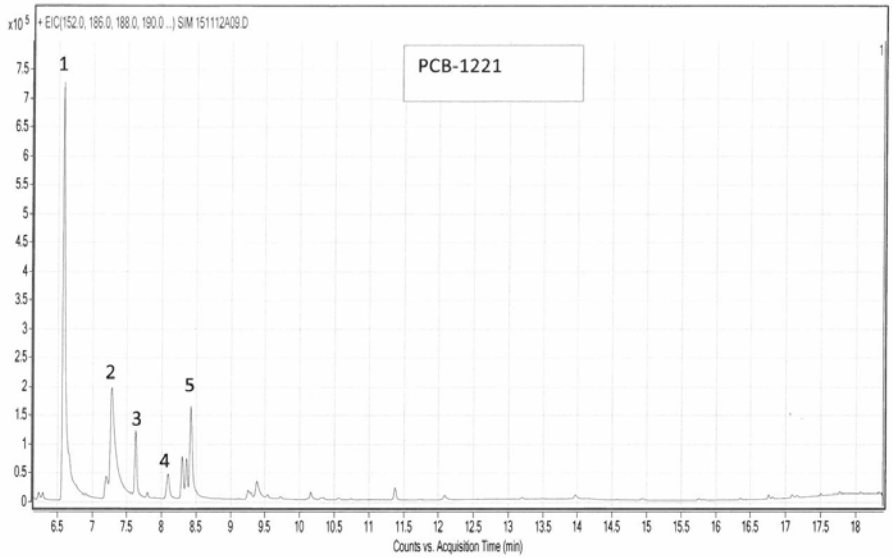
ANALYTE PROTECTANTS

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

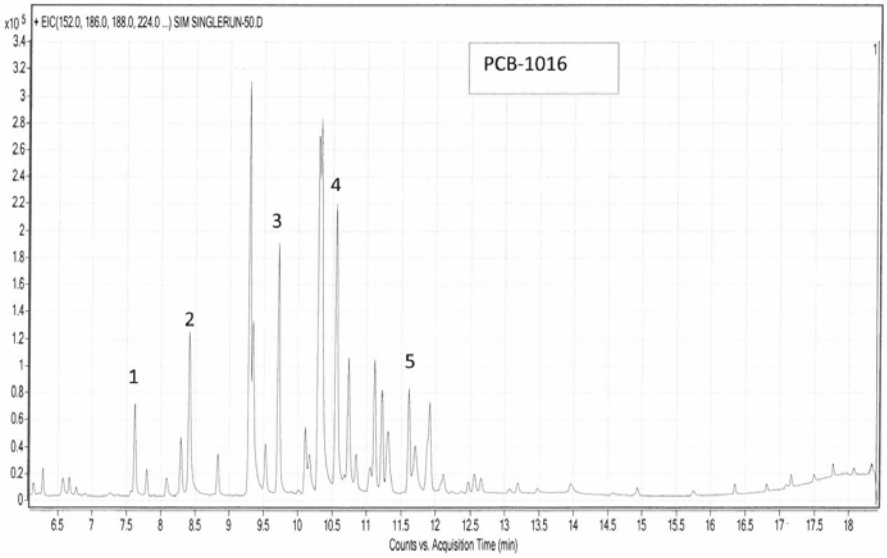
Notes:
Neat D-sorbitol is hygroscopic and should be stored in a desiccator. D-Sorbitol and, especially, gulonolactone are difficult to dissolve in MeOH. To achieve complete dissolution of these components, 1 – 3 hours of hot sonication and repeated vigorous shaking (vortexing) may be needed. To avoid 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.
AP solution used for GC/MS 5977 analysis is a two times diluted version of a standard used for GC/MS triple quad analyses.

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APPENDIX 5: PCB patterns and analytical peaks

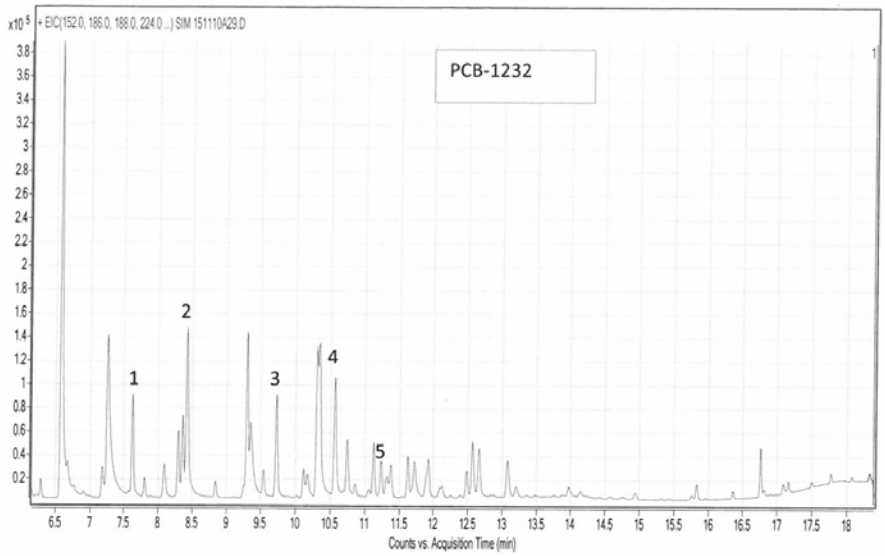


PCB-1221 pattern and five quant peaks as extracted with EIC method "Extract1221"

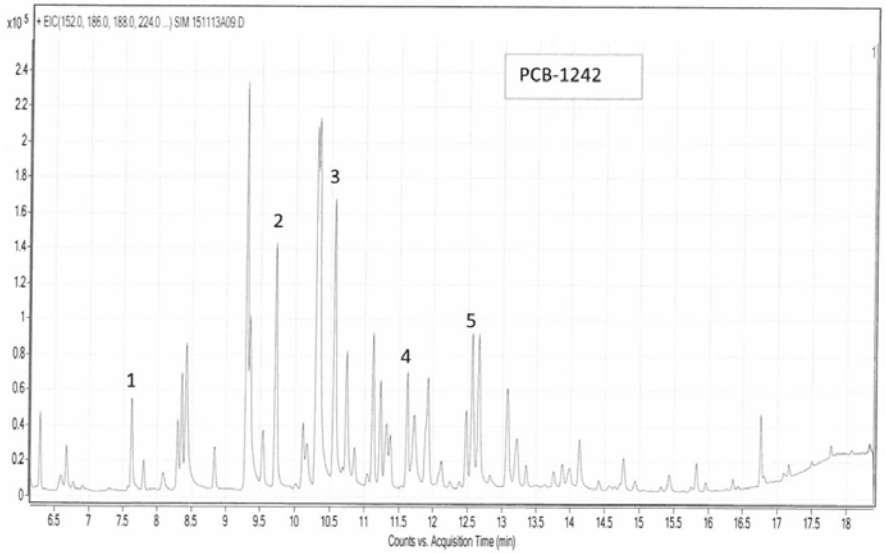


PCB-1016 pattern and five quant peaks as extracted with EIC method "Extract1016"

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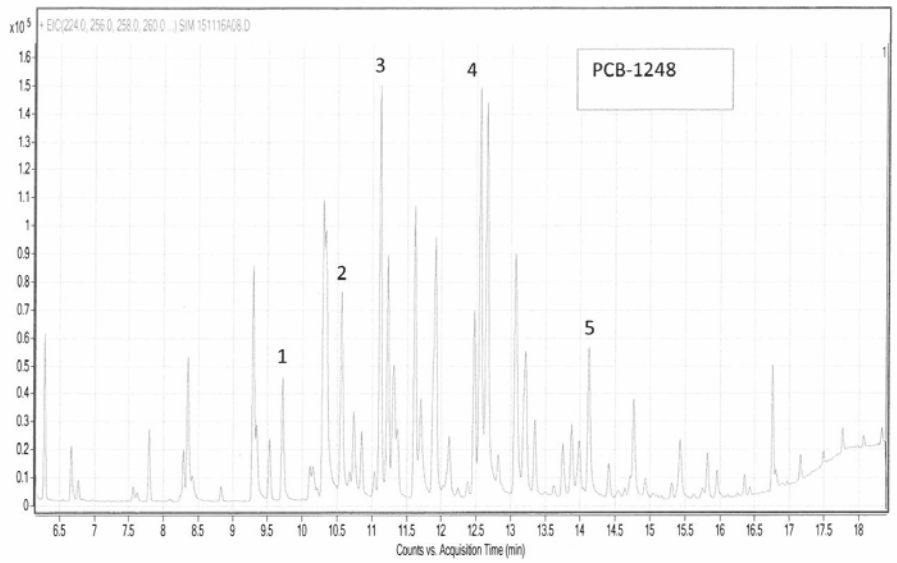


PCB-1232 pattern and five quant peaks as extracted with EIC method "Extract1232"

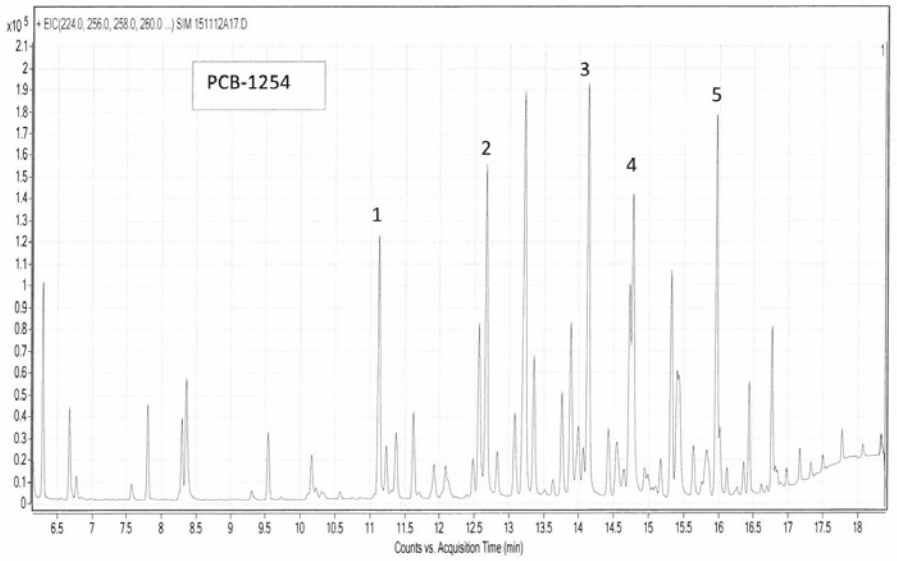


PCB-1242 pattern and five quant peaks as extracted with EIC method "Extract1242"

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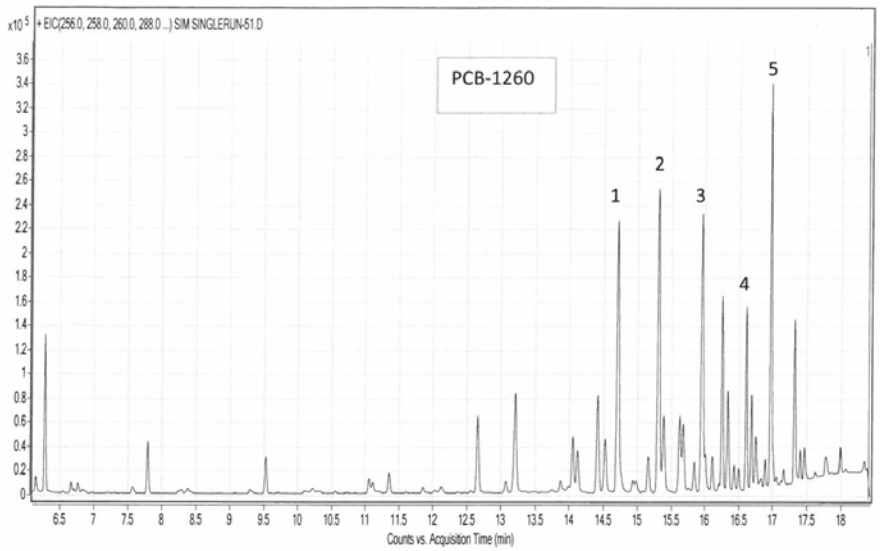


PCB-1248 pattern aned five quant peaks as extracted with EIC method "Extract1248"



PCB-1254 pattern aned five quant peaks as extracted with EIC method "Extract1254"

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PCB-1260 pattern and five quant peaks as extracted with EIC method "extract1260"

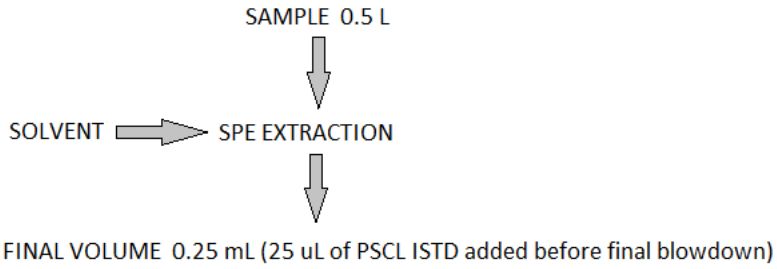
Appendix 6 preparation flowchart

Water samples GC/MS SIM PREP ID: USGS-O-1126-95

Chlorinated pesticides and PCBs in water

Tests: W-PCL-SQ-R, W-PCL-SQ, W-PCB-SQ-R, W-PCB, W-CT-CL-R, W-DIELDRIN

The USGS and RCRA tests follow the same procedure



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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
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.

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