**Standard Operating Procedure for:**

# ANALYSIS OF ENVIRONMENTAL TRACERS IN AQUEOUS SAMPLES USING GC/MS-SIM

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## 1.0 SCOPE AND APPLICATION

This method is applicable to the determination of sunscreen compounds, and flame retardants 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 3510C (ref 15.2), SOP GC-002-2 (ref 15.6). The analytical part is based on EPA 8270E (ref 15.1) Laboratory Information Management System (LIMS) test: W-TR-SQ-R.

1.2 This Standard Operation Procedure is restricted to use by an analyst experienced in the use of an Agilent 5977 GC/MS system, and in the use of appropriate computer programs. The minimum qualifications required:

- B.S. in Chemistry or Biochemistry or related discipline with a 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.

## 2.0 SUMMARY OF THE METHOD

2.1. General description.

Water samples are extracted using separatory funnel liquid-liquid extraction as per EPA 3510C. The extracts are analyzed using an Agilent 5977 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.

2.2 Modifications to analytical method as EPA 8270E:

The analysis uses analyte protectants (Ethoxyglycerin, Gulonolactone and Sorbitol). Those compounds are injected using the sandwich technique at 25,000ppm/2500ppm/5000ppm respectively. Analyte protectants are necessary to suppress matrix induced response enhancement effects. The 5977A GC/MS seem to be especially sensitive to those kinds of effects.

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

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

DFTPP tune/tune check 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 m/e fragments.

## 3.0 INTERFERENCES

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.


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

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated 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.

## 4.0 DEFINITIONS

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

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

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

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

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

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

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

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

FIELD DUPLICATES: Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers,


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and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.

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

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

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

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

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

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

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

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

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

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

where X1 and X2 are the two measurements

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

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


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

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

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

## 5. 0 APPARATUS AND EQUIPMENT

5.1 Apparatus.

Agilent 5977 GC/MS with extractor source, or equivalent is recommended. The instrument must be temperature programmable with an injector port designed for cold splitless injection. A Multi-Mode Inlet (MMI) may be used if available. The GC, GC Automatic Sampler and MSD operating parameters are summarized in Appendix 1. The analytical column is an HP-5MS UI or equivalent, fused silica capillary, 20 m x 0.25 mm x 0.25 um or similar column with Ultimate Union placed after the initial 5 m of the column (5m-15m mid-column backflash configuration).

5.2 Data system

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

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

5.3 Gases

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

## 6.0 REAGENTS AND CHEMICALS

6.1 Solvents

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

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

6.3 Stock and Intermediate Standards


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

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

6.4 Working Standard Solutions (Calibration standards)

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

Internal Standards for sunscreens analysis:

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)
Octachloronaphthalene

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

6.5 Spiking Solution

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

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

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

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

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

6.7.1 The acceptance criterion is ± 20% difference.

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

6.8 Analyte protectants.


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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. Matrix induced response enhancements make exact quantitation problematic, especially for some analytes. Analyte protectants are generally very polar organic compounds injected at very high concentrations along with every standard and sample in the analytical run sequence. Due to their polarity, they are thought to deactivate all the active sites in the system, and, due to their very high concentration, they render all the other matrices in the samples basically insignificant. In result, 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 25000 ppm, 2500 ppm and 5000 ppm respectively. Due to solubility considerations the working solution is prepared in MeOH containing 5% of DI water. It is injected along with every standard and sample using a "sandwich injection" technique. 0.4 uL of the above analyte protectants mixture is injected, which corresponds to 5.0 ug, 0.5 ug and 1 ug of the corresponding analyte protectants on column. 10% glacial acetic acid in MeOH is used in the second layer (middle) of the three layer "sandwich".

## 7.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

All samples and sample extracts must be refrigerated at 6 degrees C or less from time of collection until extraction.
All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.

## 8.0 SAMPLE PREPARATION PROCEDURE

Water samples are extracted using appropriate procedure described in SOP GC-002 (Ref 15.6). The extracts are shared with test W-PSNP-TQ.

## 9.0 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 to Agilent 5977A GC/MS with the extractor ion source. Instead, this SOP modifies the method to follow manufacturer's tuning instructions using PFTBA autotune. The PFTBA autotune is performed before each run. 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. It may also be necessary to replace the filament or certain source parts.

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

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

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

9.1.2.3. Replace the injector liner (Agilent 4 mm single gooseneck liner) is recommended. 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.


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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 260ºC 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 ºC and the oven temperature to 300 ºC. Bake for 1-2 hrs. It is beneficial and recommended to bake the ion source at 350 ºC at the same time.

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

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

9.1.2.9. Following column trimming and/or replacement the retention times in the SIM acquisition method may need to be adjusted. For that purpose, a high-level calibration standard needs to be run. 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.

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 R^2 not smaller than 0.99. If a higher order curve is to be used the correlation coefficient R^2 has to be at least 0.99. When new calibration is inspected linear fit is usually tried first, followed by average response factor (%RSD) which is equivalent to weighted linear forced through origin), then followed by quadratic fit and finally higher order curves. Do not use the “include” option for the origin. “Ignore origin” should be used preferentially though forcing through origin may have to be used under some circumstances. When calibration curve fit is selected in the Masshunter software the % calibration drift has to be monitored in order to have all the calibration levels within 70-130% of the expected value. Special care has to be taken to carefully fit the curves at the lower end of the calibration range where the vast majority of problems occur. All calibration curves should be weighted curves (1/x or 1/x2); do not use equal weighing. It is permissible to remove individual analyte calibration levels from either the lowest and/or highest levels of the curve (the PQL may have to be adjusted). Removal of interior levels is forbidden. An entire single standard calibration level may be removed from the interior of the curve whenever the standard was not correctly injected, or a wrong standard was injected. If more than 10% of the total number of analytes fail the calibration fit criteria or more than 20% of analytes fail the % 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. Approximate retention times, the primary quantitation ions and confirmatory, secondary ions are given along with SIM acquisition time segments start/stop times in


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Table 1. The primary and secondary ions should all be present, and the relative intensities should agree within ±30% absolute of the reference mass spectrum after background subtraction is performed.

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

9.3 Daily GC/MS Performance and Calibration Check

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

Degradation/tailing factor check (required by EPA 8270E)
A modified GC/MS tuning standard is used to perform this task. The standard contains 5 mg/l each of DDT-p,p' and Pentachlorophenol. Benzidine, which is also recommended by method 8270E, is usually not detectable in the presence of analyte protectants. Since the absence of benzidine peak in the chromatograms has no bearing on the chromatographic behavior of the target analytes and surrogates, only pentachlorophenol is used for the tailing factor determination. The degradation check/tailing factor standard is run at the beginning of the analytical run sequence to verify injection port inertness and GC column performance. A full scan version of the acquisition method is used for this purpose. Degradation of DDT to DDD and DDE should not exceed 20%.
The percent breakdown calculation is performed using the following formula (EPA method 8081B)

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

The following are the Relative Retention Times for DDD-p,p' and DDE-p,p' (relative to DDT-p,p'):
DDE-p,p' RRT = 0.880
DDD-p,p' RRT = 0.945

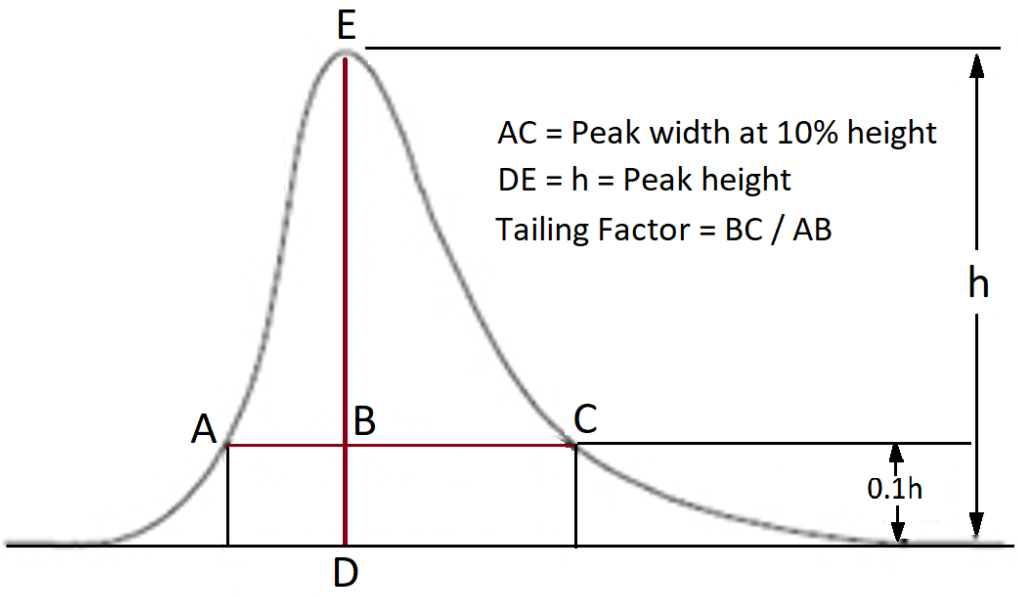
Usually it is necessary to perform spectral deconvolution of the chromatograms to remove the analyte protectants "hump" and obtain correct integration values and clean spectra for target analytes. Deconvolution for GC/MS data is the process of computationally separating co-eluting components and creating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

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

Tailing Factor = BC / AB

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


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

9.3.3 Calibration verification standard must also meet the following criteria:

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

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

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

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

9.4 GC/MS Sample Analysis.

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


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**concentration of internal standard must remain at 100 µg/L when diluting samples by adding additional internal standard to the extract.**

9.5 Analysis Run Sequence.
The analyst will set up an analysis run sequence by placing the GC vials containing the sample extracts and standards on the autosampler tray in the following order or similar:

isooctane (to clean the system)
degradation/performance check
Instrument Blank W-PSCL-ISTD (containing internal standard HCB-d3 at 100 ug/L)
Tracers calibration set (when initial calibration is run, levels 1-8)
TR ICV L-5 initial calibration verification check (when initial calibration is run)
TR CCV L-5 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)*
samples (up to 12 hours)

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

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

Data Processing using the Masshunter software.

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

9.5.2 Examine the quantitation reports soon after the samples have been analyzed. Check all 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


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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 TR surrogate spike solution currently containing p-terphenyl-d14 at 1000 ug/L. The surrogate compound is expected to be found at 200 µg/L in all the sample extracts, Blanks, LFBs, and Matrix Spikes.

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

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

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. See ref 15.8, chapter 5.3 for details. LFB and matrix spikes recovery limits are calculated independently; in some cases, the limits for LFBs may then be applied to both LFBs and matrix spikes. In case LFB failures are observed the LFBs may be rerun and reanalyzed. All the associated samples that have positives (above PQL) for the analytes failing in the LFBs must be re-run and reanalyzed as well. Similarly, if the number of matrix spikes failures is deemed excessive matrix spikes (along with the background sample) may be rerun and reanalyzed. See ref 15.8, chapter 5.3 for details on disposition of QC failures.

9.5.8 Blank contamination

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

9.5.8.2 Method Blanks. In the event a positive identification is found in both the sample(s) and the extraction blank then the unexpired sample have 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.


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The re-extraction is not necessary when the analytes in question are non-detects in the samples or whenever the values found in the samples are >10x the value detected in the method blank(s).

9.5.8.3 Field Blanks.

In case a positive identification is found in a field blank, but method blank(s) pass, all field blank detections above PQL generally need to be confirmed by re-extraction. If the field blank detections are below PQL, then the re-extraction is not necessary in the following cases:

- The same analyte is not found in the associated samples (samples in the same job),
- The same analyte is found in the associated samples at levels at least 10 times the value in the field blank.
- It is always prudent to confirm the results in extract by rerun, before sending the field blank for re-extraction. The above rules also apply to samples with matrix "DI water" even if they are not specifically called field blanks.

9.5.8.4. Equipment Blanks.

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

9.5.9 Continuing Calibration

9.5.9.1 After initial calibration, the GC/MS 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 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).

9.6. Quantitation of positives.

Positives are quantified based on their peak area. The concentration reported for an identified hit in the sample extract, expressed in ug/L, is based on calibration curve of the initial calibration. The Masshunter software used to process data will do the interpolation for the sample extract. However, the analyst must ensure that all identification criteria are fulfilled, and the peak area integration was correctly done. If not, the integration has to be corrected by choosing a new set of integration parameters or by manual integration (for manual integration procedure see 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



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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).

## 10.0 REPORTING AND DOCUMENTATION

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

TR_CCV,
SURWTR_1234567 for surrogate in sample.

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).

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.

## 11.0 QUALITY CONTROL

11.1 See DEP SOP GC-001, (ref 15.8) for detailed information on quality control, definitions and interferences. See DEP SOP LB-027 (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


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- 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

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

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 . 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_MSD3. They are then converted in QC Manager for reporting in LIMS.

## 13.0 DETERMINATION OF METHOD DETECTION LIMITS

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


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

## 14.0 SAFETY/HAZARDOUS WASTE MANAGEMENT

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

## 15. REFERENCES

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

15.2 EPA method 3510C, Separatory Funnel Liquid-Liquid Extractions, SW 846, 3rd Edition, Update 4, January 3rd, 2008.

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 GC-002-2. Extraction of Pesticides, Environmental Tracers and Polychlorinated Biphenyls (PCBs) from Water, Wastes, and Soil/Sediment Samples for Subsequent Analysis by GC/MS Techniques.

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

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


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

15.10 DEP SOP LB-031 Method Detection Limit Verification.

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

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

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

## TABLES

**TABLE 1:** Quantifier and qualifier ions, internal standard associations, MDLs, PQLs and approximate RTs for environmental tracers included in LIMS test W-TR-SQ-R. **LIMS reporting units are ng/L.**

| Analyte | Approx. Retention Time min) | Associated internal standard | Quantifier ion | Qualifier ions | MDL ug/L in extract | PQL ug/L in extract | MDL ng/L in sample | PQL ng/L in sample |
|---|---|---|---|---|---|---|---|---|
| **p-Terphenyl-d14 surrogate** | 6.27 | Octachloronaphthalene | 244.0 | 122.0, 212.0 | | | | |
| Tris(2-chloroethyl) phosphate (TCEP) | 5.07 | HCB-d3 | 205.0 | 249.0, 251.0 | 110 | 330 | 55 | 160 |
| Tris(1-chloro-2-propyl) phosphate (TCPP) | 5.18 | HCB-d3 | 201.0 | 277.0, 279.0 | 200 | 600 | 100 | 300 |
| Oxybenzone | 5.86 | HCB-d3 | 151.0 | 227.0, 228.0 | 20 | 60 | 10 | 30 |
| Pentabromotoluene | 6.55 | HCB-d3 | 485.6 | 483.6, 487.6 | 6.0 | 18 | 3.0 | 9.0 |
| Octinoxate | 655 | HCB-d3 | 178.0 | 165.0, 290.0 | 300 | 900 | 150 | 450 |
| Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) | 6.62 | HCB-d3 | 380.9 | 378.9, 382.9 | 10 | 30 | 5.0 | 15 |
| Hexabromobenzene | 7.05 | HCB-d3 | 551.5 | 549.5, 553.5 | 12 | 36 | 6.0 | 18 |
| PBDE-47 | 7.14 | HCB-d3 | 487.5 | 483.7, 487.7 | 8.0 | 24 | 4.0 | 12 |
| Tri-o-cresyl Phosphate | 7.27 | HCB-d3 | 368.1 | 181.1, 277.1 | 12 | 36 | 6.0 | 18 |
| 2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol (UV-328) | 7.45 | TCB-d5 | 322.2 | 323.2, 351.2 | 540 | 1620 | 270 | 810 |
| Avobenzone | 7.75 | Octachloronaphthalene | 310.0 | 309.0, 135.0 | 420 | 1260 | 210 | 630 |
| Dechlorane 602 | 7.81 | Octachloronaphthalene | 510.7 | 514.7, 512.7 | 10 | 30 | 5.0 | 15 |
| 2-Ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB) | 7.79 | HCB-d3 | 420.7 | 422.7, 437.7 | 100 | 300 | 50 | 150 |
| PBDE-99 | 7.80 | HCB-d3 | 565.7 | 563.7, 567.7 | 10 | 30 | 5.0 | 15 |


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| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| PBB-153 | 8.27 | Octachloronaphthalene | 625.6 | 546.6, 467.7 | 12 | 36 | 6.0 | 18 |
| Dechlorane 603 | 9.27 | Octachloronaphthalene | 600.8 | 602.8, 598.8 | 8.0 | 24 | 4.0 | 12 |
| Dechlorane Plus* | 11.28 syn<br>11.72 anti | HCB-d3 | 271.8 | 273.8, 275.8 | 60 | 180 | 30 | 90 |
| Tetradecachloro-m-terphenyl** | 17.67 | Octachloronaphthalene | 709.7 | 713.7, 711.7 | 15 | 45 | 7.5 | 23 |
| TCB-d5 | 5.70 | Internal Std | 297.0 | 295.0, 225.0 | | | | |
| HCB-d3 | 7.01 | Internal Std. | 363.0 | 365.0, 293.0 | | | | |
| Octachloronaphthalene | 7.94 | Internal Std | 403.8 | 331.8, 401.8 | | | | |

- Summary peak is used for Dechlorane Plus. This analyte is no longer analyzed in routine samples.

**Table 2A**: Analyte concentrations in calibration standards and ICV for environmental tracers (ug/L) (Test ID W-TR-SQ-R). The expected spike concentrations in LFBs/MSs are equal to 200/800 ug/L (in extract)

| | L8 | L7 | L6 | L5/CCV | L4 | L3 | L-2 | L-1 | ICV |
|---|---|---|---|---|---|---|---|---|---|
| **analyte** | ppb | ppb | ppb | ppb | ppb | ppb | ppb | ppb | ppb |
| Oxybenzone | 1600 | 1200 | 800 | 400 | 200 | 100 | 50 | 20 | 400 |
| Octinoxate | 6400 | 4800 | 3200 | 1600 | 800 | 400 | 200 | 80 | 1600 |
| Avobenzone | 6400 | 4800 | 3200 | 1600 | 800 | 400 | 200 | 80 | 1600 |
| PBDE-47 | 800 | 600 | 400 | 200 | 100 | 50 | 25 | 10 | 200 |
| PBDE-99 | 800 | 600 | 400 | 200 | 100 | 50 | 25 | 10 | 200 |
| 2-Ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB)* | 1600 | 1200 | 800 | 400 | 200 | 100 | 50 | 20 | 400 |
| Tri-o-cresyl Phosphate | 800 | 600 | 400 | 200 | 100 | 50 | 25 | 10 | 200 |
| Dechlorane Plus | 3200 | 2400 | 1600 | 800 | 400 | 200 | 100 | 40 | 800 |
| 2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol (UV-328)* | 3200 | 2400 | 1600 | 800 | 400 | 200 | 100 | 40 | 800 |
| Tris(1,3-dichloro-2-propyl) phosphate (TDCPP)* | 800 | 600 | 400 | 200 | 100 | 50 | 25 | 10 | 200 |
| Tris(1-chloro-2-propyl) phosphate (TCPP)* | 3200 | 2400 | 1600 | 800 | 400 | 200 | 100 | 40 | 800 |
| Tris(2-chloroethyl) phosphate (TCEP)* | 6400 | 4800 | 3200 | 1600 | 800 | 400 | 200 | 80 | 1600 |
| 2,3,4,5,6-Pentabromotoluene | 800 | 600 | 400 | 200 | 100 | 50 | 25 | 10 | 200 |
| Hexabromobenzene | 800 | 600 | 400 | 200 | 100 | 50 | 25 | 10 | 200 |
| Dechlorane 602 | 800 | 600 | 400 | 200 | 100 | 50 | 25 | 10 | 200 |
| Dechlorane 603 | 800 | 600 | 400 | 200 | 100 | 50 | 25 | 10 | 200 |
| PBB-153 | 800 | 600 | 400 | 200 | 100 | 50 | 25 | 10 | 200 |
| Tetradecachloro-m-terphenyl | 800 | 600 | 400 | 200 | 100 | 50 | 25 | 10 | 200 |
| p-Terphenyl-d14 | 800 | 600 | 400 | 200 | 100 | 50 | 25 | 10 | 200 |

- * These analytes are called by their acronyms in the Masshunter software


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**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 | As per QCM limits tables, 50-150% for most new analytes | Reanalyze/Re-extract/Flag |
| | Matrix Spike recoveries | As per QCM limits tables, 50-150% for most new analytes | Reanalyze/Re-extract/Flag |
| 3 | ICV | ± 30% | Reanalyze/Flag |
| 4 | CCV | ± 20% | Re-run and recalibrate/Flag |
| 5 | Surrogate recovery | p-Terphenyl-d14 52-192% | Reanalyze/Re-extract/Flag |
| 6 | Linearity criterion | 20% RSD; 0.99 R^2 | Use appropriate cal fit / Re-run/ Recalibrate |
| 7 | Internal Std. recovery | -50% to+200% | Reanalyze/recalibrate/flag |
| 8 | % cal drift | ± 30% of expected value | Change fit/ recalibrate/flag |
| 9 | Instrument performance check | < 20% DDT degradation, tailing factor not more than 2.0 for pentachlorophenol. | Perform instrument maintenance, rerun the performance check sample. |
| 10 | Method Blank | <MDL | Rerun/re-extract; qualify samples with “V” if up to 10X the value in method blank. |

Statistical recovery limits for LFB/MS and surrogates recoveries are typically based on QC Manager statistics for the last two 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. For more details refer to ref 15.8 chapter 5.3.

## APPENDICES

### APPENDIX 1
**GC/MS acquisition method for environmental tracers compounds.**

INSTRUMENT CONTROL PARAMETERS: GC_MSD-3
---

C:\MassHunter\GCMS\1\methods\TR-SIM_221213.M
Tue Dec 13 09:37:37 2022

Control Information
------- -----------

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


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No Sample Prep method has been assigned to this method.

GC
GC Summary

| | |
|---|---|
| Run Time | 19 min |
| Post Run Time | 3 min |

Oven

| | |
|---|---|
| Temperature | |
| Setpoint | On |
| (Initial) | 90 °C |
| Hold Time | 1.5 min |
| Post Run | 310 °C |
| Program | |
| #1 Rate | 40 °C/min |
| #1 Value | 310 °C |
| #1 Hold Time | 12 min |

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

ALS
Front Injector

| | |
|---|---|
| Syringe Size | 10 µL |
| Injection Volume | 1 µL |
| Solvent A Washes (PreInj) | 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 | 3000 µL/min |
| Sample Wash Draw Speed | 300 µL/min |
| Sample Wash Dispense Speed | 3000 µL/min |
| Injection Dispense Speed | 6000 µL/min |
| Viscosity Delay | 7 sec |
| Sample Depth | Disabled |
| Injection Type | 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 |


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Sample Overlap
Mode Prepare sample before end of GC run 1 min

ALS Errors Pause for user interaction

Front MM Inlet He
Front MM Inlet He Temperature
Setpoint On
(Initial) 310 °C

Mode Pulsed Splitless
Pressure On 7.1207 psi
Total Flow On 54.1 mL/min
Septum Purge Flow On 3 mL/min
Septum Purge Flow Mode Standard
3 min (Post Run Temperature) 310 °C
3 min (Post Run Total Flow) 25 mL/min
Gas Saver On 25 After 3 min mL/min
Injection Pulse Pressure 40 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 On
(Initial) 1.1 mL/min
Post Run -5.7796 mL/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) 90 °C


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| | |
|---|---|
| Pressure | 7.1207 psi |
| Flow | 1.1 mL/min |
| Average Velocity | 32.765 cm/sec |
| Holdup Time | 0.25433 min |
| Control Mode | Constant Flow |

Column #2
Flow

| | |
|---|---|
| Setpoint | On |
| (Initial) | 1.2 mL/min |
| Post Run | 1.4044 mL/min |

| | |
|---|---|
| Column Information | Agilent 19091S-433UI-25m |

HP-5ms Ultra Inert

| | |
|---|---|
| Temperature Range | -60 °C—325 °C (350 °C) |
| Dimensions | 15 m x 250 µm x 0.25 µm (Calibrated) |
| Column lock | Unlocked |
| In | Aux EPC 3 He |
| Out | MSD |
| (Initial) | 90 °C |
| Pressure | 4.3978 psi |
| Flow | 1.2 mL/min |
| Average Velocity | 57.524 cm/sec |
| Holdup Time | 0.4346 min |
| Control Mode | Constant 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 |
| Data Rate | 50 Hz |
| Dual Injection Assignment | Front Sample |


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Signal #2:
Description None

Signal #3:
Description None

Signal #4:
Description None

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

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

Acquisition Mode : SIM
Solvent Delay (minutes) : 3.5
Tune file : C:\MassHunter\GCMS\1\5977\etune.u
EM Setting mode Gain : 5.000000

Number of SIM Groups : 5
Run Time (if MS only) : 14.5 minutes

[SIM Parameters]
Group 1 Group ID : 1
Resolution : 0
Group Start Time : 3.5
Number of Ions : 21
Ions
Dwell In Group :( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
( 122.00,10 ) ( 151.00,10 ) ( 161.00,10 )
( 178.00,10 ) ( 201.00,10 ) ( 205.00,10 )
( 212.00,10 ) ( 227.00,10 ) ( 228.00,10 )
( 244.00,10 ) ( 249.00,10 ) ( 251.00,10 )
( 277.00,10 ) ( 279.00,10 ) ( 290.00,10 )
( 378.90,10 ) ( 380.90,10 ) ( 382.90,10 )
( 483.60,10 ) ( 485.60,10 ) ( 487.60,10 )

Group 2 Group ID : 2
Resolution : 0
Group Start Time : 6.85
Number of Ions : 33
Ions
Dwell In Group :( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
( 135.00,10 ) ( 181.10,10 ) ( 277.10,10 )
( 293.00,10 ) ( 309.00,10 ) ( 310.00,10 )
( 322.20,10 ) ( 323.20,10 ) ( 331.80,10 )
( 351.20,10 ) ( 363.00,10 ) ( 365.00,10 )
( 368.10,10 ) ( 401.80,10 ) ( 403.80,10 )
( 420.70,10 ) ( 422.70,10 ) ( 437.70,10 )


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( 467.70,10 ) ( 483.70,10 ) ( 485.70,10 )
( 487.70,10 ) ( 510.70,10 ) ( 512.70,10 )
( 514.70,10 ) ( 546.60,10 ) ( 549.50,10 )
( 551.50,10 ) ( 553.50,10 ) ( 563.70,10 )
( 565.70,10 ) ( 567.70,10 ) ( 625.60,10 )

Group 3 Group ID : 3
Resolution : 0
Group Start Time : 8.8
Number of Ions : 6
Ions
Dwell In Group :( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
( 271.80,50 ) ( 273.80,50 ) ( 275.80,50 )
( 598.80,50 ) ( 600.80,50 ) ( 602.80,50 )

Group 4 Group ID : 4
Resolution : 0
Group Start Time : 13
Number of Ions : 6
Ions
Dwell In Group :( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
( 73.00,50 ) ( 147.00,50 ) ( 207.00,50 )
( 281.00,50 ) ( 355.00,50 ) ( 429.00,50 )

Group 5 Group ID : 5
Resolution : 0
Group Start Time : 16
Number of Ions : 3
Ions
Dwell In Group :( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
( 709.70,100 ) ( 711.70,100 ) ( 713.70,100 )

[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)
19.00 off

END OF MS ACQUISITION PARAMETERS

TUNE PARAMETERS for SN: US1418M201
---


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Trace Ion Detection is ON.

```
  34.593   :   EMISSION
  70.007   :   ENERGY
   4.985   :   REPELLER
  89.822   :   IONFOCUS
  10.090   :   ENTRANCE_LENS
1764.695   :   EMVOLTS
                    1764.7  : Actual EMV
                     0.27   : GAIN FACTOR
1411.000   :   AMUGAIN
 123.938   :   AMUOFFSET
   1.000   :   FILAMENT
   1.000   :   DCPOLARITY
  10.773   :   ENTLENSOFFSET
   7.502   :   Ion_Body
  -1.799   :   EXTLENS
-462.000   :   MASSGAIN
 -37.000   :   MASSOFFSET

              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:


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```
History of Serial # 123546
--------------------------------------------------
123546-TR-L8
   123538-SUNSCREENS INT
      123536-SUNSCREENS-STOCK
         117568-AVOBENZONE
         117567-OXYBENZONE
         117566-OCTINOXATE
      123535-P-TERPHENYL-D14 STOCK
         121676-P-TERPHENYL-D14
   121169-PSCL IS 100 PPM
      120982-PSCL IS 1000 PPM
         113463-PSCL IS 1000 PPM
            113164-TRIFLURALIN-D14
            113162-HCB-D3
            113159-DCB-D5
            113151-ALPHA-BHC-D6
            113135-DDT-D8
            113134-TCB-D5
            112042-OCTACHLORONAPHTHALENE
```

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 must 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.

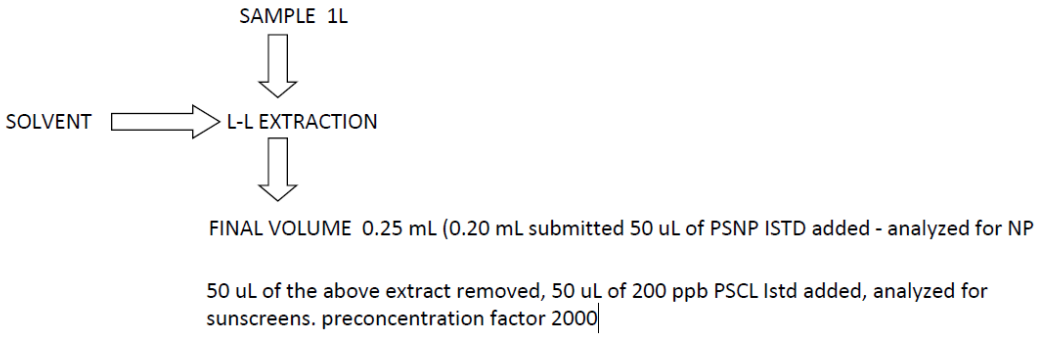

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**APPENDIX 4: Preparation Flowchart**

**Water samples GC/MS or GC/MS/MS PREP ID: EPA 3510C**

**Sunscreens and NP pesticides in water**

**W-PSNP-TQ, W-TR-SQ-R**




## Appendix of significant changes.

| | |
|---|---|
| 02/02/2022 | Updated MDLs and surrogate recovery limits. Field blanks re-extraction rules added. |
| 06/03/2022 | New analytes added to the test. Updated tables and acquisition method. Updated surrogate recovery limits. |
| 08/05/2022 | Dechlorane Plus added to the test. Updated tables and the acquisition method. |
| 02/16/2023 | New analytes added to the test. Surrogate recovery limits updated. Clarification of re-extraction rules in case of MBLK contamination. Tables updated to include new analytes. GC acquisition method updated. |
| 09/16/2023 | Addition of UV-328 to the test. MDL update to octinoxate. Addition of TCB-d5 internal standard. |
| 01/03/2024 | Updated MDLs and surrogate recoveries. Rule regarding positive in the equipment blanks added to chapter 9.5.8. Updated standards concentrations due to recent changes. |
| 10/03/2024 | Updated surrogate recovery limits. Updated MDL/PQL for TCPP. Updated re-extraction rules for field blanks. |
| 09/26/2025 | Updates to MDLs and PQLs. |
| 10/27/2026 | Updated surrogate recovery limits. Updated some MDLs and PQLs. |


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