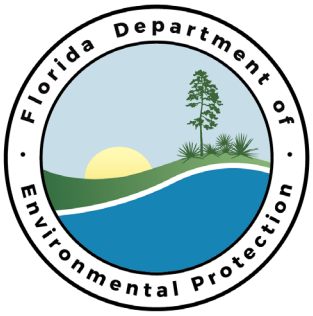
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Standard Operating Procedure For:

Analysis of Base/Neutral/Acid Extractables by Gas Chromatography/Mass Spectrometry



Department of Environmental Protection
Chemistry Section
Tallahassee Florida

Analysis of Base/Neutral/Acid Extractables by Gas Chromatography/Mass Spectrometry

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1. SCOPE AND APPLICATION

1.1 This method describes the analysis of base-neutral and acid extractable organics by GC/MS and is based on the EPA Methods 625.1 and 8270E. The analytes applicable to this method (as listed in Table 1) may be detected in ground water, surface water, sediments, and wastes. The operating procedures described here are designed to meet or exceed the requirements for EPA methods 625.1 and 8270E.

1.2 FDEP Laboratory Test IDs and equivalent methods reported by this SOP are compiled in the table below. This method follows the requirements of EPA Method 625.1 and Method 8270E for the parameters denoted as such in Table 5.1 of the laboratory's Quality Manual. EPA Method 625.1 is an approved test procedure of the National Pollutant Discharge Elimination System (NPDES) under the Clean Water Act (CWA) and Method 8270E is listed in the SW-846 publication under Subtitle C of the Resource Conservation and Recovery Act (RCRA). Furthermore, the NPDES and RCRA compliant tests employed by the laboratory using these methods are listed below.

Laboratory Test Name	Test Description
W-BNA-R	EPA Method 8270E analysis, water sample
W- BNA	EPA Method 625.1 analysis, water sample
W-PAH	EPA Method 625.1 analysis for PAHs only, water sample
W-PAH-R	EPA Method 8270E analysis for PAHs only, water sample
S- BNA	EPA Method 8270E analysis, soil sample
S-PAH	EPA Method 8270E analysis for PAHs only, soil sample
WAS-BNA	EPA Method 8270E analysis, waste sample
WAS-PAH	EPA Method 8270E analysis for PAHs only, waste sample
SPLP-PAH	EPA Method 8270E analysis of SPLP extract
SPLP-BNA	EPA Method 8270E analysis of SPLP extract
TCLP-BNA	EPA Method 8270E analysis of TCLP extract

The acceptance limits, as provided in EPA Methods 625.1 and 8270E, are programmed into the Laboratory's Information Management Systems (LIMS) and applied automatically as part of the data processing, review, and reporting procedures. Table 5.1 of the Quality Manual provides information regarding method limits of detection, accuracy, and precision.

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

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

2. SUMMARY OF THE METHOD

2.1 Extracts from water, sediment and waste samples (prepared following SOPs SV-001) are analyzed by GC/MS.

2.2 Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of two or three characteristic masses (m/z). Quantitative analysis is performed using internal standard technique.

2.3 The following compounds may require special treatment when being determined by this method.

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2.3.1 Benzidine can be subject to oxidative losses during solvent concentration, storage, and analysis.

2.3.2 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

2.3.3 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

2.3.4 N-Nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.

2.3.5 N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. For this reason, it is acceptable to report the combined result for N-nitrosodiphenylamine and diphenylamine for either of these compounds as a combined concentration.

2.3.6 1,2-Diphenylhydrazine is unstable even at room temperature and readily converts to azobenzene. Given the stability problems, it would be acceptable to calibrate for 1,2-diphenylhydrazine using azobenzene. Under these poor compound separation circumstances results for either of these compounds should be reported as a combined concentration.

2.3.7 Pyridine may perform poorly at the GC injection port temperatures listed in this method. Lowering the injection port temperature may reduce the amount of degradation. However, the analyst must use caution in modifying the injection port temperature, as the performance of other analytes may be adversely affected. Therefore, if pyridine is to be determined in addition to other target analytes, it may be necessary to perform separate analyses. In addition, pyridine may be lost during the evaporative concentration of the sample extract. As a result, many of the extraction methods listed above may yield low recoveries unless great care is exercised during the concentration steps.

2.3.8 For quantitation and reporting of Benzo(b)fluoranthene and Benzo(k)fluoranthene, the peaks must be 50% resolved. The height of the valley between the peaks should not be more than 50% of the average height of the two peaks. If peaks are not resolved, perform injection service, change column and/or use longer GC temperature program. If this separation is not performed these two analytes must be reported as both.

3. INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interference. 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. In extreme cases, it may be necessary to analyze a solvent blank between samples.

3.3 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. These materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary.

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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.

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.

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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 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 Bottles--25 mL, amber glass with Teflon-lined screw caps

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5.2 Autosampler vials - 1.5 mL and 0.35 mL, with crimp tops with Teflon-lined septa, to fit the Agilent 7683 and 7693 autosampler.

5.3 GC/MS system:

5.3.1 Gas chromatograph, Agilent 7890A, 7890B and Agilent 6890N series II or equivalent. Must be temperature programmable with an injector port designed for splitless injection. A Multi-Mode Inlet (MMI) may be used if available.

5.3.2 Autosampler, Agilent 7693 and 7683 or equivalent, capable of 1 to 2 µL injections and equipped with solvent vials for flushing syringe between injections.

5.3.3 Mass spectrometer, Agilent 5977B, 5975C and 5973 or equivalent; Must be capable of scanning from 35 to 450 amu every 7 s or less, utilizing a 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

5.3.4 Data system: A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z and plotting such m/z abundance versus time or scan number (an Extracted Ion Current Profile, or EICP). Software must also allow integrating the abundance in any EICP between specified time or scan number limits. This system currently uses the Masshunter software from Agilent Technologies Inc. For reporting data, the system currently uses DEP LIMS.

5.3.5 GC/MS Operating Conditions: (this serves as a guideline only for regular BNA analysis, different instrument may have different settings)

Parameter	Setting
Mass Range:	35-450 amu
Scan Time:	4.5 to 34 min. 1 scan/sec minimum
GC Oven Temperature Program:	45 °C for 0.5 min., °C 18 °C/min to 270 °C , hold for 1 min, 10 °C/min to 330 °C, hold for 3.5 min.
Inlet:	Temp: 275 °C; Mode: Pulse Splitless; Pressure: Constant Flow ON, 6.0 psi at 50 °C (1.2 mL/min); Purge Time 0.75 min. Purge Flow: 30 mL/min. Total Flow 23.8 mL/min. Gas Saver: ON; Saver Flow 20 mL/min. Saver Time: 3.0 min.
MS interface temperature:	280 °C
Injection Volume:	1µL
Total Run Time:	23 min.

5.4 Helium, UPC grade, is the carrier gas in the gas chromatographs. The helium must be passed through an oxygen filter before entering the gas chromatographs.

5.5 Agilent DB-5MS or HP-5MS UI capillary column (or equivalent), 30m x 0.25 mm x 0.25 µm) or equivalent

6. REAGENTS AND CHEMICALS

6.1 Standards

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6.1.1 For instrument GC-MSD5 high level calibration standards (BNA-H) are prepared at the following concentration levels: 0.75 1, 2.5 5, 10, 25 and 50 mg/L (with 1 mg/L internal standards presents in each of the seven levels). Concentrations for some of the analytes are twice the values mentioned above. Note: Some analytes will not be detectable at 1 or 2 µg/mL; do not include these when constructing calibration curves.

6.1.2 For instrument GC MSD6 low level calibration standards (BNA-L) are prepared at the following concentration levels at 50, 100, 200, 500, 750, 1000 and 2500 µg/L (with 1000 µg/L internal standards presents in each of the seven levels) and 1 µg/mL second source ICV. Concentration for some of the analytes are twice the values mentioned above.

6.1.3 Prepare a second source (ICV/CV625) check standards at 25 mg/L (for high level set) and 750 ug/L (for low level set). These standards are used as initial calibration verifications and run immediately following initial calibrations. They are also used as the daily continuing calibration verification check standards (CCVs) for method 625.1 (test IDs W-BNA, W-PAH). For 8270E based tests 25 mg/L and 750 ug/L first source standards are run as CCVs.

6.1.4 Similarly to BNA standards, two set of PAH standards (high and low) as well as ICVs/CCVs are prepared. .@

6.1.5 Internal standard solution, 10 and 1 mg/L. This solution is used when sample dilution is needed and contains the following compounds:

1,4-Dichlorobenzene-d4	Phenanthrene-d10
Naphthalene-d8	Chrysene-d12
Acenaphthene-d10	Perylene-d12

6.1.6 DFTPP (Decafluorotriphenylphosphine) Tuning Standard Mixture, 50 mg/L each.

6.2 Solvents: Methylene chloride and Methanol, HPLC grade (or equivalent).

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 plus 6 degrees C or less from time of collection until extraction.

7.3 All samples must be extracted within 7 days of collection (waters) or 14 days of collection (soils, wastes) or 365 days (tissue samples) and completely analyzed within 40 days of extraction.

8. SAMPLE PREPARATION PROCEDURE

See SOP: SV-001.

9. GENERAL DESCRIPTION OF GC/MS ANALYSIS

9.1 GC/MS Maintenance and Tuning

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9.1.1 GC/MS tuning includes periodically performed autotune and daily DFTPP tune check. For instrument GC-MSD5 (Agilent 5975C) the DFTPP tune file is used. For GC-MSD6 (Agilent 5977B) High Efficiency Source tune is performed (HES tune) The five lens High Effieciency Source cannot be tuned to DFTPP, The instrument tune has to be performed after each major MSD maintenance, like source cleaning, source parts replacement, filament changing or electron multiplier changing. Additionally, it is highly recommended to run the autotune before each initial calibration. Furthermore, for instrument GC-MSD6, the autotune can be run daily.

Additional manual steps can be taken at the beginning of each sequence run (and after any subsequent "retuning") to ensure that the spectrometer's mass calibration is accurate: Using Perfluorotributylamine (PFTBA) and the manual tune section of the Masshunter software, adjust the tuning lenses so that the PFTBA alignment ions (69, 219, 502) are centered (± 0.10 amu) on their respective amu calibration points and that their widths are 0.45 to 0.55 amu at half height. Print out a tune report from the manual tune section of the Masshunter software. This is a good time to check for air leaks with ions 18 and 28. These need to be less than 5% of ion 69. This mass calibration report is then stored in the run's QA/QC folder.

9.1.2 The DFTPP tune check analysis is performed prior to the beginning of each a seqeunce run (methods 625.1 and 8270E) and then every 12 hours thereafter (625.1 only). The DFTPP tune check analysis must meet the criteria in Table 2 for a 50-ng injection of DFTPP within two scans on either side of the DFTPP apex. The analysis of the DFTPP tune sample (along with DDT degradation, pentachlorophenol, benzidine tailing factors) is performed using Environmental Quant Masshunter software. Depending on the required tests, use either DFTPP-625 or DFTPP-8270E method, or both. If the tune check does not pass, , you can manually try to adjust the DFTPP target tune parameters (as described above in 9.1.1) and perform a DFTPP tune check by re-injecting the DFTPP standard. Otherwise, retune the instruments and rerun the tune check sample. If the tune passes, then check the DDT breakdown (only required to for method 8270E) and Tailing Factor (TF) for Benzidine and Pentachlorophenol criteria (Table 2). Once the instrument has failed to successfully tune after making several attempts, then it is time to clean the ion source and perform other preventative maintenance. Other instrumental problems, which can prevent the mass spectrometer from tuning properly, include a contaminated column, a poorly responding EM, or air leaks. Sample analyses MUST not begin until all the tuning criteria are met. Do not expect instrument GC-MSD6 to always pass the more stringent 625.1 criteria. HES tune should be performed, instead. Consequently, GC-MSD6 is not to be used for unknowns analysis.

9.1.3 Background subtraction, if needed, should be straightforward and designed only to eliminate column bleed or instrument background ions.

9.1.4 Place a hard copy of the DFTPP tuning report(s) in the batch folder. .

9.1.5 For method 625.1 Include a DFTPP standard injection at twelve hours intervals during an analysis sequence and check the tune criteria. Do not count method blank and LFB(s) into 12 hrs interval. If the tune check happens to fail any of the criteria, then re-analyze all samples that were analyzed after the failed tune check_standard. For method 8270E only initial, once daily, injection of the DFTPP standard is required.

9.1.6 The instrument tune must be maintained not only for environmental samples, but also for instrument calibration standards.

9.1.7 Perform inlet maintenance replaced the glass wool in the liner, or the liner itself. Cut 1-6 inches 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.

9.1.8 Run an Instrument Blank and look for instrument contamination.

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

9.1.10 To perform maintenance of the MMI inlet (GC-MSD6) replace the liner and septum and clean the inside of the inlet body with cotton swabs soaked with methanol and methylene chloride. **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.

9.1.11 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 basis is highly recommended.

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

9.2 Initial Calibration

9.2.1 Analyze the calibration standards at seven levels as per chapter 6.1. At each level, the internal standards should be present at 1000 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 a 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” origin option in the Masshunter software. “Ignore” origin is preferable to “force” through origin in most cases. Forcing the curve through origin is acceptable whenever ignoring origin produces nonsensical results for small peaks close to MDL (like negative values). 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 For each compound determine the retention time, the primary quantitation ion and two or three secondary ions to use for qualitative identification. The primary and secondary ions are already given in the EPA methods 625.1 and 8270E. Those ions are compiled in Table 4. 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. In cases where the qualifier has higher intensity than quantifier ions, relative ±30% is used. Additionally, a reference spectral library is created based on mid-level (CCV) calibration standard. The acceptance criterium for the reference library match is 60%. The reference library may be updated on daily basses using the CCV standard. The reference library match compares the deconvoluted

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spectrum of each peak with that stored in the reference library. 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.

9.2. 3 Initial calibration curve is always immediately checked with the second source initial calibration verification standard (ICV). The acceptance criterion is ±30%.for method 8270E and ±40% for 625.1 For method 625.1 The ICV standard is identical with the Continuous calibration standard (CCV), since that method requires the CCV to be prepared from the second source standard.

9.2.4 The initial calibration is to be run periodically based on analyst judgment regarding the instrument condition. However, following each major maintenance, the instrument must be recalibrated. Column replacement, source cleaning, source parts replacement, filament changing or electron multiplier changing are examples of major maintenance actions that trigger obligatory recalibration. Lastly, there is nothing wrong with running initial calibrations daily, if deemed practical and adventitious.

9.2.5 Masshunter software tabulates the area of the primary ions against concentration for each compound and internal standard in the calibration standard mixes and calculates response factors for each compound using the equation below.

$$RF = \frac{(A_S\ C_{is})}{(A_{is}\ C_S)}$$

where :

RF_i is the average response factor from the initial calibration
A_s is the area of the quantitation ion for the compound measured
C_{is} is the concentration for the internal standard
A_{is} is the area of the quantitation ion for the internal standard
Cs is the concentration of the compound measured

9.2.6 Some analytes are very problematic. Benzidine breaks down readily and may not be seen below a 50 µg/mL standard level. Some compounds may not be detected at the lower standard concentration levels. (i.e., Benzidine, 4-Nitrophenol). Eliminate these levels from the analyte's calibration curve. However, the analytes should have a calibration curve with 5 or more levels. In the case of Benzidine, only three levels may be feasible. The MS may have to be adjusted accordingly (i.e., increase EM voltage, etc.) to achieve appropriate sensitivity.

9.2.7 A method blank should be analyzed prior to sample analysis to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

9.2.8 Store all hard copies of the calibration and quantitation reports created in a file folder and label with the ID file name and calibration file name.

9.3 Daily GC/MS Performance and Calibration Check

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

9.3.1 Degradation/tailing factor check.

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GC/MS tuning standard is used to perform this task. The standard contains 50 mg/L each of DDT-p,p' and pentachlorophenol and benzidine along with DFTPP. 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. For method 625.1 it is also run at 12 hrs intervals afterwards.

Degradation of DDT to DDD and DDE should not exceed 20%.
The percent breakdown calculation is performed using the following formula (EPA method 8081)

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

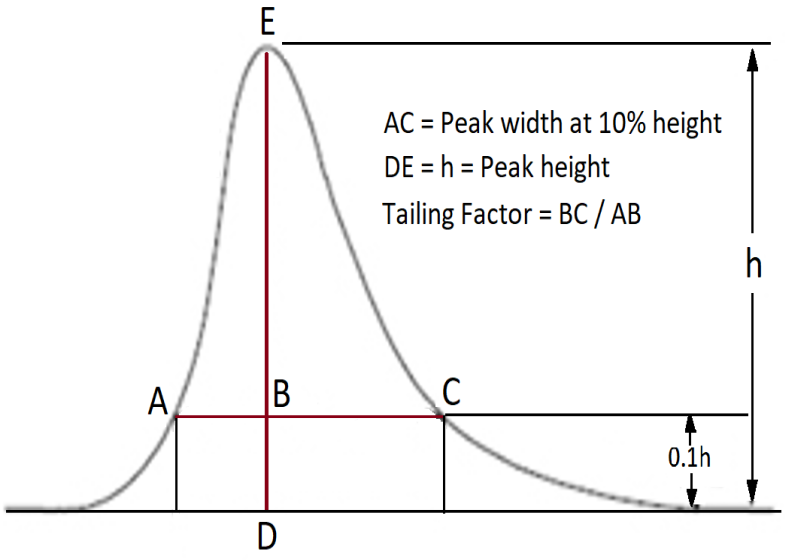
The following are the Relative Retention Times for DDD-p,p' and DDE-p,p' (relative to DDT-p,p'):

DDE-p,p' RRT = 0.885
DDD-p,p' RRT = 0.949

It is not necessary to perform the DDT degradation check for method 625.1 since this SOP does not include DDT-p,p' in its list of analytes. The degradation and tailing factors assessments are performed together with the DFTPP tune checks, using the Environmental Quant Masshunter software (see 9.1.2 above)

The tailing factors for pentachlorophenol and benzidine should not be higher than 2 (for 8270E, and less than 2.0 for 625.1) according to the following equation:

In the figure below, Tailing Factor = BC / AB



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 continuing calibration check standards. These calibration check standards must be analyzed at the start of each run (CCV for 8270E ICV/CV625 for 625.1) and at 12 hours intervals thereafter (only ICV/CV625).

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9.3.3 Calibration verification standard criteria: Each of the most common target analytes in the calibration verification standard should meet the minimum response factors as noted in Table 4. These criteria are particularly important when the common target analytes are also critical project-required compounds. This is the same check that is applied during the initial calibration.

9.3.4 The recovery limits acceptance criteria for continuous calibration verification are 80-120% method 8270E and 60-140% for method 625.1.

9.3.5 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.

9.3.6 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.

9.3.7 If any of the requirements mentioned in 9.3 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.

10 GC/MS SAMPLE ANALYSIS

10.1 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 1 µg/mL of internal standard. Any extract that is dark in color, suspected of containing petroleum hydrocarbons or high concentrations of any analytes should be screened on the GC/FID before analyzing on the mass spec. The extracts should be diluted as deemed necessary. The concentration of internal standard must remain at 1 µg/mL when diluting samples by using 1µg/mL of internal standard solution as diluting agent.

10.2 Analysis Run Sequence.
The analyst sets 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:

Methylene chloride (to clean the system)
DFTPP/degradation/performance check
Instrument Blank BNA ISTD (containing internal standards at 1000 ug/L)
BNA Continuing Calibration Verification (CCV) check.
Instrument Blank (containing internal standards at 1000 ug/L)
Extraction blank (method blank)
Laboratory fortified blank (LFB)
Laboratory fortified blank duplicate (if required)
Sample matrix spike,
Sample matrix spike duplicate.
Samples (for up to 12 hours, including QC samples)
DFTPP/degradation/performance check (method 625.1 only).
BNA Continuing Calibration Verification (CCV) check (method 625.1 only)..
Instrument Blank (containing internal standards at 100 0ug/L)
samples (up to 12 hours)

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. For method 625.1, a vial of DFTPP and the appropriate calibration check standards (dependent on the customer requested analysis) must be inserted every 22-25 samples to check the tuning and calibration response every 12 hours. If the DFTPP or calibration check standard fail their criteria, any samples run after them must be reanalyzed after the criteria have been passed.

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

10.4 Data Processing using the Masshunter software.

10.4.1 Check all of the calibration check standards and DFTPP tune standards analyzed during the run sequence and ensure that they met the criteria given above. The Environmental version of the Masshunter software is used to process the DFTPP/degradation check sample, while the single quad (MS) version of the Masshunter software is used for all other quantitative analyses.

10.4.2 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.

10.4.3 The concentration reported for an identified hit in the sample extract, expressed in ug/L or mg/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 17.6).

10.4.4 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 methylene chloride 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.

10.4.5 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 0.06 RRT from the last check calibration, then the chromatographic system must be inspected for malfunctions and corrections must be made. The m/z abundance 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 include a comment, and any positives detected must be qualified with a "J" to indicate that the result is an estimate.

10.5 Analysis of Surrogates and Spikes

10.5.1 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 BNA surrogate spike solution currently containing three acid and three base/neutral surrogates specified in the table below.

The BNA surrogates are listed in the table below. Recoveries must be within statistical limits, and calculated at least annually (10.5.2). Table 1 lists the surrogate association for all the BNA analytes. If any of these surrogates fall outside control limits (lower side), re-extract the effected sample with proper QC even after expiration and follow DEP SOP LB-027 for reporting.

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Compound	% Rec Water	% Rec Sediment
Base/Neutral Surrogates		
Nitrobenzene-d_5	Statistical*	statistical
2-Fluorobiphenyl	statistical	statistical
Terphenyl-d_{14}	statistical	statistical
Acid Surrogates		
Phenol-d_5	Statistical*	statistical
2-Fluorophenol	statistical	statistical
2,4,6-Tribromophenol	statistical	statistical

*The calculated limits for water samples cannot be outside of 15-314% for Nitrobenzene-d5 and 8-424% for Phenol-d5 per method 625.1

10.5.2 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.

10.5.3 If a surrogate recovery fails, and there is a reasonable suspicion that instrument related factors may be responsible, the sample may be 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.

10.5.4 Check the Matrix Spike and Lab Fortified Blank recoveries. They must be within the current acceptance range for each analyte and matrix, see Table 1. The acceptance range limits are statutory limits and they are set initially at the time of method set up. These limits are evaluated at least once a year or if a problem with the method performance occurs. For EPA 625.1 method the limits are set by the method. A comment must be added to the qualified data in the final report explaining any deviation from the routine limits whenever the spikes or surrogates are out of range (DEP SOP LB-027). . 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 17.8, chapter 5.3 for details on disposition of QC failures.

10.6 Blank Contamination

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

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

10.6.3 Field Blanks.

In the event a positive identification is found in a field blank, but method blank(s) pass, the field blank detection only affects the samples in the same job. If those samples do not show any detections for the analyte found in the field blank, the field blank does not need to be re-extracted. If the detections are found up to 10x the level in the field blank, all samples with such detections and the field blank must be re-extracted. If the detections are above the 10x field blank level, no re-extractions are necessary.

10.6.4. 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.

10.7 Continuing Calibration Verification

10.7.1 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. For method 625.1 the same second source ICV/CV625 standard is run as ICV and CCV. Criterion of acceptance for continuing calibration check is +/-20 % of initial calibration for method 8270E and +/-40 % for method 625.1. 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.

10.7.2 If CCVs do not meet method requirements but the associated analytical results are below the detection limit or below the quantifiable threshold (PQL) and no systematic failure is observed (i.e., the failure is deduced to be due to a statistical outlier in a multi-component analysis where results from other CCV components and LFB results do not indicate a systematic bias in the analysis or detector response), an appropriate test comment and result qualifier (J) shall be provided to indicate the CCVs are outside control limits. However, when a systematic or system failure is detected or the affected analytical data are above the quantifiable threshold, the analysis shall be re-run if possible. If re-analysis is not an option, the analytical results shall be qualified as estimates (see ref 17.8 for more details).

10.8 Data Interpretation and Quantitation

10.8.1 Two criteria must be satisfied to verify identification of a compound: 1) Elution of the sample component at the same GC relative retention time as the standard component: and 2) Correspondence of the sample component and the standard component mass spectrum. The computer system will check these criteria automatically (as long as the retention times and mass spectra have been updated recently with the calibration standard's retention times/spectra) but ALWAYS manually assess each chromatogram/mass spectrum. Spectral match is assured by passing qualifier ratios and reference library match.

10.8.2 Concentrations (Cs) of each compound and surrogate identified should be calculated as follows:

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$$Cs = \frac{(A_S)(I_{is})(V_t)(DF)}{(A_{is})(RF)(V_{H2O})}$$ **water samples**

where:

A_S is the corrected area of the compound peak.
I_{is} is the concentration of the appropriate internal standard (in µg/mL).
V_t is the total volume of the extract (usually 1 mL).
DF is the appropriate dilution factor (i.e., 1:10 dilution = a DF of 10).
A_{is} is the corrected area of the internal standard.
RF is the response factor for the compound being measured.
V_{H2O} is the volume of water extracted.

or

$$Cs = \frac{(A_S)(I_{is})(V_t)(DF)}{(A_{is})(RF)(W_S)(D)}$$ **sediment/waste samples**

where:

A_S, I_{is}, V_t, DF, A_{is}, and **RF**= same as for water.
W_S = weight of sample extracted or diluted in grams.
D = (100-% moisture in sample)/100, or 1 for a wet-weight basis.

10.9 TCLP (Toxicity Leaching Characteristic Procedure) Special Reporting/ Calculation Requirements:

10.9.1 Follow steps in section 10.8.

10.9.2 Unless a sample contains TCLP compounds at or above the Characteristic Levels listed in following table, it is NOT considered as TCLP hazardous. Some clients may, however, use different maximum leachability concentrations than those listed here.

10.9.3 The BNA TCLP analytes (with associated characteristic level) are:

Maximum Concentration of Contaminants for the Toxicity Characteristic (TCLP)

Compound	Characteristic Level (µg/L)	Compound	Characteristic Level (µg/L)
o-Cresol*	200,000	Hexachlorobutadiene	500
m,p-Cresol (total)*	200,000	Nitrobenzene	2000
Cresol (o,m and p)	200,000	Pentachlorophenol	100,000
Hexachloroethane	3000	2,4,5-Trichlorophenol	400,000
2,4-Dinitrotoluene	130	2,4,6-Trichlorophenol	2000
Hexachlorobenzene	130	Pyridine	5000

10.9.4 If the TCLP extraction resulted in two or more phases that were analyzed separately, the results from these phases must be mathematically recombined and reported as follows:

$$C_f = \frac{(V_1 \times C_1) + (V_2 \times C_2)}{(V_1 + V_2)}$$

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where:

C_f = final calculated concentration in µg/mL.
V_1 = the total volume (mL) of the liquid phase as measured after filtration.
V_2 = Total volume (mL) of the extraction fluid used in the tumbling of the solid phase.
C_1 = concentration (in µg/mL) of the analyzed liquid phase sample extract.
C_2 = concentration (in µg/mL) of the analyzed solid phase extract.

HOWEVER: If analysis result of any one of the liquid fractions of the sample indicates that a TCLP analyte is present in such a high concentration that it exceeds the TCLP limit, even accounting for the dilution from the other fractions, then the sample is considered hazardous, and it is not necessary to analyze the remaining fractions of the sample. It is acceptable to report the results from the one phase and comment the results accordingly.

11 LIBRARY SEARCH PROTOCOL FOR BNA GC/MS

11.1 If there are any unidentifiable peaks in the chromatogram that are at least 10 % of the nearest internal standards response (discounting any in-house contaminants in the extraction blank), conduct a library search. Exceptions to this rule:

11.1.1 If the unknown peaks appear to be part of a petroleum hydrocarbon pattern (like diesel or kerosene, etc.), it is unnecessary to search individual peaks, since they are mostly elements of the petroleum product.

11.1.2 If the peak pattern is a petroleum hydrocarbon, identify the petroleum hydrocarbon using pattern-std. comparison. If the pattern is unrecognizable, report as an "unidentifiable petroleum hydrocarbon pattern ". Estimate the amount of petroleum. hydrocarbons present using total ion area calculation of the envelope. Assume the RF is 1. Quantitate using Ax as the total petroleum hydrocarbon area. Report result in the comment section of LIMS (using only ONE significant figure) as follows:

Example 1:

Chromatographic pattern similar to diesel, estimated concentration = 3.0E5 µg/L.

Example 2:

Unidentifiable petroleum hydrocarbon pattern: estimated concentration = 5.0E6 µg/kg.

11.2 Use the library search program to estimate the concentrations for the unknown peaks. When reviewing the results from the library search, look at the probability value assigned to the listed compounds in addition to the mass spectra. Usually, if the search program assigns a probability of about 60% or greater, it is a pretty good match, and the compound may be reported tentatively.

11.3 If the search program resulted in multiple hits with probabilities of 60% or greater and they all look like possible matches, then you must attempt to classify the compound. For example, if you get a 80% match for undecane and a 83% match for dodecane and a 88 % match for tricosane,, and all of the spectra look like plausible matches, report result as "alkane" and give estimated concentration. If there are a lot of hits for a variety of alkanes, report as "total alkanes" with the estimated total concentration. This will simplify reporting if your sample has a lot of unknown alkanes. The same goes for other classes of organic compounds.

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11.4 If the match is below about 60%, or the search program resulted in no matches (i.e., " No database entries were retrieved") the spectra will usually suggest a poor match. In this case, the peak is an "unknown extractable organics". You only need to report the total estimated amount for all unknown extractable organics, not each individual estimated concentration.

WARNING: Do not trust any library search program over your own scientific judgment. Just because the program returns a probability of 35% does not mean that it is not a match. Look at the spectra; you may have additional information about the sample that will lead you to a different conclusion than what the search program concluded. However, it is not necessary to turn each unknown identification practice into a research project. Exercise caution when utilizing the search results and do not neglect to examine the returned spectra against the sample spectra.

11.5 The library search program returns estimated concentration results in µg/mL. You must apply the correct sample volume or weight extracted to calculate the final estimated result for water and sediment/waste samples.

11.6 Report final result in the comment section of the final report using the following format (if sample is a water, use µg/L as unit):

Sediment/Waste Example

Comments:
Estimated Values for Tentatively Identified Compounds in ug/kg:
4-hydroxy -4-methyl-2-pentanone = 2.5E+03; alpha pinene = 1900;
2-beta-pinene = 510; sub.benzenedicarboxylic acid = 340;
total alkanes = 6300.
Unknown extractable organics = 2.8E+04.

12 REPORTING AND DOCUMENTATION

12.1 When analysis is complete, generate a .txt file in the Masshunter software for all the reported samples, QC samples and CCVs. When analysis is complete, the QC Manager is 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.

12.2 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. See DEP SOP LB-027, Standard Operating Procedure for Reporting Qualified Data and Correcting Quality Control Problems for guidelines for qualifying data when quality control results are outside established control limits and re-analysis is not a viable or desired option.

12.3 Definitions of the available qualifying codes are listed in DEP SOP LB-027

12.4 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.

12.5 Enter the results for each sample in the analysis results form. Print out QC results from the QC Manager. Include a copy of the 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.

12.6 Submit the result folder to the BNA section supervisor. The supervisor will review results and then authorize the /test/sample. The supervisor will then file the folders in the GC pesticides filing cabinets.

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13 QUALITY CONTROL

13.1 See DEP SOP GC-001, (ref 17.4) for detailed information on quality control, definitions, and interferences. See DEP SOP LB-027 (ref 17.8) for guidelines for qualifying data when quality control results are outside established control limits and re-analysis is not a viable or desired option.

13.2 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 review/authorization checklist as per DEP SOP GC-001 mentioned above.

14 DATA ARCHIVAL

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

The valid data files (tune, ICALS, CCVs, QC and sample data files) are copied soon after collection from the hard disk of the instrument computers to the network drive \\TLHLAB3\GC\BACKUP_GC_MSD-5 or MSD_6
. 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_MSD5 or GC_MSD6. They are then converted by QC Manager for reporting in LIMS.

15 DETERMINATION OF METHOD DETECTION LIMITS

Refer to the SOP **LB-007** *Procedure and Policy for Demonstration of Capability for Methods, Instruments and Laboratory Staff* and refer to SOP **LB-031** *Limit of Detection Verification* for specific procedural details.

15.1 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**.**

15.2 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.

15.3 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).

15.4 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

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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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16 SAFETY/HAZARDOUS WASTE MANAGEMENT

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

17 REFERENCES

17.1 *Code of Federal Regulations, Title 40, Part 136, Vol. 49, No. 209*, Method 625.1: Base/Neutrals and Acids by GC/MS, 12/2016.

17.2 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.

17.3 Test Methods for Evaluating Solid Wastes, Third Edition, SW-846, Method 1311 (Revision 0. 7/92), Toxicity Characteristic Leaching Procedure and Method 1312 (Revision 0. 9/92), Synthetic Precipitation Leaching Procedure.

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

17.5 DEP SOP SV-001. Extraction of Base/Neutral and Acid Organic Analytes from Water, Sediments and Wastes.

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

17.7 DEP SOP SV-009. BNA Standard Preparation.

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

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

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

17.11 DEP SOP LB-031. Limit of Detection Verification.

17.12 Quality Manual for State of Florida Department of Environmental Protection Laboratory.

APPENDIX OF CHANGES

04/26/2010	Updated standards levels to reflect current use. Updated MDLs for PAHs in Table 1 and added 5 new analytes to Table 1 and Table 4.
11/22/2010	Added Soil PAH Homolog analysis test and Petroleum Hydrocarbon Pattern Identification
10/24/2012	Added low level soil PAH analysis and Table 6 in SIM mode using MSD5975C

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10/20/2014	Minor revisions to the text were made for format and clarity.
11/25/2015	Added new analytes.
12/07/2023	Removed analytes not in use.
04/16/2024	Analyses switched to the Masshunter software. Clear distinctions spelled out between 8270E and 625.1. Structural changes throughout the document to make it more in-line with other analytical SOPs in the GC Group.

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TABLES

TABLE 1: Surrogate association, MDLs/PQLs, Spike Recovery Acceptance Range and Precision in Water and Sediment for BNA analytes. *EPA 625.1 Analytes

Analyte	MDL µg/L	PQL µg/L	MDL µg/kg	PQL µg/kg	Accuracy Range Water (%)	Accuracy Range Soil (%)	Prcsn (% RPD)
Base/Neutral Extractables							
Nitrobenzene-d5 Surrogate							
Acetophenone	0.2	0.80	60	240	50 - 130	40 - 140	<40
Aniline	1.0	4.0	60	240	30 - 120	40 - 140	<40
Benzyl alcohol	0.2	0.80	30	120	50 - 130	40 - 140	<40
Bis(2-chloroethoxy)methane*	0.05	0.20	30	120	50 - 130	40 - 140	<40
Bis(2-chloroethyl)ether*	0.05	0.20	30	120	50 – 158	40 - 140	<40
Bis(2-chloroisopropyl)ether*	0.05	0.20	30	120	50 - 140	40 - 140	<40
1,3-Dinitrobenzene	0.2	0.8	60	240	50 - 130	40 - 140	<40
Ethyl Methanesulfonate	1.0	4.0	60	240	50 - 130	40 - 140	<40
Hexachlorobutadiene*	0.05	0.20	60	240	24 - 116	40 - 140	<40
Hexachloroethane*	0.05	0.20	60	240	40 - 113	40 - 140	<40
Hexachloropropene	0.05	0.20	60	240	50 - 130	40 - 140	<40
Isophorone*	0.05	0.20	30	120	50 - 130	40 - 140	<40
Isosafrole	0.05	0.20	60	240	50 - 130	40 - 140	<40
Naphthalene*	0.1	0.40	6.7	27	50 - 130	40 - 140	<40
Nitrobenzene*	0.05	0.20	30	120	50 - 130	40 - 140	<40
N-Nitrosodi-n-butylamine	0.05	0.20	60	240	50 - 130	40 - 140	<40
N-Nitrosodiethylamine	1.0	4.0	60	240	50 - 130	40 - 140	<40
N-Nitrosodimethylamine	2.0	8.0	60	240	40 - 120	40 - 140	<40
N-Nitrosodi-n-propylamine*	0.05	0.20	60	240	50 - 130	40 - 140	<40
N-Nitrosomethylethylamine	2.0	8.0	60	240	50 - 130	40 - 140	<40
N-Nitrosomorpholine	0.05	0.20	60	240	50 - 150	40 - 140	<40
N-Nitrosopiperidine	0.05	0.20	60	240	50 - 130	40 - 140	<40
N-Nitrosopyrrolidine	0.1	0.40	60	240	50 - 130	40 - 140	<40
Pentachloroethane	0.05	0.20	60	240	20 - 130	40 - 140	<40
2-Picoline	1.0	4.0	360	1440	50 - 130	40 - 140	<40
Pyridine	4.0	16	360	1440	20 - 130	40 - 140	<40
Safrole	0.05	0.20	60	240	50 - 130	40 - 140	<40
1,2,4,5-Tetrachlorobenzene	0.05	0.20	60	240	50 - 130	40 - 140	<40
1,2,4-Trichlorobenzene*	0.05	0.20	60	240	50 - 130	40 - 140	<40
o-Toluidine	0.1	0.40	180	720	50 - 130	40 - 140	<40
2-Fluorobiphenyl Surrogate							
Acenaphthene*	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
Acenaphthylene*	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
Biphenyl	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
2-Chloronaphthalene*	0.05	0.20	30	120	60 - 118	40 - 140	<40
4-Chlorophenylphenyl ether*	0.05	0.20	30	120	50 - 130	40 - 140	<40
Dibenzofuran	0.05	0.20	30	120	50 - 130	40 - 140	<40

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Analyte	MDL µg/L	PQL µg/L	MDL µg/kg	PQL µg/kg	Accuracy Range Water (%)	Accuracy Range Soil (%)	Prcsn (% RPD)
Diethylphthalate*	2.0	8.0	30	120	50 - 114	40 - 140	<40
Dimethylphthalate*	0.2	0.80	30	120	50 - 112	40 - 140	<40
2,6-Dimethylnaphthalene	0.025	0.10	6.7	27	50 - 130	40 - 140	<40
2,4-Dinitrotoluene	0.05	0.20	30	120	50 - 130	40 - 140	<40
2,6-Dinitrotoluene*	0.05	0.20	30	120	50 - 130	40 - 140	<40
Fluorene*	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
Hexachlorocyclopentadiene	0.05	0.20	30	120	20 - 130	40 - 140	<40
1-Methylnaphthalene	0.1	0.40	6.7	27	60 - 140	40 - 140	<40
2-Methylnaphthalene	0.1	0.40	6.7	27	60 - 140	40 - 140	<40
1-Naphthylamine	10	40	360	1440	30 - 130	40 - 140	<40
2-Naphthylamine	10	40	360	1440	40 - 130	40 - 140	<40
2-Nitroaniline	0.05	0.20	30	120	50 - 130	40 - 140	<40
5-Nitro-o-toluidine	0.1	0.40	60	240	50 - 130	40 - 140	<40
Pentachlorobenzene	0.05	0.20	60	240	50 - 130	40 - 140	<40
2,3,5-Trimethynaphthalene	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
Terphenyl-d14 Surrogate							
2-Acetylaminofluorene	1.0	4.0	60	240	50 - 130	40 - 140	<40
4-Aminobiphenyl	4	16	180	720	50 - 130	30 - 140	<40
Anthracene*	0.025	0.20	6.7	27	60 - 140	40 - 140	<40
Azobenzene/1,2-Diphenylhydrazine	0.05	0.20	30	120	50 - 130	40 - 140	<40
Benzidine	10	40	1300	5200	0 - 240	20 - 140	<40
Benzo[a]anthracene*	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
Benzo[b]fluoranthene*	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
Benzo[k]fluoranthene*	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
Benzo[a]pyrene*	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
Benzo[e]pyrene	0.025	0.10					
Benzo[g,h,i]perylene*	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
Bis(2-ethylhexyl)adipate*	1.0	4.0			50 - 158	40 - 140	<40
Bis(2-ethylhexyl)phthalate*	2	8	180	720	50 - 158	40 - 140	<40
4-Bromophenylphenyl ether*	0.05	0.20	30	120	53 - 127	40 - 140	<40
Butyl benzyl phthalate*	1.0	4.0	30	120	50 - 152	40 - 140	<40
Carbazole	0.05	0.20	30	120	50 - 130	40 - 140	<40
Chrysene*	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
Coprostanol	2.0	8.0	360	1080	70-130	40 - 140	<40
Dibenzo[a,h]anthracene*	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
Dibenzothiophene	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
3,3'-Dichlorobenzidine*	10	40	1300	5200	20 - 150	40 - 140	<40
p-(Dimethylamino)azobenzene	0.05	0.20	30	120	50 - 130	40 - 140	<40
7,12-Dimethylbenz(a)anthracene	0.1	0.40	60	240	50 - 130	40 - 140	<40
Dinoseb	4	16	360	1440	50 - 150	40 - 140	<40
Di-n-butyl phthalate*	2	8	180	720	50 - 118	40 - 140	<40
Di-n-octyl phthalate*	0.05	0.20	30	120	50 - 146	40 - 140	<40

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Analyte	MDL µg/L	PQL µg/L	MDL µg/kg	PQL µg/kg	Accuracy Range Water (%)	Accuracy Range Soil (%)	Prcsn (% RPD)
Fluoranthene*	0.05	0.20	6.7	27	60 - 140	40 - 140	<40
Hexachlorobenzene*	0.05	0.20	30	120	50 - 130	40 - 140	<40
Indeno[1,2,3-cd]pyrene*	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
3-Methylcholanthrene	0.10	0.40	30	120	50 - 130	40 - 140	<40
1-Methylphenanthrene	0.025	0.10	6.7	27	60 – 140	40 - 140	<40
N-Nitrosodiphenylamine/ Diphenylamine	0.1	0.40	30	120	50 - 150	40 - 140	<40
Phenacetin	0.05	0.20	60	240	50 - 130	40 - 140	<40
Phenanthrene*	0.1	0.40	6.7	27	54 - 120	40 - 140	<40
Pentachloronitrobenzene	0.05	0.20	60	240	50 - 130	40 - 140	<40
Pyrene*	0.1	0.40	6.7	27	60 - 140	40 - 140	<40
1,3,5-Trinitrobenzene	0.2	0.8	60	240	50 - 150	40 - 140	<40
Acid Extractables							
Phenol-d5 / 2-Fluorophenol Surrogates							
4-Chloro-3-methylphenol*	0.05	0.20	30	120	50 - 130	40 - 140	<40
2-Chlorophenol*	0.05	0.20	60	240	50 - 130	40 - 140	<40
2,4-Dichlorophenol*	0.05	0.20	30	120	50 - 130	40 - 140	<40
2,6-Dichlorophenol	0.05	0.20	60	240	50 - 130	40 - 140	<40
2,4-Dimethylphenol*	0.05	0.20	180	720	50 - 119	40 - 140	<40
2-Nitrophenol*	0.05	0.20	60	240	50 - 130	40 - 140	<40
Phenol*	0.05	0.20	30	120	20 - 112	40 - 140	<40
o-Cresol	0.05	0.20	30	120	50 - 130	40 - 140	<40
m, p-cresol	0.05	0.20	30	120	50 - 130	40 - 140	<40
2,4,6-Tribromophenol Surrogate							
2,4-Dinitrophenol*	10	40	360	1440	50 - 160	40 - 140	<40
2-Methyl-4,6-dinitrophenol*	3.0	12	180	720	50 - 150	40 - 140	<40
4-Nitrophenol*	10	40	180	720	15 - 110	40 - 140	<40
Pentachlorophenol*	0.5	2.0	180	720	50 - 130	40 - 140	<40
2,3,4,6-Tetrachlorophenol	0.1	0.4	60	240	50 - 130	40 - 140	<40
2,4,5-Trichlorophenol	0.05	0.20	30	120	50 - 130	40 - 140	<40
2,4,6-Trichlorophenol*	0.05	0.20	30	120	50 - 130	40 - 140	<40

TABLE 2: DFTPP Tuning Criteria for EPA 625.1

m/z	Ion Abundance Criteria
51	30 - 60 percent of m/z 198
68	Less than 2 percent of m/z 69
70	Less than 2 percent of m/z 69
127	40 - 60 percent of base peak m/z 198
197	Less than 1 percent of m/z 198
198	Base peak, 100 percent relative abundance
199	5 - 9 percent of m/z 198
275	10 - 30 percent of m/z 198

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365	Greater than 1 percent of m/z 198
441	Present but less than m/z 443
442	40 - 100 percent of m/z 198
443	17 - 23 percent of m/z 442
DDT	DDT breakdown should be less than 20%
TF	Tailing Factor (TF) for Benzidine and Pentachlorophenol (<2)

DFTPP Tuning Criteria for EPA 8270E

m/z	Ion Abundance Criteria
68	Less than 2% of m/z 69
69	Present
70	Less than 2% of m/z 69
197	Less than 2% of m/z 198
198	Base peak or present
199	5-9% of m/z 198
365	Greater than 1% of base peak
441	Less than 150% of m/z 443
442	Base Peak or present
443	15-24% of m/z 442
DDT	DDT breakdown should be less than 20%
TF	Tailing Factor (TF) for Benzidine and Pentachlorophenol (<2)

TABLE 3: Characteristic Ions For Internal Standards and Surrogates

Analyte	Primary ion	Secondary Ions
1,4-Dichlorobenzene-d4**(IS)**	152	150, 115
Naphthalene-d8 **(IS)**	136	68
Acenaphthene-d10 **(IS)**	164	160, 162
Phenanthrene-d10 **(IS)**	188	94, 80
Chrysene-d12 **(IS)**	240	120, 236
Perylene-d12 **(IS)**	264	260, 265, 132
Nitrobenzene-d5 **(S)**	82	128, 54
2-Fluorobiphenyl **(S)**	172	171
Terphenyl-d14 **(S)**	244	122, 212
2-Fluorophenol **(S)**	112	64
Phenol-d5 **(S)**	99	71, 42
2,4,6-Tribromophenol **(S)**	330	332, 141

TABLE 4: Characteristic Ions and Minimum Response Factors For Semi-volatile Compounds

Analyte	Primary ion	Secondary Ions	Minimum Response Factor
Acetophenone	105	71, 51, 120	0.010
Aniline	93	66, 65	-
Benzyl alcohol	108	79, 77	-
Bis(2-chloroethoxy)methane	93	95, 123	0.300
Bis(2-chloroethyl)ether	93	63, 95	0.700
Bis(2-chloroisopropyl)ether	45	77, 121	-

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Analyte	Primary ion	Secondary Ions	Minimum Response Factor
1,3-Dinitrobenzene	168	76, 50,75,92,122	-
Ethyl Methanesulfonate	79	109,97,45,65	-
Hexachlorobutadiene	225	223, 227	0.010
Hexachloroethane	117	201, 199	0.300
Hexachloropropene	213	211,215,117,106,141	-
Isophorone	82	95, 138	0.400
Isosafrole	162	131,104,77,51	-
Naphthalene	128	129,127	0.700
Nitrobenzene	77	123,65	0.200
N-Nitrosodi-n-butylamine	84	57,41,116,158	-
N-Nitrosodiethylamine	102	42,57,44,56	-
N-Nitrosodimethylamine	42	74, 44	-
N-Nitrosodi-n-propylamine	70	42,101,130	0.500
N-Nitrosomethylethylamine	88	42,43,56	-
N-Nitrosomorpholine	56	116	-
N-Nitrosopiperidine	114	42,55,56,41	-
N-Nitrosopyrrolidine	100	41,42,68,69	-
Pentachloroethane	117	167, 119, 165	-
2-Picoline	93	66, 93	-
Pyridine	79	52, 78	-
Safrole	162	104,77,103,135	-
1,2,4,5-Tetrachlorobenzene	216	214,179,108,143,218	0.010
1,2,4-Trichlorobenzene	180	182, 145	-
o-Toluidine	106	107,77,51,79	-
Acenaphthene	154	153, 152	0.900
Acenaphthylene	152	151, 153	0.900
2-Chloronaphthalene	162	127, 164	0.800
4-Chlorophenylphenyl ether	204	206, 141	0.400
Dibenzofuran	168	139	0.800
Diethylphthalate	149	177, 150	0.010
Dimethylphthalate	163	194, 164	0.010
2,4-Dinitrotoluene	165	63, 89	0.200
2,6-Dinitrotoluene	165	63, 89	0.200
Fluorene*	166	165, 167	0.900
Hexachlorocyclopentadiene	237	235, 272	0.050
1-Methylnaphthalene	142	141, 115	-
2-Methylnaphthalene	142	141	0.40
1-Naphthylamine	143	115, 89, 63	-
2-Naphthylamine	143	115, 116	-
2-Nitroaniline	65	92, 138	0.010
5-Nitro-o-toluidine	152	77, 79, 106, 94	-
Pentachlorobenzene	250	252,108,248,215,254	-
2-Acetylaminofluorene	181	180, 223, 152	-
4-Aminobiphenyl	169	168,170,115	-
Anthracene	178	176, 179	0.700

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Analyte	Primary ion	Secondary Ions	Minimum Response Factor
Azobenzene/1,2-Diphenylhydrazine	77	182, 51	-
Benzidine	184	92, 185	-
Benzo[a]anthracene	228	229, 226	0.800
Benzo[b]fluoranthene	252	253, 125	0.700
Benzo[k]fluoranthene	252	253, 125	0.700
Benzo[a]pyrene	252	253, 125	0.700
Benzo[e]pyrene	252	253, 125	0.700
Benzo[g,h,i]perylene	276	138, 277	0.500
Bis(2-ethylhexyl)adipate	129	147, 112	
Bis(2-ethylhexyl)phthalate	149	167, 279	0.010
4-Bromophenylphenyl ether	248	250, 141	0.100
Butyl benzyl phthalate	149	91, 206	0.010
Carbazole	167	166, 168	0.010
Chrysene	228	226, 229	0.700
Coprostanol	215	233, 388	-
Dibenzo[a,h]anthracene	278	139, 279	0.400
3,3'-Dichlorobenzidine	252	254,126	0.010
Dimethylaminoazobenzene	225	120,77,105,148, 42	-
7,12-Dimethylbenz(a)anthracene	256	241, 239, 120	-
Dinoseb	211	163, 147, 117, 240	-
Di-n-butyl phthalate	149	150, 223	0.010
Di-n-octyl phthalate	149	167, 43	0.010
Fluoranthene	202	101, 203	0.600
Hexachlorobenzene	284	142, 249	0.100
Indeno[1,2,3-cd]pyrene	276	138. 277	0.500
3-Methylcholanthrene	268	252, 253, 126, 134, 113	-
N-Nitrosodiphenylamine/ Diphenylamine	169	168, 167	0.010
Phenacetin	108	180, 179, 109, 137, 80	-
Phenanthrene	178	179, 176	0.700
Pentachloronitrobenzene	237	142, 214, 249, 295, 265	-
Pyrene	202	200, 203	0.600
1,3,5-Trinitrobenzene	75	74, 213, 120,91, 63	-
4-Chloro-3-methylphenol	107	144, 142	0.200
2-Chlorophenol	128	64, 130	0.800
2,4-Dichlorophenol	162	164, 98	0.200
2,6-Dichlorophenol	162	164, 98	-
2,4-Dimethylphenol	122	107, 121	0.200
2-Nitrophenol	139	109, 65	0.100
Phenol	94	65, 66	0.800
o-Cresol	107	108, 77, 79, 90	0.700
m, p-cresol	107	108, 77, 79,80	0.600
2,4-Dinitrophenol	184	63, 154	0.010
2-Methyl-4,6-dinitrophenol	198	51, 105	0.010
4-Nitrophenol	139	109, 65	0.010

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Analyte	Primary ion	Secondary Ions	Minimum Response Factor
Pentachlorophenol	266	264, 268	0.050
2,3,4,6-Tetrachlorophenol	232	131, 230, 166, 234, 168	0.010
2,4,5-Trichlorophenol	196	198, 97, 132, 99	0.200
2,4,6-Trichlorophenol	196	198, 200	0.200
Biphenyl	154	153, 152	
2,6-Dimethylnaphthalene	156	155, 141, 115	
2,3,5-Trimethylnaphthalene	155	169, 170	
Dibenzothiophene	184	185, 139	
1-Methylphenanthrene	192	191, 189, 165	

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