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Standard Operation 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 8270D. 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 8270D.

1.2 There are few differences between EPA 625.1 and EPA 8270D methods. Scince both methods are used at same time, more stringent requirements of these two methods are used. These differences are listed below.

	Method-625.1	DEP	Method-8270D
Injection Volume	1 µL	1 – 2 µL	1 – 2 µL, (used)
DFTPP Ions and abundance criteria	Mass 51, 30-60%, (used) Mass 127. 40-60%, (used) Mass 197, <1, (used) Mass 275, 10-30%, (used) Mass 443, 17-23%, (used)	Mass 51, 127.10-80%, MSD5977 Mass 275, 10-60%, MSD5977	10-80% 10-80% <2 10-60% 15-24%
TF for benzidine	<2	<3	<2
TF for Pentachlorophenol	<2	<5	<2
%RSD of the response factors for each of the target compounds	≤35%	≤20%	≤20%
Sample storage temperature	≤4 °C, (used)		≤6 °C

1.3 FDEP Laboratory Test IDs and equivalent methods reported by the SOP
This method is in compliance with the requirements of EPA Method 625.1 and Method 8270D 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 8270D 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-625	EPA Method 625.1 analysis, water sample with separate extraction/analysis
W-BNA-R	EPA Method 8270D 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-SIM	EPA Method 8270D analysis for PAHs only using SIM, water sample
W-PAH-R	EPA Method 8270D analysis for PAHs only, water sample
W-PAH-PA	EPA Method 8270D analysis for PAHs only, water sample profile analysis
S- BNA	EPA Method 8270D analysis, soil sample
S-PAH	EPA Method 8270D analysis for PAHs only, soil sample
S-PAH-SIM	EPA Method 8270D analysis for PAHs only using SIM, soil sample
S-PAH-EXT	EPA Method 8270D analysis for PAHs extended list, soil sample (homolog)

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S-PAH-PA	EPA Method 8270D analysis for PAHs only, soil sample (profile analysis)
S-PAH-E-PA	EPA Method 8270D analysis for PAHs extended list, soil sample (profile analysis)
WAS-BNA	EPA Method 8270D analysis, waste sample
WAS-PAH	EPA Method 8270D analysis for PAHs only, waste sample
WAS-PAH-PA	EPA Method 8270D analysis for PAHs only, waste sample profile analysis
SPLP-BNA	EPA Method 8270D analysis of SPLP extract
TCLP-BNA	EPA Method 8270D analysis of TCLP extract
SA-BNA	EPA Method 8270D analysis, surface area wipe sample
GCMSSCREEN	EPA Method 8270D analysis, unknown screening sample

The acceptance limits, as provided in EPA Methods 625.1 and 8270D, 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.

1.4 This GC/MS analysis method can be used to tentatively identify, in a sample extract, a target crude oil source if the target crude oil source standard is available. The probable source for a spill can be determined by certain unique biomarkers resistant to weathering. For this visual comparison of weather resistant biomarkers, The standards and samples are subjected to the same extraction and clean up procedures. The silica gel fractions I and II are analyzed in a selected scan range of 80 to 290 amu and visually compared using four biomarker ions 85 (Alkanes), 191 (Triterpanes), and 217/218 (Steranes) in both the standards and samples to screen for potential match (ref. 14.4). For the quantitative determination of degree of weathering of oil sample, ions 85 (Alkanes), weather resistant stable biomarkers 191 (Terpanes), 217/218 (Steranes) and 19 PAHs homologs are integrated induvidually or in group. The area of each ion is used in calculations to determine % weathering. Biomarker ions 191, 217 and 218 is assumed as stable and 100%, and used as internal standard. Amount of ion 85 (Alkanes) is determined by area of ion 85 divided by area of ion 191 (Terpanes).

1.5 Homolog analysis in soil samples for the test S-PAH-EXT is designed to quantitate some of the toxic alkylated PAHs. This test result may provide composition of weathering in the samples. Table 5 lists all the homologs identified and quantitated in this method.

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.

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.

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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 can not 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.

2.4 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.5 Interference:

2.5.1 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.

2.5.2 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.

2.5.3 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.

3 Apparatus and Equipment

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

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

3.3 GC/MS system:

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3.3.1 Gas chromatograph, Agilent 7890A, 7890B and Agilent 6890N series II or equivalent. Must be temperature programmable with an injector port designed for splitless injection.

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

3.3.3 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 decafluorotriphenyl phosphine (DFTPP) is injected through the GC inlet.

3.3.4 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. See the Enviroquant soft ware manual for details.

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., to 330 °C at 18 °C/min., hold at 330 °C for 4 min.
Inlet:	Temp: 275 °C; Mode: 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:	20 min.

Or

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 1 min., ramp to 250 °C at 15 °C/min. hold for 1 min, ramp to 325 °C at 4 °C/min and hold for 1 min.
Inlet:	Temp: 275 °C; Mode: 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:	35 min.

GC/MS Operating Conditions for the Screening of a Potential Crude Oil Source: (this serves as a guideline only, different instrument may have different settings)

Parameter	Setting

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Mass Range:	80-290 amu, narrow range for better sensitivity
Scan Time:	4.5 to 34 min. 1 scan/sec minimum
GC Oven Temperature Program:	55 °C for 2 min., to 270 °C at 6 °C/min. to 300 °C at 3 °C/min., hold at 300 °C for 2 min., at 20 °C/min.to 325 °C hold at 325 °C for 14 min.,
Inlet:	Temp: 290 °C; Mode: Pulse Splitless; Inj Pulse Pressure: 40 psi until 1.5 min. Purge flow to split vent: 60 mL/min at 1.75. Gas Saver: ON; Saver Flow 20 mL/min. Saver Time: 3.0 min.
MS interface temperature:	300 °C
Injection Volume:	1µL
Total Run Time:	65 min.

GC/MS Operating Conditions for soil PAHs homolog analysis: (this serves as a guideline only, 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:	55 °C for 2 min., to 325 °C at 10 °C/min., hold at 325 °C for 20 min.
Inlet:	Temp: 290 °C; Mode: Pulse Splitless; Inj Pulse Pressure: 40 psi until 1.5 min. Purge flow to split vent: 60 mL/min at 1.75. Gas Saver: ON; Saver Flow 20 mL/min. Saver Time: 3.0 min.
MS interface temperature:	280 °C
Injection Volume:	1µL
Total Run Time:	49 min.

3.4 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.

3.5 J&W Scientific DB-5MS capillary column (or equivalent), 30m x 0.25 mm x 0.5 µm (or 0.25 µm). Zebron Capillary GC Column, Phenomenex (ZB-5ms), 30m x 0.25 mm x 0.5 µm (or 0.25 µm).

4 Reagents and Chemicals

NOTE: Record Lot Numbers of all the reagents and solvents used in the Note Book.

4.1 Standards (see Standard Preparation SOP SV-009 for instructions)

4.1.1 Calibration Standards 625.1 and 8270D mixes at the following concentration levels: 1, 2.5 (or PQL), 5, 10, 25 and 50 µg/mL (with 1 µg/mL internal standards presents in each of the six levels). Note: Some analytes will not be detectable at 1 or 2 µg/mL; do not include these when constructing calibration curves.

NOTE: For low level 625.1 (drinking water) analysis (MSD 5977B), prepared concentration levels at 0.05, 0.1, 0.2, 0.5, 1 and 2.5 µg/mL (with 1 µg/mL internal standards presents in each of the six levels) and 1 µg/mL second source CCV.

NOTE: Prepare CCV check standards as they expire every 3 months (25 µg/mL and 1 µg/mL, with 1 µg/mL internal standards). These standards are also used as the daily continuing calibration check standards and are prepared from a standard acquired from a second source.

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NOTE: For low level PAHs analysis, prepared concentration levels at 0.05, 0.2, 1, 5, 10, 25 and 50 µg/mL (with 5 µg/mL internal standards presents in each of the seven levels) and 5 µg/mL second source CCV. For alkylated PAH Homolog analysis, a longer GC oven temperature program (section 3.3) may be used for better separation of pattern. Each PAH Homolog pattern is identified and quantified by its charecterstic primary ion peaks in the expected retention time window using its representative analyte response (Table 5).

NOTE: For low level PAHs analysis in SIM mode (MSD 5975C), prepared concentration levels at 2, 5, 10, 25, 100, 500 and 1000 µg/L (with 100 µg/L internal standards presents in each of the seven levels) and 100 µg/L second source CCV.

NOTE: For the screening of crude oil source for oil spill samples is carried out by a visual comparision of chromatoghraphic profile in sample extracts to the known crude oil (for example MS 252) and/or any other requested known suspect source standards. A longer GC oven temperature program for better separation of pattern, and a selected scan range to cover the four Biomarker ions 85, 191, 217 and 218 for good sensitivity (section 3.3) is used. Silicagel fractions I and II prepared in the same extraction batch for reference crude oil standard and samples are analyzed.

NOTE: For low level Coprostanol, Galaxolide and Tonalide (PCP) analysis by SIM mode, prepared concentration levels at 0.2, 0.5, 1, 2, 5, 10 and 20 µg/mL for coprostanol and 0.1, 0.25, 0.5, 1, 2.5, 5 and 10 µg/mL for Galaxolide and Tonalide (with 2 µg/mL internal standards presents in each of the seven levels). The second source CCV was prepared at 5 µg/mL.

4.1.2 Matrix and Lab Fortified Spiking Standard: Contains all the 625.1 analyte spike mixture for routine use for EPA 625.1 and 8270D analyses. Refer to SOP SV-009 for details. Spike for each matrix at least once a year all the 625 and 8270 mixes.

4.1.3 Internal standard solution, 50 µg/mL and 5 µg/mL. 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

4.1.4 DFTPP (Decafluorotriphenylphosphine) Tuning Standard Mixture, 50 µg/mL each. For MSD 5977, prepared DFTPP (Decafluorotriphenylphosphine) Tuning Standard Mixture, 2 µg/mL each.

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

5 Sample Preparation Procedure

See following SOPs: SV-001 and SV-004.

6 GC/MS Tuning/Calibration

6.1 Tuning

6.1.1 At the beginning of a run (and after any subsequent “retuning”) ensure that the spectrometer’s mass calibration is accurate: Using Perfluorotributylamine (PFTBA) and the manual tune section of Chemstation, adjust the tuning lenses so that the PFTBA alignment ions (69, 219, 502) are centered (± 0.10 amu) on their respective amu

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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 Chemstation. 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.

6.1.2 Tune the GC/MS system prior to the beginning of an analysis run and every 12 hours thereafter. The tune 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. Check the scan at the apex first. If the tune does not pass, then use the auto find DFTPP feature in the Enviroquant software, which averages 3 scans around the apex. If the tune fails again, then adjust DFTPP target tune parameters and perform a DFTPP tune by re-injecting the DFTPP standard. If the tune pass, then check the DDT breakdown 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.

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

6.1.4 Place a hard copy of the DFTPP tuning report(s) in the daily QA/QC folder for the instrument that was tuned.

6.1.5 Include a DFTPP standard injection at twelve hour intervals during an analysis sequence and check the tune criteria. 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.

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

6.1.7 For MSD 5973 and 5975, initially the MSD is tuned using Target Tune and MSD 5977B is tuned using High Efficiency Source Autotune (HES Tune).

6.1.8 GC/MS Tune Verifications: Verify that all samples, blanks, and standards associated with a given instrument tune are analyzed within twelve (12) hours of DFTPP, as applicable to the specific analytical method.

Verify that spectra were generated using appropriate background subtraction techniques, as applicable to the specific analytical method.

Verify the GC/MS Tune results are included in the instrument's daily QA/QC folder.

6.2 Initial Calibration

6.2.1 Analyze the 625 and 8270 calibration standards at the following levels: 50, 25, 10, 5, 2 and 1 µg/mL. At each level, the internal standards should be present at 1 µg/mL.

Analyze low level 625 (drinking water) calibration standard at the following levels: 0.05, 0.1, 0.2, 0.5, 1 and 2.5 µg/mL. At each level, the internal standards should be present at 1 µg/mL.

Analyze the PAH calibration standards at the following levels: 50, 25, 10, 5, 2, 1 and 0.2 µg/mL. At each level, the internal standards should be present at 5 µg/mL. For alkylated

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PAH Homolog analysis, build the calibration curve for each homolog with its own primary ion and by manually entering responses of its representative analyte (Table 5).

Analyze the low level PAH calibration standards in SIM mode using MSD 5975C at the following levels: 1000, 500, 100, 25, 10, 5 and 2 µg/L. At each level, the internal standards should be present at 100 µg/L.

Analyze the PCP calibration standards, see details in sec. 4.1.1 (Note) for the levels.

6.2.2 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 8270D. The major ions (>10% of the most abundant ion) should be present and the relative intensities of the major ions should agree within ±20% of the reference mass spectrum. For each homolog, determine the retention time window manually before quantitation by its primary ion (Table5). Visually check Ion Chromatogram of homolog primary ion and enter the retention time range in calibration curve. Total area of all the peaks in this retention time window represents the response for each homolog.

6.2.3 Enviroquant 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

6.2.4 The initial calibration curve must meet the following criteria:

6.2.4.1 The %RSD of the response factors for each of the target compounds must be ≤20% for linear fit (or correlation coefficient must be equal or greater than 0.99 for quad. fit), or the instrument system is considered to be out of calibration. It is also recommonded that a minimum response factor for the most common target analytes, as noted in Table 4, be demonstrated for each individual calibration level as a means to ensure these componds are behaving as expected. In addition , meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. However, the %RSD must be <30 % for each of the calibration check compounds. If the %RSD for the compounds are out of these ranges, then the instrument system must be corrected. Some possible problems include standard mixture degradation, injection port inlet contamination, and analytical column contamination and active sites in the column or chromatographic system.

6.2.5 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

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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.

6.2.6 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.

6.2.7 The relative retention time (RRT) of each target analyte in each calibration standard, CCV and samples should agree within 0.06 RRT units.

6.2.8 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.

6.3 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 from a second source.

6.3.1 Analyze continuing calibration check standards. These calibration check standards must be analyzed at the start of each run and at 12 hour intervals thereafter.

6.3.2 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.

6.3.4 If the minimum response factors are not met, the system should be evaluated, and corrective action should be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

6.3.5 Calibration Check Compounds (CCC): After the system performance check is met, CCCs listed in Table 1 are used to check the validity of the initial calibration. Enviroquant software calculates the relative percent difference (RPD) for linear fit using:

$$RPD = \frac{(RF_I avg - Rf_C) \times 100\%}{RF_I avg}$$

where:

$RF_I avg$ is the average response factor from the initial calibration
RF_C is the response factor from current verification check standard

or calculates percent difference for quad. fit.

** The RPD for all compounds should be less than 30 %. The RPD for any CCC must be less than 30%. If the percent difference for each CCC is less than 30%, then the initial calibration is assumed to be valid. If the percent difference is greater than 30% for any

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one CCC, corrective action must be taken. Problems similar to those listed for SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before sample analysis begins.

6.4 The Screening for a Potential Crude Oil Source by GC/MS analysis

6.4.1 Analyze 1 µg/mL internal standard (IS) instrument blank prior to sample analyses to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. Perform a DFTPP tune prior to the analysis as described in section 6.1, and every 12 hours thereafter.

6.4.2 Analyze Resolution Mix standard (Resolution Mix Standard consists of pristane, phytane, n-heptadecane (C_{17}) and n-octadecane (C_{18}) in equal concentration of 50 to 150 µg/mL in cyclohexane) at the beginning of the run and at the end of the run (use full scan mode and long 65 minutes GC oven temperature program). The pristane and phytane should be resolved 80% or greater from C_{17} and C_{18} respectively.

6.4.3 Analyze Mass Discrimination Check standard (Mass Discrimination Check standard consists of naphthalene, fluoranthene and benzo(ghi)perylene in equal concentration of 50 to 150 µg/mL in cyclohexane) after the Resolution Mix standard at the beginning of the run and at the end of the run (use full scan mode and long 65 minutes GC oven temperature program). Integrate the total ion chromatogram and calculate the area ratio of naphthalene to fluoranthene (the ratio must be less than or equal to 2), and benzo(ghi)pereylene to fluoranthene (the ratio must be greater than or equal to 0.2). If the resolution is less than 50% and the Mass Discrimination Check standard ratios fail the criteria then take corrective action like injection service before going to the next step.

6.4.4 Analyze 17 compounds TRPH standard which includes C_8 to C_{40} to make sure all the hydrocarbon range is covered by the current GC oven temperature program. The retention time of each peak helps to identify the specific hydrocarbon range.

6.4.5 Analyze all the five-gram silica gel clean up fractions I and II in 1 mL methylene chloride prepared in the extraction batch (DEP SOP SV-001). This extraction batch includes five gram silica blank, reference crude oil at 20, 000 µg/mL, sample and one sample duplicate.

6.4.6 Generate Extracted Ion Chromatograms for each oil spill sample and the known crude oil reference standard for chromatographic profile comparisons.

6.4.7 Direct visual comparison of Extracted Ion Chromatograms for reference source oil is compared to the appropriate Extracted Ion Chromatograms of spilled oil. Evaluation of the Extracted Ion Chromatograms patterns is performed as a peak-to-peak comparision simply by placing the Extracted Ion Chromatograms one over the other to identify qualitatively pattern.

Table: Petroleum Profile Analyses by GC/MS for PAHs and PAH Homologues				
Sample Name: 1452694 4281 Fr1 & Fr2; Data File: 12919410-12919413				
		m/z	**RT Window min**	**Findings**
1	Alkanes	85	4 to 65	used in calculations
2	Isoprenoids (Diterpanes) - C19 to C22	183	18 to 28	not used in calculations
3	Terpanes	191	30 to 53	used in calculations

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4	Steranes	217	25 to 44	used in calculations
5	Steranes	218	27 to 44	used in calculations
6	Methylsteranes	232	20 to 46	not used in calculations
7	Methylsteranes	245	26 to 48	not used in calculations
8	Tri aromatic steranes	231	28 to 44	not used in calculations
9	Mono aromatic steranes	253	19 to 53	not used in calculations
10	Diasteranes	259	26 to 44	not used in calculations
11	C1 Naphthalenes	142	13 to 16	used in calculations
12	C2 Naphthalenes	156	15 to 18	used in calculations
13	C3 Naphthalenes	170	17 to 23	used in calculations
14	C4 Naphthalenes	184	19 to 24	used in calculations
15	C1 Fluorenes	180	21 to 24	used in calculations
16	C2 Fluorenes	194	23 to 26	used in calculations
17	C3 Fluorenes	208	25 to 29	used in calculations
18	C1 Dibenzothiophenes	198	24 to 27	used in calculations
19	C2 Dibenzothiophenes	212	26 to 30	used in calculations
20	C3 Dibenzothiophenes	226	27 to 31	used in calculations
21	C1 Phenanthrenes	192	25 to 28	used in calculations
22	C2 Phenanthrenes	206	26 to 30	used in calculations
23	C3 Phenanthrenes	220	28 to 33	used in calculations
24	C4 Phenanthrenes	234	29 to 35	used in calculations
25	C1 Pyrenes	216	29 to 33	used in calculations
26	C2 Pyrenes	230	31 to 35	used in calculations
27	C3 Pyrenes	244	32 to 37	used in calculations
28	C1 Chrysenes	242	34 to 37	used in calculations
29	C2 Chrysenes	256	36 to 40	used in calculations

6.4.8 Ion 85 (Alkanes) serves to provide a chromatographic trace for alkanes. This alkanes group assess gross weathering effects since this class is very weathering sensitive. Losses in the rapidly eluting, early part of the spill Extracted Ion Chromatograms relative to the source are to be expected due to various weathering phenomena (evaporation, dissolution, and biodegradation).

6.4.9 Ion 191 serves to provide a chromatogrphic trace for the basic structures for stereoisomers of haptane A and B present in the sample and are impartant due to their resistivity to weathering. Ion 191 is used as internal standard for % weathering quantitation in each sample compared to source oil.

6.4.10 Ions 217/218 represent stereoisomeric steranes. These steranes reflect different processes of maturation undergone by the source crude oils. They are highly resistant to biodegradation and weathering since they are both virtually nonvolatile and water insoluble. Their chromatographic profiles remain unaltered effectively. These Extracted Ion Chromatograms traces remain as virtual overlays despite severe weathering. The use of these Extracted Ion Chromatograms would be most desirable since they demonstrate exceptional stability to weathering while generally providing unique chromatograms for

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identification purposes. These two ions 217/218 may be used as internal standard for % weathering quantitation in each sample compared to source oil.

6.4.11 In addition to qualitative assessment of the Extracted Ion Chromatograms, spill oil samples may also be assessed for the degree of weathering they have undergone by examining the relative changes in distributions of the various homologous series.

6.4.12 Report results as similar if all of the Extracted Ion Chromatograms examined for two oil samples display the same qualitative pattern by visual examination. In addition, the oils are similar if either anticipated changes due to weathering are escertained.

6.4.13 Report results are inconclusive when the Extracted Ion Chromatograms for two oil samples display no qualitative differences, that is, the chromatographic patterns are the same visually, but one or more differences between analogous Extracted Ion Chromatograms is or are encountered that is or are greater than any observed for the duplicate samples. Then reprepare and reanalyze these samples if possible. They are inconclusive if similar results are still obtained.

6.4.14 Report results are dissimilar if analogous Extracted Ion Chromatograms for a spill or source show discrepancies, that is, qualitatively different patterns, particularly for the most weathering stable compounds.

6.4.15 For % weathering quantitation for each ion chromatogram individual peaks or group of peaks are manually integrated in both fractions I and II and determined area and tabulated in excel for calculations. From integration results total area of ion 85 (Alkanes as group), ion 191 (Terpanes, total area of individual ions and used as internal standard), ion 217/218 (Steranes, total area of group and may be used as internal sandards), and total area of 19 PAH homologs. See below an example of recent oil sample quantitation.

	Sept 2012	Sept 2012 dup	MC 252	ratio	MC252/Sept12	MC252/Sept12Dup
191	4901414	4048437	734712		0.149898	0.18148
217 group	8042378	7151016	1269372		0.1578354	0.177509
218 group	4667974	4105666	716182		0.1534246	0.174437
85	201255625	185946385	180422056			
aromatics	9529455	9531317	37729633			
ratio						
191/217group	0.6094483	0.5661345	0.5787996			
191/218group	1.0500088	0.986061	1.0258733			
85 Normalized to 191	41.060728	45.930413	245.56841			
%weather	83.28%	81.30%	0.00%			
aromatics normalized to 191	1.9442257	2.3543202	51.352956			
% weather	96.21%	95.42%	0.00%			

Note the aromatics calculations were only based on 19 weather-resistance homologues which were detected in Sept 19 sample. The actual total% weather for all aromatics would be significantly greater. However, aromatics

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contribution in original crude oil is only a little more than 10%, for the sake of est % weather of the sample it was not included.

7 GC/MS Sample Analysis

Load each run sequence separately for proper association of CCV data for each sample.

7.1 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.

7.2 Analyze the extracts by GC/MS by loading the auto sampler tray and setting up a run sequence in the GC/MS software. 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.

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

7.4 Examine the quantitation reports soon after the samples have been analyzed.

7.4.1 Check all of the calibration check standards and DFTPP tune standards analyzed during the run sequence and insure that they met the criteria given above.

7.4.2 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.

7.4.3 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 be commented and any positives detected must be qualified with a "J" to indicate that the result is an estimate.

7.4.4 Surrogate Recoveries: The recoveries must be within the following acceptance limits. Table 1 lists the surrogate association for all the BNA analytes. If any of these surrogates fall out side control limits (lower side), re-extract the effected sample with proper QC even after expiration and follow DEP SOP LB-027 for reporting.

Compound	% Rec Water & Sediment
Base/Neutral Surrogates	
Nitrobenzene-d_5	30-150
2-Fluorobiphenyl	30-150
Terphenyl-d_{14}	30-150
Acid Surrogates	

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Phenol-d_5	20-150
2-Fluorophenol	20-150
2,4,6-Tribromophenol	30-150

7.4.5 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 statutary limits and they are set initialy at the time of method set up. These limits are evaluated once a year or problem with the method performance. 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).

7.4.6 Check the method blank for any interfering contaminants. The MDL's may have to be elevated if the blank(s) indicate contamination.

7.5 Data Interpretation and Quantitation

7.5.1 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.

7.5.2 Concentrations (Cs) of each compound and surrogate identified should be calculated as follows (the computer program will automatically calculate the concentrations for water samples, including any dilution factors entered; the calculations for sediments must be adjusted for the weight of the sample and conversion of units to µg/kg):

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

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D = (100-% moisture in sample)/100, or 1 for a wet-weight basis

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

7.6.1 Follow steps in section 7.4.

7.6.2 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.

7.6.3 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

7.6.3 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:

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

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.

7.7 For samples containing components not associated with the calibration standards, a library search is made for the purpose of tentative identification. Guidelines for making tentative identifications are given in section 8, Library Search Protocol For BNA GC/MS.

8 Library Search Protocol For BNA GC/MS

8.1 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:

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8.1.1 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.

8.1.2 If the peak pattern is a petroleum hydrocarbon, identify the petroleum hydrocarbon using pattern-std. comparison. If the pattern is unrecognizable, report as "unidentifiable petroleum hydrocarbon pattern ". Estimate the amount of pet. hydrocarbon present using total ion area calculation of the envelope. Assume the RF is 1. Quantitate as in step 7.5.2., 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.

8.2 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.

8.3 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 class of organic compounds.

8.4 If the match is below about 60%, or the search program resulted in no matches (i.e., " No data base 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 <u>total</u> 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.**

8.5 The library search program returns estimated concentration results in µg/mL. You must apply the correct sample volume or weight extracted to correct the result and calculated the final estimated result as in step 7.5.2 for water and sediment/waste samples.

8.6 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):

<u>Sediment/Waste Example</u>

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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.

9 Reporting and Documentation

9.1 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.

9.2 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.

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

9.4 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.

9.5 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 print out of sample positives from the data review and file it in the data folder.

9.6 Submit the result folder to the BNA section supervisor. The supervisor will review results and then authorize the sample. The supervisor will then file the folders in the BNA GC/MS lab.

10 Data Archival

10.1 For the Enviroquant GC-MS system:

10.1.1 Move the valid data files (tune, ICALS, CCC, QC and sample data files) soon after collection from the hard disk of the instrument computers to the network drive to archive. Raw data files on the hard disk of each instrument may be deleted after 3 to 4 months or they are no longer in need.

10.1.2 Copy the processed data files (quantitation reports) for each calibration method (625.1 and 8270) into network drive to convert in QC Manager for reporting in LIMS. These files may be deleted after all results are authorized.

10.1.3 The archived data may be retrieved by making a request to the data group or the BNA supervisor. Make sure when setting up an injection sequence to write down the name of the data files with the associated sample information in the injection log. Include mass spectrometer number in the data file name. (Example: 07502100.d indicates - year 2007; month 1 to 9 and o, n, d; day 01 to 31; instrument number 1 to 3; and file number 00 to 99) This is the only way that data files may be cross referenced to their sample ID.

11 Quality Control

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11.1 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 Determination of Method Detection Limits

12.1 Determination of Method Detection Limits and Demonstration of Capability

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

The LOD and Demonstration of Capability (DOCs) shall be determined for each main quality system matrix group identified by NELAP (air, drinking water, non-potable water, biological materials and solids/chemical materials). These groups represent the minimum matrix distinctions for LOD determinations and DOCs where there is evidence that the method performance will not be affected by sub-matrix distinctions within these group, Otherwise LODs and DOCs shall be determined separately for the quality system matrix sub-groups listed below. Where a suitable matrix cannot be found for preparing samples for LOD determinations or DOCs, another similar matrix type may need to be used or samples may need to be prepared in the absence of a matrix (e.g. method blanks). Reasons for matrix substitution may include (but are not limited to): inappropriate background analyte levels in the matrix for the intended study, no analyte-free matrix is available for method blanks, no reference materials are available for a matrix, etc,

12.1.1 Quality System Matrices:

- Aqueous – all aqueous samples excluding drinking water (see below) and salt or estuarine waters;
- Drinking Water – water from a designated potable source;
- Saline/Estuarine – an aqueous sample from an ocean or estuarine. The effects of this matrix type may from analysis to analysis and with salt content. Therefore, the decision to what extent if any this matrix has on the LOD and what salt levels may affect the LOD is left to the discretion of experienced supervisory staff;

12.1.2 MDL Determination Procedures

12.1.2.1 The MDLs were established using procedures given in EPA Chapter 40 Part 136, Appendix B of the Federal Register. Also refer to **Reference 14.1 and 14.2.**

12.1.2.2 Seven replicate samples are analyzed near the MDL. The MDL is the concentration of analyte at which there is analyte present with 99% confidence.

12.1.2.3 The results of the seven replicate data sets are tabulated and the statistical calculations are performed electronically on at least an annual basis to establish or update the MDLs and PQLs for each analyte and matrix. A list of MDLs is given in the Laboratory Comprehensive Quality Control Plan, see Reference 14.14.

12.2 Table lists the LOD check for all the tests performed

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Table: LOD Check – Amount of Spike Standard Required Check Spike concentration for all the BNA methods.

Method	Reported MDL in LIMS In PPB	On Column Conc. (µg/mL) Required for MDL	Lowest ICAL Standard (µg/mL) Used for Analysis	Routine LFB's (µg/mL)	LOD Check Conc. on Column (µg/mL))	LOD Check Spike Amount (mL)	LOD Spike Conc.
W-BNA/ W-BNA-R	1	1	1	25.0	4	0.08(625/8270)	50 ppm
W-BNA/W-BNA-R	0.05	0.05	0.05		0.2	0.04	5 ppm
S-BNA	60	1.8	1	25.0	7	0.140	50 ppm
W-PAH	0.025	0.025	0.050	5.0	0.1	0.02	5 ppm
S-PAH	6.66	0.2	0.2	5.0	0.8	0.16	5 ppm
W-FL-PRO	0.25(mg/L)	85	125	850	425	0.1	500 ppm
S-FL-PRO	10(mg/kg)	85	125	850	425	0.1	500 ppm
A-PAH	100 ug	0.1	0.1	0.5	0.25		

13 Safety/Hazardous Waste Management

13.1 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.

14 References

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

14.2 Test Methods for Evaluating Solid Wastes, Third Edition, SW-846, Method 8270D, Semi-volatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS).

14.3 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.

14.4 ASTM D 5739-06. Standard Practice for Oil Spill Source Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectrometry.

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

14.6 DEP SOP SV-004. Extraction and Fractionation of Petroleum Range Organics from Waters and Sediments (FL-PRO and MADEP-EPH)

14.7 DEP SOP SV-009. BNA Standard Preparation.

14.8 DEP SOP LB-027. Standard Operating Procedure for Reporting Qualified Data and Correcting Quality Control Problems .

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

14.10 Florida Department of Environmental Protection, Standard Operating Procedure **LB-007** *Procedure and Policy for Demonstration of Capability for Methods, Instruments and Laboratory*

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Staff.

14.11 Florida Department of Environmental Protection, Standard Operating Procedure **LB-031** *Limit of Detection Verification.*

14.12 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

10/20/2014 Minor revisions to the text were made for format and clarity.

11/25/2015 Added new analytes.

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	0.1	0.40	60	240	50 - 130	40 - 140	<40
Aniline	1.0	4.0	60	240	30 - 120	40 - 140	<40
Benzaldehyde	2.0	8.0			50 - 130		<40
Benzyl alcohol	0.05	0.20	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
2-Butoxy ethanol	2.0	8.0			50 - 130		<40
1-Butoxy-2-propanol	2.0	8.0			50 - 130		<40
1,3-Dinitrobenzene	0.1	0.4	60	240	50 - 130	40 - 140	<40
Ethyl Methanesulfonate	1.0	4.0	60	240	50 - 130	40 - 140	<40
Glutaraldehyde	2.0	8.0			50 - 130		<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*	0.05	0.20	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

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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	0.05	0.20	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
alpha-Terpineol	2.0	8.0			50 - 130		<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	0.05	0.20	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
Diethylphthalate*	2.0	8.0	30	120	50 - 114	40 - 140	<40
Dimethylphthalate*	0.05	0.20	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	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
2-Methylnaphthalene	0.025	0.10	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	0.05	0.20	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	20	80	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					

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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*	20	80	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	0.05	0.20	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
Fluoranthene*	0.025	0.10	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	0.05	0.20	30	120	50 - 150	40 - 140	<40
Phenacetin	0.05	0.20	60	240	50 - 130	40 - 140	<40
Phenanthrene*	0.025	0.10	6.7	27	54 - 120	40 - 140	<40
Pentachloronitrobenzene	0.05	0.20	60	240	50 - 130	40 - 140	<40
Pyrene*	0.025	0.10	6.7	27	60 - 140	40 - 140	<40
Triethyl-2-acetylcitrate	2.0	8.0			50 - 150		<40
1,3,5-Trinitrobenzene	0.1	0.4	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

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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

m/z	Ion Abundance Criteria
51	30-60% of Base Peak
68	less than 2% of mass 69
70	less than 2% of mass 69
127	40-60% of base peak 198
197	less than 1% of mass 198
198	Base peak, or >50% of Mass 442
199	5-9% of mass 198
275	10-30% of Base Peak
365	greater than 1% of mass 198
441	Present but <24% of mass 442
442	Base Peak, or greater than 50% of mass 198
443	17-23% of mass 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	-

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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	-
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	-

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4-Aminobiphenyl	169	168,170,115	-
Anthracene	178	176, 179	0.700
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
Benzoic acid	105	122, 77	-
2,4-Dinitrophenol	184	63, 154	0.010
2-Methyl-4,6-dinitrophenol	198	51, 105	0.010

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4-Nitrophenol	139	109, 65	0.010
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	

TABLE 5: Homolog Analysis of Soil PAHs

PAH Homolog	Representative Analyte Response Used for Quantitation	Primary Quantitation Ion	MDL µg/kg	PQL µg/kg
C1 Naphthalenes	Naphthalene	142	14	56
C2 Naphthalenes	Naphthalene	156	14	56
C3 Naphthalenes	Naphthalene	170	14	56
C4 Naphthalenes	Naphthalene	184	14	56
C1 Fluorenes	Fluorene	180	14	56
C2 Fluorenes	Fluorene	194	14	56
C3 Fluorenes	Fluorene	208	14	56
C1 Phenanthrenes	Phenanthrene	192	14	56
C2 Phenanthrenes	Phenanthrene	206	14	56
C3 Phenanthrenes	Phenanthrene	220	14	56
C4 Phenanthrenes	Phenanthrene	234	14	56
C1 Pyrenes	Pyrene	216	14	56
C2 Pyrenes	Pyrene	230	14	56
C3 Pyrenes	Pyrene	244	14	56
C4 Pyrenes	Pyrene	258	14	56
C1 Dibenzothiophenes	Dibenzothiophene	198	14	56
C2 Dibenzothiophenes	Dibenzothiophene	212	14	56
C3 Dibenzothiophenes	Dibenzothiophene	226	14	56
C4 Dibenzothiophenes	Dibenzothiophene	240	14	56
C1 Chrysenes	Chrysene	242	14	56
C2 Chrysenes	Chrysene	256	14	56
C3 Chrysenes	Chrysene	270	14	56
C4 Chrysenes	Chrysene	284	14	56

TABLE 6: Surrogate association, MDLs/PQLs, Spike Recovery Acceptance Range and Precision in Sediment and Water for low level PAH's analytes in SIM mode using MSD 5975C. *EPA 625.1 Analytes

Analytes	MDL µg/L	PQL µg/L	MDL µg/kg	PQL µg/kg	Accuracy Range Water (%)	Accuracy Range Soil (%)	Prcsn (% RPD)
Base/Neutral Extractables							

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Nitrobenzene-d5 Surrogate							
Naphthalene*	0.002	0.008	0.440	1.76	50 - 130	40 - 140	<40
2-Fluorobiphenyl Surrogate							
2-Methylnaphthalene	0.002	0.008	0.330	1.32	60 - 140	40 - 140	<40
1-Methylnaphthalene	0.002	0.008	0.330	1.32	60 - 140	40 - 140	<40
Biphenyl	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
2,6-Dimethylnaphthalene	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
Acenaphthylene*	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
Acenaphthene*	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
2,3,5-Trimethylnaphthalene	0.002	0.008	0.330	1.32	60 - 140	40 - 140	<40
Fluorene*	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
Terphenyl-d14 Surrogate							
Dibenzothiophene	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
Phenanthrene*	0.002	0.008	0.330	1.32	60 - 140	40 - 140	<40
Anthracene*	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
1-Methylphenathrene	0.002	0.008	0.100	0.400	60 - 140	40 - 140	<40
Fluoranthene*	0.003	0.012	0.330	1.32	60 - 140	40 - 140	<40
Pyrene*	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
Benzo (a) anthracene*	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
Chrysene*	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
Benzo (b) fluoranthene*	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
Benzo (k) fluoranthene*	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
Benzo (a) pyrene*	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
Indeno (1,2,3-cd) pyrene*	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
Dibenzo (a,h) anthracene*	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40
Benzo (g,h,i) perylene*	0.002	0.008	0.067	0.268	60 - 140	40 - 140	<40

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