

**STANDARD OPERATING PROCEDURE**  
**FOR**  
**GASOLINE RANGE ORGANICS BY METHOD 8015D**

**PHILIS SOP L-A-104 Rev. 2**

**Revision Date: 06-21-2024**

**EPA Contract No. 68HERH21D0002**

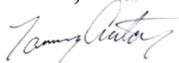
**PREPARED BY**

**PHILIS**

**PREPARED FOR**

**U.S. Environmental Protection Agency  
Office of Emergency Management  
Washington, DC 20460**

**Approvals:**

 _____ PHILIS, Castle Rock Lead Chemist	<b>June 21, 2024</b> Date
 _____ PHILIS, Edison Lead Chemist	<b>June 21, 2024</b> Date
 _____ PHILIS, Quality Assurance Manager	<b>June 21, 2024</b> Date
 _____ PHILIS, Program Manager	<b>June 21, 2024</b> Date

**CONTROLLED DOCUMENT**

Users are responsible for ensuring they work to the latest approved revision.  
Printed or electronically transmitted copies are uncontrolled.

**Revision History**

<b>Revision</b>	<b>Name</b>	<b>Date</b>	<b>Description of Change</b>
A	James Travis	04/01/2021	Transitional Issue
0	James Travis	03/21/2022	Program Issue
1	James Travis	04/12/2023	Annual Review
2	Thomas Antony	04/25/2024	Annual Review

<b>SOP REVISION FORM</b>
--------------------------

<b>SOP Name: Gasoline Range Organics by Method 8015D</b>			
<i>Purpose: (Review or Revise)</i>	<i>SOP #:</i>	<i>Rev. #: (Being Reviewed or Revised)</i>	<i>Origination / Release Date:</i>
Annual Review	SOP No. L-A-104	1	08/31/2023
Requested by:	Thomas Antony	Date:	04/25/2024

<b>New SOP Revision Date:</b>	<b>6/21/2024</b>	<b>New SOP Revision #:</b> <i>(If Applicable)</i>	<b>2</b>
-----------------------------------	------------------	--	----------

**For Revision: Summary of Revisions (specify sections)**

2.3, 8.2	Replaced sodium bisulfate with water
7.3.2	Removed this section; it is unnecessary
7.3.3	Added the addition of preservatives
7.4.1	Removed "20% sodium bisulfate solution." Not necessary.
7.4.2	Added the addition of preservatives to QC to match samples
8.0	Addition of preservation of Encore samples
8.3	Added section pertaining to Encore samples
8.10	Removed "QA 015." Not necessary.
9.2	Added statement about adding method blanks to MDL study
10.2	Added section about running RT markers
10.3	Added section about calibration standards and autointegration
10.8	Added "The lowest point of the calibration curve must be at or below the reporting limit"
10.9	Added that a closing CCV must be run
12.2	"uses" changed to "used"
Table 7	Changed "Low point and mid point" to "All calibration points" must be recalculated.
Table 10	Removed "low" within "ICAL Point Eval" because all points are recalculated
Forms	Updated to current release

**For Review: Comments**

**Standard Operating Procedure  
Gasoline Range Organics By Method 8015D  
L-A-104 Rev. 2**

**TABLE OF CONTENTS**

1.0	Scope and Application .....	1
2.0	Summary of Method .....	1
3.0	Definitions.....	3
4.0	Interferences.....	6
5.0	Safety .....	6
6.0	Equipment and Supplies .....	8
7.0	Reagents and Standards .....	9
8.0	Sample Collection, Preservation, and Storage.....	13
9.0	Quality Control .....	15
10.0	Calibration and Standardization.....	16
11.0	Procedure .....	17
12.0	Data Analysis and Calculations .....	21
13.0	Method Performance.....	26
14.0	Pollution Prevention.....	27
15.0	Waste Management.....	28
16.0	References.....	28
17.0	Tables, Figures, and Attachments.....	28

**TABLES, FIGURES, AND ATTACHMENTS**

Table 1. Example MDL's and RL's for C6 to C10 Gasoline Range Organics for Different Matrices..... 29  
Table 2. Example Preparation of PDS Standards in Methanol for Analyses of Aqueous Samples and Medium Level Soil Analysis..... 29  
Table 3. Example Preparation of PDS Standards i for Analyses of Low-Level Soils and Solids30  
Table 4. Example Preparation of Aqueous Working Standards ..... 30  
Table 5. Example Preparation of Working Standards for Analyses of Low Level Soil/Solids... 31  
Table 6. Recommended GRO Sample Preservation Techniques and Holding Times taken from SW 846 Method 5035A Appendix A..... 32  
Table 7. Example EPA Method 8015D Analysis Sequence with QC and Instrument Calibration Frequency and Acceptance Criteria ..... 33  
Table 8. Example Purge and Trap Parameters for GRO Analysis..... 34  
Table 9. Example GC 6890 Parameters for GRO Analysis..... 34  
Table 10. Method 8015D Method Acceptance Criteria..... 36  
Figure 1. Example Auto Integration Parameter File..... 37  
Figure 2. FID Chromatogram of a 1000ug/L Gasoline Standard ..... 38  
Figure 3. Example GC-FID Data Review Form ..... 39

## **Standard Operating Procedure Gasoline Range Organics By Method 8015D L-A-104 Rev. 2**

### **1.0 Scope and Application**

This standard operating procedure (SOP) documents CSS-Inc's application of EPA Method 8015D dated June 2003 used in conjunction with EPA method 5030C Rev. 3 dated May 2003 and EPA method 5035A Rev. 1 dated July 2002 for the qualitative and quantitative determination of Gasoline Range Organics in the C6 to C10 range.

This SOP is executed in accordance with the U.S. Environmental Protection Agency and National Environmental Laboratory Accreditation Program (NELAP).

#### **1.1 Applicable Matrix or Matrices**

This method is to be used for the identification and measurement of Gasoline Range Organics in finished potable water, ground water, surface water, liquid and aqueous waste samples, product samples, and soil and solid samples.

#### **1.2 Scope and Application, and Components to be Analyzed**

1.2.1 GRO corresponds to the range of alkanes from C6 to C10 and covering a boiling point range of approximately 60°C - 170°C. This SOP is applied for GRO from a variety of matrices as specified in Section 2.0.

1.2.2 This method may be applicable to other petroleum based liquid products, fuel types and petroleum hydrocarbons other than those listed in Sec. 2. However, in order to be used for additional analytes, fuel types, or petroleum hydrocarbons, the analyst must demonstrate that the gas chromatographic conditions, including the GC column, and purge and trap conditions are appropriate for the analytes of interest. The analyst must also perform the initial demonstration of proficiency described in Method 8000.

### **2.0 Summary of Method**

2.1 Aqueous Samples (Based on SW-846 Method 5030C): Helium is bubbled through 5 mL of water in a purge and trap sparge vessel. The purgeable hydrocarbon product is efficiently transferred from the liquid phase to the gaseous phase. The vapor is swept onto a sorbent trap where the purgeable product is trapped. After purging is completed, the trap is heated and backflushed with helium to desorb the product components onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the product components out into a distinctive multicomponent pattern with chromatographically resolved peaks. Prior to data acquisition of calibration standards,

- a retention time marker standard consisting of a three component mix containing 50 to 100ppb each of hexane, decane and dodecane is prepared in either water or soil. This mixture undergoes the same purge and trap and GC cycles as the calibration standards. The retention times of the leading edge of hexane and the tailing edge of decane is used to determine the boundaries of the C6-C10 range for gasoline. Data is then acquired for calibration standards prepared from a certified stock solution covering the concentration range for analysis. The area sum of the peaks generated by the FID signal is integrated within the boundaries determined from the retention time marker. Sample peak area summations are determined and used to quantitate concentrations based on the calibration curve. One microliter of surrogate solution is added to all calibration standards, QC samples and samples to monitor system performance.
- 2.2 Medium level soil and solid samples (based on SW846 Method 5035A): medium level samples are collected in the field and added directly into a pre-tared vial containing 5mL methanol in the field. As an alternative, samples are collected in an EnCore® sampler and added to a pre tared vial containing 5mL methanol in the lab. A maximum of 1mL of methanol extract is added to 50ml water in a volumetric flask. Lesser volumes of extract require the addition of additional methanol to maintain a constant ratio of 1mL methanol to 50mL water to be consistent with the LCS and blanks which are also prepared as extracts. Samples and QC are then run similar to the aqueous procedure in Section 5.1.
- 2.3 Low level soil and solid samples (based on SW846 Method 5035A). 5g or less of a solid sample are added in the field (or collected in the field in 5g EnCore® samplers and added in the lab) to a pre-tared 40ml vial containing a clean magnetic stir bar and 5ml of water. Calibration standards are prepared by directly injecting aliquots of the gasoline primary dilution standard into the soil/water mixture. The sealed vial is then placed on the auto sampler where surrogate and an additional 5ml of water is added through a 2-stage needle. Sample is heated to 40C and purged while stirring into a concentrator where the organics are trapped and desorbed into the GC. Retention time marker is prepared in a similar manner to a soil calibration standard or sample, FID signal is integrated and data is processed as described in Section 5.1.
- 2.4 Oily Samples (SW 846 Method 3585): Samples that contain oily material are assessed to determine water-miscibility. Samples that are soluble in methanol may be weighed and diluted with methanol for analysis as in 5.2. Samples that are not soluble in water miscible solvents are prepared by dilution with hexadecane, or other suitable solvent, and directly injected for analysis. The gas chromatograph is temperature programmed to separate the components which are then detected with an FID detector. The hexadecane method needs to undergo method development.

### 3.0 Definitions

3.1 Batch<sup>‡</sup>: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24hours. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

A volatiles analytical batch will consist of no more than twenty (20) environmental samples in addition to the SOP Quality Control requirements.

All batches require one MB, LCS, and MS/MSD pair or MS and Sample Duplicate when possible.

3.2 Chain of Custody (COC)<sup>‡</sup>: Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers; the mode of collection; the collector, the time of collection, preservation, and requested analyses. See also Legal Chain of Custody Protocols.

Each time the samples are transferred, the document should be signed by the person releasing the samples and by the person receiving the samples. A date and time must also be recorded.

3.3 Continuing Calibration Verification (CCV): A standard analyzed at the beginning of each analytical sequence that contains all method analytes at a concentration near the mid-range of the calibration curve. Each analyte must have a recovery within a percentage range specified in the method to validate that analyte in the calibration curve. A CCV is not required if a calibration curve is analyzed at the start of an analysis sequence. Some methods require additional CCV's. The CCV frequency will be stated in the method SOP.

3.4 Holding Time: The maximum amount of time permitted between sampling and sample preparation and/or sample preparation and sample analysis. Also the period of time a sample may be stored prior to analysis when there is no preparation step. See the specific method or SW846 8000B table 4.1.

- 3.5 Instrument Calibration Standards (ICS): A solution prepared from the primary dilution standard solution or stock standard solutions, internal standards and surrogate analytes. The ICS solutions are used to calibrate the instrument response with respect to analyte concentration.
- 3.6 Laboratory Control Sample (LCS)<sup>‡</sup>: (however named, such as laboratory fortified blank, blank spike (BS), or QC check sample). A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.
- The standard source can be the same as the calibration or a second source. The LCS is analyzed exactly like a sample to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.
- 3.7 Laboratory Duplicate (LD): Two sample aliquots taken in the laboratory and analyzed separately with identical procedures. Analyses of the aliquots indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
- 3.8 Matrix Spike (spiked sample of fortified sample)<sup>‡</sup>: A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of the sample for which an independent test results of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.
- 3.9 Matrix Spike Duplicate (spiked sample or fortified sample duplicate)<sup>‡</sup>: A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.
- 3.10 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. Method Blank analytical results are evaluated to determine the presence of contamination in the analytical method process.
- 3.11 Method Detection Limit (MDL): The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined by analyzing seven or more replicates of a spiked analyte free matrix and the resulting statistical calculation, in accordance with 40 CFR 136, Appendix B, Revision 2.

- 3.12 Primary Dilution Standard (PDS): A solution of one or several analytes prepared in the laboratory from SSS and diluted as needed to prepare calibration solutions and other needed analyte solutions.
- 3.13 Quality Control Sample (QCS)<sup>‡</sup>: A sample used to assess the performance of all or a portion of the measurement system. One of any number of samples, such as Certified Reference materials, a quality system matrix fortified by spiking, or actual samples fortified by spiking, intended to demonstrate that a measurement system or activity is in control.
- 3.14 Reporting Limit (RL): The reporting limit, also known as the LOQ is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample. This value can be no lower than the concentration of the lowest calibration standard.
- 3.15 Required Detection Limit (RDL): Detection limits established by a client or regulatory authority for analytes of concern. The laboratory MDL values must be equal or lower than the RDL. This is also known as the CRQL, the contract-required quantitation limit.
- 3.16 Second Source Calibration Verification (SCV): A solution prepared from a source that is different from the calibration standards. The SCV is immediately following the ICS, and is used to verify calibration standard accuracy.
- 3.17 Stock Standard Solution (SSS): A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased as certified from a reputable commercial source.
- 3.18 Surrogate Standard (SS): Organic compounds which are similar to the target analytes in chemical composition and mimic the behavior of the target analytes throughout the analytical process. Surrogate compounds are not normally found in environmental samples. Each calibration standard, sample, MB, LCS, MS, and MSD is spiked with surrogate standards. Surrogates are used to evaluate analytical efficiency by measuring recovery. See analytical method SOP for a list of specific surrogate compounds that are appropriate for sample-specific analysis.
- 3.19 Working Standards (WS): Instrument calibration/calibration verification standards and quality control standards used in an analytical sequence such as ICS, CCV, ICV, MS, and MSD.

<sup>‡</sup> EL-V1M2-ISO-2016, 2016 NELAP Standard definition.

#### **4.0 Interferences**

- 4.1 Samples for GRO are susceptible to laboratory chemical contaminants (e.g.: methylene chloride, acetone) which may elute during the gasoline range and create high bias. Samples may become contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage.
- 4.2 Carryover contamination may occur when a sample containing low levels of GRO are analyzed immediately following a sample containing high levels of GRO. If this situation occurs during a non-monitored analysis, the sample containing the low concentration GRO may require reanalysis. If the situation occurs during monitored analysis, a blank should be run to ensure that the system is free of contamination, and in addition, the sample should be re-analyzed at a higher dilution factor.
- 4.3 Other contamination or interferences could be present in laboratory glassware, chemicals, and reagents used.
- 4.4 A wide range of constituents may elute in the gasoline range. Other classes of compounds which may not be gasoline include halogenated organics, volatile solvents, or the leading edge of diesel range products which may significantly contribute to the total detection of organics in the gasoline range of interest creating high bias. Weathering of gasoline may also create a positive or negative bias. Particular attention should be paid the chromatographic pattern to determine the usefulness of the data. Tentative identification of individual peaks in the GRO range by reanalyzing the sample on a GC/MS system may be useful in the interpretation of the results. Any QAPP using this method should define how the data is used and the analyst's interpretation of this data should be based on this information.
- 4.5 Baseline fluctuations, especially where there is a presence of additional hydrocarbon fractions can bias the results. Careful observation of the baseline to assure that integration is tight to the baseline is necessary. Adjustment of the threshold in the auto-integration parameter file or manual integration may be necessary to eliminate baseline interference.

#### **5.0 Safety**

Laboratory personal are required to be familiar with the general laboratory safety plan including the location and proper use of safety/emergency equipment.

- 5.1 Employees must abide by the policies and procedures in the Chemical Hygiene Plan and this document. This procedure involves hazardous material, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow the appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are hazardous. Standard laboratory safety procedures should be followed when working with all samples.
- 5.2 **Specific Safety Concerns or Requirements**
- Eye protection that satisfies ANSI Z87.1, laboratory coat, and disposable nitrile or Silver-Shield® gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately. Latex and Vinyl gloves provide no protection against the organic solvents used in this method.
- 5.3 Each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation must be performed in a fume hood.
- 5.4 Extraction solvents such as acetone, hexane and especially methylene chloride have appreciable vapor pressure that requires proper venting if using a separatory funnel. After a few manual shakes, hold the funnel upside down, open the stopcock and position the funnel to be directed in the hood and away from the individual(s) to release buildup of solvent pressure, repeat as necessary.
- 5.5 Safety Data Sheets (SDS) for each analyte and reagent used in the mobile laboratory are available to all employees. The SDS and the PHILIS Chemical Hazard Summary Sheet must be read and understood by the analyst prior to initial use of a chemical.
- 5.6 This method does not address all safety issues associated with its use. Laboratory personnel are responsible for maintaining a safe work environment and a current awareness of the Chemical Hygiene Plan regarding the safe handling of the chemicals listed in this method.
- 5.7 The toxicity and/or carcinogenicity of the other reagents and analytes used in this method have been defined; however, each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation should be performed in a fume hood.

- 5.8 Laboratory personnel are required to be familiar with the general laboratory safety including the location and proper use of safety/emergency equipment.
- 5.9 Gasoline and petroleum products are highly flammable and volatile, the use of prepared standards avoids handling pure product, but if handling pure petroleum products as standards is unavoidable use sealed methods of transfer to avoid contact and the high potential for airborne cross contamination.
- 5.10 Hydrogen is generated for use in the FID, it is a highly flammable gas. Monitor for leaks in instrumentation or delivery lines.

## **6.0 Equipment and Supplies**

- 6.1 Sampling equipment for aqueous samples
  - 6.1.1 40 mL pre-cleaned VOA vials fitted with Teflon<sup>®</sup> septa.
  - 6.1.2 1:1 HCL for preserving water samples.
  - 6.1.3 pH test strips capable of measuring a pH of 0-14
  - 6.1.4 Other equipment may be necessary as per the QAPP and sample collection protocol.
- 6.2 Sampling equipment for soil samples, product or liquid waste samples
  - 6.2.1 Pre-weighed 40 mL pre-cleaned VOA vials containing 5 mL of 20% sodium bisulfate solution and magnetic stir bar fitted with Teflon septa.
  - 6.2.2 Pre-weighed 40 mL pre-cleaned VOA vials containing 5 mL of purge and trap methanol and magnetic stir bar fitted with Teflon septa.
  - 6.2.3 5g EnCore<sup>®</sup> samplers.
  - 6.2.4 Top loading balance capable of weighing to the hundredth of a gram.
  - 6.2.5 4-oz or 8-oz soil jars for moisture determination.
  - 6.2.6 Other equipment may be necessary as per the QAPP and sample collection protocol.
- 6.3 Glassware
  - 6.3.1 Volumetric Flask- Class A, various sizes.
  - 6.3.2 Disposable Pasteur pipettes.
  - 6.3.3 2ml screw cap vials.

- 6.3.4 1-L or 2-L Erlenmeyer Flask(s).
- 6.3.5 OI Analytical 5ml or 25ml Sparge Vessel.
- 6.4 Syringes
  - 6.4.1 Gas-tight micro syringes – various sizes.
- 6.5 Instrumentation
  - 6.5.1 Agilent 6890N Gas Chromatograph or equivalent.
  - 6.5.2 Agilent FID Part# AG-7890-8015 or equivalent.
  - 6.5.3 OI Analytical Eclipse 4660 Purge and Trap Concentrator or equivalent.
  - 6.5.4 OI Analytical Archon 4552 Water/Soil Autosampler or equivalent.
  - 6.5.5 Agilent MSD ChemStation G1701 DA software (or higher revision).
  - 6.5.6 Restek RTX-Volatiles 30M x 250um x 1.00 um or equivalent.
  - 6.5.7 OI Analytical Trap #10 or equivalent.
- 6.6 Equipment
  - 6.6.1 Heated Stirrer.
  - 6.6.2 Nitrogen purge line for reagents.
  - 6.6.3 Moisture analyzer or drying oven (for analyses of % solids).
  - 6.6.4 Hydrogen generator/air compressor FID1000 Parker/Balston/Thomas IT617-HDN or equivalent.
- 6.7 Supplies
  - 6.7.1 Magnetic stir bars.
- 7.0 Reagents and Standards**
  - 7.1 Reagents

- 7.1.1 Organic Free Reagent Water – Water that does not contain analytes of interest or interferences that would prevent detection of analytes of interest at the reporting limit. Poland Spring water or Millipore water that is heated and purged with nitrogen for at least one hour are examples that fit this criterion.
- 7.1.2 Methanol- Purge and Trap grade only.
- 7.1.3 Helium carrier gas: 99.999% (UHP) grade or better.
- 7.1.4 Nitrogen- purge gas, 99.999% (UHP) grade or better.
- 7.1.5 Original containers of reagents must be labeled with an expiration date. All containers of prepared reagents must bear a name, preparation date, and must be recorded in the LIMS system or in a preparation log.
- 7.1.6 Sodium bisulfate monohydrate, 97% (or better) for analyses of soils/solids. ACS reagent grade chemicals should be used and if ACS grade is not available, use the best available.
- 7.1.7 Ottawa Sand- Reagent Grade (for analyses of soils/solids). Other sands may be used provided they do not contain analytes of interest or interferences that would prevent reporting analytes at their reporting limits.
- 7.1.8 Concentrated HCL (ACS grade) for making of 1:1 dilution in water for preservation of aqueous samples, standards and QC.
- 7.2 Standards
- 7.2.1 Stock Standard Solutions (SSS)-Certified standards are purchased from approved vendors. The standards listed in this SOP are examples. SSS are used to prepare primary dilution standards (PDS), Working Standards (WS), and second source calibration verification standards (SCV). Depending on the QAPP, it may be useful to create stock standards by diluting the actual product from a targeted suspected source of a leak. Also available from vendors are stock standards of gasoline in varying stages of weathering, which may be useful on identifying detected concentrations of product as gasoline. Table 2 and Table 3 outlines the preparation of standards used to develop the base methods for GRO in PHILIS's Edison lab.
- 7.2.2 Standards should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards may need to be replaced after one or two weeks for working standards and one month for opened stocks or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented.

- 7.2.3 Certificates of analysis are attached to the standard in LIMS for easy reference and may also be stored on servers that are available to personnel. The certificates shall be used each time the method standards are logged in to confirm the concentration of analytes. Each stock standard is to be individually logged in so that the date opened can be documented and the expiration date can be changed appropriately. Two weeks after opening should be entered into LIMS as the expiration for gasoline standards. Stock standard for Surrogates and Retention time markers should be expired two months after opening.
- 7.2.4 Primary Dilutions Standards PDS are prepared using SSS from approved vendors and expire two weeks after preparation.
- 7.2.5 Surrogate solutions are prepared as described in Table 2 & 3 and immediately transferred to the Archon standard vessel. PDS for Surrogates can be used for up to 2 months as long as integrity of this standard has not degraded and level of standard in the autosampler vial is not below 1/3.
- 7.2.6 Labeled PDSs are stored in the freezer and replaced every one-two weeks or sooner when analytical results indicate a problem. Each vial containing the PDS shall be labeled in a standard format including the expiration date. Preparation of standards is documented in LIMS which ties the standard to the parent stock standard.
- 7.3 Working standards (WS) for aqueous samples.
- 7.3.1 Working standards are prepared in water according to Table 4. Working standards are used for the instrument performance check, calibration, and calibration verification.
- 7.3.2 All standards, QC, blanks and samples are decanted into 40ml vials leaving no headspace and placed in the tray of the Archon auto-sampler. They are automatically spiked with 1.0 $\mu$ L of a 200ug/ml surrogate solution by the Archon auto sampler as 5ml is transferred into a sparge vessel for the final purge. Resulting surrogate concentration is 40ug/L. Preservatives are added to blanks and QC samples to match the preservation of the samples in the batch.
- 7.3.3 Standards and reagent preparations are documented in the LIMS system. All standards in LIMS reference to the method of preparation, date of preparation, expiration date of prepared solution and preparer's initials, as well as trace them to their parent stock solutions.
- 7.4 Working standards (WS) for low level soil/solids
- 7.4.1 Working standards are prepared as per Table 5. They are used for the instrument performance check, calibration, and calibration verification. Aliquots of the PDS are spiked directly into a vial containing a magnetic stir bar and 5g of pre-cleaned Ottawa sand.

- 7.4.2 Soil samples, standards, and QC are spiked with 1.0 $\mu$ L of a 200ug/ml surrogate solution while adding an additional 5ml of water to the vial by the Archon auto sampler resulting in a concentration of 40 $\mu$ g/Kg. Preservatives are added to QC sample to match the preservation of samples in the batch.
- 7.4.3 Standards, QC and samples undergo a heated purge while being stirred by an external magnet.
- 7.5 Analysis of medium level soils and methanol miscible products
- 7.5.1 The aqueous calibration is used for quantifying samples extracted or diluted in methanol.
- 7.5.2 VOA free “reagent sand” is prepared by pouring purchased Ottawa sand into a large beaker and placing in a muffle furnace for 4 hours and transferring to a sealed 8 oz jar for later use.
- 7.5.3 Medium soil blanks are extracted by weighing 5g of reagent sand into a 40ml vial and then adding 5ml of P&T grade methanol. A 1mL aliquot of the extract methanol is transferred to a 50ml volumetric flask with reagent water then brought up to the mark with water and then decanted into a 40ml vial for analysis. The standard dilution factor is 50.
- 7.5.4 Example preparation of a medium level soil LCS follows:
- 7.5.4.1 A 5000ug/ml standard is prepared by adding 900ul of methanol and 100ul of a 50000ug.ml stock gasoline standard in a 2ml vial.
- 7.5.4.2 50uL of the 5000ug/mL PDS is added to 5g of reagent sand in a 40mL vial and 5mL of P&T methanol is added resulting in a 50ug/mL extract.
- 7.5.4.3 1mL of the 50ug/ml extract is added to 50ml of water in a volumetric flask, inverted 3 times and transferred to a 40ml vial leaving no headspace. Final aqueous LCS is 1000ug/L at a dilution of 50.
- 7.5.5 The final aqueous dilution of a sample extract should maintain the methanol water ratio of 100uL to 5mL. If a lesser aliquot of extract are required for a dilution to be in range, clean P&T methanol should be added to the water solution to adjust the amount of methanol 1mL methanol in 50mL water.

## 8.0 Sample Collection, Preservation, and Storage

PHILIS personnel do not take field samples, however this section describes sample collection and preservation and the rationale for using particular preservation methods. PHILIS PT and QC samples should be treated exactly as actual samples even though some are received in sealed glass ampoules. Use the date received as the sample date and allow LIMS to assign the standard hold times as per the method being analyzed. Do not crack open the ampoule until analysis is ready to begin. If the holding time is exceeded, document that it is a PT or QC sample that was received in a sealed ampoule and not opened until analysis. Once extracted or opened, normal holding times would be used and if times were exceeded, then the results would not be used.

EPA Method 5035A Appendix A provides the guidance for sample preservation techniques to maintain the integrity of samples when sampling for volatile organics including gasoline run under method 8015D. For aqueous samples with respect to gasoline a major concern is the effect of biological activity on aromatic constituents. Since shallow groundwater and surface water are a probable source for sampling and are likely to have biological activity, and one of the primary classes of compounds in gasoline are aromatics, it is advised that the sample be preserved by acidification with HCL. Performance data for fuel oxygenates using acid preservation and run at PHILIS by Method 8260 under the same purge and trap conditions indicates that the fuel oxygenate ethers are stable under these conditions. If fuel oxygenates constitute a concern in preparing a QAPP, a second set of non-preserved samples can be collected. Table 8 summarizes preservation techniques which are probable for a future PHILIS project. Similarly, for low level soil samples the default preservation method can be collection of Encore samples which are frozen or analyzed immediately upon receipt by the lab or collection in the field with acid preservation using Sodium Bisulfate. Other preservation techniques are outlined in Appendix A of Method 5035A.

- 8.1 Aqueous samples are collected in multiple 40 mL pre-cleaned VOA bottles with or without HCL preservative.
- 8.2 Solid samples for low level analysis are collected in multiple 40 mL pre-tared VOA vials containing 5 mL of water and a magnetic stir bar. Alternatively, solid samples can be collected in 5g EnCore sample containers and added to the above in the lab. Acidification with NaHSO<sub>4</sub> is dependent on the project.
- 8.3 Alternatively, solid samples can be collected in 5g EnCore sample containers and added to the above in the lab. Ecore samples can be added to a vial with a stir bar and 5ml water and analyzed as a low level soil, extracted in methanol and analyzed as a medium level soil, or stored in a freezer provided that either of these 3 options is accomplished within 24 hours of collection.
- 8.4 Solid samples for medium level analysis can be collected by adding 5g or less of soil to a pre-tared vial containing 5ml of purge and trap grade methanol. Alternatively, solid sample can be collected in 5g EnCore containers and added to the above in the lab.

- 8.5 Samples are delivered to the PHILIS or appropriate field refrigerator for shipment to the lab for analysis within holding time
- 8.6 The samples delivered to the PHILIS on the collection day must be transported in coolers containing ice to demonstrate the cooling process has begun. Samples shipped overnight to PHILIS must have temperatures that do not exceed 6 °C.
- 8.7 Store samples at 4°C until analysis. The sample storage area must be free of organic solvent vapors and direct or intense light. Analyze all samples within the stated holding times. Samples not analyzed within this period must be discarded and replaced.
- 8.8 Field Reagent Blanks (FRB) Duplicate FRBs must be handled along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill field blank sample bottles with reagent water and sample preservatives, seal, and ship to the sampling site along with empty sample bottles and back to the laboratory with filled sample bottles. Wherever a set of samples is shipped and stored, it is accompanied by appropriate blanks. FRBs must remain hermetically sealed until analysis. Use the same procedures used for samples to add preservative to blanks. The same batch of preservative is to be used for the field reagent blanks as for the field samples. If the sampler adds preservative in the field preservative must be added in the field. If all preservatives are added by the lab then FRBs can double as Trip blanks, if not a second set of vials with reagent water preservatives added by the lab must be prepared and added to the empty vial shipment and analyzed as Trip blanks.
- 8.9 Detailed instructions on sampling and the inclusion of trip and field reagent blanks and as disclaimer on the validity of data should these instructions not be followed should be included with the vial shipment. Copies of these instructions should be saved in the documents package attached to the work order and perhaps included in the data package.
- 8.10 If trip blanks and field blanks are not returned to the lab, this will be documented in the sample receipt checklist and the client must be notified and the result of the conversation recorded.
- 8.11 If there is a site-specific sampling procedure as a part of the QAPP, then it automatically supersedes this SOP.

## 9.0 Quality Control

QC requirements include the demonstration of capability and ongoing QC requirements that must be met when preparing and analyzing samples.

- 9.1 DEMONSTRATION OF CAPABILITY (DOC) – must be successfully performed by the analyst prior to analyzing any field samples and any time major method modifications are made. The following is done to demonstrate laboratory capability to perform this method: Prior to conducting the DOC study, the analyst tunes the instrument and generates an acceptable instrument calibration following the procedure outlined in Section 13 of this SOP. A MB is analyzed to demonstrate that the background contamination is low enough to not interfere with the analyte. Method precision and accuracy are demonstrated by analyzing 4 replicate LCS's fortified at a midlevel concentration appropriate for the matrix and analyzed according to the procedure described in Section 14 of this SOP. Calculate the measured GRO concentration in each replicate, the mean concentration of GRO in all replicates, and mean accuracy (as mean percentage of true value), and the precision (as relative standard deviation, RSD). The mean accuracy must be 70-130% (i.e. an accuracy of  $\pm 30\%$ ). The precision of the recovery (accuracy) for each analyte must be less than twenty percent ( $<20\%$ ). If these criteria are not met take remedial action and repeat the measurements until satisfactory performance is achieved.
- 9.2 MDL verification is performed at the time of initial method development, and anytime major changes are made to the instrument and on an annual basis. Each time the MDL study is performed, analyze a standard 1-4 times the expected MDL level. A positive detection is required to verify the MDL. MDL's are determined by analyzing seven or more replicates of a spiked GRO free matrix and seven or more method blanks and the performance statistical calculations in accordance with 40 CFR 136, Appendix B, and Revision 2.
- 9.3 Example detection limits for GRO as determined by EPA Method 8015D are listed in Table 1. Medium level soils, methanol miscible liquids and products are extracted and analyzed by the aqueous method by diluting an extract or methanol dilution at a maximum dilution factor of 100 for a 5g to 5ml methanol extract.
- 9.4 Ongoing QC applied when performing this method includes analyzing acceptable instrument calibration/calibration verification standards, method blanks, LCS/LCSD, and/or MS/ MSD. Surrogates must be acceptable with all QC samples and with test samples. Refer to EPA Method 8000D Revision 4 July 2014 for formulas for the calculation of laboratory generated limits when sufficient data has accumulated.

## 10.0 Calibration and Standardization

- 10.1 Prior to the analysis of samples, performance of the instrument is optimized, and an instrument calibration curve is developed.
- 10.2 A retention time marker containing 10ppb of hexane and 100ppb of Decane is run to verify the retention time window for the integration c6-c10 hydrocarbons.
- 10.3 Calibration standards are run and an auto integration parameter is created which is able to demonstrate a consistent integration pattern across the entire concentration range of the calibration.
- 10.4 Rejection of calibration points
- 10.4.1 It is not generally acceptable to remove internal points from a calibration curve. Typically instrument maintenance and the accuracy of the calibration standards should be examined if the calibration acceptance criteria are not met.
- 10.4.2 If no problems are found, then a point(s) can be rejected as long as it meets the following criteria.
- 10.4.3 If the rejected point is the highest or lowest point in the ICAL, then the rejection is valid as long as the reporting limit and the upper range of the calibration are adjusted, and the reporting limit meets the requirements of the QAPP. If the rejected point is an internal point on the ICAL, it may be removed if the reason is obvious and documented. Examples for level removal are; a bad injection, surrogates or internal standards low or missing.
- 10.4.4 The calibration must have a minimum of 5 points for quantitation by average response factor or linear regression or 6 points for a quadratic regression fit.
- 10.5 A response factor calibration curve is generated for GRO by plotting the response factor as a function of concentration ratio. An RSD of 20% is required for quantitation by average response otherwise choose a linear or quadratic regression curve which must have a coefficient of determination of 0.990 or greater for the curve to be acceptable.
- 10.6 The lowest point and midpoint in a curve must be evaluated against the curve. Acceptable re-quantitation limits are 70% to 130% accuracy.
- 10.7 The calibration is verified by analysis of a second source calibration verification standard (SCV) prepared from a secondary product source. Prepare and analyze a standard at mid-range of the calibration. Calculate the % recovery. Recovery criteria is 70 to 130.

- 10.8 The lowest point of the calibration curve must be at or below the reporting limit. Concentrations above the highest level of the calibration curve may not be reported unless flagged as estimated.
- 10.9 Calibration is verified by running a retention time marker and CCV every 12 hours. A closing CCV must be run at the closing of every analytical sequence. If analyzing samples containing product analyte, more frequent CCV analysis should be performed. Prepare and analyze a standard from the primary calibration source at the middle range of the calibration. All data, to be deemed acceptable must be bracketed by CCVs which exhibit no more than 20% Drift (80 to 120 recovery) for GRO and surrogates.
- 10.10 Table 7 summarizes all QC criteria and frequency of analysis.

## **11.0 Procedure**

### 11.1 Organic Free Water Preparation

- 11.1.1 Purchase distilled water.
- 11.1.2 Obtain a 1L or 2L Erlenmeyer flask and fill it with reagent water.
- 11.1.3 Place a magnetic stir bar into an Erlenmeyer flask or appropriate apparatus, and then place it on top of the heater.
- 11.1.4 Turn the stirrer on, verify that the stir bar is stirring, and turn the heater on low heat.
- 11.1.5 Place the 25 mL transfer pipette or glass tubing that is installed to the nitrogen line into the Erlenmeyer flask. Do not allow it to touch the stir bar. Turn the nitrogen valve until the water is being purged by the nitrogen.
- 11.1.6 Water should undergo a heated purge for a minimum of 1 hour.
- 11.1.7 Once purging is complete, remove the transfer pipette and plug the Erlenmeyer flask.
- 11.1.8 Allow the reagent water to cool to room temperature before using it to prepare working standards.
- 11.1.9 Document the preparation and use of this reagent. in LIMS.
- 11.2 Preparation of sodium bisulfate preservative (20%) for analyses of soils and solids
- 11.2.1 Ensure that the analytical balance has been calibrated.
- 11.2.2 Weigh 57.6 g of sodium bisulfate in a 150 mL beaker.

- 11.2.3 Dissolve the sodium bisulfate using the reagent grade water and transfer to a 250 mL volumetric flask.
- 11.2.4 Dilute the volumetric flask to the mark using reagent water and invert the flask to mix.
- 11.2.5 Decant the solution into a 250cc wide mouth amber bottle or another suitable container. Document the reagent in LIMS and print a container label and affix to the bottle.
- 11.2.6 Add 5ml of this sodium bisulfate solution and a stir bar to each 40ml vial to be analyzed for soil using an Eppendorf pipette
- 11.2.7 As an alternative, add approximately 1 g of sodium bisulfate to each vial. If samples markedly smaller or larger than 5 g are to be collected, then adjust the amount of preservative added by 0.2 g of preservative for each 1 g of sample. Also add 5ml of reagent water to the vial. Enough sodium bisulfate should be present to ensure a sample pH of 2.
- 11.3 Preparation of 1:1 HCL: Carefully add concentrated HCl to an equal volume of water measuring with an appropriate size graduated cylinder in a 40ml vial. Use 2 to 3 drops to 40 or 50ml of aqueous standard or water to acidify to a pH of <2.
- 11.4 Sample preparation for aqueous samples based on SW846 Method 5030C. It is recommended that samples be screened by headspace analysis prior to purge and trap analysis to prevent cross contamination and avoid contamination of the instrumentation. Historical site data and communication of the potential for heavily contaminated samples by the sampling team can be useful tools to prevent problems.
- 11.4.1 Remove samples from the laboratory refrigerator.
- 11.4.2 Verify that they have been logged into the LIMS, and are within the holding time. If the sample exceeds holding time, notify the Lead Chemist and follow the corrective action plan.
- 11.4.3 Ensure that the 40 mL sampling bottles are free of headspace. If headspace is noticed, notify the Lead Chemist and follow the corrective action plan. Headspace is considered a problem if the bubble is greater than ¼ inch in diameter (the size of a pea).
- 11.4.4 Also invert the vial to verify that the sample is completely aqueous and there is no undissolved product in the sample. Multi-phase samples must undergo phase separation and separate analysis of each phase. The lead chemist should be notified before analysis proceeds if this is the case.
- 11.4.5 Allow samples to equilibrate to ambient temperature before running.
- 11.4.6 For samples to be analyzed as MS/MSD follow the procedure below:

- 11.4.6.1 Additional sets of vials should be collected by the sampling team to ensure that there are sufficient unused vials available for reanalysis if necessary.
- 11.4.6.2 Spike an appropriate aliquot of spiking solution using a gas tight syringe through the vial septum. Shake vial for 1 minute before analysis.
- 11.5 Sample preparation for low/level soil/solid samples is based on SW846 Method 5035A.
  - 11.5.1 Remove samples from refrigerator and allow to equilibrate to room temperature.
  - 11.5.2 Verify that they have been logged into LIMS and are within holding time. If the sample exceeds holding time, notify the Lead Chemist and follow the corrective action plan.
  - 11.5.3 Determine final un-tared weight of sample to the hundredth of a gram on a properly calibrated balance and subtract the tare weight of the individual/NaHSO<sub>4</sub> tare weight. Record weights in balance log and in the LIMS bench sheet and in any logs created for the project. If the tare weight was lost damaged or destroyed notify the lead chemist.
  - 11.5.4 Matrix spikes are prepared by adding an appropriate aliquot of spiking solution by gas tight syringe through the vial septum into the NaHSO<sub>4</sub> solution. Invert vial a few times to mix. Making sure stir bar is buried under the soil after settling in the upright position.
- 11.6 Preparation of medium level soils
  - 11.6.1 Remove sample extracts from refrigerator and allow to equilibrate to room temperature.
  - 11.6.2 Verify that they have been logged into LIMS, and are within holding time. If the sample exceeds holding time, notify the Lead Chemist and follow the corrective action plan.
  - 11.6.3 Determine final un-tared weight of sample to the hundredth of a gram on a properly calibrated balance and subtract the tare weight of the individual/NaHSO<sub>4</sub> tare weight. Record weights in balance log and in the LIMS bench sheet and in any logs created for the project. If the tare weight was lost damaged or destroyed notify the lead chemist.
  - 11.6.4 Remove a measured aliquot of methanol from the extract using a gas tight syringe and transfer into a 50ml volumetric flask filled to near the mark with water. If sample aliquot is less than the default amount of 1mL methanol to 50ml water, then add purge and trap methanol to make up the difference. Add water to the mark, invert no more than three times and gently decant into a 40ml vial leaving no headspace.

- 11.6.5 Matrix spike/ matrix spike duplicates are spiked directly into the methanol extract/soil mix, LCS's are spiked into 5g of blank sand where 5ml of purge and trap methanol have been added. Remove a measured aliquot of methanol from the extract and transfer into 50ml volumetric flask filled to near the mark with water. If sample aliquot is less than the default amount of 1mL methanol to 50ml water then add purge and trap methanol to make up the difference. Add water to the mark, invert no more than three times and gently decant into a 40ml vial leaving no headspace.
- 11.6.6 Method blanks are 5g of blank sand extracted with 5ml methanol and prepared the same way in water as samples and QC samples.
- 11.7 Preparation of dilutions for of methanol miscible products and solvents.
- 11.7.1 Remove samples from refrigerator and allow to equilibrate to room temperature.
- 11.7.2 Verify that they have been logged into the LIMS and are within the holding time. If the sample exceeds holding time, notify the Lead Chemist and follow the corrective action plan.
- 11.7.3 Transfer a 20ml aliquot of purge and trap grade methanol to a 40ml vial and carefully mark the meniscus with a fine point permanent marker. Remove an aliquot of methanol. Cap vial and determine the tare weight to the hundredth of a gram using a properly calibrated balance. Transfer an aliquot of sample using a dedicated thoroughly rinsed gas tight syringe from the sample vial to the dilution vial through the septa of both vials. Make sure to transfer only the product phase of the sample. Determine the final weight and subtract the tare weight to determine the sample weight. Add purge and trap methanol to bring the sample up to the meniscus mark. Samples may be serial diluted from this initial dilution. An aliquot of the final dilution is added to 50mL of reagent water in a volumetric flask. Clean methanol is added to the water dilution to adjust to the default methanol to water ratio and water is added to the flask to bring up to the mark. Invert the flask no more than 3 times and gently decant into a 40mL vial. Place dilution into the 4552 tray and run by the water method. Final results can be reported in ug/Kg or % by weight.
- 11.7.4 All weights must be recorded in the balance log. All dilution procedures must be appropriately documented in any logs created for the project and on the bench sheet in LIMS. Final dilution factors as well as traceability to the sample container used must be included on the ChemStation quant report, the ChemStation sequence log and the LIMS preparation bench sheet.
- 11.7.5 Method blanks are aliquots of the same purge and trap methanol used for dilution and is added to water at the default methanol to water ratio and run by purge and trap,

- 11.7.6 LCS samples and matrix spikes are spiked into methanol at an appropriate stage of dilution and are added to the final methanol water purge dilution while adjusting for the default methanol to water ratio.
- 11.8 Setting up an analytical sequence (regardless of matrix)
- 11.8.1 In ChemStation, load the “default” or the previous day’s sequence. Make sure the sequence ties to the correct acquisition method used in the calibration curve for the samples being analyzed. Make the changes as necessary to reflect the QC and samples that you will be analyzing. A typical sequence would start with the Tune, CCV, MB, and LCS/LCSD It would then contain samples and an MS/MSD or MS/Dup. At the close of the sequence run another CCV.
- 11.8.2 Verify that the correct parameter program is loaded on the OI 4660 and the 4552 is programmed for soils or water as appropriate to the samples being run.
- 11.8.3 Load the Archon Auto sampler with Standards, QC and samples as entered into the ChemStation sequence.
- 11.8.4 Check the helium supply, water supply, and the Surrogate reservoir to make sure that adequate amounts are available to complete the sequence.
- 11.8.5 Check that the hydrogen generator and air compressor are operational.
- 11.8.6 Check that the FID settings are correct and that air and hydrogen flows are being properly maintained,
- 11.8.7 Start the sequence.
- 11.9 Moisture analysis for soil samples

Moisture analysis must be performed if results of solid samples are to be reported on a dry weight basis Follow SOP No L-A-100 for moisture analysis. The aliquot of soil for this analysis will come from the 8-oz soil jar.

## **12.0 Data Analysis and Calculations**

- 12.1 The c6-c10 fraction of gasoline in this method is the sum of all peaks between the leading edge of hexane and the tailing edge of decane as determined by the analysis of the retention time marker. Automated integration is suggested as the most efficient way to assure consistent integration, however careful attention must be paid to assure that the integration is tight to the baseline and includes all peaks in the range of interest.

- 12.2 In Enviroquant software load the midrange calibration standard. Under the Integrate pull down menu, left click on select integrator and choose ChemStation, the left click on Signal 1 integration parameters. Set integrator off at 0.1 minutes, integrator on at the retention time corresponding to the leading edge of hexane and integrator off at the time corresponding to the tailing edge of decane. Example settings for other parameters are shown in Figure 1. Save the parameter file with a unique name. Click integrate and observe the results paying careful attention to the baseline. It is up to the analyst's judgement to include peaks or clusters in close proximity to the retention time boundary settings. Optimization of the integration so that it yields an acceptable integration across all calibration levels is accomplished by trial and error through adjustment of the initial threshold value the final auto integration parameter should be used throughout the entire calibration.
- 12.3 Save the integration parameter and choose this parameter file in "Set Up Quantitation". The compound type for GRO must be set to H for hydrocarbon and the surrogate set to S. Quantify the midrange standard and set start and stop windows in Easy ID for graphical purposes. Quantify calibration standards, QC and samples but pay careful attention to the quality of integration in all cases. Adjustment of integration parameters or manual integration may be need if visual observation warrants it.
- 12.4 The concentration of GRO is calculated using Agilent MSD ChemStation software using an average response factor or linear or quadratic regression curve as established in Section 13 of this SOP. Response factors and GRO concentrations are calculated by the equations below:

- 12.5 Response factor (RF)

$$RF = \frac{(A_x)}{(C_x)}$$

Where:

- A<sub>x</sub> = Area of the quantitation ion for the surrogate or compound being measured.  
C<sub>x</sub> = Calibration concentration of the surrogate or compound being measured.

- 12.6 Average RF:

$$\overline{RF} = \frac{\sum_1^n RF}{n}$$

Where n= number of initial calibration standards

12.7 Percent Relative Standard Deviation

$$\%RSD = (s / \bar{x}) * 100$$

Where:

$$s = \sqrt{\frac{(\sum_{i=0}^n (\bar{x} - x_i)^2)}{n - 1}}$$

and

$$\bar{x} = \overline{RF}$$

$$x_i = RF_i$$

12.8 Sample concentration using average response factor

$$C_x = A_x D / \overline{RF}$$

Where:

$A_x$  = area of quantitation ion for compound being measured  
 $(RF)_{\overline{}}$  = mean relative response factor for compound being measured  
 $D$  = Dilution Factor  
 $C_x$  = Concentration of the sample.

12.9 Percent recovery for CCV, ICV, LCS, and MS are performed using the following equation

Where:

$C_{\text{spk}}$  = the concentration of the analyte in the spiked sample  
 $C_x$  = the concentration of the analyte in the reference (parent) sample; ( $C_x = 0$  for CCV, LCS and ICV.)  
 $C_t$  = the theoretical spike concentration.

12.10 Relative percent difference for duplicate is calculated using the following equation:

Where:

$C_1$  = concentration of the first sample

$C_2$  = concentration of the second sample

12.11 Data Qualification

12.11.1 The identification of fuels, especially gasoline, is complicated by their inherent volatility. The early eluting compounds in fuels are obviously the most volatile and the most likely to have weathered unless the samples were taken immediately following a spill. The most highly volatile fraction of gasoline constitutes 50% of the total peak area of a gasoline chromatogram. This fraction is the least likely to be present in an environmental sample (due to weathering or biodegradation) or may be present at only very low concentration in relation. While gasoline contains a large number of compounds that will produce well-resolved peaks in a GC/FID chromatogram, gasoline may contain many other components that are not chromatographically resolved. This unresolved complex mixture results in the "hump" in the chromatogram that is characteristic of these fuels. In addition, although the resolved peaks are important for the identification of the specific fuel type, the area of the unresolved complex mixture contributes a significant portion of the area of the total response. to the remainder of a gasoline chromatogram. Figure 1 shows a typical chromatogram for gasoline.

12.11.2 A wide range of constituents may elute in the gasoline range. Other classes of compounds which may not be gasoline include halogenated organics, volatile solvents, or the leading edge of diesel range products where more than one product is present may significantly contribute to the total detection of organics in the gasoline range of interest creating high bias. Weathering of gasoline may also create a positive or negative bias. Particular attention should be paid the chromatographic pattern to determine the usefulness of the data.

12.11.3 Overlaying the standard chromatogram with the sample chromatogram may be useful in determining a quality match for gasoline.

12.12 Data Assessment and Acceptance Criteria for Quality Control Measures

Instrument generated data goes through a series of reviews prior to being submitted to the client. First the analyst reviews the data to ensure method and client requirements are met. Then the instrument data goes through a peer review covering the same items as the analyst. Both reviews are documented on Form QA-022, which is provided in

Figure 2. The Quality Assurance Manager also reviews a minimum of 10 % of data to evaluate the QA process.

- 12.13 Analytical data generated by the instrument software is reviewed and evaluated by the analyst and peer as follows:
  - 12.13.1 The instrument calibration relative response factor and percent relative standard deviation.
  - 12.13.2 QA-QC check report for percent recovery for the surrogate.
  - 12.13.3 GRO percent recoveries CCV, LCS, SCV, MS, and RPD for MSD.
- 12.14 In order for the analytical data to be acceptable, the calibration standards and quality control measures must meet the criteria listed in Sections 12 and 13 of this SOP including Tables 9-10 and 14.
- 12.15 All GRO results are reported to LIMS.
- 12.16 All integrations must be performed in a consistent manner for all calibration standards, QC and field samples.
- 12.17 If the QAPP requires it, chromatograms of all field samples are examined to detect and identify individual peaks. Peaks should be reported in a manner specified by the QAPP.
- 12.18 Discrepancies in the analytical run are documented on the “Data Review Form, QA-022” and discussed with the Lead Chemist.
- 12.19 Reviewed data is entered into LIMS, hard copies of LIMS report is printed and compared to the original data or may be reviewed in LIMS.
- 12.20 All records derived from the analytical process are assembled in the analytical data packages that consist of:
  - 12.20.1 Analytical run sheet.
  - 12.20.2 “Data Review Form Q-020A” signed by the Lead Chemist or designee.
  - 12.20.3 QA-QC check report.
  - 12.20.4 Quantitation Report for each Sample and QCS.
  - 12.20.5 Evaluation reports for CCV, SCV, LCS/LCSD, and MS, MSDs.
  - 12.20.6 Initial calibration form.

- 12.21 Data packages are assembled in PDF packages and are stored electronically. Electronic data, including reports are maintained on servers in multiple locations.
- 12.21.1 In water samples with floating product, the product phase will contain the overwhelming majority of the gasoline rang organics. The numbers generated for concentration represent the concentration only for that particular phase not the sample as collected. It may be useful to run the to identify the water soluble components which have “:washed out” of the organic phase as these are likely to be the oxygenate additives, The total sample concentration can be estimated by measuring the height of the aqueous phase and the total height of the vial and calculating based on the percentage of each phase in the sample. This approach can only be as accurate as the sample process is in collecting a sample which representative of this ratio of water to product.
- 12.21.2 The QAPP should specify whether GRO reporting is to be done on an “as is” basis (reporting a GRO concentration regardless of the quality match) or whether positive detection for GRO is to be qualified and what criteria will be used to qualify the data.

### **13.0 Method Performance**

- 13.1 Demonstration MDL data is presented in Table 1 and 2. MDL’s are analyzed at least annually or with instrumentation changes. Lab Accuracy and Precision data are used to calculate lab specific acceptance criteria. Precision and Accuracy data are recalculated and evaluated every six months. Limit acceptance criteria will be established no tighter than 70 % to 130 % for accuracy and 20% for precision.
- 13.2 Other specific Quality Assurance Objectives (QAO) may be found in the appropriate statement-of-work or Quality Assurance Project Plan (QAPP) for specific projects.
- 13.3 Corrective Actions for Out of Control

In cases where quality control measures do not meet acceptance criteria, the quality of the analytical data is not acceptable, and the analyst does the following:

- 13.3.1 If the acceptance criteria listed in Table 10 of this SOP are not met for ICAL, SCV, CCV, MB, LCS, MS, MSD, internal standards, and surrogates, the affected QCs and associated samples should be treated as per laboratory or QAPP protocols. All samples and QC must be bracketed by acceptable CCV’s.
- 13.3.2 If after analysis, any of the criteria for quality control are not met, or the sample is not available for reanalysis, the analyst must notify the Lead Chemist. The Lead Chemist will implement the corrective action plan.
- 13.3.3 The analyst shall report to the Lead Chemist and indicate on the “Data Review Form QA-022” any out control event. Such events include:

- 13.3.4 Damage to the sample.
- 13.3.5 Headspace in the sample bottle.
- 13.3.6 Floating product in the sample.
- 13.3.7 Holding time exceeded.
- 13.3.8 Inadequate sample preservation.
- 13.3.9 Sample results exceeds the Agency's action limit
- 13.3.10 Samples do not reflect historical data.
- 13.3.11 Upward trending or sample results approaching interval warning limits.
- 13.3.12 Any obvious non-gasoline peak present on the instrument generated chromatogram that will create significant bias to the GRO results.
- 13.4 The Lead Chemist will implement the corrective action plan described in the PHILIS corrective action plan document.

See the QAPP that the samples were analyzed under for guidance.

#### **14.0 Pollution Prevention**

- 14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. The EPA places pollution prevention as the management option of first choice with regard to laboratory waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.
- 14.2 The Environmental Protection Agency requires that laboratory waste management practices be compliant with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the PHILIS Chemical Hygiene Plan and the PHILIS Waste Management Plan.
- 14.3 The waste produced from EPA Method 8015Bd, 5030C and 5035A consists of waste collected from the purge and trap system, excess sample, standards (stock mixes, PDS, WS), and methanol.
- 14.4 Waste from the purge and trap system from field samples are disposed in the Hazardous Waste container.

- 14.5 Excess reagents are disposed following the MSDS instructions.
- 14.6 Glass pipettes are disposed of as Lab scraps.
- 14.7 For information about pollution prevention that may be applicable to laboratories and research institutions consult “Less is Better: Laboratory Chemical Management for Waste Reduction”, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036.

## **15.0 Waste Management**

Waste management procedures are specified in the Hazardous Waste Management Plan.

## **16.0 References**

- 16.1 EPA Method 8015D Non-Halogenated Organics Using GC/FID, Revision 4, June 2003
- 16.2 EPA Method 5030C, Purge-And-Trap of Aqueous Samples, Revision 3, May 2003; U.S. EPA Office of Solid Waste.
- 16.3 EPA Method 5035A, Closed System Purge and Trap and Extraction for Volatile Organics in Soil and Waste Samples, Revision 1, July 2002.
- 16.4 2003 and 2009 NELAC manuals
- 16.5 40 CFR 136, Appendix B, Revision 1.11.
- 16.6 U.S. EPA Contract Laboratory Program Statement of Work OLM 04.2.
- 16.7 EPA Method 8260C, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Revision 3, August 2006; U.S. EPA Office of Solid Waste
- 16.8 EPA Method 8000D, Determinative Chromatographic Separations, Revision 4, July 2014.

## **17.0 Tables, Figures, and Attachments**

**Table 1. Example MDL's and RL's for C6 to C10  
 Gasoline Range Organics for Different Matrices**

Matrices	Analyte	CAS#	MDL (ug/) or (ug/Kg)	RL (ug/L)
WATER	Gasoline Organics Range c6-c10	8006-61-9	6.21	20
MEDIUM LEVEL SOIL	Gasoline Organics Range c6-c10 Gasoline Organics Range	8006-61-9	621	1000
LOW LEVEL SOIL	Gasoline Organics Range c6-c10 Gasoline Organics Range	8006-61-9	31.5	100

**Table 2. Example Preparation of PDS Standards in Methanol for  
 Analyses of Aqueous Samples and Medium Level Soil Analysis**

PDS Name	SSS Mix Used				Methanol	PDS description		
	Source/catalog#	Analytes	Conc. µg/mL	Volume µL	Volume mL	Conc. µg/mL	Final Volume mL	Application
PDS 5000	Restek/30205	Unleaded Gasoline Composite	50000	200	1.8	5000	2.0	ICAL, CCV, LCS/LCSD, MS/MSD
PDS 500	Restek/30205	Unleaded Gasoline Composite	50000	20	1.98	500	2.0	ICAL
PDS 50	In House	Unleaded Gasoline Composites	500	200	1.8	50	2.0	ICAL
SS	Restek 30049	1,2-Dichlorbenzene-D4	2000	1000	900	200	10.0	All Samples, Standards and QC
SCV-PDS	SpexCertiPrep SR-G-20K	Regular Unleaded Gasoline	20000	500	1.5	5000	2.0	SCV

**CONTROLLED DOCUMENT**

Users are responsible for ensuring they work to the latest approved revision.  
 Printed or electronically transmitted copies are uncontrolled.

**Table 3. Example Preparation of PDS Standards i for Analyses of Low-Level Soils and Solids**

PDS Name	SSS Mix Used				Methanol	PDS description		
	Source/catalog#	Analytes	Conc. µg/mL	Volume µL	Volume mL	Conc. µg/mL	Final Volume mL	Application
PDS	Restek/30205	Unleaded Gasoline Composites	50000	200	1.8	5000	2.0	ICAL
PDS	Restek/30205	Unleaded Gasoline Composites	50000	20	1.98	500	2.0	ICAL, CCV, LCS/LCSD, MS/MSD
PDS	In House	Unleaded Gasoline Composites	500	200	1.8	50	2.0	ICAL
SS	S Restek 30049	1,2-Dichlobenzene-D4	2000	1000	9	200	10	All Samples, QC
								& Standards
SCV-PDS	SpexCertiPrep SR-G-20K	Regular Unleaded Gasoline Unweathered	20000	50	1.95	500	2.0	SCV

**Table 4. Example Preparation of Aqueous Working Standards**

Working Standard Name	WS Conc. (µg/L) GRO C6-C10	Vol (µL)				Final Volume Water (mL)
		PDS Conc.			SCV	
		50ug/ml	500ug/ml	5000ug/ml	5000ug/ml	
Cal 1	20	20			-	50.0
Cal 2	50	-	5		-	50.0
Cal 3	100	-	10		-	50.0
Cal 4	250	-	25		-	50.0
Cal 5	500	-	50		-	50.0
Cal 6	1000	-		10	-	50.0
Cal 7	2500	-		25	-	50.0
Cal 8	5000	-		50	-	50.0
Cal 9	7500	-		75	-	50.0
Cal A	10000	-		100	-	50.0
SCV	1000				10	50.0
CCV	1000	-		10	-	50.0
LCS	1000	-	20	10	-	50.0

**Table 5. Example Preparation of Working Standards for  
 Analyses of Low Level Soil/Solids**

Working Standard Name	WS Conc. (µg/kg) Analytes	Vol (µL)				Mass Sand (g)	Vol 20% NaHSO <sub>4</sub> (mL)
		PDS-50ug/ml	PDS 500 ug/ml	PDS 5000 ug/ml	SCV/PDS -500 ug/ml		
Cal 1	50	5	-		-	5.0	5.0
Cal 2	100	10	-		-	5.0	5.0
Cal 3	250	25	-		-	5.0	5.0
Cal 4	500	50			-	5.0	5.0
Cal 5	1000		10		-	5.0	5.0
Cal 6	2500	-	25		-	5.0	5.0
Cal 7	5000	-		5	-	5.0	5.0
Cal 8	7500	-		7.5	-	5.0	5.0
Cal 9	10000			10			
SCV	1000	-			10	5.0	5.0
CCV	1000	-	10		-	5.0	5.0
LCS	1000	-	10		-	5.0	5.0

**Table 6. Recommended GRO Sample Preservation Techniques and Holding Times taken from SW 846 Method 5035A Appendix A**

Sample Matrix	Preservative	Holding Time	Comment
Aqueous Samples with No Residual Chlorine Present	1:1 HCL. Cool to 4+/- 2C.	-14days	Adjust the pH of all samples to < 2 at the time of collection by carefully adding two drops of 1:1 HCl for each 40 mL of sample. Seal the sample bottles, Teflon face down, and mix for 1 min...If-MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples. If aromatic and biologically active compounds are analytes of interest, acid preservation is necessary
Aqueous Samples with Residual Chlorine Present	Ascorbic Acid + 1:1HCl.Cool to 4 ± 2° C.≤ 6 °C-and adjust pH to less than 2 with HCl.	14days	Dechlorinate with 25mg of Ascorbic acid per 40ml sample vial. Adjust the pH of all samples to < 2 at the time of collection, but after dechlorination by carefully adding two drops of 1:1 HCl for each 40 mL of sample. Seal the sample bottles, Teflon face down, and mix for 1 min. <b>NOTE:</b> Do not mix the ascorbic acid with the HCl.in the sample bottle prior to sampling.
Acid reactive samples and samples where fuel oxygenate ethers may be of concern.	No preservation Cool to 4 ± 2° C.≤ 6 °C	7 days	If a sample foams vigorously when HCl is added, discard that sample. Collect a set of duplicate samples but do not acidify them. These samples must be flagged as "not acidified" and must be stored at 4°C or below. These samples must be analyzed within 7 days of collection if the sample is not biologically active.
Solid Samples <sup>2</sup>	Sample is extruded into a vial containing reagent water and 1 g NaHSO <sub>4</sub> and cooled to ≤ 6 °C.	14 days <sup>1</sup>	Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.
	Sample is extruded into a vial containing methanol and cooled to ≤ 6 °C.	14 days <sup>1</sup>	Additional methanol extract storage time beyond 14 days may be acceptable if the desired VOC constituent stability can be demonstrated from appropriate performance data.

**Table 7. Example EPA Method 8015D Analysis Sequence with QC and Instrument Calibration Frequency and Acceptance Criteria**

Analysis #	Sample Name	QC and Instrument Calibration Acceptance Criteria	QC and Instrument Calibration Frequency
	RT Marker	Used to define retention time range boundaries.	Set integration parameters from hexane to Decane for C6 to C10 range every 12 hours
2	Cal 1	1. Instrument Calibration must have %RSD $\leq$ 20%. or use regression fit with Coefficient of Determination $>$ 0.990, Minimum of 5 points for Average response. Six points for regression fit. If criteria not met, instrument maintenance performed. All calibration points are recalculated with the completed curve to return a concentration within 30% of the true value.	Analyzed anytime CCV fails criteria
3	Cal 2		
4	Cal 3		
5	Cal 4		
6	Cal 5		
7	Cal 6		
8	SCV	Resulting concentration must be 70% to 130% of true value. Surrogate must be within 30% recovery and retention time of surrogate must be within 0.5min of midpoint level.	Analyzed immediately after Cal curve
9	CCV	1. GRO result must be within 80% to 120% of true value. 2. Surrogate % Recovery must be within 20% and Retention time within 0.5 minutes.	Analyzed initially with each-batch, at the end of every sample run and at the start of every 12 hour work shift.
10	MB	Must be free from contamination that could prevent determination of GRO at the RL. Must be $<$ RL.	With every preparation batch of 20 or less samples.
11,12	LCS/LCSD	1. Percent Recovery of Target must meet in house or default 30% limits or data flagged. SS Percent Recovery must meet 30% limits or data flagged. 2. RPD must meet in house limits or 30% default limits.	1. LCS is analyzed with each batch of 20 of less samples. 2. LCSD analyzed only if no MS/MSD or sample duplicate is in batch
13	Sample 1	1. 30% Recovery limits or inhouse limits on surrogates or Data flagged. GRO results must be in calibration range.	
14	Sample 2 to n	n./= to 20	
15	MS	1. Percent Recovery of GRO meet in-house limits or 30% default limits or data flagged 2. SS Percent Recovery must meet in house limits or 30% default limits or data flagged.	Run with every batch of 20 samples.
16	MSD	1. Recovery results same as above. 2. Surrogate limits same as above. 3. RPD must be within 30% or data flagged.	Run with every batch of samples. Sample Duplicate or LCSD may be substituted for an MSD:-
17	CCV	Same as line 11.	All sample runs must be bracketed with a CCV that passes acceptance criteria.

**Table 8. Example Purge and Trap Parameters for GRO Analysis**

GC/FID Settings for EPA Method 8015D GRO			
Archon Autosampler		Eclipse Purge and Trap	
Water Only	Soil Only	Trap:	#10
Standard 1 Only	Standard 1 Only	Purge Flow rate:	40 mL/min
Desorb 0.7 min	Desorb 0.7 min	Purge Time:	11 min
Sample Vol 5 mL	Sample Heat: 40 °C	Sample Temp.:	45°C
Rinse Vol: 17 mL	Stir: Yes	Mount Temp:	45°C
Standard 1: Yes	Standard 1: Yes	Dry Purge:	0 min
Standard 2: No	Standard 2: No	Desorb Preheat:	180 °C
	Fill volume: 5 mL	Desorb:	190 °C for 0.7min
		Bake:	210 °C for 9min
		Transfer Line:	140 °C

**Table 9. Example GC 6890 Parameters for GRO Analysis**

INSTRUMENT CONTROL PARAMETERS: APL02C	
6890 GC METHOD	
Control Information	
Sample Inlet: GC	
Injection Source: External Device	
<b>OVEN</b>	<b>FRONT INLET</b>
Initial temp: 50 °C (On)	Mode: Split
Initial time: 0.00 min	Initial temp: 125 °C (Off)
Ramps:	Pressure: 5.31 psi (Off)
# Rate Final temp Final time	Split ratio: 1:1
1 10.00 100 1.00	Split flow: 1.0 mL/min
2 40.00 220 5.00	Total flow: 5.1 mL/min
3 0.0(Off)	Gas saver: Off
Post temp: 220 °C	Gas type: Helium
Post time: 0.00 min	
Run time: 14.00 min	
Maximum temp: 280 °C	
Equilibration time: 0.50 min	

<b>INSTRUMENT CONTROL PARAMETERS: APL02C</b>	
<b>BACK INLET</b>	<b>COLUMN 2</b>
Mode: Split	Capillary Column
Initial temp: 185 °C (On)	Model Number: Restek 10990
Pressure: 12.26 psi (On)	RTX-VOLATILES
Split ratio: 100:1	Max temperature: 280 °C
Split flow: 99.8 mL/min	Nominal length: 30.0 m
Total flow: 103.8 mL/min	Nominal diameter: 250.00 um
Gas saver: Off	Nominal film thickness: 1.00 um
Gas type: Helium	Mode: constant flow
	Initial flow: 1.0 mL/min
	Nominal init pressure: 12.27 psi
<b>COLUMN 1</b>	Average velocity: 26 cm/sec
None	Inlet: Back Inlet
FRONT DETECTOR (NO DET)	Outlet: Back Detector
	Outlet pressure: ambient
<b>THERMAL AUX 2</b>	
Use: MSD Transfer Line Heater	BACK DETECTOR (FID)
Description:	Temperature: 250 °C (On)
Initial temp: 150 °C (Off)	Hydrogen flow: 30.0 mL/min (On)
Initial time: 0.00 min	Air flow: 300.0 mL/min (On)
# Rate Final temp Final time	Mode: Constant makeup flow
1 0.0(Off)	Makeup flow: 25.0 mL/min (On)
	Makeup Gas Type: Helium
<b>SIGNAL 2</b>	Flame: On
Data rate: 20 Hz	Electrometer: On
Type: back detector	Lit offset: 1.0
Save Data: On	
Zero: 0.0 (Off)	
Range: 0	
Fast Peaks: Off	
Attenuation: 0	

**Table 10. Method 8015D Method Acceptance Criteria**

Item	Measure	Action
Initial Calibration (ICAL)	Average Response Factor > 20.0 % RSD	Evaluate points in the curve for use of linear or quadratic regression ( $r^2$ must be $\geq 0.990$ ). Also evaluate upper and lower points for removal. Criteria still not met perform instrument maintenance and/or recalibrate.
ICAL Point Eval	Not within $\pm 30$ % of True Value	Recalibrate if % deviation or bias is not met and compound.
Second Source Calibration Verification (SCV)	Not within $\pm 30\%$ of true value for deviation or drift	Recalibrate if % deviation or drift is not met.
Continuing Calibration Verification (CCV)	No greater than 20% Drift	Evaluate the system for problems, correct method or standard, perform routine maintenance, etc. Reanalyze standard and if failure repeats, then analyze a new ICAL All samples must be bracketed by a passing CCV.
Method Blank	No detection of GRO above reporting limits.	If the associated samples are non-detect, no action is required. If GRO is detected in the sample, flag with a "b" or reanalyze. If the GRO level in the sample is 10 times or greater than the blank contamination, the results are not affected. Locate the source of the contamination.
Laboratory Control Spike (LCS)	% Recovery. Laboratory acceptance criteria are evaluated every six months. Acceptable values are stored in LIMS. Default acceptance limit is 30% in the absence of sufficient data to calculate limits.	If the LCS % Recovery is high and the sample is non- detect, no action is required. If the LCS is high and the sample has detects, reanalyze the sample. If the LCS is low, the sample(s) should be reanalyzed.
Laboratory Control Spike Duplicate (LCSD)	Same criteria as the LCS with the addition of RPD. RPD should be no greater than 30% or as calculated based on lab performance.	% Recovery same as the LCS. If the RPD value is above the acceptance criteria, then evaluate the system for possible problems. Reanalyze samples as necessary.
Matrix Spike(MS)	Recovery are evaluated every six months. Acceptable values are stored in LIMS. Default acceptance limit is 30% in the absence of sufficient data to calculate limits.	If the % Recovery is outside laboratory acceptance criteria, evaluate the LCS. If the LCS is in control, then there is a possible matrix effect. The sample should be flagged appropriately.
Matrix Spike Duplicate (MSD)	Same criteria as the MS with the addition of RPD. Acceptance criteria are evaluated every six months with values stored in LIMS. Default acceptance limit is 30% in the absence of sufficient data to calculate limits.	% Recovery same as the MS. If the RPD value is above the acceptance criteria, then evaluate the system for possible problems. Reanalyze the MS/MSD samples if possible or flag the results.
Surrogate(s)	Laboratory acceptance criteria are evaluated every six months. Acceptable values are stored in LIMS–Default acceptance limit is 30% in the absence of sufficient data to calculate limits.	If the % Recovery is outside <del>laboratory</del> acceptance criteria on a QC sample, evaluate the system. Surrogate recalibration may be necessary. Reanalyze the QC samples.
		If the % Recovery is on a client sample, reanalyze. If the % Recovery is within criteria, report the sample within limits. If the % Recovery outside criteria is confirmed, there is a matrix effect. Flag the results as estimated and report both results.

**Figure 1. Example Auto Integration Parameter File**

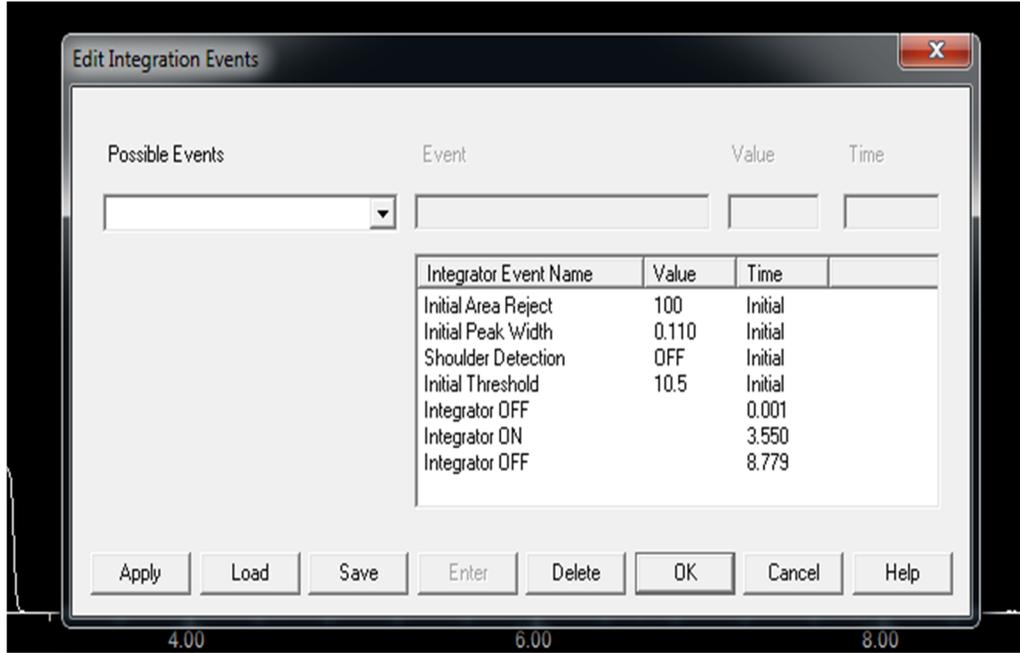


Figure 2. FID Chromatogram of a 1000ug/L Gasoline Standard

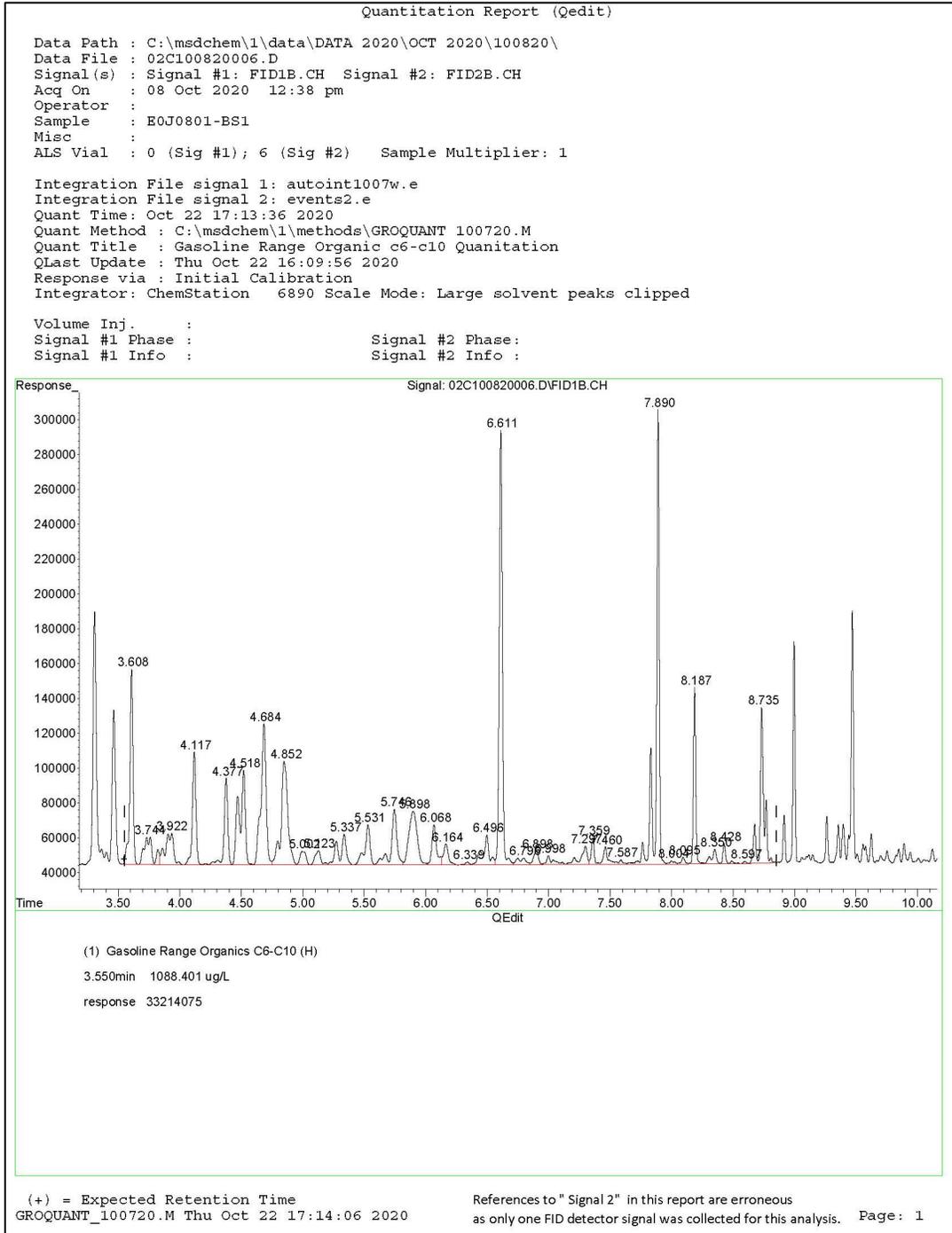


Figure 3. Example GC-FID Data Review Form

PHILIS Program 

---

**DATA REVIEW FORM – GC/FID**

Instrument and Date: \_\_\_\_\_ Sequence #: \_\_\_\_\_  
 Analysis:  GRO  DRO  Other \_\_\_\_\_

	Yes	No	Peer Rvw	QA Rvw	Comments
<b>Analyst Report</b>					
PHILIS narrative is complete	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Reported data matches the raw data	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Reporting limits and qualifiers are correct	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
<b>Sample Receiving</b>					
Samples received in acceptable condition and compliant with COC	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Samples properly preserved	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Sample receipt checklist filled out	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
<b>Instrument Calibration</b>					
A minimum 5 point calibration curve is generated for average response or linear regression	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Quadratic regression requires a minimum of six points	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
The %RSD of Response Factors is $\leq 20\%$ or curve fit meets criteria of $COD \leq 0.990$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Do the reporting limit and midpoint levels return a value within 30% of true value when quantified with the curve	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
SCV is within 30% of true values for deviation or drift	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Are integrations consistent and free from baseline bias	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Are all samples and QC bracketed by a CCV which meets 20% drift criteria	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Does CCV analysis fall within a 12 Hour time window	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
<b>Method Blank</b>					
Analyses detected at or above their reporting limits are flagged	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
<b>Samples</b>					
Samples prepared and extracts analyzed within holding time limits	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Target compound report included and Chromatograms provided	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Manual integration/Q-Deletion initialed and dated by analyst and reviewer	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Has the chromatogram been assessed for product match and documented	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Calculations have been verified—see calculations sheet	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
<b>Surrogate</b>					
Surrogate recovery meets acceptance criteria	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Sample results are properly flagged	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
<b>Preparation batch summary</b>					
All samples are accounted for	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Results reflect sample mass/volume prepared	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Solid results are provided dry weight basis	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
<b>Matrix spike/matrix spike duplicate</b>					
MS/MSD percent recoveries are within limits	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Relative percent differences are within limits	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Sample results been flagged appropriately	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
<b>Laboratory control spike/laboratory control spike duplicate</b>					
LCS/LCSD recoveries are within limits	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Relative percent differences are within limits	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Have sample results been flagged appropriately	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	

Analyst review signature \_\_\_\_\_ Date \_\_\_\_\_ Peer review signature \_\_\_\_\_ Date \_\_\_\_\_ QA review signature \_\_\_\_\_ Date \_\_\_\_\_

PHILIS Form ID#: QA-022 / Release Date: 09/18/2023

**\*\*\* *This Page Intentionally Blank* \*\*\***