STANDARD OPERATING PROCEDURE

FOR

DIESEL RANGE ORGANICS BY METHOD 8015D

PHILIS SOP L-A-205 Rev. 1

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PREPARED BY

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U.S. Environmental Protection Agency
Office of Emergency Management
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Revision History

Revision	Name	Date	Description of Change
A	James Travis	04/01/2021	Transitional Issue
0	James Travis	03/21/2022	Program Issue
1	James Travis	04/12/2023	Annual Review

SOP REVISION FORM

SOP Name:	**Diesel Range Organics by Method 8015D**		
Purpose: *(Review or Revise)*	*SOP #:*	*Rev. #:* *(Being Reviewed or Revised)*	*Origination / Release Date:*
Annual Review	*SOP No. L-A-205*	0	04/05/2022
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For *Revision* : Summary of Revisions (specify sections)

Signature Page	Changed Project Manager to Program Manager
Document	Updated section headings to current format
9.2.1.1 & Table 4	Added ½ the RL
13.12.2	Changed to the appropriate review form # QA-022

For *Review*: Comments

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Diesel Range Organics by Method 8015D
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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 3510C Rev. 3 dated May 2003 and EPA method 3545A Rev. 1 dated February 2007 for the qualitative and quantitative determination of Diesel Range Organics in the C10 to C28 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 Diesel 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

1.3 DRO corresponds to the range of alkanes from C10 to C28 and covering a boiling point range of approximately 170ºC - 430ºC. This SOP is applied for DRO from a variety of matrices as specified in section 2.0.

1.4 This method may be applicable to other petroleum based liquid products, fuel types and petroleum hydrocarbons other than those listed in Secs. 4.1 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. Expansion of this method to other fuel types or petroleum hydrocarbons will also require that the boiling point range or carbon number range of the material be carefully defined, and the quantitation approach be modified to match such ranges. Analysts are advised to consult authoritative sources, such as the American Petroleum Institute (API), for appropriate definitions of other fuel types or petroleum fractions.

2.0 Summary of Method

2.1 This method provides gas chromatographic conditions for the detection of Diesel Range Organics (DRO). Detection is achieved by a flame ionization detector (FID). The GC columns and conditions listed have been demonstrated to provide separation of those target analytes. Other columns and conditions may be employed, provided that the analyst demonstrates adequate performance for the intended application. Given the large number of components to be separated, fused-silica capillary columns are necessary for the analysis of DRO.

2.2 Soil or solid samples are extracted using pressurized solvent extraction (PSE).

2.3 Aqueous samples are extracted with methylene chloride using separatory funnel extraction. The extract is typically concentrated to 1mL before injection into the GC. Other final volumes for extract concentration are allowed based on data requirements.

3.0 Definitions

3.1 Batch‡: 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.

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

3.2 Chain of Custody (COC)‡: 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)∓: (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 or fortified sample)∓: 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)‡: 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)‡: 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.

╪ EL-V1M2-ISO-2016, 2016 NELAP Standard definition.

4.0 Interferences

4.1 Samples for DRO are susceptible to laboratory chemical contaminants which may elute during the diesel range and create high bias.

4.2 The quantitative analysis of DRO are based on the procedures described in Sec. 14. The identification of specific fuel types may be complicated by environmental processes such as evaporation, biodegradation, or when more than one fuel type is present. Methods from other sources may be more appropriate for DRO, since these hydrocarbons are not regulated under RCRA. Consult State and local regulatory authorities for specific requirements.

4.3 Carryover contamination may occur when a sample containing low levels of DRO are analyzed immediately following a sample containing high levels of DRO. If this situation occurs during a non-monitored analysis, the sample containing the low concentration DRO 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

4.4 Other contamination or interferences could be present in laboratory glassware, chemicals, and reagents used.

4.5 A wide range of constituents may elute in the diesel range. Other classes of compounds which may not be diesel fuel include halogenated organics, pesticides, phthalates or the other products which may significantly contribute to the total detection of organics in the range of interest creating a high bias. Weathering 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 DRO 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.

4.6 Baseline fluctuations 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 autointegration 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 Laboratory personnel are required to be familiar with the general laboratory safety including the location and proper use of safety/emergency equipment.

5.3 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.

5.4 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.

5.5 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.

5.6 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.

5.7 Petroleum products are flammable. 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.

5.8 Hydrogen is generated for use in the FID, it is a highly flammable gas. Monitor for leaks in instrumentation or delivery lines and avoid use of heat sources, sparks or open flames in the SLA laboratory where hydrogen is in use.

6.0 Equipment and Supplies

6.1 Glassware

6.1.1 5 mL, 40 mL, or 60 mL vials are used for storage of standards and spiking solutions.

6.1.2 Disposable Pasteur pipettes.

6.1.3 Volumetric Flask- Class A, various sizes.

6.1.4 Small glass vials (1mL or 2 mL) are used for storage of sample extracts, calibration standards and stock standards.

6.1.5 Gas-tight micro syringes- various sizes for transferring the concentrated extracts, diluting samples, adding internal standards to extracts, and preparing calibration standards.

6.2 Solvents

6.2.1 Acetone—Capillary GC, GC/MS, pesticide or equivalent grade.

6.2.2 Methylene Chloride—Capillary GC, GC/MS, pesticide or equivalent grade.

6.3 Instrumentation

6.3.1 Gas chromatograph: analytical system, complete with a temperature-programmable gas chromatograph suitable for solvent injections, equipped with all necessary accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

6.3.2 Column: RXI-5 Sil MS 30m x 0.25mm ID, 0.25-µ m film thickness fused silica capillary column coated with 1,4-bis(dimethylsiloxy)phenylene dimethyl polysiloxane (RESTEK cat. 13623) or equivalent.

6.3.3 Auto sampler: Hewlett Packard HP 6890 or equivalent.

6.3.4 Data System: The data system is equipped with the Agilent Chemstation software for data acquisition, Enviroquant for data processing. Other equivalent software may be used.

6.3.5 Detector: Flame Ionization Detector (FID) Agilent part # AG-7890-8015 or equivalent.

6.3.6 Hydrogen Generator/Air Compressor FID1000 Parker/Balston/Thomas lT617-HDN.

6.3.7 Syringe: 10 µL Agilent syringe, or equivalent.

7.0 Reagents and Standards

Note: Original containers of reagents shall be labeled with expiration dates in accordance with the OSHA Hazard Communication Program. All containers of prepared reagents must bear a name, preparation date, and must be linked to the preparation records.

7.1 Reagents

7.1.1 Reagent water can be Milli-Q water, distilled water or any other water provided no interferences are noted.

7.1.2 Reagent soil is TCL-free sand is used for QC samples. Ottawa Sand that has been processed through the Fast PSE may also be used for QC samples.

7.1.3 Helium carrier gas is 99.999% (UHP) or greater such as Research Grade, 99.9999%.

7.1.4 Nitrogen- gas is 99.999% (UHP) grade.

7.2 Standards

7.2.1 Stock solutions may be prepared from pure standard materials or purchased as certified solutions stock standards.

7.2.2 Diesel Fuel # 2: 20,000 ug/mL (SPEX S-DF2-20K).

7.2.3 O-Terphenyl: 10,000 ug/mL (Restek # 31097).

7.2.4 Second source: Diesel Fuel # 2 10,000 ug/mL (Restek # 31233 or equivalent).

7.2.5 Retention marker standard solution: Standard mix containing at least Decane and Octacosane, DRO Mix 2,000 ug/mL (Restek # 31064 or equivalent).

7.2.6 Calibration standards. A minimum five-point calibration curve is prepared for establishing average response factors or linear regression curve fitting. The stock standard solutions are used to prepare the calibration curve. Six calibration points are required for quadratic (second-order) curve fits. The low point of the calibration curve must be equal to or less than the reporting limit. The high standard defines the calibration range. See Table2 below for the preparation of the ICAL levels. Other amounts of the standards listed below may be used based on the sensitivity of the instrument.

7.2.7 Laboratory Control Spiking Solution: The DRO and surrogate stock solution are used for spiking the Laboratory control sample thus there's no need to prepared secondary dilutions.

7.2.8 Matrix Spike Solution: Matrix Spike samples are prepared with the stock solutions as well.

8.0 Sample Collection, Preservation, and Storage

8.1 Samples are collected by field sampling teams in 1000-mL amber bottles or 8-oz amber jars and are put on ice to maintain a temperature of ≤ 6°C and submitted to the laboratory. See SOP sample login procedures, for sample acceptance criteria. Other containers may be used provided the size is adequate for the reporting limits required, are clean, and do not add any interferences.

8.2 Samples received on the collection day shall be considered acceptable if there is evidence that the chilling process has begun such as arrival on ice. In such cases, sample temperatures that are in excess of 6 °C upon receipt are acceptable.

8.3 Samples are maintained at the temperature of ≤ 6 °C.

8.4 Sample extraction holding time is 7 days for aqueous samples and 14 days for soil samples.

9.0 Quality Control

QC requirements include the Initial Demonstration of Capability and ongoing QC requirements that must be met when preparing and analyzing samples.

9.1 Initial Demonstration of Capability (IDOC) is an evaluation that must be successfully performed by an 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

9.1.1 Method precision and accuracy is demonstrated by analyzing four (4) replicate LCSs fortified at a known concentration (e.g. 500µg/mL) typically around the midpoint of

the calibration. Calculate the average recovery and the standard deviation of the recovery for each analyte of interest using the four results.

9.1.2 MDLs are established by analyzing a minimum of seven replicates of a known concentration and a minimum of seven blanks over a three day period.

9.2 Ongoing QC is applied when performing this method and includes analyzing an acceptable instrument calibration, verification standard, MB, LCS, MS, MSD, with samples. Every batch must contain at least one MB, LCS, MS, and MSD. If there is not enough volume for an MS/MSD pair, then a sample DUP or an LCSD must be performed for precision data Control Limits.

9.2.1 Method Blank: For aqueous samples, the method blank is reagent water, and for soil samples it is Ottawa sand or an analyte-free sand. The method blank is free of the analytes of interest and is spiked with the surrogates. At least one method blank must be prepared with every batch.

9.2.1.1 Acceptance Criteria: The result for the method blank must be less than 1/2 the RL or less than 10% of the analyte concentration found in the associated samples, whichever is higher, to report definitive results.

9.2.1.2 Corrective Action: If a compound fails to meet these criteria, the lead chemist will be informed. In general, batch samples, other than those that are non-detect for the contaminant compounds will be re-extracted. However, if the analyte in the method blank was not detected in any of the associated samples, the data can still be reported, but flagged accordingly.

9.2.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix..

9.2.2.1 Acceptance Criteria: All analytes must be within the control limits to report definitive data. Example control limits are in Table 4.

9.2.2.2 Corrective Action: If any analyte in the LCS is outside the established control limits, a corrective action must be performed. A corrective action may consist of a data evaluation to determine the effect on data, to complete re-prep and reanalysis. All corrective actions must be documented.

9.2.2.3 If the batch is not re-extracted or re-analyzed, the reasons for accepting the batch must be clearly presented in the report. An example of acceptable reasons for this might be that the MS/MSD are acceptable and sample surrogate recoveries are within control limits, showing that the problem was just on the LCS. This is also applicable if the analyte that failed is not a target analyte for the project, or if the analyte recovered above the control limit, but was not detected in the associated samples.

9.2.2.4 If re-extraction and re-analysis of the batch are not possible due to limited sample volume, the LCS is reported, all associated samples are flagged accordingly, and the appropriate comments are made in the report.

9.2.3 The matrix spike is a second aliquot of one of the samples in the batch, and the matrix spike duplicate is a third aliquot of the same sample. The MS/MSD are spiked with the same analytes and concentration as the LCS. The MS and MSD samples are prepared with every batch.

9.2.3.1 Acceptance Criteria: The percent recovery must be within the control limits. The RPD for the pair must be less than or equal to the control limit.

9.2.3.2 Corrective Action: If the recovery or RPD of an analyte is outside of its control limits, or if an RPD fails, then a corrective action must be performed. Typically, if the recoveries of the MS/MSD are similar but not within control limits and the recoveries of the LCS are within control limits, then the analysis can continue. This is documented as matrix interference.

9.2.3.3 If there are recovery failures in the MS/MSD and the LCS, then the batch must be reextracted and/or re-analyzed. Or, all associated data must be qualified and a reason must be included in the data package detailing the batch was not re-extracted and reanalyzed.

9.2.3.4 If re-extraction is not possible due to limited sample volume, then a duplicate LCS (LCSD) must be run with the re-extraction batch. The RPD of the LCS/LCSD must be less than or equal to the established control limit.

9.2.4 Control limits are determined for surrogates, laboratory control samples, matrix spike samples and precision and accuracy. Limits can be calculated when 15 – 20 data points are available and monitored every 20 – 30 data points thereafter. They should be evaluated at least every 6 months. The recovery limits are the mean recovery ±3 standard deviations for surrogates, MS, and LCS. Precision limits for the MS/MSD or LCS/LCSD pair are the absolute value of the mean relative percent difference (RPD) ±3 standard deviations.

9.2.5 All surrogates, LCS, and MS recoveries (except for dilutions) must be entered into Element so that historical control limits can be generated. For multiple dilutions, reported from the same extract, surrogates will be reported for all dilutions of less than 4x.MDL Procedure

9.3 MDLs and RLs are established by analyzing a minimum of seven replicates of a standard at or near the estimated MDL. Tabulation of results and MDL calculations are performed by the method in 40 CFR, Part 136, Method Update Rule Revision 2.

9.3.1 Initial MDLs are established by analyzing a minimum of seven replicates of the low-level calibration standard and a minimum of seven blanks prepped and analyzed over three separate days. The MDL should be spiked 1 to 5 times the estimated MDL. Extract and analyze the MDL standards and blanks with the same procedure as regular samples.

9.3.2 For each compound, calculate the mean and standard deviation of the replicates in micrograms per liter (µg/L). Then calculate the MDL by multiplying the standard deviation by the Student's t value. The one sided (single-tailed) Student's t values at the 99% confidence levels are used (e.g., t = 3.143 at the 99% confidence level for n = 7). MDL studies are repeated annually and verified each time they are prepared. MDL results are stored in Element each time they are calculated. This calculation must be performed separately for the spikes and blanks. The larger of the two values will be used.

9.3.3 Ongoing MDLs are determined by preparing and analyzing two spiked standards at 1-5 times the estimated md and two blanks once per quarter for a minimum of seven determinations. The blanks and spikes may be analyzed in the same prep batch, but is not required. If the instruments are being used regularly, the mdl spikes may be added to the routine batches and the regular blanks used. All blanks analyzed during the evaluation period should be used.

9.4 Example detection limits for DRO as determined by EPA Method 8015D are listed in Table 1.

10.0 Calibration and Standardization

Prior to the analysis of samples, performance of the instrument is optimized, and an instrument calibration curve is developed.

10.1 GC Conditions. Establish the GC operating conditions appropriate for the GC column being utilized and the target analytes specified in the project plan. Optimize the instrumental conditions for resolution of the Diesel Range Organics and sensitivity. Suggested operating conditions are given below in table 3. The column listed in section 9.3.2 was the column used to develop the method performance. PHILIS may use this columns or other columns provided that they document method performance data (e.g., chromatographic resolution and sensitivity) that meet the data quality needs of the intended application.

10.2 Retention time marker. The calibration of DRO is markedly different from that for single component analytes. In particular, the response used for calibration must represent the entire area of the chromatogram within the retention time range for the fuel type, including the unresolved complex mixture that lies below the individual peaks. The retention time range for DRO is defined before the initial calibration. The range is established by injecting a Retention time marker standard (section 10.2.5) using the retention times of the C10 and C 28 alkanes. A retention time marker must be analyzed at a minimum of every twelve hours or with each analytical batch.

10.3 Initial Calibration.

10.3.1 A minimum five-point calibration curve is prepared. This is valid for average response factors or linear regression curve fitting. A minimum of six calibration points is required for quadratic curve fits. The low point of the calibration curve must be at or below the reporting limit. The high standard defines the range of the calibration. See Tables 8 and 9 for the preparation of the ICAL levels.

10.3.2 Acceptance criteria for the Instrument Calibration and CCVs, and the required frequency of their analysis are summarized in Table 4.

10.3.3 Rejection of Calibration Points

10.3.3.1 It is not generally acceptable to remove internal points from a calibration. Typically, instrument maintenance and the accuracy of the calibration standards should be examined if the calibration acceptance criteria are not met.

10.3.3.2 If no problems are found, then a point can be rejected as long as it meets the following criteria: The rejected point is the highest or lowest point in the ICAL. This may be done by analyte. An internal calibration point may also be removed if the reason is obvious. Examples are; a bad injection, detector flame out, gross contamination, etc. In these cases, the entire point, including all analytes, must be removed and the reason documented.

10.3.4 The lowest remaining calibration point is still at or below the reporting limit. If the calibration point is higher, then the reporting limit must be raised.

10.3.5 The highest remaining calibration point defines the upper concentration of the working range, and all samples above this concentration must be diluted and reanalyzed.

10.3.6 The calibration must still have the minimum number of calibration levels required by the method. [Five levels for average response factors and linear curve-fits, six levels for quadratic (second-order) curve-fits].

10.3.7 Analyze each calibration level. Calculate the response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in the calculation section of this SOP. Samples may not be analyzed unless the ICAL meets the following criteria:

10.3.8 The RSD must be < 20% for each compound and surrogate.

10.3.9 If the RSD for a compound in the initial calibration is >20%, then the calibration points may be fit to a linear or a nonlinear curve, such as a second-order polynomial. A curve fit should not be employed in lieu of the average RF to compensate for instrumentation problems or needed maintenance.

10.3.10 Linear curve-fits may be used if there are five (5) or more ICAL levels. Quadratic (second-order) curve-fits may be used if there are 6 or more ICAL levels. The use of a weighted linear regression is recommended to improve accuracy of quantitation at the low end of the curve. Curve-fits can be used if it is determined that the curve will generate accurate results across the calibration range. If a curve-fit is used, a requantitation of the low point of the ICAL against the ICAL must show acceptable accuracy.

10.3.11 If a linear curve-fit is used, the coefficient of determination (r^2) must be greater than 0.990. For quadratic curve-fits, the intercept and degree of curvature should be examined to be sure that the results will be reliable throughout the working range and the coefficient of determination is greater than 0.990. There must not be two levels that would produce the same value. Quadratic curve-fits should not be used to compensate for detector saturation or to avoid proper instrument maintenance.

10.3.12 The second source calibration verification (SCV) standard, made from a different source than the ICAL (an alternate vendor or a unique lot from the same vendor) must be analyzed immediately after the calibration. The value determined from the second source check should be within 30% of the expected concentration. An alternative recovery limit may be appropriate based on the desired project-specific data quality objectives.

10.3.13 Weighting of Calibration Data Points. In a linear regression curve-fit, the lower points of the ICAL have a significant bias over the higher points in determining the generated curve. This is not seen in quadratic regression. However, in environmental analysis, accuracy at the low end is very important. For this reason, it is preferred that the weighting of the lower concentrations is increased. 1/Concentration^2or 1/Concentration weighting will improve accuracy at the low end of the ICAL and should be used for curve-fits. All compounds using linear or quadratic regression must have the low point quantitated against the curve and the resulting value must be within 30 % of the true value. Quantitation is performed using the calibration curve or average response factor from the initial curve, not the continuing calibration.

10.3.14 Continuing calibration verification. The initial calibration and retention times must be verified at the beginning of each 12-hour work shift, at a minimum. Verification is accomplished by the measurement of the fuel standard and the hydrocarbon retention time standard. Additional analyses of the Calibration verification standard throughout a 12-hour shift and at the end of the sequence are required.

11.0 Procedure

11.1 Sample extraction

11.1.1 See extraction SOP's L-P-101 and L-P-200 for extraction procedure.

11.2 Sample Preparation

11.2.1 Remove samples from the laboratory refrigerator.

11.2.2 Verify that the samples 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.

11.2.3 Batch up to 20 environmental samples for extraction.

11.2.4 For samples to be analyzed as MS/MSD follow the procedure below: The client must provide enough volume for a parent sample and the MS/MSD. If performing a 1L extraction, this means the client must provide 3L of sample.

11.2.5 For the MS/MSD samples, transfer the samples into their appropriately marked containers (1L bottles, 40mL VOA vials, or PSE metal tubes).

11.2.6 Spike the MS/MSD with the appropriate amount of surrogates and spikes.

11.2.7 Refer to the extraction SOPs for the preparation procedures.

11.3 Standard Preparation

11.3.1 Follow the example procedure listed in Table 2.

11.4 Sample Analysis

11.4.1 Analysis is performed using an automated injection GC/FID instrument.

11.4.2 In Chemstation (or Gerstel software), load the sequence from the previous run and enter in the sequence information for the day. A typical sequence will have one or two rinses, a retention time standard, the CCV, an instrument blank, the QC's from the batch, then the samples and a closing CCV. If the samples being analyzed are suspicious or possibly high of non-target analytes, running a rinse pattern of MeOH and MeCl2 at the end of the sequence will help maintain the quality of your instrument.

11.4.3 All samples must be analyzed using the same GC conditions as the preceding CCV analysis.

11.4.4 Inject 1µL of the extract using the sample injection technique as used for the standards.

11.4.5 The data system will determine the concentration of each analyte in the extract using calculations in Section 15. Quantitation is based on the initial calibration, not the continuing calibration verification.

11.4.6 Sample concentrations are calculated by comparing the sample response with the response from the initial calibration of the system. Therefore, if the sample response exceeds the limits of the initial calibration range, a dilution of the sample or sample extract must be analyzed.

11.5 Instrument Maintenance

11.5.1 Injection of sample extracts from waste sites often leaves a high boiling residue in the injection port area, splitters (when used), and the injection port end of the chromatographic column. This residue affects chromatography in many ways (i.e., peak tailing, retention time shifts, analyte degradation, etc.) and, therefore, instrument maintenance is very important. Residue buildup in a splitter may limit flow through one leg and therefore change the split ratios. If this occurs during an analytical run, the quantitative data may be incorrect. Proper cleanup techniques will minimize the problem and instrument QC will indicate when instrument maintenance is necessary.

11.5.2 Column rinsing - The column should be rinsed with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be acetone, followed by methanol; methylene chloride is a satisfactory final rinse and in some cases may be the only solvent necessary. The column should then be filled with methylene chloride and allowed to remain flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen passing through the column.

12.0 Data Analysis and Calculations

12.1 The C10-C28 fraction of diesel fuel in this method is the sum of all peaks between the leading edge of Decane and Octacosane. 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 uses throughout the entire calibration.

12.3 Save the integration parameter and choose this parameter file in "Set Up Quantitation". The compound type for DRO 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 DRO 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 DRO concentrations are calculated by the equations below:

12.5 Response factor (RF)

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

Where:
Ax = Area of the quantitation ion for the surrogate or compound being measured.
Cx = 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:

and

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

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

$$x_i = RF_i$$

12.8 Sample concentration using average response factor

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

Where:
Ax = area of quantitation ion for compound being measured
$(RF)^{-}$ = mean relative response factor for compound being measured
D = Dilution Factor
Cx = Concentration of the sample.

12.9 Data Qualification

12.9.1 While diesel fuel 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 DRO chromatogram. Figure 2 shows a typical chromatogram for diesel fuel. A wide range of constituents may elute in the DRO range. Other classes of compounds which may not be diesel include halogenated organics, phthalates, or complex chromatograms where more than one product is present may significantly contribute to the total detection of organics in the diesel range of interest creating high bias. Weathering of product may also create a positive or negative bias. Particular attention should be paid the chromatographic pattern to determine the usefulness of the data. Over laying the standard chromatogram with the sample chromatogram may be useful in determining a quality match for diesel fuel.

12.9.2 In water samples with floating product, the product phase will contain the overwhelming majority of the diesel range organics. The numbers generated for concentration represent the concentration only for that particular phase not the sample as collected. 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.

12.9.3 The QAPP should specify whether DRO reporting is to be done on an “as is” basis (reporting a DRO concentration regardless of the quality match) or whether positive detection for DRO is to be qualified and what criteria will be used to qualify the data.

13.0 Method Performance

Demonstration MDL data is presented in Table 1. 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.

Other specific Quality Assurance Objectives (QAO) may be found in the appropriate statement-of-work or Quality Assurance Project Plan (QAPP) for specific projects.

13.1 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-020, which is provided in Figure 2. The Quality Assurance Manager also reviews a minimum of 10 % of data to evaluate the QA process.

13.2 Analytical data generated by the instrument software is reviewed and evaluated by the analyst and peer as follows:

13.3 The instrument calibration relative response factor and percent relative standard deviation.

13.4 QA-QC check report for Percent recovery for the surrogate.

13.5 DRO percent recoveries CCV, LCS, SCV, MS, and RPD for MSD.

13.6 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 Table 4.

13.7 All DRO results are reported to LIMS.

13.8 All integrations must be performed in a consistent manner for all calibration standards, QC and field samples.

13.9 If the QAPP requires it, chromatograms of all field samples are examined for comparison to the product. Quality matching should be reported in a manner specified by the QAPP.

13.10 Discrepancies in the analytical run are documented on the "Data Review Form, QA-020F" and discussed with the Lead Chemist.

13.11 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.

13.12 All records derived from the analytical process are assembled in the analytical data packages that consist of:

13.12.1 Analytical run sheet.

13.12.2 "Data Review Form QA-022" signed by the Lead Chemist or designee.

13.12.3 QA-QC check report.

13.12.4 Quantitation Report for each Sample and QCS.

13.12.5 Evaluation reports for CCV, SCV, LCS/LCSD, and MS, MSDs.

13.12.6 Initial calibration form.

13.12.7 Low Level and Mid-level calibration standard quantitation showing calculated recovery of these standards using the initial calibration.

13.12.8 Example Calculations.

13.13 Data packages are assembled in PDF packages and are stored electronically. Electronic data, including reports are maintained on servers in multiple locations

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 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.

14.4 Corrective Actions for Out of Control

14.4.1 If the acceptance criteria listed in Table 4 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.

14.4.2 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.

14.4.3 The analyst shall report to the Lead Chemist and indicate on the "Data Review Form QA-020F" any out of control event. Such events include:

14.4.3.1 Damage to the sample.

14.4.3.2 Floating product in the sample.

14.4.3.3 Holding time exceeded.

14.4.3.4 Inadequate sample preservation.

14.4.3.5 Sample results exceeds the Agency's action limit

14.4.3.6 Samples do not reflect historical data.

14.4.3.7 Upward trending or sample results approaching interval warning limits.

14.4.3.8 Any obvious non-diesel peak present on the instrument generated chromatogram that will create significant bias to the DRO results.

14.5 The Lead Chemist will implement the corrective action plan described in the PHILIS corrective action plan document.

14.6 Contingencies for Handling Out of Control or Unacceptable Data

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

15.0 Waste Management

Waste management procedures are specified in the Hazardous Waste Management Plan and the SOP's for specific preparatory methods (3510C and 3445A). which are used to prepare samples for analysis of DRO by 8015D.

15.1 Additional waste specific to the analytical method would be expired standards, extracts and solvent rinse waste in addition to disposable glassware, chem wipes and gloves.

15.1.1 Disposable solid waste would be disposed as lab scraps in a five gallon pail.

15.1.2 Extracts and expired standards in vials would be disposed in a sealed and labeled metal can layered with absorptive material. Storage and final disposal of the collected waste would be in a tertiary containment vessel (5 gallon pail).

15.1.3 Solvent waste is decanted into a solvent carboy.

16.0 References

16.1 EPA Method 8015D Non-Halogenated Organics Using GC/FID, Revision 4, June 2003.

16.2 2016 NELAP manual.

16.3 40 CFR 136, Appendix B, Rev U.S. EPA Contract Laboratory Program Statement of Work OLM 04.2 Revision 2.0.

16.4 EPA Method 8000D, Determinative Chromatographic Separations, Revision 4, July 2014.

17.0 Tables, Figures, and Attachments

Table 1. Example MDLs and RLs Diesel Range Organics for Different Matrices

Matrices	Analyte	CAS#	MDL (mg/L) or (mg/Kg)	RL (mg/L) or (mg/Kg)
WATER	Diesel Organics Range C10-C28	68334-30-5	0.2	0.5
SOIL	Diesel Organics Range C10-C28	68334-30-5	0.9	1.67

Table 2. Example of Preparation of Calibration Standards

Calibration level	Concentration (ug/mL)		Vol used (uL)		Final vol (mL)
	DRO	O-Terphenyl	DRO	O-Terphenyl	
Cal 1	50	10	5	2	2
Cal 2	100	20	10	4	
Cal 3	250	40	25	8	
Cal 4	500	50	50	10	
Cal 5	1000	60	50	6	1
Cal 6	2500	80	125	8	
Cal 7	5000	100	250	10	

Table 3. Example GC Conditions

GC Conditions	
Inlet tem.	280 °C
Capillary Column	Restek RXI-5silMS, 30M length, 0.25mm ID, 0.25um film thickness
Column Mode	1.2 mL/min, constant flow.
Temperature Program	Initial tem = 60°C, hold for 2 min.
	12°C/min ramp to 275°C, hold 6 min.
	Run time = 25.95 min
Injection Volume	1 uL
Inlet mode	Split
Split Ratio	10:01
Split Flow	11.9 mL/min
FID Conditions	
Heater	250°C
H2 flow	30 mL/min
Air flow	300 mL/min
Make up flow	25 mL/min

Table 4. Method 8015D Method Acceptance Criteria

Item	Measure	Action
Retention Time Marker	Validates the integration stat and finish	If not within limits, then reset to the proper times.
Initial Calibration (ICAL)	Average Response Factor > 20.0 % RSD	Evaluate points in the curve for use of linear or quadratic regression (r2 must be ≥ 0.990). Also evaluate upper and lower points for removal. Criteria still not met perform instrument maintenance and/or recalibrate.
ICAL Low and Mid-Point Eval	Not within ± 30 % of True Value	Recalibrate if % deviation or bias is not met and compound.
Second Source Calibration Verification (SCV)	Not within ± 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 DRO above ½ the reporting limits.	If the associated samples are non-detect, no action is required. If DRO is detected in the sample, flag with a "b" or reanalyze. If the DRO 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 laboratory 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. Retention Marker Chromatogram

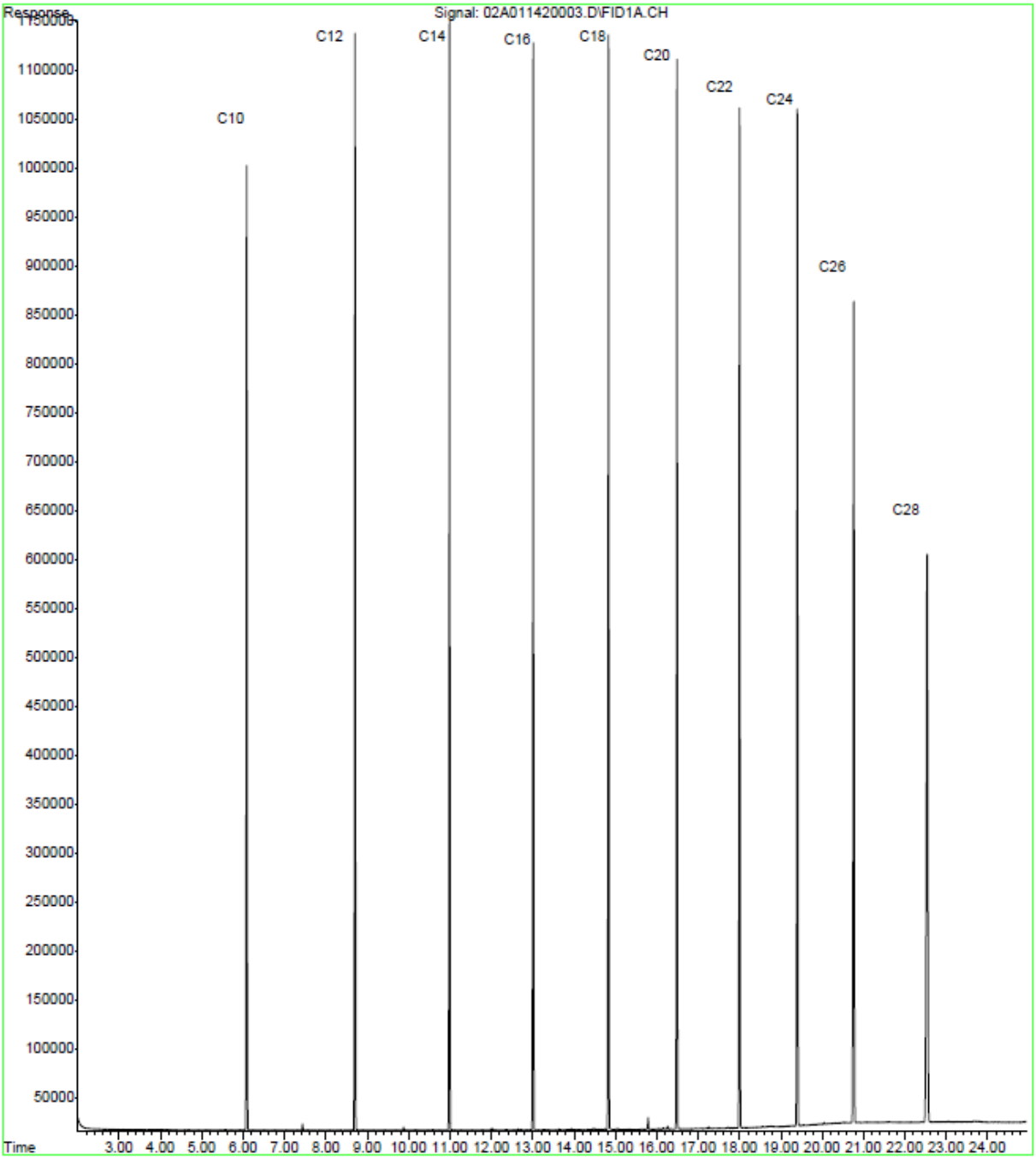
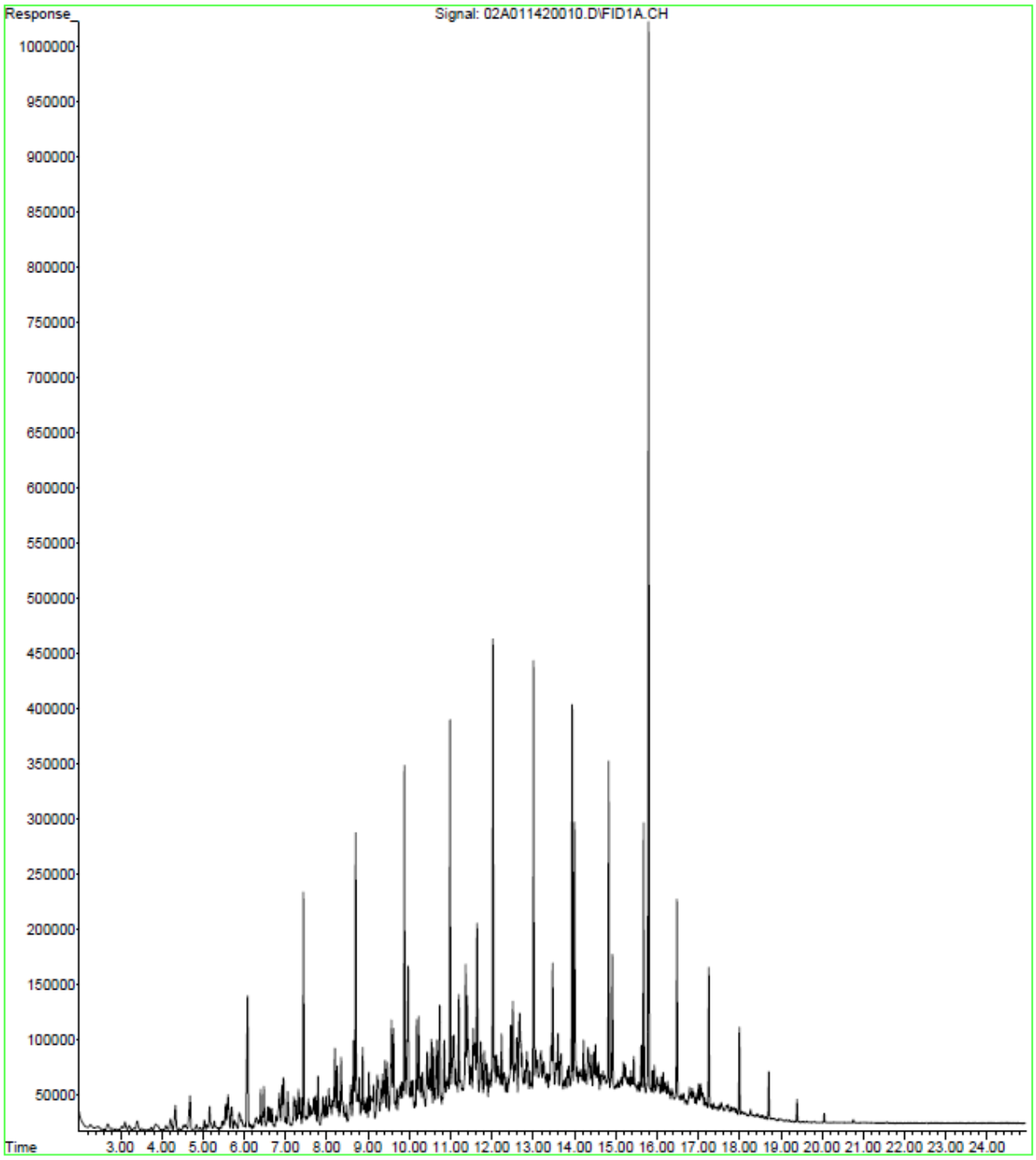


Figure 2. Chromatogram of a 500 ug/mL Diesel Standard



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