

Method 1663

Differentiation of Diesel and Crude Oil by GC/FID

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1. SCOPE AND APPLICATION

- 1.1** This method differentiates between diesel oil and crude oil in drilling muds and other sources by comparing the ratio of n-alkanes in the C₉-C₃₀ range as determined by gas chromatography (GC) with a flame-ionization detector (FID).
- 1.2** This method is for use in the Environmental Protection Agency's survey programs and may be used for compliance monitoring as part of the "Effluent Limitations Guidelines and New Source Performance Standards for the Offshore Subcategory of the Oil and Gas Extraction Point Source Category" [50 FR 34592].
- 1.3** For oil in drilling muds, this method is designed to be used in conjunction with the extraction procedure in EPA Method 1662.
- 1.4** This method cannot differentiate between mineral oil and diesel crude oil. EPA Method 1654A can be used to determine that the oil is not mineral oil by measurement of the polynuclear aromatic (PAH) content.
- 1.5** When used in conjunction with EPA Method 1662, the estimated detection limit for diesel or crude oil in drilling mud is 100 mg/kg, excluding interferences caused by other materials in the mud.
- 1.6** Any modification of this method beyond those expressly permitted shall be considered as a major modification subject to application and approval of alternative test procedures under 40 CFR 136.4 and 136.5.
- 1.7** The gas chromatography portions of this method are restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Each laboratory that uses this method must generate acceptable results using the procedures described in Sections 7.1, 8.2, and 12 of this method.

2. SUMMARY OF METHOD

- 2.1** An oil sample is diluted in methylene chloride. An internal standard is added and an aliquot is injected into a gas chromatograph (GC). The components of the oil are separated by the GC and detected by a flame-ionization detector (FID).
- 2.2** Identification of diesel oil or crude oil (qualitative analysis) is performed by comparing ratios of groups of n-alkanes.
- 2.3** Quantitative analysis is performed by calibrating the GC/FID with hexadecane using an internal standard technique. The calibration factor is then used to determine the amounts of the groups of n-alkanes. A quotient of these amounts establishes that the oil is diesel or crude.
- 2.4** Quality is assured through reproducible calibration and testing of the extraction and GC systems.

3. CONTAMINATION AND INTERFERENCES

- 3.1** Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms.
 - 3.1.1** All materials used in the analysis shall be demonstrated to be free from interferences by running method blanks initially and with a sample batch (samples started through the extraction process at the same time, to a maximum of ten). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.
 - 3.1.2** Glassware and, where possible, reagents are cleaned by rinsing with solvent or baking at 450°C for a minimum of 1 hour.
- 3.2** Interferences co-extracted from samples may vary from source to source, depending on the diversity of the site being sampled.

4. SAFETY

- 4.1** The toxicity or carcinogenicity of each reagent used in this method has not been defined. Therefore, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available.
- 4.2** The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety can be found in References 1 through 3.

5. APPARATUS AND MATERIALS

NOTE: Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance maybe achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance meeting the requirements of this method is the responsibility of the laboratory.

- 5.1** Equipment for glassware cleaning.
 - 5.1.1** Laboratory sink with overhead fume hood.
 - 5.1.2** Kiln: Capable of reaching 450°C within 2 hours and holding 450°C within ±10°C, with temperature controller and safety switch (Cress Manufacturing Co., Santa Fe Springs, CA. B31H or X31TS, or equivalent).
- 5.2** Equipment for sample preparation.
 - 5.2.1** Laboratory fume hood.
 - 5.2.2** Analytical balance: Capable of weighing 0.1 mg.
 - 5.2.3** Glassware.

- 5.2.3.1** Disposable pipettes: Pasteur, 150 mm long by 5 mm i.d. (Fisher Scientific 13-678-6A, or equivalent).
 - 5.2.3.2** Glass pipettes: 0.1-, 1.0-, and 10-mL, accurate to 1% or better.
 - 5.2.3.3** Volumetric flasks: Glass, 10- and 100-mL.
 - 5.2.3.4** Sample vials: Amber glass, 1- to 3-mL with PTFE-lined screw- or crimp-cap, to fit GC autosampler.
- 5.3** Gas Chromatograph (GC): Analytical system with split injection, capillary column, temperature program with initial and final isothermal holds, and all required accessories, including syringes, analytical columns, gases, detector, and recorder. The analytical system shall meet the performance specifications in Section 12.
 - 5.3.1** Column: 30 m long (± 5 m) by 0.25 mm i.d. (± 0.02 mm), 99% methyl, 1% vinyl, 1.0 μ m film thickness, bonded-phase fused-silica capillary (Supelco SPB-1, or equivalent).
 - 5.3.2** Detector: Flame ionization. Capable of detecting 10 ng of hexadecane.
- 5.4** GC data system: Shall collect and record GC data, store GC runs in magnetic memory or on magnetic disk or tape, process GC data, compute peak areas, store calibration data including retention times and the response factor, identify GC peaks through retention times, and compute concentrations.
 - 5.4.1** Data acquisition: GC data shall be collected continuously throughout the analysis and stored on a magnetic storage device.
 - 5.4.2** Response factor: The data system shall be used to record and maintain the response factor (Section 7). Computations of relative standard deviation (coefficient of variation; CV) are used for testing calibration linearity. Statistics on initial (Section 8.2) and ongoing (Section 12.5) performance shall be computed and maintained.
 - 5.4.3** Data processing: The data system shall search, locate, identify, and quantify the compounds of interest in each GC analysis. Software routines shall be employed to compute and record retention times and peak areas. Displays of chromatograms and library comparisons are required to verify results.

6. REAGENTS

- 6.1** Methylene chloride: ACS grade or equivalent.
- 6.2** Standards: Purchased as solutions or mixtures with certification as to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If compound purity is 96% or greater, the weight may be used without correction to compute the concentration of the standard. If diesel oil in drilling mud is to be tested, the diesel oil standard used in this method should be from the diesel oil added to the mud on the drilling rig from which the mud sample is taken. If this oil is not available, No. 2 diesel oil from a local source may be substituted.
 - 6.2.1** Stock solutions: Prepare in methylene chloride for injection into the GC. Observe the safety precautions in Section 4.
 - 6.2.1.1** Diesel oil (62.5 mg/mL): If QC extracts from Method 1662 are to be tested, use the oil that was spiked to produce these extracts.

Weigh 6.25 g of diesel oil to three significant figures in a 100-mL ground-glass stoppered volumetric flask and fill to the mark with methylene chloride. After the oil is completely dissolved, transfer the solution to a 150-mL bottle with PTFE-lined cap.

- 6.2.1.2** Normal hydrocarbons - decane (C_{12}), hexadecane (C_{16}), and tetracosane (C_{24}): Dissolve an appropriate amount of reference material in a suitable solvent. For example, weigh 10.0 mg of decane in a 10-mL volumetric flask and fill to the mark with methylene chloride. After the decane is completely dissolved, transfer the solution to a 15-mL vial with PTFE-lined cap.
- 6.2.1.3** Internal standard: Dissolve 1.0 g of 1,3,5-trichlorobenzene (TCB, Kodak No. 1801 or equivalent) in 100 mL methylene chloride. After the TCB is completely dissolved, transfer the solution to a 150-mL bottle with PTFE-lined cap. Label with the concentration and date. Mark the level of the meniscus on the bottle to detect solvent loss.
- 6.2.1.4** Stock solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards.
- 6.2.2** Normal hydrocarbon calibration standards (GAL): Dilute and mix the stock solutions (Section 6.2.1.2) in methylene chloride to produce the calibration standards shown in Table 1. The three solutions permit the response of hexadecane to be measured as a function of concentration, and decane and tetracosane permit the retention-time window of diesel oil to be defined. The medium-level solution is used for calibration verification.
- 6.2.3** Precision and recovery standard: Dilute the stock solution of diesel oil (Section 6.2.1.1) to produce a concentration of 1.25 mg/mL in methylene chloride. This standard is used for initial precision and recovery (IPR, Section 8.2) and ongoing precision and recovery (OPR, Section 12.5).
- 6.2.4** Addition of internal standard: Using a micropipette or microsyringe, transfer 100 μ L of each standard solution (Section 6.2.2 or 6.2.3) to a GC injection vial. Add 100 μ L of the TCB internal standard (Section 6.2.1.3) to each vial and mix thoroughly. Calibration and precision and recovery standards are made fresh daily to avoid solvent loss by evaporation.
- 6.2.5** Stability of standards.
- 6.2.5.1** When not being used, standards are stored in the dark at -20 to -10°C in screw-capped vials with PTFE-lined lids. A mark is placed on the vial at the level of the solution so that solvent loss by evaporation can be detected. The vial is brought to room temperature prior to use. Any precipitate is redissolved and solvent is added if solvent loss has occurred.
- 6.2.5.2** Standard solutions used for quantitative purposes (Sections 6.2.1 through 6.2.3) shall be analyzed within 48 hours of preparation and on a monthly basis thereafter for signs of degradation. Standards will remain acceptable if the peak area remains within $\pm 15\%$ of the area obtained in the initial analysis of the standard.

7. CALIBRATION

- 7.1** Establish gas chromatographic operating conditions given in Table 2. Verify that the GC meets the minimum level in Table 4. The gas chromatograph is calibrated using the internal standard technique.

NOTE: Because each GC is slightly different, it may be necessary to adjust the operating conditions (carrier gas flow rate and column temperature and temperature program) slightly until the retention times in Table 3 are met.

- 7.2** Internal standard calibration procedure: 1 ,3,5-Trichlorobenzene (TCB) has been shown to be free of interferences from the diesel and crude oils tested in the development of this method. Check for acceptability by injecting 0.5 μL of the internal standard solution (Section 6.2.1.3) into the GC\FID. If a major peak other than the TCB peak appears in the chromatogram, interference with the peaks used for determination of diesel/crude oil may occur. In this case, the analyst must choose an alternative internal standard that is free from interferences.

- 7.2.1** Inject 1 μL of each calibration standard containing the internal standard (Table 1 and Section 6.2.2) into the GC\FID. The TCB will elute approx 8.5 minutes after injection. For the GC\FID used in the development of this method, the TCB internal standard peak was 30 to 50% of full scale at an attenuator setting of 8×10^{-11} amp.

- 7.2.2** Response factor of hexadecane (C_{16}).

- 7.2.2.1 Tabulate the peak areas against concentration for the TCB and C_{16} peaks. Calculate response factors (RF) at each concentration for C_{16} using the following equation:

Equation 1

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Area of the peak to be measured

C_{is} = Concentration of the internal standard, in $\mu\text{g}/\text{kg}$

A_{is} = Area of the internal standard peak

C_s = Concentration of the peak to be measured, in $\mu\text{g}/\text{kg}$

- 7.2.2.2** Calculate the average, standard deviation, and relative standard deviation (RSD) of the response factors. If the RF is constant (<15% RSD) over the calibration range, linearity through the origin can be assumed and system performance is acceptable; if not, the system must be recalibrated.

- 7.2.2.3** The average response factor is verified on each working 8-hour shift by measurement of the medium-level calibration standard (Section 12.4).

- 7.2.3** Single-point calibration for diesel oil: Inject the precision and recovery standard (Section 6.2.3) to which the internal standard has been added (Section 6.2.4) to produce a single calibration point for diesel oil.

- 7.2.3.1** Integrate the area of the C_{16} peak.

- 7.2.3.2** Determine the response factor for diesel oil using Equation 1.

8. QUALITY ASSURANCE/QUALITY CONTROL

- 8.1** Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 4). The minimum requirements of this program consist of an initial demonstration of laboratory capability, an ongoing analysis of standards and blanks as a test of continued performance, analyses of spiked samples to assess accuracy, and analysis of duplicates to assess precision. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method. If the determination of diesel/crude oil is to be made on extracts from Method 1662, the quality control samples for initial precision and recovery (IPR), spiked samples, duplicates, and ongoing precision and recovery (OPR) from Method 1662 shall be substituted for those in the QC tests below, and the specifications in Table 4 of this method for extracts from Method 1662 shall be met.
- 8.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.
- 8.1.2 The analyst is permitted to modify this method to improve separations or lower the costs of measurements, provided all performance requirements are met. Each time a modification is made to the method, the analyst is required to achieve the minimum level (Section 7.1) and to repeat the procedure in Section 8.2 to demonstrate method performance.
- 8.1.3 Analyses of spiked samples are required to demonstrate method accuracy when extracts from Method 1662 are analyzed. The procedure and QC criteria for spiking are described in Section 8.3.
- 8.1.4 Analyses of duplicate samples are required to demonstrate method precision when extracts from Method 1662 are analyzed. The procedure and QC criteria for duplicates are described in Section 8.4.
- 8.1.5 Analyses of blanks are required to demonstrate freedom from contamination. The procedures and criteria for analysis of a blank are described in Section 8.5.
- 8.1.6 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and the analysis of the precision and recovery standard (Section 6.2.3) that the analysis system is in control. These procedures are described in Section 12.
- 8.1.7 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in Sections 8.3.2 and 12.5.4.
- 8.2** Initial precision and accuracy: The initial precision and recovery test is performed using the precision and recovery standard. If extracts from Method 1662 are to be analyzed, the extracts from the initial precision and recovery test in that method shall be used; otherwise, the laboratory shall generate acceptable precision and recovery by performing the following operations.
- 8.2.1 Using diesel oil, prepare four separate aliquots of the precision and recovery standard (Section 6.2.3) using the procedure in Section 10. Add the internal standard to each aliquot (Section 6.2.4). Analyze these aliquots using the procedure in Section 11.

- 8.2.2** Using results of the set of four analyses, compute the average recovery (X) in mg/mL and the standard deviation of the recovery (s) in mg/mL for each sample by the internal standard method (Sections 7.2 and 14.2).
- 8.2.3** For each compound, compare s and X with the corresponding limits for initial precision and accuracy in Table 4. If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the range for accuracy, system performance is unacceptable. In this event, review this method, correct the problem, and repeat the test.
- 8.3** Method accuracy: If extracts from Method 1662 are to be analyzed, the extract from the accuracy test in that method shall be used; otherwise, an accuracy test is unnecessary. The procedure for determining method accuracy is given in Section 8.3 of Method 1662, and the specification for accuracy is given in Table 4 of this method.
- 8.3.1** Compare the percent recovery for diesel oil with the corresponding QC acceptance criteria in Table 4. If the results of the spike fail the acceptance criteria, and the recovery of the QC standard in the ongoing precision and recovery test (Section 12.6.3) is within the acceptance criteria in Table 4, an interference may be present. In this case, the result may not be reported for regulatory compliance purposes. If, however, the results of both the spike and the ongoing precision and recovery test fail the acceptance criteria, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected and the sample batch reanalyzed.
- 8.3.2** As part of the QA program for the laboratory, method accuracy for samples shall be assessed and records shall be maintained. After the analysis of five spiked samples in which the recovery passes the test in Section 8.3.1, compute the average percent recovery (P) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $P - 2s_p$ to $P + 2s_p$. For example, if $P = 90\%$ and $s_p = 10\%$ for five analyses of diesel oil, the accuracy interval is expressed as 70 to 110%. Update the accuracy assessment on a regular basis (e.g., after each five to ten new accuracy measurements).
- 8.4** Duplicates: If extracts from Method 1662 are to be analyzed, the extracts from the duplicates test in that method shall be used. The procedure for preparing duplicates is given in Section 8.4 of Method 1662, and the specification for RPD is given in Table 4 of this method. If extracts from Method 1662 are not to be analyzed, duplicates of the precision and recovery standard (Section 6.2.3) are analyzed, and the specification for RPD is given for diesel oil in Table 4 of this method.
- 8.4.1** Analyze each of the duplicates per the procedure in Section 11 and compute the results per Section 14.
- 8.4.2** Calculate the relative percent difference (RPD) between the two results per the following equation:

Equation 2

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

D_1 = Concentration of diesel oil in the sample

D_2 = Concentration of diesel oil in the second (duplicate) sample

- 8.4.3** The relative percent difference for duplicates shall meet the acceptance criteria in Table 4. If the criteria are not met, the analytical system shall be judged to be out of control, and the problem must be immediately identified and corrected and the sample batch reanalyzed.
- 8.5** Blanks: If extracts from Method 1662 are to be analyzed, the extracts from blanks in that method shall be analyzed in addition to the blanks in this method.
- 8.5.1** Rinse the glassware used in preparation of the extracts in this method with hexane and analyze a 1- μ L aliquot of the rinsate using the procedure in Section 11. Compute the results per Section 14.
- 8.5.2** If any peak is detected in a blank at greater than the minimum level in Table 1, analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination.
- 8.6** The specifications contained in this method can be met if the apparatus used is calibrated properly, then maintained in a calibrated state. The standards used for initial precision and recovery (IPR, Section 8.2) and ongoing precision acid recovery (OPR, Section 12.5) precision and recovery should be identical, so that the most precise results will be obtained. The GC instrument will provide the most reproducible results if dedicated to the settings and conditions required for the analyses given in this method.
- 8.7** Depending on specific program requirements, field replicates and field spikes of diesel oil into samples may be required when Method 1662 and this method are used to assess the precision and accuracy of the sampling and sample transporting techniques:

9. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 9.1** Oil samples are collected in 20- to 40-mL vials with PTFE- or aluminum-foil-lined caps and stored in the dark at -20 to -10°C.
- 9.2** If extracts from Method 1662 are to be analyzed, the laboratory should be aware that sample and extract holding times for this method have not yet been established. However, based on tests of wastewater for the analytes determined in this method, samples shall be extracted within seven days of collection and extracts shall be analyzed within 40 days of extraction.
- 9.3** As a precaution against analyte and solvent loss or degradation, sample extracts are stored in glass bottles with PTFE-lined caps, in the dark, at -20 to -10°C.

10. DILUTION OF OIL AND EXTRACTS

- 10.1** Neat oil samples: If oil is received in neat form, it should be diluted to bring the concentration within the range of the instrument. If the oil is No. 2 diesel oil, the appropriate concentration will be approximately 1.25 mg/mL.
- 10.2** Extracts from Method 1662: If extracts of samples from Method 1662 are to be analyzed, these extracts (from Section 10.4.2 of that method) are analyzed undiluted unless diesel oil is known or suspected to be present.
- 10.3** Neat oil expected to be diesel oil.
 - 10.3.1** Weigh 100 mg into a 1.0-mL volumetric flask and dilute to the mark with methylene chloride to produce a concentration of 10 mg/mL. Stopper and mix thoroughly.
 - 10.3.2** Using a calibrated 1.0-mL volumetric pipette, withdraw 1.0-mL of the solution created in Section 10.3.1.1 and place in a 10-mL volumetric flask. Then withdraw an additional 0.25 mL of the solution and add it to the 10-mL volumetric flask (for a total of 1.25 mL). Fill to the mark with methylene chloride to produce a concentration of 1.25 mg/mL (1250 µg/mL). This solution will be near, but not above, the limit of the calibration range and will match the concentration of the QC samples from Method 1662 (assuming 100% recovery).

11. GAS CHROMATOGRAPHY

- 11.1** Table 2 summarizes the recommended operating conditions for the GC. Retention times for the n-alkanes obtained under these conditions are given in Table 3. An example of the separation achieved for diesel oil is shown in Figure 1. Other columns, chromatographic conditions, or detectors may be used if the minimum level (Section 7.1) and the initial precision and accuracy requirements (Section 8.2) are met.
- 11.2** Using a micropipette or microsyringe, transfer equal 100-µL volumes of the sample, sample extract, or QC standard extract (Section 10.2) and the TCB internal standard solution (Section 6.2.1.3) into a GC injection vial. Cap tightly and mix thoroughly.
- 11.3** Inject 1 µL of the sample extract or standard into the GC, using the conditions in Table 2.
- 11.4** Begin data collection and the temperature program at the time of injection.
- 11.5** If the area of any peak exceeds the calibration range of the system, dilute a fresh aliquot of the extract by a factor of 10, mix 100 µL of internal standard with a 100-µL aliquot of the extract, and reanalyze.
- 11.6** Compute the concentrations of the individual n-alkane peaks using the response factor for hexadecane from the calibration data (Section 7.2.2.2).

12. SYSTEM AND LABORATORY PERFORMANCE

- 12.1** At the beginning of each 8-hour shift during which analyses are performed, GC calibration and system performance are verified. For these tests, analysis of the medium-level calibration standard (Table 1) and of the precision and recovery standard (Section 6.2.3) shall be used to verify all performance criteria. Adjustment and/or re-calibration (per Section 7) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples and blanks be analyzed.
- 12.2** Inject 1 μ L of the medium-level calibration standard (Table 1) into the GC instrument according to the procedure in Section 11.
- 12.3** Retention times.
- 12.3.1 Retention time of the internal standard: The absolute retention time of the TCB internal standard shall be within the range of 7.96 to 8.08 minutes.
- 12.3.2 Relative retention times of the n-alkanes: The retention times of the n-alkanes relative to the TCB internal standard shall be within the limits given in Table 3.
- 12.4** Calibration verification: Compute the concentration of hexadecane based on the average calibration factor (Section 7.2.2.2). The concentration shall be within the limits in Table 4. If calibration is verified, system performance is acceptable and analysis of blanks and QC samples may begin. If, however, the concentration falls outside of the calibration verification range, system performance is unacceptable. In this case, correct the problem and repeat the test, or recalibrate (Section 7).
- 12.5** Ongoing precision and recovery (OPR): If the extract is from Method 1662, the OPR standard from that method shall be used and the specification for the OPR from Method 1662 in Table 4 shall be met; if not, a sample of diesel oil shall be diluted per the procedure in Section 10 and shall be used for the OPR test.
- 12.5.1 Analyze the appropriate OPR standard.
- 12.5.2 Compute the concentration of diesel oil in this standard per Section 14.2.
- 12.5.3 Compare the concentration with the limits for ongoing precision and recovery in Table 4. If the concentration is in the range specified, the analytical processes are in control and analysis of blanks and samples may proceed. If, however, the concentration is not in the specified range, these processes are not in control. In this event, correct the problem, re-extract the sample batch if the OPR is from Method 1662, or redilute the oil sample (per Section 10.3) and repeat the ongoing precision and recovery test.
- 12.5.4 Add results that pass the specifications in Section 12.5.3 to initial and previous ongoing data. Update QC charts to form a graphic representation of continued laboratory performance. Develop statements of laboratory data quality for diesel oil by calculating the average percent recovery (R) and the standard deviation of percent recovery (s_r). Express the accuracy statement as a recovery interval from $R - 2s_r$ to $R + 2s_r$. For example, if $R = 95\%$ and $s_r = 5\%$, the accuracy is 85 to 105%.

13. QUALITATIVE IDENTIFICATION

- 13.1** Qualitative identification is accomplished by comparison of data from analysis of a sample or blank with data from analysis of the calibration verification standard (Section 12.4). Diesel and crude oil are differentiated by the presence and concentration of the C₉-C₃₀ n-alkane peaks in the chromatogram of extracts of the sample.
- 13.1** Using the calibration data, establish the identity of the C₉-C₃₀ n-alkane peaks in the chromatogram of the sample.
- 13.2** Diesel oil is not present in the sample if there are less than 10 n-alkane peaks present in the C₉-C₂₄ range at a signal-to-noise ratio equal to or greater than 3 for each peak, and if the QC tests (Sections 8 and 12) for the sample set are acceptable. The experience of the analyst shall weigh heavily in the determination of the presence of peaks at a signal-to-noise ratio of 3 or greater.
- 13.3** If ten or more n-alkane peaks are present in the analysis of the sample, diesel oil, mineral oil, or crude oil may be present. Mineral oil can be distinguished by its lower polynuclear aromatic hydrocarbon content using Method 1654A. Some crude oils may be distinguished by the presence and concentration of n-alkanes in the C₂₅-C₃₀ range. If peaks are present in the C₂₅-C₃₀ range, the quantitative measurements in Section 14 are used as a final determination that the oil is crude oil.

14. QUANTITATIVE DETERMINATION

- 14.1** Differentiation between diesel and crude oil.

14.1.1 Using the concentrations of the individual n-alkane peaks determined in Section 11.6, sum the concentrations of the n-alkanes from C₉-C₃₀ inclusive. Similarly, sum the concentrations of the n-alkanes from C₂₅-C₃₀ inclusive.

14.1.2 Calculate the percentage of C₂₅-C₃₀ n-alkanes as follows:

Equation 3

$$\text{Percent (C}_{25}\text{-C}_{30}\text{)} = \frac{\text{Sum of C}_{25}\text{-C}_{30} \text{ n - alkanes}}{\text{Sum of C}_9\text{ - C}_{30} \text{ n - alkanes}} \times 100$$

14.1.3 If the percent of C₂₅-C₃₀ n-alkanes is greater than 1.2, the oil is crude oil.

- 14.2** Determination of diesel oil: Compute the concentration of diesel oil in the standard or QC extract using the hexadecane peak only, and the response factor given in Section 7.2.2.2, using the following equation:

Equation 4

$$C_{ex}(\text{mg/mL}) = \frac{(C_{is})(A_s)}{(A_{is})(RF)}$$

where:

C_{ex} = Concentration of oil in the sample

C_{is} = Concentration of the internal standard, in mg/mL

A_s = Area of the peak to be measured

A_{is} = Area of the internal standard peak

(For RF, see Equation I)

15. COMPLEX SAMPLES

- 15.1** The most common interferences in the determination of diesel oil are from mineral oil and proprietary additives in drilling fluids, and from naturally occurring hydrocarbons from crude oil-bearing formations.
- 15.2** Mineral oil can be identified by its lower polynuclear aromatic hydrocarbon content using Method 1654A.
- 15.3** Crude oils can usually be distinguished by the percentage of C₂₅-C₃₀ n-alkanes per Section 14 of this method. However, some crude oils may not produce peaks in the C₂₅-C₃₀ range.
 - 15.3.1** Oil condensates from gas wells are low in molecular weight and will normally produce chromatographic peaks in the C₈-C₁₆ range. If a sample of the gas condensate crude oil from the formation is available, the oil can be distinguished from diesel oil using the extract from this method and the n-alkane ratio determinations in the section on qualitative determination in Method 1651.
 - 15.3.2** Asphaltene crude oils with API gravities <20 may not produce chromatographic peaks in the C₂₅-C₃₀ range. In this instance, the lack of peaks in the C₂₅-C₃₀ range cannot be used to prove that the oil is crude oil and not diesel oil. However, the absence of ten peaks in the C₉-C₂₄ range can be used to demonstrate that diesel oil is not present, per Section 13 of this method.

16. METHOD PERFORMANCE

Specifications in this method are adopted from EPA Method 1651 (Reference 5). Example chromatograms of diesel oil and crude oil are shown in Figure 1.

References

1. "Carcinogens-Working With Carcinogens." Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control [available through National Technical Information System, 5285 Port Royal Road, Springfield, VA 22161, document no. PB277256]: August 1977.
2. "OSHA Safety and Health Standards, General industry [29 CFR 1910], Revised." Occupational Safety and Health Administration, OSHA 2206. Washington, DC: January 1976.
3. "Safety in Academic Chemistry Laboratories (3rd Edition)." American Chemical Society Publication, Committee on Chemical Safety. Washington, DC: 1979.
4. "Handbook of Analytical Quality Control in Water and Wastewater Laboratories." USEPA, EMSL-Ci, EPA-600/4-79-019. Cincinnati, OH: March 1979.
5. "Method 1651, Total Oil and Diesel Oil in Drilling Muds and Drill Cuttings by Retort, Gravimetry, and GC/FID." Available from the EPA Sample Control Center, 300 N. Lee St., Alexandria, VA 22314.

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Table 1. Concentration of Calibration Standards

Analyte	Calibration Solution Concentration ($\mu\text{g/mL}$)		
	Low	Medium	High
n-decane	--	40	--
n-hexadecane	10	40	200
n-tetracosane	--	100	--
Diesel Oil	--	1250	--

Table 2. Gas Chromatographic Operating Conditions

Injection port, transfer line, and detector temperatures: 275 °C

Column temperature program:

Initial temperature: 90 °C

Initial time: 0 minutes

Ramp: 90 °C–250 °C @ 5 °C per minute

Final temperature: 250 °C

Final hold: 10 minutes or until all peaks have eluted

Carrier gas and flow rates:

Carrier: Nitrogen or helium

Velocity: 20–40 cm/sec @ 90 °C

Split ratio: 0–120:1**

Makeup gas: As required by manufacturer

Hydrogen and air flow rates: As specified by manufacturer

Detector amplifier settings: 10⁻¹¹ amp full scale. Attenuation is adjusted so that the highest peaks are on scale in the most concentrated standard.

Recorder: Chart speed of 1–2 cm/min (fixed)

* Conditions are approximate and can be adjusted to meet the performance criteria in Section 12 (see the note in Section 7.1).

**Lower split ratios may give more reproducible results.

Table 3. Retention Times and Relative Retention Time Limits for n-Alkane Peaks

<i>Compound</i>	<i>Retention Time</i>	
	<i>Mean (minutes)</i>	<i>Relative</i>
TCB	8.0	1.00-1.00
n-C ₁₂	9.9	1.22-1.24
n-C ₁₃	12.6	1.55-1.57
n-C ₁₄	15.3	1.89-1.92
n-C ₁₅	17.9	2.21-2.25
n-C ₁₆	20.4	2.52-2.56
n-C ₁₇	22.9	2.82-2.88
n-C ₁₈	25.2	3.12-3.15
n-C ₁₉	27.3	3.39-3.43
n-C ₂₀	29.4	3.66-3.71
n-C ₂₁	31.5	3.90-3.97
n-C ₂₂	33.4	4.14-4.21
n-C ₂₃	35.3	4.37-4.45
n-C ₂₄	37.1	4.58-4.69

Table 4. QC Acceptance Criteria

<i>Criterion</i>	<i>Units</i>	<i>Diesel Oil¹</i>	<i>Oil from Method 1662</i>	<i>n-hexadecane</i>
Minimum Level ²	µg/mL	100		10
Method Detection Limit ³	mg/kg	100		
Initial Precision and Recovery				
Precision (RSD) ⁴	mg/mL		0.23	
Recovery	mg/mL		1.00-1.35	
Calibration Verification ⁵	µg/mL			34-46
Ongoing Precision and Recovery ⁴	mg/mL		0.98-1.37	
Matrix Spike Recovery ⁴	pct		0.73-1.14	
Duplicates	RPD		16	

1 CAS Registry number 68534-30-5; #2 diesel oil used for these tests.

2 This is a minimum level at which the analytical system shall give recognizable signals and acceptable calibration points.

3 Estimated; 40 CFR Part 136, Appendix B; MDL is diesel oil in mud.

4 Test concentration in diluted extract = 1.25 mg/mL

5 Test concentration = 40 µg/mL

Method 1663

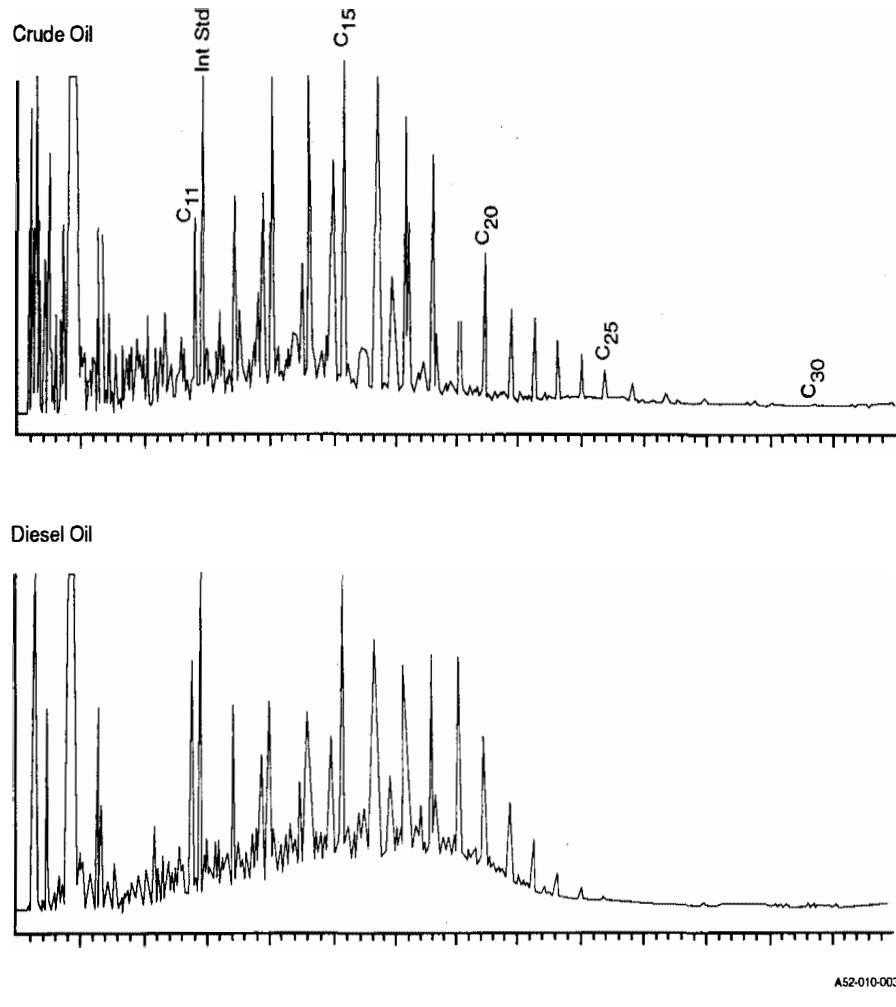


Figure 1. Chromatograms of Crude Oil and Diesel Oil, Showing Differences in the C₂₅–C₃₀ Range