

**New Jersey Department of Environmental Protection
Office of Quality Assurance
Analytical Method**

Title:	Document #: OQA-QAM-025-02/08
Quantitation of Semi-Volatile Petroleum Products in Water, Soil, Sediment and Sludge	Revision: 7, 2/25/08 Supersedes: Revision 6, 4/17/06
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1.0 SCOPE OF APPLICATION

1.1 Scope

This method utilizes a gas chromatograph fitted with a flame ionization detector (FID). The following petroleum analyses are included in the method:

1.1.1 Quantitative analysis of environmental samples (water, soil, sediment, and sludge) for residues from commercial petroleum products such as crude oil, diesel fuel, waste oil, fuels oils Nos. 2-6, lubricating oil, processed oils and bunker fuel.

The method determines Total Semi-Volatile Petroleum Products (TPH), also known as Total Petroleum Hydrocarbons. TPH includes paraffinic, naphthenic, and polynuclear aromatic hydrocarbons (PAHs).

The method shall not be used for gasoline contaminated sites.

1.1.2 Fingerprint Identification of unknown petroleum products by comparison of their chromatograms with chromatograms of known petroleum product profiles. Products that can be identified include diesel fuel, fuel oils Nos. 2-6, lubricating oils, bunker fuel and processed oils (1, 2).

1.2 Applicable NJDEP Programs

Underground Storage Tanks (UST), New Jersey Spill Fund, Comprehensive Environmental Response Compensation and Liability Act (CERCLA), Industrial Site Recovery Act (ISRA), Sludge Residuals, and Resource Conservation and Recovery Act (RCRA).

1.3 Method Advantages

1.3.1 The method partially replaces the TPH method (EPA Method 418.1) based on Freon 113 extraction and analysis by infrared spectroscopy.

1.3.2 The FID response produces a TPH chromatogram that can be used to identify the type of petroleum product present by matching the chromatogram of the unknown sample with the chromatograms of known petroleum products.

1.4 Method Limitations

1.4.1 Quantitative Studies

1.4.1.1 The TPH is quantitatively restricted to the semi-volatile components since partial loss of volatiles (b.p. < 60°C) occurs during the extraction and/or concentration process.

1.4.1.2 The gas chromatographic conditions are not designed for compounds with carbon numbers greater than about C50.

1.4.1.3 Benzene and hydrocarbons that elute from the column before heptane co-elute with the extraction solvent methylene chloride.

1.4.2 Identification Studies

1.4.2.1 The method is most successful with fresh spills of petroleum products. Weathering changes the chromatographic profile. Weathering can be simulated in the laboratory.

1.4.2.2 Absorption, adsorption, biological reactions, and chemical reactions occur in soil, changing the chromatographic profile which reduces the ability to make positive identifications. ASTM Method “Standard Practice for Oil Spill Source Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectroscopy,” D5739-00 can be used for more detailed product analysis (28).

1.5 Matrix

1.5.1 Surface water, ground water, wastewater and low solids sludge (<10%).

1.5.2 Soil, sediments or high solids sludge (>10%).

2.0 SUMMARY OF METHOD

- 2.1 This quantitative TPH method is adopted from the "Leaking Underground Fuel Tanks Field Manual" of the California State Water Resources Control Board (3). This method is also derived from "Test Methods for Evaluating Solid Waste" USEPA Method 8015B and the Florida Department of Environmental Protection, "Method for the Determination of Total Petroleum Range Organics" (4, 25).**
- 2.2 This petroleum method is also adapted with modifications from ASTM Method D3328-82, and the US Coast Guard Oil Spill Identification Procedure for Total Petroleum (1, 2).**
- 2.3 Petroleum residues are extracted from sample matrices with methylene chloride. Surrogate compounds are added to all samples before extraction. The methylene chloride extract is analyzed with a gas chromatograph fitted with a capillary column attached to a FID.**
- 2.3.1 The TPH is determined by integration of the FID chromatogram. Calibration of the gas chromatograph is done with a hydrocarbon standard C8-C40 or where justified and documented, based on historic site-specific data, a standard reference petroleum product.**
- 2.3.2 Identification of unknown residues may be done by comparing their chromatograms with chromatograms of known petroleum products. Samples from old spills are compared to synthetically weathered samples if available. Identification is established when chromatograms match. NJ Method QAM-018 or ASTM Method "Standard Practice for Oil Spill Source Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectroscopy," D5739-00 must be used for detail pattern recognition (6, 28).**
- 2.3.3 The sensitivity of the method is dependent on the level of interferences rather than on instrument limitations. The method detection limit (MDL) for TPH in soil is approximately 10 ug/g and water 80 ug/L. These MDLs can be achieved without concentrating the extract.**
- 2.3.4 Dynamic Range**
- 2.3.4.1 TPH**
- | | |
|---------|---------------|
| Soil | 30-1000 mg/Kg |
| Aqueous | 0.5-500 mg/L |
- 2.3.4.2 Individual Compounds**

Soil 1-500 mg/Kg
Aqueous 1-200 ug/L

2.4 Performance Based Measurements

The laboratory is permitted to modify the method to overcome interferences or improve efficiency of measurements, provided that all performance criteria in this method are met. The laboratory shall determine the equivalency of the revised method.

3.0 INTERFERENCES

3.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with tap water, distilled water, methanol, and methylene chloride.

3.2 High purity reagents such as Burdick and Jackson GC2 methylene chloride, Baker capillary grade methylene chloride or equivalent must be used to minimize interference problems.

3.3 Before processing any sample, the analyst should demonstrate daily, through the analysis of a method blank, that the entire system is interference-free.

3.4 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interference will vary considerably from source to source (e.g. fatty acids, biogenic materials, oxidized biodegradation products), depending upon the nature and diversity of the site being sampled. The silica gel cleanup procedure, EPA Method 3630B can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the method detection limit (MDL) (4).

3.5 Naturally occurring alkanes may be detected by this method and may interfere with product identification. Naturally occurring plant waxes include odd carbon number alkanes from n-C₂₅ through n-C₃₅, and exhibit a dominant odd/even chain length distribution. Leaf hydrocarbons also may be detected.

3.6 A vial septum should be penetrated and extracted with methylene chloride to evaluate the potential alkane distribution that could occur in re-analyzed extracts. Vial septums should be changed after each analysis.

3.7 Particulates interfere with the determination of dissolved petroleum products in ground water. Petroleum products adsorb on the surface of particulates. The groundwater samples should be filtered through glass fiber filters to determine dissolved TPH.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been defined precisely. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Additional reference to laboratory safety are available and have been identified for use by the analyst (8,9).

5.0 APPARATUS AND EQUIPMENT

5.1 Sampling Containers

5.1.1 Prior to use, wash bottles and cap liners with aqueous detergent solutions and rinse with tap water, distilled water, and methylene chloride. Allow the bottles and containers to air dry at room temperature, place in a 150°C oven for one hour, then remove and allow cooling in an area known to be free of organic analytes.

5.1.2 Screw cap bottle - 40 mL PTFE-faced silicone cap liners.

5.1.3 Narrow mouth bottles - 1 liter, amber, PTFE faced silicone cap liners.

5.1.4 Wide-mouth glass jar-four ounce, amber, PTFE faced silicone cap liners

5.2 Glassware

5.2.1 Serum bottles - 100 mL, 10 mL, 2 mL crimp-top, PTFE-faced silicone cap liners.

5.2.2 Pasteur pipets

5.2.3 Screw-cap Erlenmeyer flasks - 250 mL, with PTFE faced silicone cap liners.

5.2.4 Volumetric flasks - 10 mL, 25 mL, 100 mL

5.2.5 Kuderna-Danish apparatus (KD)

5.2.6 Separatory funnels - 2 L Pyrex, Teflon stopcock

5.2.7 Soxhlet Extractor

5.3 Apparatus

5.3.1 Rotary shaker table, 350 rpm minimum

5.3.2 Analytical balance capable of accurately weighing 0.0001 g.

5.3.3 A gas chromatograph with split/splitless injector, equipped with a capillary column, capable of temperature programming.

5.3.3.1 Column-30m long x .53mm ID, .5um film thickness poly dimethyl siloxane coating (Restek, J&W Scientific or equivalent). This column will allow for the resolution of alkanes from nC8 to nC40, as well as the resolution of phytane/nC18 and pristane/nC17. This column will also allow for the resolution of the petroleum products listed in Section 1.1 (21). Low bleed columns must be used. Equivalent columns may be used.

5.3.3.2 Column - 30m long x 0.32mm ID, 0.25um film thickness, 95% dimethyl-5% diphenyl polysiloxane (J&W Scientific, Restek or equivalent). This column has similar resolution to 5.3.3.1 but high bp compounds elute later. Equivalent columns may be used.

5.3.3.2 Column - 100m long x .25mm ID., 0.5um film thickness, capillary, Protocol DH (Supelco or equivalent (22)).

5.3.3.3 Detector - Flame Ionization Detector (TPH only)

5.3.4 An autosampler is recommended.

5.3.5 Boiling chips - Solvent extracted approximately 10/40 mesh.

5.3.6 Water bath - Top, with concentric ring cover, capable of temperature control. The bath should be used in a hood.

5.3.7 Gas-tight syringe - One milliliter (mL) with chromatographic needles.

5.3.8 Microsyringes – 10uL, 100uL, 200uL

5.3.9 Continuous liquid-liquid extraction apparatus.

5.3.10 Liquid chromatographic column - 400 x 20mm with coarse frit, Teflon stopcock.

5.3.11 Magnetic stirrer and 2-inch Teflon coated stirring bars.

5.3.12 Nitrogen concentration system composed of a precleaned Pasteur pipet, with a small plug of glass wool loaded at the tip end, and filled with approximately 1-2 cm of precleaned alumina. The top of the pipet is attached to a hydrocarbon free nitrogen gas source using precleaned Teflon tubing. This concentration step should be performed at room temperature or lower to retain light end compounds.

6.0 REAGENTS

- 6.1 Purity of Reagents - Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee and Analytical Reagents of the American Chemical Society.**
- 6.2 Reagent water - Reagent water is defined as a water in which an interference is not observed at the MDL of each parameter of interest. (ASTM Specification D1193, Type ii).**
- 6.3 Methylene chloride, methanol, carbon, disulfide and hexane - pesticide grade, Burdick and Jackson GC2, Baker Capillary Grade or equivalent.**
- 6.4 Sodium sulfate - (ACS) granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray, cool in a desiccator and store in a sealed glass bottle.**
- 6.5 Silica gel - Grade 923 (100/200) desiccant. Before use, activate for at least 16 hours at 130°C in a shallow glass tray that is loosely covered in foil. Cool and store as in Section 6.4.**
- 6.6 Silica granular, fine (60-120 mesh) Fisher 5151-10. Purify by Soxhlet extraction with methylene chloride for four hours. Dry at 80°C. Store in glass bottle.**
- 6.7 Hydrochloric acid, 1:1 - Mix equal volumes of (ACS) concentrated HCl and distilled water.**
- 6.8 Stock Standards**
- 6.8.1 Normal Paraffinic Hydrocarbons Standard - Prepare a methylene chloride solution containing a mixture of components ranging from**

octane to tetracontane (nC8-nC40), or selected individual normal paraffins (2 mg/ml ea). The standard must include a minimum of 12 compounds including C8, C18, C20, C32, and C40. For product identification purposes the mixture also may contain C17, pristane and phytane (2 mg/ml ea.). A separate pristane, phytane, C17, and C18 column resolution standard may be used. An appropriate dilution of the mixture is analyzed under normal analytical conditions to determine retention times and the Relative Response Factors for the Compounds. A 10% carbon disulfide/ 90% methylene chloride solvent mixture may be used if standards do not remain in solution. (Mixtures are available from Supelco, Restek (31266), and NSI Solutions).

- 6.8.2 Diesel and Fuel Oil Profile Standards -** Where applicable prepare commercial diesel, waste motor oil and/or fuel standards in methylene chloride. Weigh 300mg oil to the nearest 0.1 mg, into a 10 mL volumetric flask. Dilute to volume with methylene chloride (30 mg/ml). Standards are available from Restek Inc., Bellefonte, PA.
- 6.8.3 Initial Calibration Verification Standard (ICV) –** A calibration standard from a different source or lot number containing the compounds in 6.8.1 shall be obtained.
- 6.8.4 Internal Standards (IS) –** The internal standard 5-androstane is prepared by carefully weighing 100 mg of the compound into a 100 mL volumetric flask. Dilute to volume with methylene chloride. The final concentration of the compound is one ug/ul.
- 6.8.5 Surrogates (SS) -** The surrogates chlorobenzene, ortho-terphenyl [OTP] and tetracosane-d50 are prepared by carefully weighing 100 mg of each compound into a 100 mL volumetric flask. Dilute to volume with methylene chloride. The final concentration of each compound is one ug/ul. The laboratory is free to choose any two or more surrogates that cover the carbon range (C8 - C40). However chlorobenzene is required. Poor recovery of chlorobenzene indicates the loss of low boiling hydrocarbons, standards are available from Restek Inc.
- 6.8.6 Quality Control Check Standard (Blank Spike) -** The QC check standard concentrate (30 mg/ml) of fuel oil #2 must be prepared by the laboratory using stock standards prepared independently from those used for calibration (Section 6.8.2). If the contamination at the site is known, other fuel standards can be used. Standards are available from Supelco, or Restek.

6.8.7 Matrix spiking standard (MSS) - Prepare the MSS in methylene chloride from a Fuel oil #2 standard in Section 6.8.2 or another oil for site specific work . The laboratory may use the hydrocarbon calibration standard noted in section 6.8.1 as the MSS for unknown petroleum sources.

7.0 CALIBRATION

7.1 Initial Calibration

7.1.1 Retention time windows

- a. Before establishing windows, make sure the GC system is within optimum operating conditions. Serial injections over less than a 72 hr period result in retention time windows that are too tight.**
- b. Calculate the mean and the standard deviation of the three retention times (use any function of retention time; including absolute retention time, or relative retention time) for each surrogate.**
- c. Plus or minus three times the standard deviation of the mean retention times for each surrogate will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. The default value for the retention time shall be a minimum of +/- 0.05 minutes, if the standard deviation is zero.**
- d. Establish the midpoint of the retention time window for each surrogate by using the absolute retention for each surrogate from the mid-concentration standard of the initial calibration. The absolute retention time window equals the midpoint ± 3 SD, where the standard deviation is determined as described in Section b.**
- e. The laboratory must calculate retention time windows for each surrogate on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.**

7.1.2 FID Internal Standard Calibration for Quantitation of TPH - - Calibrate the GC-FID with an initial five point, (i.e., concentration of individual components 1ng/uL, 5ng/uL, 10ng/ul, 20ng/uL, 50ng/uL), Total Petroleum Hydrocarbons calibration curve (Section 6.8.1). The lowest concentration point in the calibration curve should be near the MDL (4-5 x MDL). The highest concentration point should be twice

the expected sample concentration and within the linear instrument range. To maintain the standards in solution, a 10% carbon disulfide/90% methylene chloride solvent may be required. Prepare the calibration standard to contain 5.0 ng/ul of surrogate and of internal standard. The relative standard deviation (RSD) for the surrogates and each calibration compound's relative response factor (RRF) must be less than or equal to 20%. If not, the calibration curve must be used to determine concentration. A minimum correlation coefficient of 0.95 is required. Also calculate the response for total petroleum hydrocarbons (TPH) which is the average of the RRFs for the nC8-nC40 compounds (Section 11.2.1). The RSD must be less than 20%. The chromatograms should be checked for mass discrimination (Section 7.3). Standards with concentrations greater than 20 mg/L may need to be equilibrated to room temperature prior to analysis.

- 7.1.3 FID External Standard Calibration for Quantitation of TPH -** The laboratory has the option of using an external calibration procedure. Prepare the standards as directed in Section 7.1.2 omitting the internal standard. Calculate response factors (RF) instead of relative response factors for each compound and the surrogates. The relative standard deviation (RSD) of each calibration compound's response factor (RF) must be less than 20%. If not the calibration curve must be used to determine concentration. A minimum correlation coefficient of 0.95 is required. Also calculate the response for total petroleum hydrocarbons (TPH) which is the average of the RFs for the nC8-nC40 compounds (Section 11.3). Figure 1, is an example of an n-hydrocarbon standard (sec. 6.8.1) calibration chromatogram.
- 7.1.4 TPH Petroleum Product Calibration -** If the laboratory has a site specific project and the petroleum product contamination is known the GC_FID maybe calibrated using a reference petroleum product (Section 6.8.2). Calibrate the GC-FID with an initial five point, (i.e. concentration total petroleum 0.1 mg/ml, 0.2mg/ml, 1.0mg/ml, 2.0mg/ml, 5.0mg/ml) calibration curve. Calculate the response factor (RF) for TPH (Section 11.2). The RSD of the TPH response factor must be less than 20%. If not the calibration curve must be used to determine concentration. A minimum correlation coefficient of 0.95 is required. Figure 2, is an example of a TPH (sec. 6.8.2 Fuel Oil #2) calibration chromatogram.
- 7.1.5 Petroleum Profile Calibration -** If the method is used only for qualitative petroleum product profiling, a single point GC-FID retention time calibration is required. Prepare a 2 mg/ml standard

from the products in section 6.8.2 (23). Prepare a 20 ng/ul carbon number standard from section 7.12.

7.1.6 Initial Calibration Verification – The initial calibration shall be verified by a calibration standard from a different source or lot than used to construct the calibration curve. A mid-range standard is recommended.

7.2 Daily Calibration

7.2.1 The resolution check is required for fingerprint determination. The resolution of the chromatographic column should be checked daily. Inject two uL of the calibration mixture (10 ng/ul) (section 7.1.2) into the chromatograph. Visually inspect the chromatograms for separation between phytane and nC18, pristane and nC17. Figure 1 is a chromatograph of a 10 ng/ul calibration standard.

If a standard fuel oil #2 is used as the calibration mixture, the resolution of the chromatograph column can be monitored by visually checking the resolution of the pair, nC17-Pristane and nC18-phytane. These compounds occur in all fuel oil #2 products.

7.2.2 The working calibration curves or calibration factors for TPH, must be verified on each working day and after every 12 hours by the measurement of one or more continuing calibration standards. Calculate the percent difference (D%) between the verified RF or RRF and the initial RF or RRF for TPH and the surrogates. The %D must not exceed 20%. If the %D exceeds 20% the instrument must be recalibrated. Reanalysis of all samples analyzed after a non compliant standard is required.

7.2.3 The retention times of surrogates in the calibration verification standard analyzed at the beginning of the analytical shift must fall within the absolute retention time windows calculated in Sec. 7.1.1b. The purpose of this check is to ensure that retention times do not continually drift further from those used to establish the widths of the retention time windows. If the retention time of any surrogate at the beginning of the analytical shift does not fall within the ± 3 SD window (less than +/- 0.05 min.), then a new initial calibration is necessary unless system maintenance (Sec. 7.11) corrects the problem.

In addition, the retention times of all surrogates in the subsequent calibration verification standards analyzed during the analytical shift must fall within the absolute retention time windows established in Sec. 7.1.1d.

7.2.4 Surrogate Standards (SS), GC Internal Standard (IS) - The SS and IS responses and retention times in the calibration check standard must be evaluated during or immediately after data acquisition. If the retention time(s) for the SS or IS are outside the determined RT window, the chromatographic system must be inspected for malfunctions and corrections must be made. If the area(s) for the SS or IS changes by +/- 50% from the last daily calibration standard check, the GC must be inspected for malfunctions and corrections must be made.

7.3` Mass discrimination

7.3.1 Mass discrimination can take place in the injection port. The heavier molecules do not enter the column as a defined plug of vapor with the lighter molecules.

7.3.2 Mass discrimination is minimized by placing a small plug of silanized glass wool one centimeter from the base of the glass injection liner. The end of the capillary column is placed just below the glass wool.

7.3.4 The calibration chromatogram (Section 7.1.2 or 7.1.3) is inspected for mass discrimination. The response factor ratio C32/C20 should be greater than 0.8. If the ratio is less, reposition the column in the glass liner until mass discrimination is minimized.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality control program which conforms to New Jersey Regulation N.J.A.C. 7:18-4.7 (13). The minimum requirements of this program consist of an initial demonstration of laboratory capability (IDOC) and an ongoing analysis of Laboratory Control Samples (LCS) to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with laboratory established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

8.1.1 The analyst must make an initial, one-time demonstration of the ability to generate acceptable accuracy and precision with this method (Section 8.2).

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted to improve the separations by changing the GC conditions or column. Each time such a modification is made to the method, the analyst is required to repeat and document the procedure in Section 8.2.

- 8.1.3** Each day before calibration and after the calibration, the analyst shall analyze a reagent blank (instrument blank) to demonstrate that interferences from the analytical system are under control.
- 8.1.4** The analyst shall analyze a method blank, with each sample batch, to demonstrate that interferences from sample extraction are under control. Target compounds' concentrations in the blank should be no more than 5x MDL. If blank levels for any component are above 5x MDL and the sample concentrations present in the samples are greater than 10x blank level then the samples may be quantified and qualified. If the blank concentration is greater than 5X MDL and the sample concentrations present in the samples are less than 10 X the blank level, the affected samples should be re-extracted and re-analyzed. If a sample cannot be re-extracted or re-analyzed, the data should be qualified as such. Samples should not be blank corrected.
- 8.1.5** The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.3. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed.
- 8.1.6** The laboratory must spike all samples with the surrogates to monitor recovery. This procedure is described in Section 8.4.
- 8.1.7** The laboratory must spike a minimum of five percent or one per batch, whichever is more frequent of all samples in each matrix, with the MSS (Section 6.8.5) to monitor and evaluate laboratory data quality. This procedure is described in Section 8.5.
- 8.2** In order to establish the ability to generate acceptable precision and accuracy, the analyst must perform the following IDOC study.
- 8.2.1** A quality control (QC) check sample concentrate is required containing fuel oil #2 at a concentration of 30 mg/ml in methylene chloride (Section 6.8.4). The QC check sample concentrates must be prepared by the laboratory using stock standards prepared independently from those used for calibration.
- 8.2.2** Aqueous
- Analyze four 1 L aliquots (TPH) of the well-mixed reagent water spiked with 0.5 mL QC check sample concentrate and 20 uL of each surrogate according to the method beginning in Section 10.1.

8.2.3 Soil and Sediment

- a. Prepare a TPH QC check sample to contain 200 ug/g of reference oil (6.8.2) by adding 0.2 mL of QC standard concentrate to 30g of reagent sodium sulfate (6.4). Also add the appropriate surrogates.
- b. Analyze four aliquots of silica spiked with QC check standard concentrate according to the method beginning in section 10.3.

8.2.4 For each matrix calculate the average recovery (\bar{X}) and the standard deviation of the recovery (s) for #2 Fuel, using the four results. The average percent recovery should be between 70 - 120%. The laboratory is to establish the criteria for the standard deviations as described in USEPA Method 8000C (4).

8.2.5 The FID retention times of the surrogates and internal standards must match the calibration standard as described in 7.2.3.

8.3 The laboratory must analyze a Total Petroleum Hydrocarbon (TPH) QC check (LCS) sample with every 5% of the samples. The check sample shall be prepared as directed in Section 8.2.1. The recovery of TPH shall be in ranges specified in Section 8.2. The FID retention times of the surrogates and internal standards must match the previous calibration as described in 7.2.3.

8.4 As a quality control check, the laboratory must spike all samples with the surrogates chosen in Section 6.8.3 and calculate the percent recovery (R_{SS}) of the Surrogate based on the FID response.

$$\%R_{SS} = \frac{A_x}{A_s} \times 100$$

A_x = Area response of SS or IS in check sample

A_s = Average area response of SS or IS in standard

8.4.1 For the surrogate standards, the laboratory must develop separate accuracy statements of laboratory performance for each matrix. An accuracy statement for the method is defined as Percent Recovery \pm Standard Deviation ($R_{SS} \pm s$). The accuracy statement should be developed by the analysis of four aliquots as described in Section 8.2, followed by the calculation of R_{SS} and s . Alternatively, the analyst may use four data points gathered through the requirement for continuing quality control in Section 8.3. The accuracy statements should be updated regularly. The initial recovery may be set at 60 to 120 percent.

8.4.2 Calculate upper and lower control limits, %R_{SS}, for the surrogate standard in each matrix.

$$\text{Upper Control Limit (UCL)} = R_{SS} + 3s$$

$$\text{Lower Control Limit (LCL)} = R_{SS} - 3s$$

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance (14).

8.4.3 The following corrective actions can be taken when the percent recoveries of chlorobenzene, androstane and/or tetracosane-d50 are outside of the recovery range:

8.4.3.1 Check calculations to assure there are no errors.

8.4.3.2 Check instrument performance, check the sample preparation procedure for losses due to temperature control and the internal standard and surrogate solutions for degradation or contamination, etc.

8.4.3.3 Reanalyze the sample or extract if the steps above fail to reveal a problem. If reanalysis yields surrogate recoveries within the stated limits, the reanalysis data should be used.

8.4.3.4 If the surrogate could not be measured because the sample was diluted prior to analysis, qualify the surrogate recovery. If the surrogate co-elutes with a compound (as in coal tar), report only the recovery of the backup surrogate tetracosane-d50. Qualify the out of range surrogate on the data table. No additional corrective action is required.

8.5 Matrix Spike Analysis - The laboratory must, on an ongoing basis, spike (MS) and analyze at least 5% of the samples for each matrix from each sample site being monitored to assess accuracy. The spike should be the matrix spiking standard (MSS) (Section 6.8.5).

8.5.1 Report the recovery as the average of the individual recoveries of the components nC8-nC40, if the hydrocarbon standard is used.

8.5.2 The laboratory should establish their own acceptance criteria for % recovery (R_{MS}) as in Section 8.2.4. Recoveries of > 70% < 130% should be achieved.

8.6 Sample Duplicate - The laboratory must, on an ongoing basis, analyze 5% of the samples for each matrix in duplicate. Both results are to be reported.

(No specific criteria concerning the relative percent difference (RPD) exists at this time. However, results should not differ by more than 50%.) The laboratory should establish their own acceptance criteria for RPD based on control charts. A matrix spike duplicate may be used if no positive TPH samples are in the batch.

- 8.7 Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.
- 8.8 The laboratory shall determine the method detection limits (MDLs) for the fuels of interest using the methods of 40 CFR 136 Appendix B (7). The MDLs must be confirmed by analyzing a low level standard (2-3x MDL).

9.0 SAMPLE COLLECTION PRESERVATION

9.1 Aqueous Matrix

- 9.1.1 Collect a representative water sample in a 1L narrow mouth bottle. A delay between sampling and analysis of greater than four hours requires sample preservation by the addition of 5ml HCl (Section 6.7). Confirmation of a pH < 2 must be obtained in the field.
- 9.1.2 Sample must be chilled to 4+/-2°C on the day of collection and stored at 4+/-2°C until analyzed.
- 9.1.3 Samples must be extracted within 14 days from the time of collection or 12 days from verified sample time of receipt (VSTR). Extracts must be analyzed within 40 days of extraction.

9.2 Solid Matrix

- 9.2.1 Collect a representative soil-sediment sample in a four-ounce, wide-mouth jar with a minimum of air space.
- 9.2.2 Samples must be chilled at 4+/-2°C on the day of collection and stored at 4+/-2°C until analyzed.
- 9.2.3 Samples must be extracted within 14 days from the time of collection or 12 days from VSTR. Extracts must be analyzed within 40 days of extraction.

10.0 PROCEDURES

10.1 Dissolved Product

10.1.1 Sealed Extraction (14)

- a. **Mark the liquid level on the outside of the one liter bottle. Check the sample for floating product. Measure/adjust pH to 2 with 6N HCl if necessary.**
- b. **Add a two inch Teflon stirring bar, 30 ul of surrogate standards (Section 6.8.3), and 30 mL of methylene chloride. Seal the sample bottle.**
- c. **Place the bottle on a magnetic stirrer. Adjust the speed so that there is a vortex. Stir for five minutes and then release any pressure. Continue stirring for 15 minutes.**
- d. **Transfer the methylene chloride extract to a serum bottle for storage using a Pasteur pipet. Add 30 mL of methylene chloride to the sample bottle, seal, return to the magnetic stirrer and stir for twenty minutes. Fill the empty sample bottle to the mark with water. Determine the sample volume in a liter graduated cylinder.**
- e. **Combine the methylene chloride extracts, filter and dry the extract through glass wool and sodium sulfate. Adjust the extract volume to 50 mL in a volumetric flask. Store the extract in a 100 mL crimp top serum bottle at 4°C.**
- f. **Emulsions**
 - 1. **Emulsions can be broken by centrifugation**
 - 2. **Continuous extraction can be used on samples known to form emulsions; USEPA Method 3520 (4).**
- g. **Screen the extract before concentrating (Section 10.4). Dry and Concentrate the extract as in section 10.1.2.e through 10.1.2i.**

10.1.2 Separatory Funnel Extraction (7)

- a. **Aqueous samples are usually extracted using separatory funnel techniques. If emulsions prevent achieving acceptable solvent recovery with separatory funnel extraction, continuous extraction (Section 10.1.2) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When a sample volume of 2 L is to be extracted, use 250, 100 and 100-mL volumes of methylene chloride for the serial extraction.**

- b. Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2 L separatory funnel. Measure/adjust pH to 2 with 6N HCL. Pipet 30 uL of the surrogate standard spiking solution into the separatory funnel and mix well (Section 6.8.3).**
- c. Add 60 mL of methylene chloride to the sample bottle seal and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min.**

If the analyst must employ mechanical techniques to the complete phase separation, the optimum technique depends upon the sample. The techniques may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250 mL Erlenmeyer flask with a glass stopper.

If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride); transfer the extract to the chamber of a continuous extractor and proceed as described in Section 10.2.3.

- d. Add a second 60 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract. Screen the extract (Section 10.4) before concentrating.**
- e. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.**
- f. Pour the combined extract through a solvent rinsed drying column (Section 5.3.10) containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.**
- g. Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction.**

Prewet each Snyder column; by adding about 1 mL of methylene chloride to the top of the column. Position the K-D apparatus in a hot water bath (60°C to 65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of the distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with one to two mL of methylene chloride. A five mL syringe is recommended for this operation.

- h. Add another one or two clean boiling chips to the concentrator tube of each fraction and attach a two ball micro Snyder column. Prewet the Snyder column by adding about 0.5 mL of methylene chloride to the top of the column. Place the KD apparatus on a hot water bath and reduce the extract volume to about 0.5mL. Allow The KD cloumn to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL with the solvent. If the internal standard method is used, transfer to a 1 ml GC auto-sampler vial and add 20 uL of the GC internal standard (5-androstane) (internal calibration only).
- i. Determine the original sample volume by refilling the sample bottle to the mark with water and transferring the liquid to a 1000 mL graduated cylinder. Record sample volume to the nearest five mL.
- j. Other extract concentration methods can be used if the recoveries of the surrogates and the QC check samples meet the requirements of the method.

10.2.3 Continuous Extraction (4)

- a. Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Transfer the sample to the continuous extractor. Measure/adjust pH to 2 with 6N HCl. Using a pipet, add 30uL of surrogate standard spiking

solution and mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor.

- b. Repeat the sample bottle rinse with an additional 50 to 100 mL portion of methylene chloride and add the rinse to the extractor.
- c. Add 200 to 500 mL of methylene chloride to the distilling flask, and sufficient reagent water to ensure proper operation, and extract for 24 hours. Allow to cool, and then detach the distilling flask. Screen the extract (Section 10.4) before concentrating. Dry and concentrate the extract as in section 10.1.2.e through 10.1.2.i.

10.3 Sample preparation, soils and sediments (1, 12)

10.3.1 Homogenize the soil sample with a solvent-rinsed stainless steel spatula. Weigh about five grams of the sample to ± 0.01 g into a tared aluminum pan. Dry at 105 degrees Celsius for 12 hours and calculate the percent solids content (Section 11.3.4).

10.3.2 Soxhlet Extraction – If the samples contain residual oil and tar, the EPA Soxhlet extraction Method 3540 should be used (2). Method 3540 may be used for all solid sample types.

a. Quickly blend 10-30g of solid sample with 10 – 30g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 30uL of the surrogate standard spiking solution (6.8.3) onto the sample. The blending of the soil with the anhydrous sodium sulfate can lead to the loss of volatile components (C8-C12). If the sample is expected of containing a large volatile component such as Jet fuel, this drying process may be omitted.

b. Place 300 mL of the extraction solvent into a 500-mL round-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract sample for 16-24 hours at 4-6 cycles/hr.

c. Allow the extract to cool after the extraction is complete. Screen the extract before continuing (Section 10.4).

Dry and concentrate the extract as in Section 10.1.2e through 10.12h.

10.3.3 Gyrotory Shaker Extraction

- a. Add 30g (+/- .1 g) (wet weight) of the sample with a stainless steel spatula to a 250 mL acid-cleaned, solvent-rinsed, capped Erlenmeyer flask. Mix in 30 g of sodium sulfate. If the sample has excessive moisture, add additional amounts of sodium sulfate. This procedure must be done quickly to reduce evaporation losses.
- b. Add 30 uL of surrogate standard spiking solution to 50 mL of methylene chloride, screw on the top, and shake the mixture vigorously for 1 minute, vent the flask (Section 6.8.3).
- c. Place the 250 mL flask on a rotary shaker unit, positioned behind a safety shield, in a fume hood. Adjust the agitation rate of the shaker device to 400 RPM and extract the samples under these conditions for exactly 30 minutes.
- d. After 30 minutes, the rotary shaker should be turned off and Erlenmeyer flasks removed to a stationary location. The analyst should permit suspended solids and particulate matter in the flasks to settle for approximately 30 minutes.
- e. Using a pasteur pipet, carefully transfer the supernatant extract to a 100 mL crimp top serum bottle for storage. Do not agitate the sediment layer.
- f. Extract the sample with two additional 30mL volumes of methylene chloride. The sample should be sonicated for 0.5 minutes before the last extraction. This will insure the complete dispersion of the soil. Combine all of the extracts, in the serum bottle for storage. Screen the extract before continuing (Section 10.4). Dry and concentrate the extract as in section 10.1.2e through 10.1.2.h.

10.3.5 Other Extraction Methods

- a. Extraction methods listed in SW846 may be used such as 3545 Pressurized Fluid Extraction, 3541 Automated Soxhlet Extraction and 3550 Sonication.
- b. The laboratory must conduct a one time demonstration of the ability to generate acceptable accuracy and precision (Section

8.2). The demonstration must include comparison results with real samples that cover the C8-C40 carbon range. The laboratory must meet the sensitivity requirements of Section 2.3.3, the dynamic range of section 2.3.4, and the surrogate recovers of section 8.4.1.

- c. Routine analysis using alternate extraction methods must meet the surrogate requirements of section 8.4.1.

10.4 Preliminary Analysis of Extracts (Screening)

10.4.1 Adjust the chromatograph for maximum sensitivity.

10.4.2 Inject 1 uL of the sample extract using an auto sampler.

10.4.3 A complete profile of the extract should be obtained without saturating the detectors. The largest peak should be a minimum of 50% and a maximum of 90% full span. If the response is too high, the extract should be diluted. if the response is too low, concentrate the extract. If the response meets the criteria, determine the extract volume and go to section 10.5 or 10.6.

10.5 Cleanup for Quantitation (4)

10.5.1 Should the sample require additional cleanup due to interfering compounds, polar compounds or a large unresolved hump without distinct peaks, in the chromatogram, use EPA Method 3630 - silica gel cleanup. Combine fraction 1 (pentane; aliphatics) and fraction 2 (methylene chloride/pentane [2 : 3 v/v] aromatics) for total petroleum hydrocarbons (TPH) analysis.

10.5.2 Figure 4 is a chromatogram of a diesel contaminated soil.

10.6 Chromatographic Analysis

10.6.1 One milliliter of extract ready for analysis should be transferred to a one mL GC auto sampler vial.

10.6.2 All extracts, standards and blanks, should contain the GC internal standard (30 ug/L) when applicable.

10.6.3 Inject one to two uL of extract using an auto-sampler device or the solvent plug method.

10.7 Recommended Chromatographic Conditions (21)

10.7.1 Suggested Temperature Program for RTX-1 Column:

Initial Value	40°C
Initial Time	2.00 min
Program Rate	12.00°C/min
Final Value	320°C
Final Time	10 min
Total Run Time	35 min
Carrier Gas	He

10.7.2 Injection Port Temperature 330°C

10.7.3 Detector Temperature 330°C

10.7.4 Instrument Performance

- a. All of the peaks contained in the standard chromatograms must be sharp and symmetrical. Peak tailing must be corrected. If only the compounds eluting before ethylbenzene give random response, have unusually wide peak width, are poorly resolved, or are missing, the problem is usually traceable to the injection port temperature.
- b. Check the precision between consecutive QC check samples. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks.
- c. Monitor the retention time for each analyte using data generated from calibration standards. If individual retention times vary by more than ± 3 standard deviations (7.1.1) over a twelve hour period, the source of retention data variance must be corrected before acceptable data can be generated.
- d. The instrument sensitivity must be maximized. Injection of 2ul of a 1ng/ul hydrocarbon standard should yield a detector signal-to-noise ratio of between 5:1 and 15:1 for the individual alkanes.

10.8 Analysis Sequence

10.8.1 This method uses a 12hr clock. The time sequence begins with the analysis of the initial calibration verification standard. Continuing calibrations must be verified every 12hrs.

10.8.2 Sequence

1. Instrument Blank
2. Initial Calibration
3. Initial Calibration Verification
4. Calibration Blank
5. Method Blanks
6. Samples (20)
7. LCS, MS, Duplicate
6. Continuing Calibration (every 12hrs. or 20 samples)
7. Calibration Blank

11.0 CALCULATIONS

11.1 Concentration of Petroleum Hydrocarbons

11.1.1 To calculate the concentration of total petroleum hydrocarbons in the sample, the area response attributed to the petroleum must first be determined. This area includes all of the resolved peaks and the unresolved "envelope". This total area must be adjusted to remove area response of the internal standards, solvent, surrogates and the GC column bleed.

11.1.2 Establishing the baseline

- a. Column bleed is defined as the reproducible baseline shift that occurs during temperature programming of the GC column oven. To determine this area, a methylene chloride blank injection should be analyzed at the beginning of the day and after every 12 hours to determine the baseline response (Figure 3). The baseline area response shall be within +/- 20% of the initial baseline response. The baseline integration point is then set at a stable reproducible point just after the solvent peak. This baseline should be extended horizontally to the end of the run. The area of the blank run shall be subtracted from the actual sample run.
- b. The baseline for the sample should be set in the same manner. The area in the sample will contain the area attributed to petroleum and that attributable to the baseline. The petroleum area shall be calculated by subtracting the baseline, internal standard and surrogate areas from the total area. The TPH is then calculated according to the equation in Section 11.1.4.
- c. As the concentration of TPH in the sample approaches the detection limit, the baseline correction becomes more critical.

11.2 Concentration based on Internal Standard

The calculations are based on EPA SW846 Method "Determinative Chromatographic Methods" 8000B (4).

11.2.1 Determine the total area (A) from sample analysis, of the unknown and calculate the concentration. The analyst must take care when calculating total product areas that the appropriate baseline is used.

(a) Aqueous Matrix

$$C \text{ (ug/L)} = \frac{(A) (C_{is}) (D) (V_i)}{(RRF) (A_{is}) (V_s) (1000)}$$

Where:

C = Concentration of Analyte or concentration of Total Petroleum Products, ug/L

A = Area response of compound or TPH to be measured.

D = Dilution Factor

C_{is} = Concentration of internal standard added to extract ug/L

A_{is} = Area response of internal standard

RRF = Relative response factor of analyte (section 11.2). For TPH RRF is the average of all the nC8-nC40 RRFs in the initial calibration.

V_i = Volume of extract injected, uL

V_s = Volume of sample, ml

(b) Soil and Sediment

$$C \text{ (ug/kg)} = \frac{(A) (C_{is}) (D) V_t}{(RRF) (W_s) (A_{is}) V_i (1000)}$$

C = Concentration of compound to be measured, or Concentration of TPH, ug/Kg

W_s = Dry sample weight, g

(c) The FID Relative Response Factor (RRF) calculation for a specific compound or TPH.

$$\text{RRF} = \frac{C_{is} \times A_{cs}}{A_{is} \times C_{cs}}$$

Where: C_{cs} = Concentration of calibration compound or TPH standard, ug/L

C_{is} = Concentration of internal standard, 5-androstane, ug/L

A_{is} = Area Response of internal standard

A_{cs} = Area of calibration compound or TPH standard

11.3 Concentration based on External Standard

11.3.1 The concentration of each analyte in the sample may be determined by calculating the amount of analyte injected, from the peak response, using the calibration curve or the calibration factor (RF) determined in Step 7.1.3. The concentration of a specific analyte is calculated as follows:

(a) Aqueous samples

$$\text{Concentration (ug/L)} = \frac{(A) (D) (V_t)}{RF (V_s) (V_i)}$$

RF = Calibration factor of an analyte (Section 7.1.3) or TPH average response of all the nC8 - nC40 RFs in the initial calibration.

(b) Non-aqueous

$$\text{Concentration (ug/Kg)} = \frac{(A) (D) (V_t)}{RF (W_s) (V_i)}$$

RF = Calibration Factor (area/ng)

11.4 Matching Chromatographic Patterns – The following provides the basis for identification of the type of petroleum product. ASTM Method “Standard Practice for Oil Spill Source Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectroscopy,” should be used to make more definitive identifications.(27)

11.4.1 Interpretation (From ASTM D3328, (1))

a .

Basis of Matching – The source of petroleum oil can be identified by comparison of the chromatogram to that of a suspected source oil or that of a reference oil. Identical petroleum products give matching chromatographic peak patterns.

b. Chromatogram Features - The major features of the chromatogram that are used for comparison are listed as follows:

A FID chromatogram shows the features of a homologous series of normal paraffins, the isoprenoid hydrocarbons pristane and phytane, the other resolved peaks and the unresolved envelope. All of these features are used to characterize petroleum oil.

c. Weathering effects: - When petroleum is spilled on open water or spilled on open ground, weathering will progress rapidly. A thin slick on open water may lose significant amounts of its components, up to nC15, 271°C, atmospheric boiling point, within 48 hours of being spilled. Soil samples will lose the soluble fraction through leaching. Biological degradation of petroleum begins within seven days. It is important to be aware of the effects of weathering when matching chromatograms of spill samples more than a few hours old. It is advisable to compare only those portions of chromatograms boiling above pentadecane in order to minimize the difference resulting from weathering. Reference oils can be weathered in the laboratory using the method of Reference 10.

Light distillate fuels cannot survive heavy weathering and have few hydrocarbons above C15. Comparison of the residues of these oils can only be done qualitatively - from about C8-C15.

d. A direct comparison of chromatograms will establish identity or nonidentity between samples. The comparison involves a peak-for- peak matching, noting differences or similarities in

relative peak height. If the chromatograms are the same on the basis of the peak-for-peak matching, there is a high probability that the samples are from the same source. A mismatch occurs when the chromatograms are different. The differences may be due to the presence of one or more components or petroleum products in one sample relative to another. Spill samples may contain components such as cleaning detergents, plasticizer, paint vehicles, etc. The presence of one or two components in a spill sample which are absent in a suspect petroleum oil is not absolutely indicative of non-identity.

- e. If the ratio of pristane/phytane in the unknown and reference petroleum oil match within $\pm 15\%$, the fingerprint match is confirmed.

11.5 Percent Recovery of Surrogate Standards (section 6.8.3) (5)

Percent recovery is calculated using the surrogate and the 5-androstane GC internal standard, (C_{is}).

$$\% R_{SS} = \frac{(A_{ot})(C_{is}) \times 100}{(C_{ot})(A_{is})}$$

Where: C_{ot} = Concentration of surrogate

A_{ot} = Area of surrogate

Percent recovery based on External Calibration

$$\% R_{SS} = \frac{C_{of}}{C_{ot}} \times 100$$

Where: C_{of} = Concentration of surrogate found

11.6 Percent Solids (P)

$$P = \frac{D_s}{T_s} \times 100$$

D_s = Weight dry Sample, g

$T_s = \text{Weight wet Sample, g}$

11.7 Dry Weight (S)

$$S = \frac{\text{Wet Weight} \times P}{100}$$

12.0 REPORTING REQUIREMENTS AND DELIVERABLES

The following minimal information must be provided to the Department on request. The Laboratory must keep this information on file and available for inspection by the Department as per N.J.A.C. 7:18 (16).

12.1 Chain of custody documents. For every sample submitted to the laboratory, both field and laboratory chain of custody documents **MUST** be provided at the end of the final data report. The chain of custody must show the signatures of the sample custodian, extraction supervisors and any other personnel who handled the sample. It must clearly track the movement of the sample through the laboratory by showing the relinquishing and acceptance of the sample by each person.

12.2 Methodology Review

The laboratory shall provide a brief narrative outlining the essential points of each method actually employed in the analysis of the samples submitted to the laboratory.

12.3 Non-Conformance Summary Report

The laboratory shall describe in narrative and/or tabular form any item which does not conform to the requirements of this method. This shall include but is not limited to a discussion of missed holding times, of failed Quality Assurance/Quality Control criteria, sample matrix effects on the analysis, sample dilutions, re-analyses, corrective actions taken and deviations from the analytical method specified on the analytical request form or the preparative methods permitted.

12.4 Sample Data Package - must contain the following information in sequence:

12.4.1 Quantitative Sample Results Summary (uncorrected for blank), Blank Results and Method Detection Limits.

12.4.2 Qualitative Sample Result Summary (For fingerprint work)

12.4.3 Quantitation Reports

12.4.4 Sample Chromatograms

The chromatograms must be clearly labeled with the following information:

- a. Sample identification number.**
- b. Volume injected.**
- c. Date and time of injection.**
- d. GC Column identification.**
- e. GC instrument identification - exact instrument employed.**
- f. Positively identified compounds, either directly above the peak or on a printout of retention times, if the retention times are printed on chromatograms.**
- g. Internal Standards labeled.**
- h. Surrogate labeled.**
- i. Analyst signature.**

12.5 Quality Control Summary - must contain the following items:

- a. Surrogate Recovery Summary**
- b. QC Check Sample Recovery**
- c. Method Blank Summary**
- d. Matrix Spike Summary**
- e. Duplicate Summary**

12.6 Standard Data Packages - must contain the following items:

- a. Initial Calibration Data Summary**
- b. Continuing Calibration Data Summary**
- c. Chromatograms of Standards and Quantitation Reports**
- d. Chromatograms of Reference Standards where applicable**
- e. Chromatograms of Samples**

12.7 Raw QC Data

- a. Blank Chromatograms**
- b. LCS Chromatograms**
- c. MS Chromatograms**

12.8 Qualitative sample Results Summary - list sample fingerprint Matches (ASTM D3328 (1))

- a. Based upon the visual comparison of source urine chromatograms, and after considering weathering, report the sample of unknown origin as belonging to one of the categories below:**

1. **Match** - The chromatogram is identical to one, or more, of the samples submitted for comparison.
 2. **Probable Match** - The chromatogram is similar to one, or more, of the samples submitted for comparison, except: (a) for changes which can be attributed to weathering, or (b) differences attributable to specific contamination.
 3. **Indeterminate** - The chromatogram is similar to one, or more, of the samples submitted for comparison, except for certain differences as in 2, of such magnitude that it is impossible to determine whether the unknown is the same petroleum oil heavily weathered, or a totally different oil.
 4. **Mismatch** - Unlike the samples submitted for comparison.
- b. Compare unknowns to a library of the products listed in Section 1.1.

13.0 REFERENCES

1. ASTM, "Comparison of Waterborne Petroleum Oils by Gas Chromatography", Method D3328-00, Annual Book of ASTM Standards, Volume 11.02, Philadelphia, PA, 2000.
2. Staff, Oil Spill Identification System, Report No. GCD-52-77, U.S. Coast Guard R & D Center, page DI. National Technical Information Center, Springfield, VA, 1977.
3. Leaking Underground Fuel Tank, Task Force "Leaking Underground Fuel Tanks Field Manual," Appendix C, State Water Resources Control Board, Sacramento, CA 1988.
4. U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste -- Physical Chemical Methods, Office of Solid Waste, Washington, DC, Publication SW846, 3rd ed. update III 1996.
5. Douglas, G.S., "Total Petroleum Hydrocarbons in water and Soil", Verbal Communication, Enseco Corp., Cambridge, MA 1988.
6. Miller, M., Analytical Chemistry Manual for Petroleum Products in the Environment, NJDEPE OQA-QAD-002, 1992.
7. U.S. Environmental Protection Agency, Federal Register, 40 CFR 136, Appendix A and B, Volume 49, No. 209, July 1, 1990.

8. "OSHA Safety and Health Standards, General Industry," (29CFR1910), occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).
9. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
10. ASTM, "Practice for Preparation of Samples for Identification of Waterborne Oils," "Method 3326-90, Annual Book of ASTM Standards, Vol. 11.02, Philadelphia, PA, 2000.
11. ASTM, "Practice for Identification of Waterborne Oils," "Method 3415-98, Annual Book of ASTM Standards, Vol. 11.02 Philadelphia, PA, 1998.
12. Zafiriou, O., Stainken, D. et al, "Correlation of Oils and Oil Products by Gas Chromatography," Environmental Protection Technology Series, EPA-600/2-77-163, August 1977.
13. Potter, Thomas, "Fingerprinting Petroleum Products, Unleaded Gasolinell , Proceeding of the Fourth National Conference of Hydrocarbons Contaminated Soils, Chapter 8, page 83, Lewis Publishers, Chelsea, MI, 1990.
14. Remeta, D.P., and Grundfeld, M. "Emergency Response Analytical Methods for Use On Board Mobile Laboratories," Internal Communication, USEPA Hazardous Waste Engineering Research Laboratory Release Control Branch, 1987.
15. Dudenbostel, B.F., "Use of GC Peak Height Ratios for Passive Tagging of Petroleum Oils", Anal. Quality Control Newsletter, #18, July 1973.
16. NJDEPE, "Regulations Governing Laboratory Certification and Standards of Performance", N.J.A.C. 7:18 as amended July 1984.
17. Taylor, J.K. Quality Assurance of Chemical Measurements, Chapter 14, Page 129, Lewis Pub. Chelsea, MI, 1987.
18. Driscoll, J.D. , Ford, J. et.al, "Gas Chromatographic Detection and Identification of Aromatic and Aliphatic Hydrocarbons in Complex Mixtures by Coupling Photoionization and Flame Ionization Detectors", J. Chromatography, 158, pp. 171-180, 1978.
19. Cox, R.D. and Earp R.F., "Determination of Trace Level Organics in Ambient Air by High resolution Gas Chromatography with simultaneous Photoionization and Flame Ionization Detection," Anal. Chem. 54 pp. 2265-2270, 1982.

20. **Davis, K.V., "A New Photoionization/Flame Ionization Series Detector for Gas Chromatography," presentation, Pittsburgh Conference, March 1990.**
21. **"High Resolution Chromatography Products," J&W Scientific; Folsom, CA, p. 38, 1990.**
22. **"Petroleum/Chemical Applications Guide," Supelco Inc., Bellefonte, PA, 1990.**
23. **Thomas, D.H. and Delfino, I.I., "A Gas Chromatographic/Chemical Indicator Approach to Assessing Ground Water contamination by Petroleum Products," Ground Water Monitoring Research, p.90, fall, 1991.**
24. **Miller, M.W., Appleby, C. Wright, D., Skelton, P., "A Gas Chromatography Method to Replace Method 418.1 for the Determination of Total Petroleum Hydrocarbons", Presented at National Conference on Contaminated Soils, Amherst, MA, October 1997. Available on OQA web site (www.**
25. **Florida Department of Environmental Protection, "Method for Determination of Petroleum Range Organics," Method #FL-PRO, rev.1a, March 14, 1997.**
26. **Schumacher, D.K., direct communication, "The Use of Chlorobenzene as a Low Temperature Surrogate," Lancaster Laboratories, Inc., Lancaster, PA August 1998.**
27. **ASTM, "Standard Practice for Oil Spill Source Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectroscopy," Method, D5739-00, volume 11.02, Philadelphia, PA, 2000.**
28. **Wright, Daniel, direct communication, "Method Comparisons of Total Petroleum Hydrocarbons: Quantitation of Semi-Volatile Petroleum Products in Water, Soil Sediment and Sludge" OQA-QAM-025 vs EPA Method 418.1," Fort Monmouth Environmental Testing Laboratory, Monmouth, NJ January 1996, June 2005.**

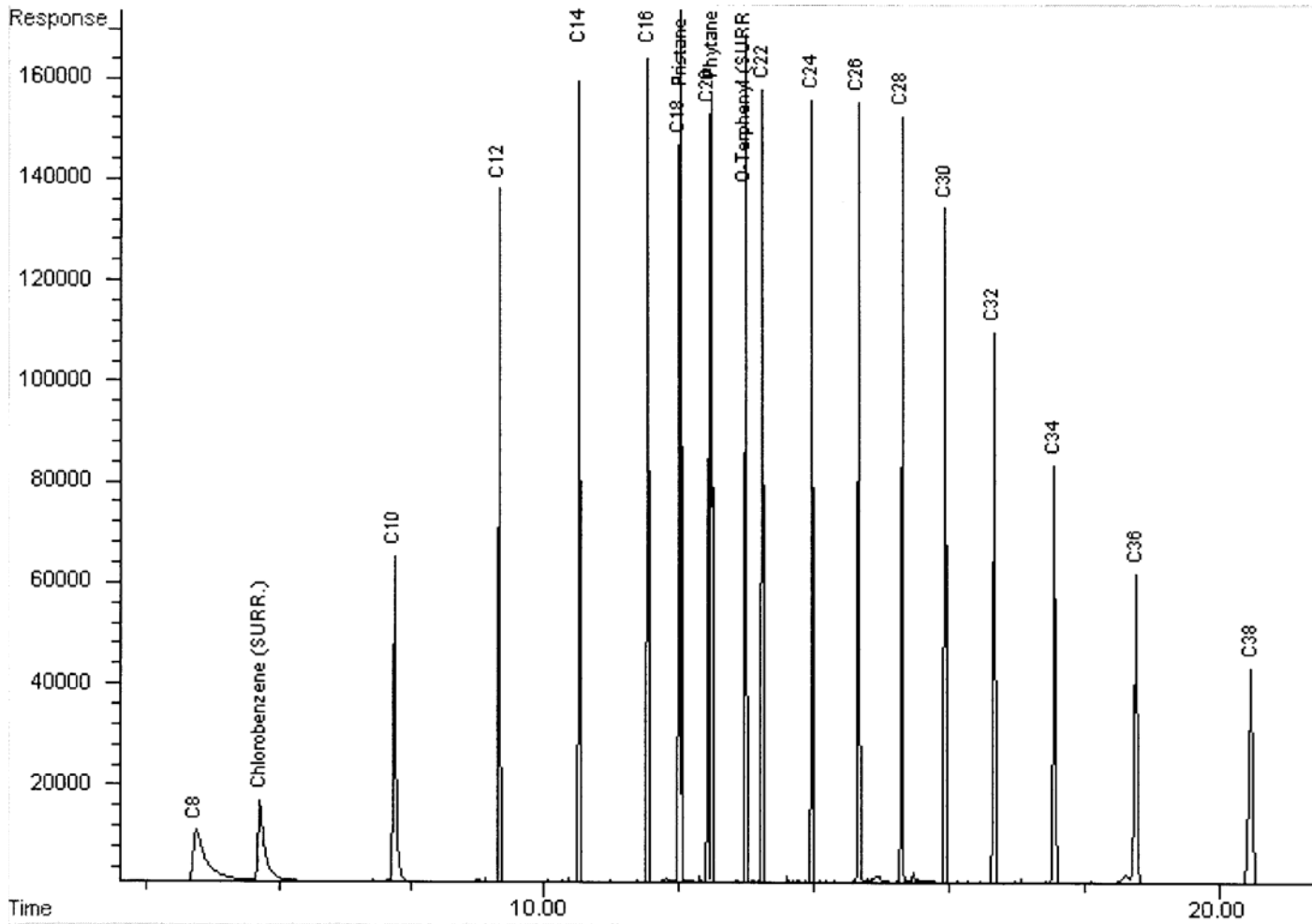


Figure 1. Normal Paraffinic Hydrocarbon Standard (50 PPM TPHC on column).

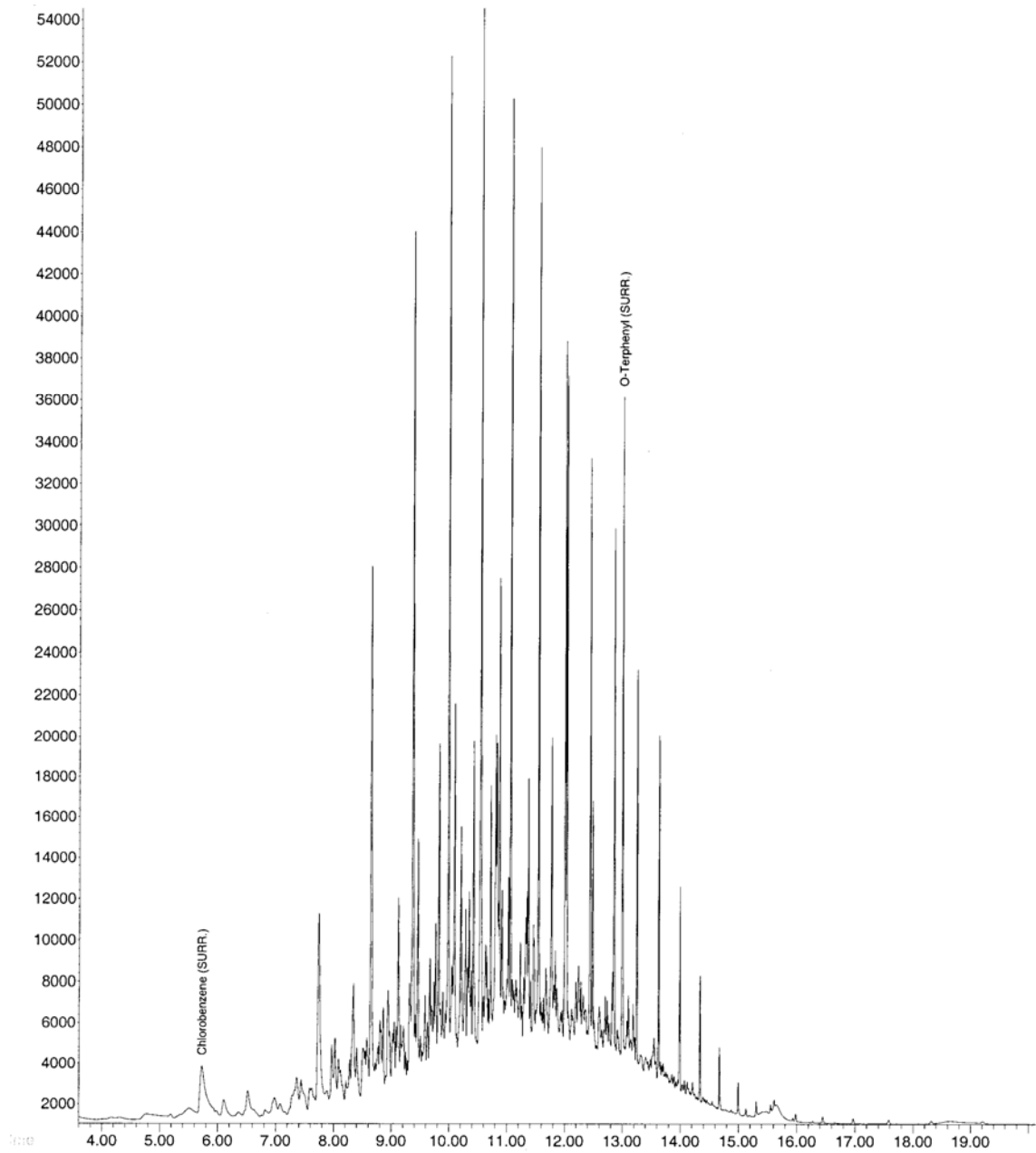


Figure 2. Diesel, Fuel Oil # 2 Standard (50 PPM TPHC on column).

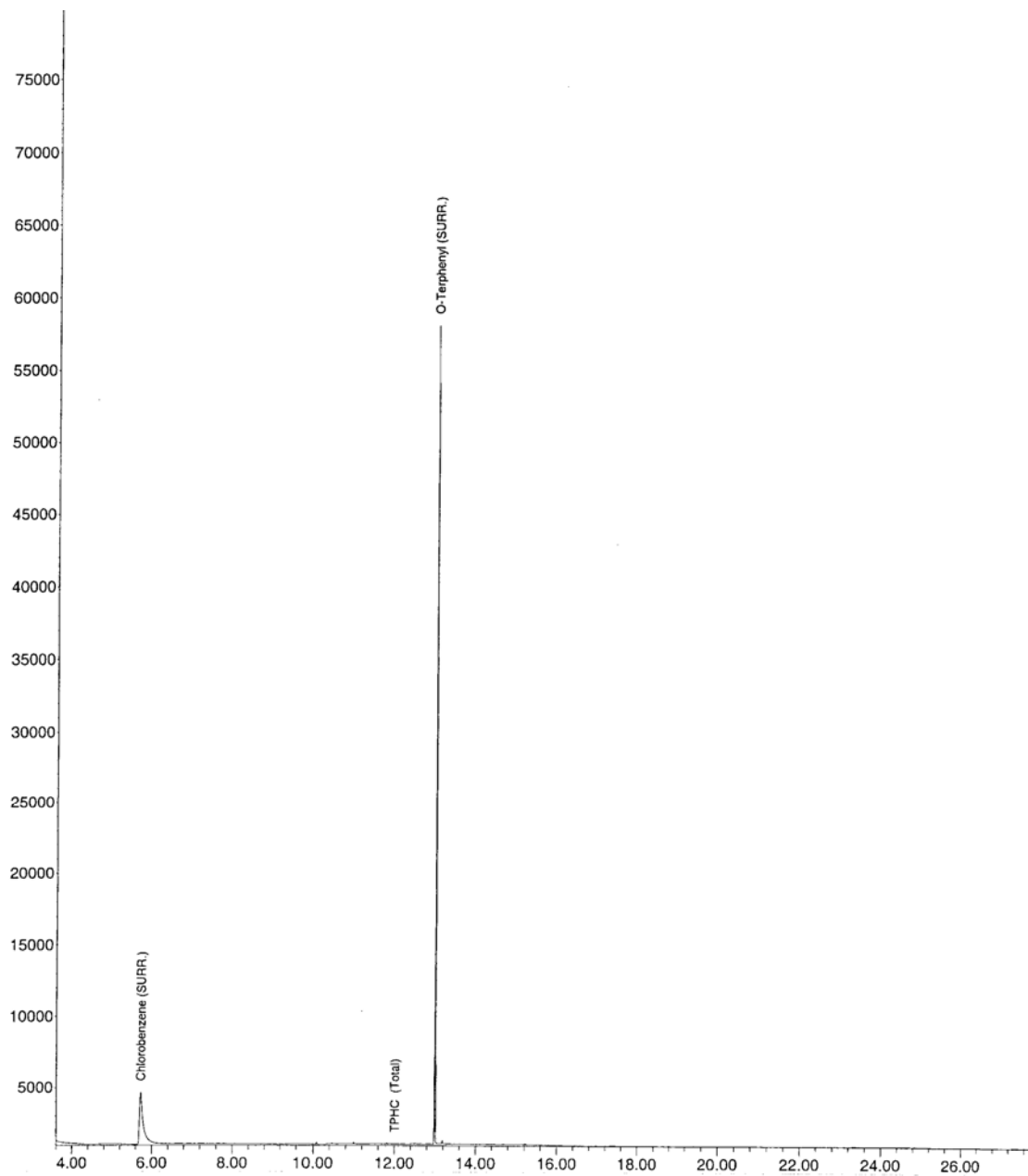


Figure 3. Method Blank.

VISION LOG:

<u>Version #</u>	<u>Effective Date</u>	<u>Change</u>
05	02/05/01	6.8.3 addition of chlorobenzene as a surrogate
06	09/19/05	Major changes as follows: 1.4.1.2 Reference to ASTM Method “Standard Practice for Oil Spill Source Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectroscopy,” 2.4 Performance Based Measurement statement 7.1.3 Addition of Figure 1. Normal Paraffinic Hydrocarbon calibration standard gas chromatogram 7.1.4 Addition of Figure 2. Diesel, Fuel Oil #2 calibration standard gas chromatogram 7.1.6 Addition of the requirement to analyze an Initial Calibration Verification Standard. 8.4 Surrogate percent recovery, %P replaced by %R _{SS} 8.5.2 Matrix Spike (MS) percent recovery %R _{MS} Limits 70 – 130% 8.8 MDL confirmed at 2-3 x MDL 10.3.5 Addition of Figure 4. Diesel Contaminated soil extract (3550) gas chromatogram 10.8 Addition of the requirement to analyze a Calibration Blank after the Initial Calibration Verification Standard and continuing Calibration Standard. 11.1.2 Baseline area response discussion AND Addition of Figure 3. Method Blank

<u>Version #</u>	<u>Effective Date</u>	<u>Change</u>
07	03/01/08	<p>Major Changes as Follows:</p> <p>9.1.3 (Aqueous holding time) Samples must be extracted within 14 days from the time of collection or 12 days from verified sample time of receipt (VSTR). Extracts must be analyzed within 40 days of extraction.</p> <p>9.2.3 (Solids holding time) Samples must be extracted within 14 days from the time of collection or 12 days from VSTR. Extracts must be analyzed within 40 days of extraction.</p> <p>13.0 References</p> <p>#24. Miller, M.W., Appleby, C. Wright, D., Skelton, P., "A Gas Chromatography Method to Replace Method 418.1 for the Determination of Total Petroleum Hydrocarbons", Presented at National Conference on Contaminated Soils, Amherst, MA, October 1997. Available on OQA web site (www.nj.gov\dep\oqa\doc)</p>