

Interlaboratory Study of Three Methods for Analyzing Petroleum Hydrocarbons in Soils

- Diesel-Range Organics (DRO)
- Gasoline-Range Organics (GRO)
- Petroleum Hydrocarbons (PHC)

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Health and Environmental Sciences Department

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**PREPARED UNDER CONTRACT BY:
TISCHLER/KOCUREK
ENESCO-ROCKY MOUNTAIN
ANALYTICAL LABORATORY**

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ABSTRACT

This report presents the results of an interlaboratory study conducted by the American Petroleum Institute (API) to validate three methods for analyzing petroleum hydrocarbons in soil: diesel-range organics (DRO) for C_{10} to C_{28} hydrocarbons, gasoline-range organics (GRO) for C_6 to C_{10} hydrocarbons, and petroleum hydrocarbons (PHC) for C_6 to C_{28} hydrocarbons. Secondary goals of the study were to estimate interlaboratory practical quantification levels (PQLs) for the three methods; and to demonstrate that the GRO method with optional photoionization detection (PID) could be used to analyze for benzene, toluene, ethylbenzene, and total xylenes (BTEX) so that both BTEX and total hydrocarbons could be obtained from the same method and the same sample.

Method performance was judged by accuracy, overall precision, and single analyst precision. Accuracy for DRO and PHC was 82-84% while GRO accuracy was 70%. Overall precision, as relative standard deviation (RSD), averaged 27% for the three methods. Single analyst precision, as RSD, was about half of the overall precision (14%). Overall precision as RSD for BTEX analysis by GRO/PID were 27% for benzene, 19% for toluene, 44% for ethylbenzene, and 15% for total xylenes. Since accuracy and precision were found to be concentration-dependent, regression equations were developed to describe expected method performance at different concentrations. Practical quantification levels (PQLs) were estimated by two different methods. The range in PQLs was 12-20 mg/kg for DRO, 17-130 mg/kg for GRO, and 50-104 mg/kg for PHC.

Acceptable method performance for the DRO, GRO, and PHC methods was demonstrated by this interlaboratory study. Performance in accuracy and precision was comparable to the results of other validation studies conducted by the U.S. Environmental Protection Agency (EPA).

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EXECUTIVE SUMMARY

This report presents the results of an interlaboratory study conducted by the American Petroleum Institute (API) for the purpose of validating three methods for the analysis of petroleum hydrocarbons in soil. These methods overcome many of the limitations of currently available methods and if validated, could be considered for use as consensus methods for petroleum hydrocarbons in soils.

The three methods which were the subject of this interlaboratory study are:

- Diesel-Range Organics (DRO) for C_{10} to C_{28} hydrocarbons
- Gasoline-Range Organics (GRO) for C_6 to C_{10} hydrocarbons
- Petroleum Hydrocarbons (PHC) for C_6 to C_{28} hydrocarbons

The GRO and DRO methods were developed by API, and the PHC method was developed by Shell Development Company.

A secondary goal of the study was to estimate interlaboratory practical quantification levels (PQLs) for each method. A third goal was to demonstrate that the GRO method with optional photoionization detection (PID) could be used to analyze for benzene, toluene, ethylbenzene, and total xylenes (BTEX) so that both BTEX and total hydrocarbons could be obtained from the same method and the same sample.

Results and conclusions from this study are:

- Acceptable method performance for the DRO, GRO, and PHC methods has been demonstrated by this interlaboratory study. Performance in accuracy and precision is comparable to the results of other validation studies conducted by the U.S. Environmental Protection Agency (EPA).
- Method performance was judged by accuracy, overall precision, and single analyst precision. With the exception of GRO accuracy, the performance among the three methods was essentially the same. Accuracy for DRO and

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PHC was 82-84% while GRO accuracy was 70%. Overall precision, as relative standard deviation (RSD), averaged 27% for the three methods. Single analyst precision, as RSD, was about half of the overall precision (14%).

- Since accuracy and precision were found to be concentration-dependent, regression equations were developed for all three methods to describe expected method performance at different concentrations. A reliable regression equation could not be developed for PHC single analyst precision, however, so the average precision was used to describe method performance for this parameter. The PHC single analyst precision regression could be improved with data from future studies.
- Precision as measured by average relative standard deviation (RSD) for benzene, toluene, ethylbenzene, and xylene isomers (BTEX) analyses by GRO/PID were 27% for benzene, 19% for toluene, 44% for ethylbenzene, and 15% for total xylenes.
- Some laboratories did not strictly follow method protocols. Alternative standards, detectors, and integration techniques were used by some laboratories. Recurrence of such deviations from method protocols can be minimized by emphasizing the requirements already specified in the methods and pointing out problems that result if they are not followed.
- Practical Quantification Levels (PQLs) were estimated by two different methods. The range in PQLs was 12-20 mg/kg for DRO, 17-130 mg/kg for GRO, and 50-104 mg/kg for PHC.
- False positive rates were 22% for GRO and 20% for PHC. The false positive rate for DRO was not calculated because all laboratories reported measurable DRO concentrations in DRO blank samples. The blank samples were either inadvertently spiked with diesel fuel or were low-level DRO samples mislabeled as blanks.
- False negatives were reported for low-concentration samples only. The false negative rate for DRO and GRO was 22% at concentrations of about 5 mg/kg; the PHC false negative rate was 3% at concentrations of 50 to 100 mg/kg.
- The average rejection rate for outliers was 25%, slightly higher than for similar interlaboratory studies conducted by EPA.

Section 1. INTRODUCTION

BACKGROUND

Since 1987, the American Petroleum Institute (API) has funded efforts to establish reliable analytical laboratory methods for the measurement of a wide range of petroleum hydrocarbons in soil. Currently available methods, although many are approved by the U.S. Environmental Protection Agency (EPA) and are in wide use by laboratories, are generally limited to certain analytes and/or are lacking in rigorous method performance data. For example, many total petroleum hydrocarbon (TPH) tests use Freon-113[®], which is not effective in extracting heavy distillates. TPH tests also have low recoveries for volatile hydrocarbon components of gasoline. Results from analyte-specific methods, such as EPA's SW-846 methods and 600 series, are difficult to correlate to particular petroleum products.

As a consequence, API sought to develop improved methods for gasoline-range and diesel-range organics in soil. API conducted a literature search and symposium to identify an analytical procedure for gasoline-range organics, originally defined as hydrocarbons in the C₆-C₁₀ range, at environmental (ppb or ppm) concentrations. The selected method was to rely on existing technology and consider regulatory guidelines. The method selected was a capillary column gas chromatography/flame ionization detector (GC/FID) technique, with sample introduction by extraction in methanol followed by purge-and-trap. A single laboratory validation study was conducted, as well as an evaluation of sampling techniques. The initial draft of the GRO method, the results of the single laboratory validation study, and the evaluation of sampling techniques are presented in Enseco (1991).

The interlaboratory study presented in this report is a continuation of the GRO research reported in Enseco (1991). Since that study, two additional methods - a diesel-range organics (DRO) method to measure C₁₀-C₂₈ hydrocarbons, and a

petroleum hydrocarbons (PHC) method to measure C₆-C₂₈ hydrocarbons - have been drafted and are also addressed by this interlaboratory validation study. The GRO and DRO methods were developed by API, and the PHC method was developed by Shell Development Company.

RATIONALE FOR METHOD VALIDATION

According to EPA (1988), validation consists of the selection of a cost-effective method capable of producing measurements of the type and quality desired for a particular application; and the verification that the selected method is technically sound and has been reduced to practice for practical purposes. General validation consists of testing, evaluating, and characterizing the method to the extent necessary to demonstrate that the method achieves a specified performance. General validation includes (EPA, 1988):

- Formal performance testing
- Peer review and comment
- Development of acceptance criteria
- Specification of QA/QC requirements

This report documents the results of multiple laboratory performance testing of the GRO/DRO/PHC methods on prepared soil samples, the modification of method protocols in response to subsequent peer review and comment, and the development of method acceptance criteria based on performance data. The resulting revised method protocols, including QA/QC requirements, are provided in Appendix A.

VALIDATION STUDY GOALS AND OBJECTIVES

The primary goal of this study was to validate the GRO, DRO, and PHC methods with acceptable accuracy and precision. If validated, the methods could be considered for use as consensus methods for petroleum hydrocarbons in soils. A secondary goal of the study was to estimate interlaboratory practical quantification levels (PQLs). A third goal was to demonstrate that the GRO method with optional photoionization detection

(PID) could be used to analyze for benzene, toluene, ethylbenzene, and total xylenes (BTEX) so that the analytical results for both BTEX and total volatile hydrocarbons could be obtained from the same method and the same sample.

Detailed descriptions of these methods and the single laboratory validation results have been described previously (Walters *et al.*, 1992; Parr *et al.*, 1991; Enseco, 1991; Rhodes *et al.*, 1991a,b). All three methods are based on determination by gas chromatography-flame ionization detection (GC/FID) and are derived from EPA SW-846 Methods 8000, 8015, and 8100, and The American Society of Testing and Materials (ASTM) Method D 3328-78. All three methods have extensive quality control requirements, including quality control (QC) check sample analyses, surrogate spikes, blank analyses, and calibration. Matrix spikes, duplicates, field blanks, and other related QC samples are recommended as necessary to meet specific project objectives. The primary goal of each method is to determine the total concentration of chromatographable material that responds to an FID within a given hydrocarbon range. Where possible, the methods allow for identification of various petroleum products. Extensive single laboratory validation data previously presented for each method indicate that the methods are suitable for environmental application within the limitations described in the methods.

The February 1992 final drafts of the methods were sent to 15 participating laboratories. Copies of these methods, which have been revised to include the method performance data developed by this study, are included in Appendix A.

General descriptions of the methods are as follows:

- **Diesel-Range Organics** - This method was designed to quantify distillate petroleum products such as diesel fuel, jet fuels and home heating oil. The sample is extracted with methylene chloride, then after a concentration step, the extract is analyzed by GC/FID. Sample results are based on the total chromatographic area between and including C₁₀ and C₂₈ alkanes. Calibration is based on a synthetic blend that contains ten even n-alkanes (n-C₁₀ through n-C₂₈). However, an authentic standard such as diesel fuel or fuel oil

may be used. Internal or external standard calibration may be used.

- **Gasoline-Range Organics** - This method is based on purge and trap GC/FID analysis of a methanol extract of the sample. A key element in the method is field preservation with methanol, which stabilizes organic components by solubilization and minimizes microbial degradation. Sample results are based on the total chromatographic area between and including C₆ and C₁₀ alkanes, as compared to a synthetic blend of gasoline components or an authentic standard such as gasoline. The method contains an option to measure volatile aromatic components using a PID.
- **Petroleum Hydrocarbons** - This method covers a wider hydrocarbon boiling range than either the DRO or GRO methods, and complements them as a total petroleum hydrocarbon (TPH) technique. The method is based on micro-extraction with methylene chloride followed by GC/FID analysis. Results are based on the total chromatographic area between and including C₆ and C₂₈ alkanes. Calibration using a gasoline and/or diesel standard is preferred over a synthetic multicomponent hydrocarbon standard.

The PHC method can be used for the estimation of boiling point distribution and/or identification of the type of petroleum product present. This type of information is extremely useful in selection of remediation techniques and in risk assessment.

Section 2

STUDY DESIGN

Procedures for use in conducting interlaboratory studies are thoroughly described in a number of reference documents (ASTM, 1986; Taylor, 1983; EPA, 1987; Youden and Steiner, 1975). These procedures typically involve the analysis of stable test materials by multiple laboratories. Generally, at least three concentrations are analyzed and a minimum of six valid data sets are required for each concentration.

SAMPLE PREPARATION

Soil samples for this interlaboratory validation study were prepared by Environmental Resource Associates. Each laboratory received eight prepared soil samples for each analytical method. Of the eight, one sample was a blind, unspiked blank and one was a blind, spiked sample near the practical quantification level (PQL) recommended in the method protocol. The other six samples were set up as three Youden pairs - low, medium, and high concentrations - to cover typical analytical ranges. A Youden pair consists of two samples with different, but similar, concentrations. Instead of duplicates, Youden pairs are used in performance tests to prevent any tendency on the laboratory's part to second-guess the analytical result. Youden pairs are also useful in identifying systematic errors in individual laboratories.

Table 2-1 shows the prepared sample GRO, DRO, and PHC concentrations in milligrams per kilogram (mg/kg). The GRO, DRO, and PHC concentrations in Youden pairs were verified by GC/FID analysis following methanol extraction; at least three randomly selected ampules were obtained from each lot for verification analysis. Average recoveries for the Youden pairs were 98% for DRO, 81% for GRO, and 94% for PHC samples (see Appendix B for verification data).

Table 2-1. Sample Concentrations

Concentration	Diesel Range Organics [mg/kg]	Gasoline Range Organics [mg/kg]	Petroleum Hydrocarbons [mg/kg]
Low	19.3 20.7	18.5 21.6	93.6 104
Medium	77.1 82.6	55.4 65.2	374 416
High	193 204	111 130	748 831
Near-PQL	4.99	5.02	50.4
Blank	0	0	0

GRO samples were spiked with an API reference gasoline (API 91-1) weathered to 50% of its initial volume by evaporation under a constant stream of helium in a 60°C water bath. DRO samples were spiked with diesel fuel from a local gas station. PHC samples were spiked with a mixture of weathered API gasoline (50.4% by weight) and diesel fuel (49.6% by weight).

Soil used to prepare the samples was topsoil that had been dried and sieved. Laboratories were instructed to use the entire, preweighed sample for analysis. Each ampule was coded (e.g., GRO-1), and the laboratories were not informed of the experimental design or the expected concentration range.

PARTICIPATING LABORATORIES

API's intent was for participating laboratories to have prior experience in the GC analysis of soil samples containing petroleum hydrocarbons. At the "Analytical Methods for Petroleum Hydrocarbons Workshop," held in Colorado Springs, Colorado, in February 1992, API gave initial notice of its intent to conduct this study. API gave formal notice to interested laboratories in April 1992. API sent notices to the Association of California Testing Laboratories (ACT); the International Association of Environmental Testing Laboratories (IAETL); various state underground storage tank program managers; specific laboratories identified by API's Environmental Monitoring Workgroup; and other state, commercial, and API member company laboratories. API considered six as the minimum number of laboratories necessary for reliable statistical

analysis of the data. Laboratories were selected based on interest in participating in the study and on a statement from each indicating an ability to perform the methods.

In total, fifteen laboratories participated in the round robin, although not every laboratory analyzed all three groups of samples. Thirteen laboratories analyzed DRO samples, eleven analyzed GRO samples, and twelve analyzed PHC samples. In addition, following API's suggestion, six of the laboratories measured BTEX concentrations using the GRO method with the optional PID.

The participating laboratories are shown in Table 2-2. To protect confidentiality, each laboratory received an arbitrary number for data coding. These laboratory numbers, which appear in numerical order in tables throughout this report, do not follow the same order as the listing in Table 2-2.

Table 2-2. Participating Laboratories

Participating Laboratories	DRO	PHC	GRO	GRO BTEX
California Department of Health Services	X	X	X	
Core Labs	X	X	X	
Enseco-Erco	X	X	X	
Enseco-RMAL	X		X	X
ETC	X		X	X
Mid-Continent Testing		X	X	X
Montgomery Laboratories	X	X		
Pacific Northwest Environmental Laboratories	X	X	X	X
Pennsylvania Department of Environmental Resources	X	X		
Resource Consultants, Inc.	X	X		
Shell Development Co, Westhollow Research Ctr.		X		
University of Iowa Hygienic Lab	X	X	X	
Wadsworth Alert Laboratories - Florida	X	X	X	X
Wadsworth Alert Laboratories - Ohio	X	X	X	
Wisconsin State Laboratory of Hygiene	X		X	X
<i>Total</i>	13	12	11	6

Laboratories received copies of the methods, instructions for performing the study, and a form for data entry. The instructions and data entry format were comparable to those issued by EPA and ASTM for similar studies.

DATA ANALYSIS

Data analysis covers outliers, accuracy and precision, PQLs, and false positives/negatives. Original data and data calculations are provided in Appendix C.

Outliers

The raw data and worksheets from the laboratories were initially reviewed by API's Environmental Monitoring Workgroup to determine obvious outliers. Laboratories were contacted to resolve errors in calculation and data transcription. These errors were corrected before statistical tests for outliers were performed.

Two statistical methods were used to identify outliers in the data. Outliers identified by these methods were not considered in any of the method performance calculations (i.e., in accuracy and precision, PQL, and false positive/negative determinations). The first method, Youden's ranking test (ASTM, 1986; Youden and Steiner, 1975), was used to identify laboratories that had values that were consistently too high or too low. Youden's test was done separately for each of the three data sets (DRO, GRO, and PHC) using only the low-, medium-, and high- concentration sample pairs; since these were the data that would be used to determine precision and accuracy. If Youden's test identified a laboratory as an outlier, then that laboratory's data were deleted from the data set. For example, Laboratory 7 values for the PHC samples were deleted because Youden's test showed that they were too high compared with the PHC data from the other laboratories.

The second method, Grubb's outlier test (ASTM, 1986; ASTM, 1989; Taylor, 1990), was applied to the data remaining after Youden's test. Grubb's test checks for outliers within each sample. For example, in the PHC data set, Laboratory 3 reported a value of 220 mg/kg for the sample that had a prepared concentration of 93.6 mg/kg. Since

220 mg/kg exceeded the expected upper limit for this sample calculated by Grubb's test (208 mg/kg), this value was deleted as an outlier.

Accuracy and Precision

Accuracy as recovery in mg/kg and overall interlaboratory precision were calculated following ASTM D 2777-86 (ASTM, 1986). For recovery percentage calculations, the prepared concentration was used as the true value. Single analyst intralaboratory precision was calculated using the Youden sample pairs with Youden's technique (Youden and Steiner, 1975) of calculating precision without duplicates. Data pairs with missing values, outlier values, or values below the detection limit were not considered. Regression equations for accuracy and precision were developed using simple linear regression.

Practical Quantification Levels (PQLs)

There is no standard method for calculating PQLs. Of the many methods which have been used before, API selected two that would work within the study design; one developed by EPA and the other by Shell Development Company. EPA's method is based on its definition introduced in the drinking water regulations: the PQL is the lowest value at which 80% of the laboratories can measure within $\pm 40\%$ of the true value (i.e., the prepared concentration). For example, if the PQL under this definition is 100 mg/kg, at least 80% of the laboratory results must fall between 60 mg/kg and 140 mg/kg. The second method was suggested by Shell Development Company in own of its own laboratory performance evaluation studies for volatile organics: the PQL is the lowest value at which at least 95% of the laboratories report a measurable value.

False Positives and False Negatives

False positives occurred when laboratories reported measurable values for samples that were not spiked (i.e., were blanks). Some of the laboratories reported blank concentrations which were below the PQL; however, only blank concentrations above

the PQL were counted as false positives. False negatives occurred when laboratories reported nondetects for spiked samples.

BTEX

Because limited BTEX data restricted statistical analysis, only relative standard deviations for overall precision were calculated from the Youden pairs. The data from one laboratory were deleted as outliers because the values were ≈ 100 times the data from the other five laboratories reporting BTEX. The blank and PQL samples were not included in the overall precision calculations. Also not included in the calculations were data reported below the detection or reporting limit.

Section 3. DISCUSSION

OUTLIERS

Outlier rejection rates were based on the total number of analyses for the low-, medium-, and high-concentration sample pairs, since these were the data that were used to determine method performance in precision and accuracy.

Overall, 25% of the data for these three methods were rejected. The tables in Appendix C include all of the original laboratory values and those identified as outliers in the DRO, GRO, and PHC data sets.

Rejection rates for individual methods were: 31% of the 78 DRO values, 25% of the 60 GRO values, and 19% of the 72 PHC values. In the GRO data set, Laboratory 4 was rejected outright before any outlier statistics were calculated, because its values were ≈ 100 times the prepared concentrations. Possibly a calculation error was involved; the source of the error was never discovered. As this data set did not represent normal analytical deviations, it was not considered in calculation of the GRO outlier rejection rate.

The rejection rates in this study are slightly higher than similar interlaboratory studies conducted by EPA. For example, in the 600 series methods for organics, the rejection rates were 15% for Method 624 (purgeables), 20% for Method 625 (base/neutrals, acids, and pesticides by purge and trap), 17% for Method 601 (purgeable halocarbons by purge and trap), and 20-23% for Method 604 (phenols) (EPA, 1984a-d).

Some of the outlying values may have been caused by the failure of certain laboratories to strictly follow method protocols. Even though the requirements were clearly stated in the method protocols, some laboratories did not use the specified standards, detectors, and/or integration techniques. Laboratories were not deleted, however, unless the statistical tests identified them as outliers.

Since gasoline-range organics, diesel-range organics, and petroleum hydrocarbons as analytes are defined by the particular analytical method employed, deviations in the method will introduce a deviation in the true value of the analyte, i.e., a bias. In practice, the significance of these deviations depended on the particular method and calibration standard used. In general, the significance of the deviation depended on how well the calibration standard matched the sample.

For example, a valley-to-valley integration using PID with gasoline calibration will have significant bias for GRO if unresolved hydrocarbons are present in the standard and are not in the sample. However, this approach can provide accurate quantification for gasoline, provided the calibration standard and unknown have the same hydrocarbon profile. The effect of calibration standard selection was most pronounced for the GRO samples and least for the DRO samples, due to compositional changes associated with weathering the gasoline standard.

Because not all laboratories will realize the impacts certain method deviations will have on their analytical results, API decided to revise the DRO, GRO, and PHC methods to include a discussion of these impacts in order to minimize deviations that would give biased results.

ACCURACY AND PRECISION

The primary objective of this study was to verify that the DRO, GRO, and PHC methods can reliably produce adequate measurements. To meet this objective requires the determination, and subsequent evaluation, of method performance in terms of accuracy and precision.

Determination of Method Performance

After eliminating outliers, the remaining data were plotted to see if accuracy and precision were concentration-dependent. These plots are shown in Figures 3-1 through 3-3. With the exception of PHC single analyst precision, accuracy and precision are shown to vary linearly with concentration.

Regression equations were then calculated to describe method performance criteria. These regression equations are summarized in Table 3-1.

Table 3-1. Regression Equations for Accuracy and Precision

Method	Range for Equations (mg/kg)	Accuracy, as Recovery X (mg/kg)	Overall Precision S (mg/kg)	Single Analyst Precision Sr (mg/kg)
Diesel Range Organics (DRO) Probability*	19.3-207	$X=0.83C-1.20$ [<<0.1%]	$S=0.23X-0.03$ [2%]	$Sr=0.12X+2.01$ [3%]
Gasoline Range Organics (GRO) Probability*	18.5-130	$X=0.66C+1.34$ [<<0.1%]	$S=0.23X+0.39$ [2%]	$Sr=0.13X-0.55$ [1%]
Petroleum Hydrocarbons (PHC) Probability*	93.6-831	$X=0.81C+7.29$ [<<0.1%]	$S=0.30X+0.45$ [<<0.1%]	$Sr=0.07X+16.35$ [51%]

- *Probability distribution from F-test on the regression equation. Regression equations with probabilities of 5% or less would be considered reliable predictors of method performance.*

The reliability of these regression equations was tested by the F-test; the probabilities from the F-test are shown below each regression equation. The probability represents how often one might see such a relationship merely by chance. Therefore, if the probability is low, the relationship is unlikely to occur by chance and the regression equation is considered a reliable predictor of method performance.

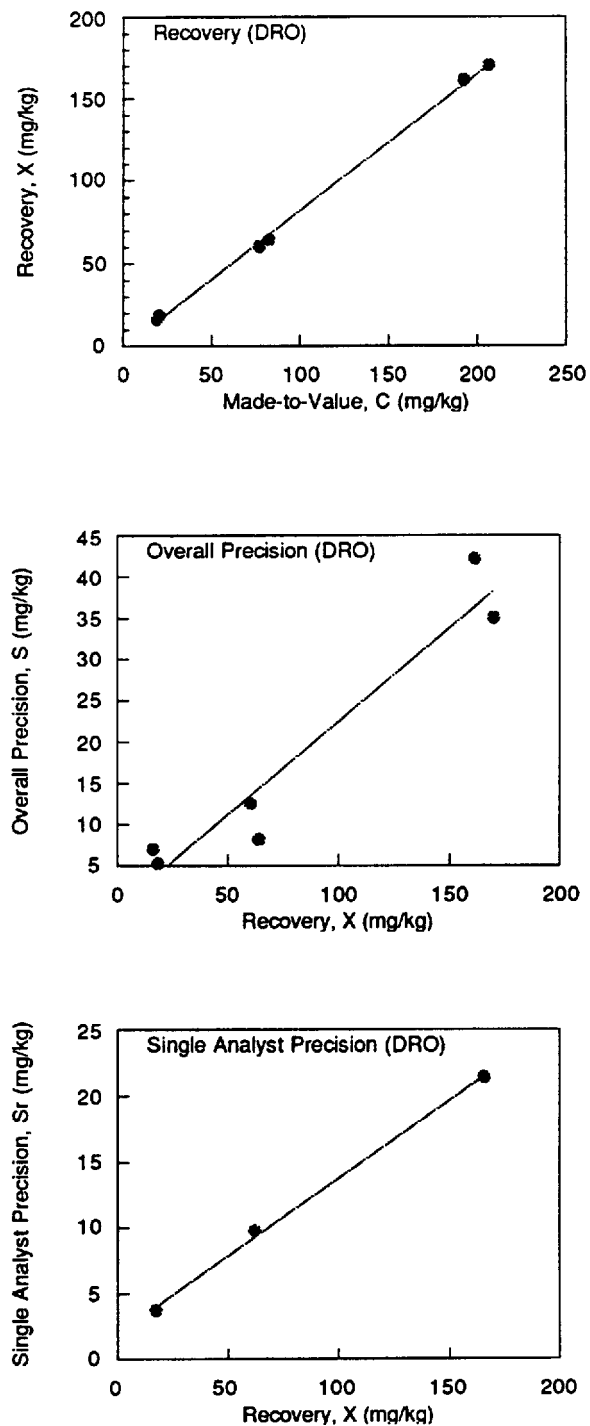


Figure 3-1. DRO Recovery and Precision

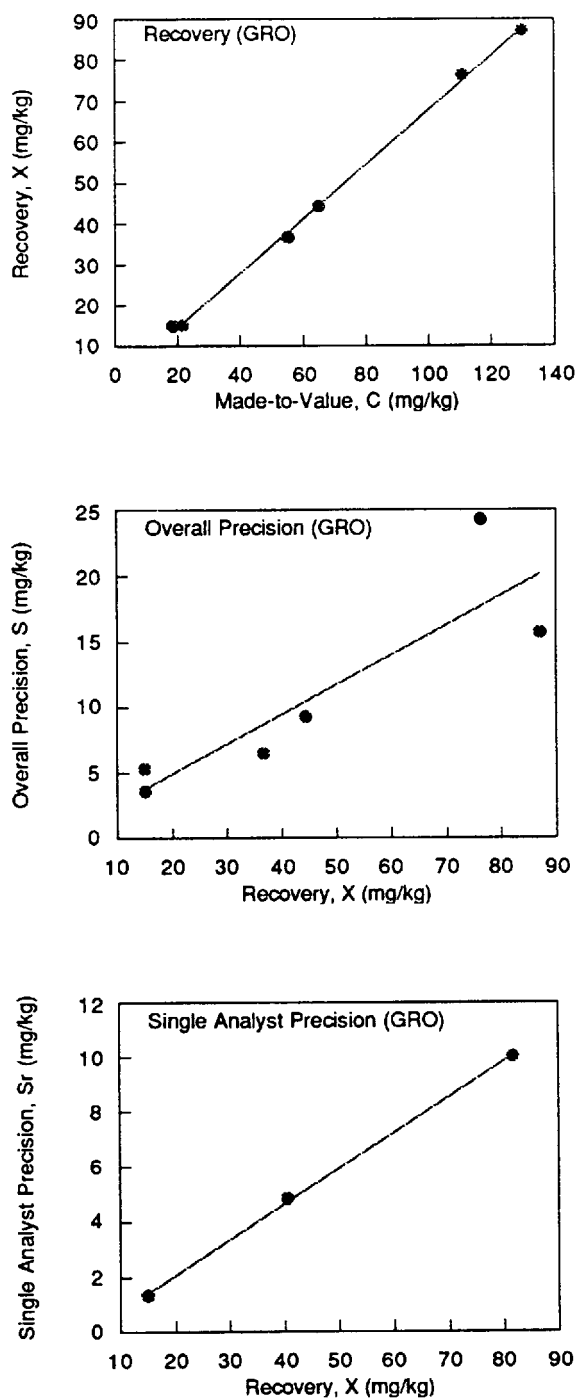


Figure 3-2. GRO Recovery and Precision

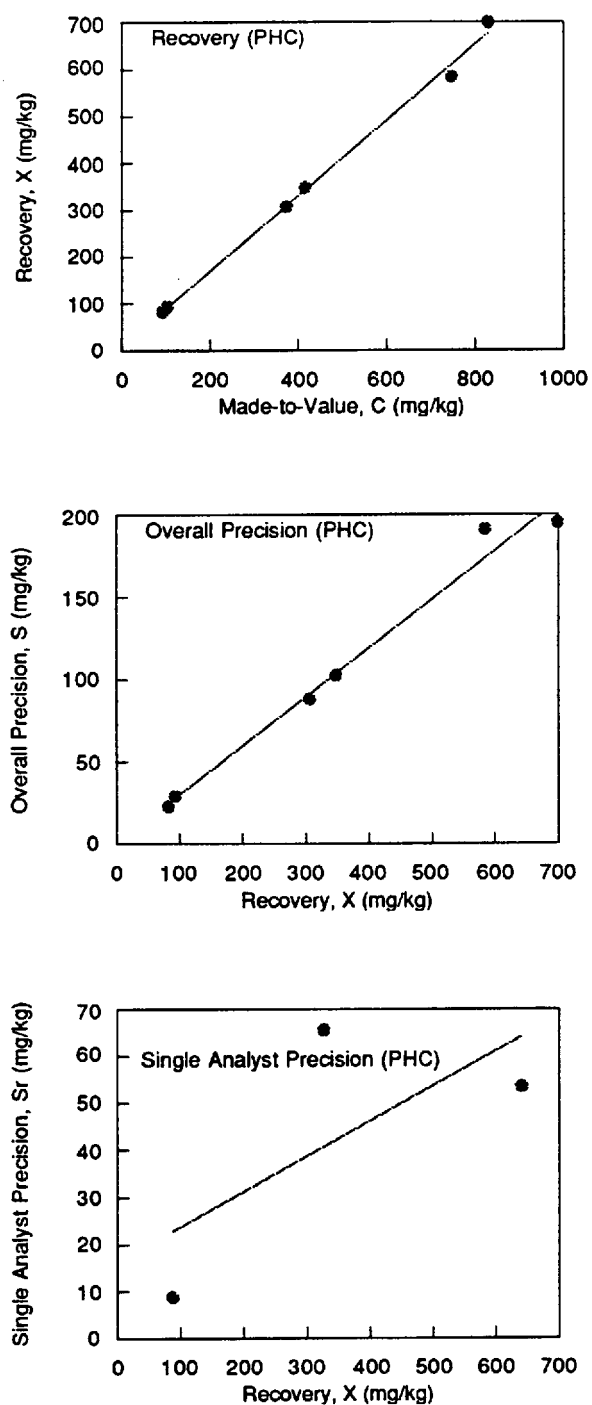


Figure 3-3. PHC Recovery and Precision

There is no established cutoff on the probability level for deciding whether a regression equation can be used as a statement of method performance in an analytical method; however, 5% is a commonly used significance level in statistics tests. On this basis all of the regression equations for method performance shown in Table 3-1, with the exception of PHC single analyst precision, are considered "good fits" and are considered reliable predictors of method performance.

Average values for accuracy and precision for each of the three methods are shown in Table 3-2. These values can be used to describe overall method performance. In the case of PHC single analyst precision, the average value can be used in lieu of a regression equation to describe expected method performance.

Table 3-2. Average Performance: Accuracy and Precision

Method	Average Accuracy (%)	Average Single Analyst RSD* (%)	Average Overall RSD* (%)
Diesel Range Organics (DRO)	82%	17%	25%
Gasoline Range Organics (GRO)	70%	11%	25%
Petroleum Hydrocarbons (PHC)	84%	13%	30%

* Relative Standard Deviation: $(\text{standard deviation} \div \text{mean recovery}) \times 100\%$

With the exception of GRO accuracy, the performance among these three methods was essentially the same. Accuracy for DRO and PHC was 82-84%, while GRO accuracy was 70%. Overall precision, as a relative standard deviation (RSD), averaged 27% for the three methods. Single analyst precision, as RSD, was about half of the overall precision (14%).

Evaluation of Method Performance

Method validation is a value judgement based on an evaluation of method performance in terms of precision and accuracy. One procedure for classifying the level of precision and accuracy of analytical methods has been specified by Taylor

(Taylor, 1987), a recognized expert in statistics and method verification. Taylor's classification system for trace analysis methods is shown in Table 3-3.

Table 3-3. Classes of Trace Analysis Methods

Class	Precision (RSD)	Accuracy (% Recovery)	Nomenclature
C	1 - 10%	90 - 99%	Intermediate
D	10 - 35%	65 - 90%	Low
E	>35%	<65%	Semiquantitative

Based on this classification system, the performance of the DRO, GRO, and PHC methods would be in Class D, quantitative but with low precision/accuracy (compare Table 3-2 with Table 3-3). Since Taylor's system is a general approach to the entire field of analytical chemistry, this classification is in reference to the performance of all analytical methods and all sample matrices. Within this wide spectrum is included method performance in measuring concentrations in simple matrices, for which high precision and accuracy are relatively easy to attain. In contrast, because of the intrinsic complexity of the soil sample matrix, the high performance classifications of the Taylor system may be impossible to attain when attempting to measure trace (ppm) concentrations of target analytes in soil.

An alternative classification procedure is to compare DRO, GRO, and PHC method performance with the performance of established EPA methods for analyzing concentrations in environmental matrices. Since there are no published performance data for EPA's soil analytical methods, it is not possible to make a direct comparison of method performance for the soil matrix. Performance data for the DRO, GRO, and PHC methods, however, are comparable to published performance data for EPA's "600 method series" for analysis of organics in water samples. For example, EPA's published data for the overall precision for benzene and toluene by Method 624 were 21% and 18%, respectively, and the overall precision for naphthalene by Method 625

was 26% (EPA, 1984c,d; details of these calculations are provided in Appendix C). DRO, GRO, and PHC method precision is similar (see Table 3-2).

Given these findings, API concludes that the GRO, DRO, and PHC methods provide acceptable levels of precision and accuracy for analysis of ppm concentrations of petroleum hydrocarbons in soils.

PRACTICAL QUANTIFICATION LEVELS (PQLs)

The protocol for each method gives recommended PQLs which a laboratory is expected to achieve if the protocol is properly followed. Protocol PQLs prior to the interlaboratory study are listed in the first column of Table 3-4. These PQLs are single laboratory estimates, and have been previously documented in Enseco (1991), Walters *et al.* (1992), and Rhodes *et al.* (1991b).

One of the purposes of this study was to determine if these PQLs are actually achieved in practice. To test PQLs, two methods were used: the $80\% \pm 40\%$ rule, and the 95% rule. The $80\% \pm 40\%$ rule, taken from an EPA discussion on drinking water analyses (52 *Federal Register* 25699), defines an achievable PQL as the minimum concentration at which 80% of the laboratories can measure within $\pm 40\%$ of the true value. The 95% rule (Stanko and Hewitt, 1990), suggests that an achievable PQL is the minimum concentration measurable by 95% of the laboratories.

Table 3-4. Method PQLs

Method	PQL Stated in Method (mg/kg)	PQL by $80\% \pm 40\%$ Rule* (mg/kg)	PQL by 95% Rule** (mg/kg)
Diesel Range Organics (DRO)	4	20	12
Gasoline Range Organics (GRO)	5	130	17
Petroleum Hydrocarbons (PHC)	50-100	104	50

* 52 *Federal Register* 25699

** *Performance Evaluation of Contract Laboratories for Purgeable Organics*, G.H. Stanko and R.W. Hewitt, Twelfth Annual Symposium, May 10 & 11, 1989, U.S. EPA, September, 1990.

The study results provided in Table 3-4 show that only the method PQL for PHC was achieved, and only by the 95% rule. The PQL for PHC by the 80% $\pm$ 40% rule (104 mg/kg) was a little higher than the upper limit given in the method (100 mg/kg). Study PQLs for GRO were 3 to 26 times the recommended method PQL of 5 mg/kg. Study PQLs for DRO were 3 to 5 times the recommended method PQL of 4 mg/kg.

The method protocols in Appendix A have been revised to incorporate the interlaboratory PQL data shown in Table 3-4.

FALSE POSITIVES AND FALSE NEGATIVES

False positive rates were 22% for GRO and 20% for PHC. The false positive rate for DRO was not calculated because all laboratories reported measurable DRO concentrations in DRO blank samples. The blank samples were either inadvertently spiked with diesel fuel or were low-level DRO samples mislabeled as blanks. False negatives were reported for low-concentration samples only. The false negative rate for DRO and GRO was 22% at concentrations of about 5 mg/kg; the PHC false negative rate was 3% at concentrations of 50 to 100 mg/kg.

BTEX BY GRO/PID

Since only 6 laboratories reported the optional BTEX data by GRO/PID, there were not enough data to perform rigorous statistical analyses. Instead, relative standard deviation (RSD) for overall precision was used as a general indicator of method performance. Table 3-5 shows the average and range in RSDs for BTEX. Average RSDs were 27% for benzene, 19% for toluene, 44% for ethylbenzene, and 15% for total xylenes.

Table 3-5. Relative Standard Deviation for BTEX by GRO/PID

	Benzene	Toluene	Ethylbenzene	Total Xylenes
Relative Standard Deviation%				
Average	27%	19%	44%	15%
Range	16 - 37%	11 - 50%	32 - 77%	6 - 33%

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APPENDIX A

METHOD PROTOCOLS

Diesel-Range Organics

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METHOD FOR DETERMINATION OF DIESEL RANGE ORGANICS

1. SCOPE AND APPLICATION

1.1 Analytes

1.1.1 This method is designed to measure the concentration of diesel range organics in water and soil. This corresponds to an alkane range of C_{10} - C_{28} and a boiling point range between approximately 170°C and 430°C.

1.1.2 The method is designed to measure mid-range petroleum products such as diesel or fuel oil. Components greater than C_{28} present in products such as motor oils or lubricating oils are detectable under the conditions of the method. If, based on a review of the chromatogram, the presence of these product types is suspected, additional efforts may be performed including, but not limited to, analysis of additional reference materials. These additional efforts are not contained within this method.

1.2 Quantitation Limits

1.2.1 Quantitation limits are based on 100 µg/mL of diesel in the extract and are 0.10 mg/L for waters and 4.0 mg/kg for soils. (Note: The word "diesel" corresponds to diesel #2 or fuel oil #2.)

1.3 Dynamic Range

1.3.1 Dilutions should be performed as necessary to put the chromatographic envelope within the linear range of the method. In general, the individual compound range is 1.0 µg/mL to 50 µg/mL in the final extract. This is approximately equivalent to 100 µg/mL to 5000 µg/mL of diesel.

1.4 Experience

1.4.1 This method is based on a solvent extraction, Gas Chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of solvent extractions and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

2. METHOD SUMMARY

2.1 One liter of water or 25 grams of soil is spiked with a surrogate compound and extracted with methylene chloride. The extract is dried

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and concentrated to a volume of 1.0 mL. The extract is injected into a capillary column gas chromatograph equipped with a flame ionization detector (FID). Quantitation is performed by comparing the total chromatographic area between $n\text{-C}_{10}$ and $n\text{-C}_{28}$, including resolved and unresolved components, to the response of a ten-component calibration standard.

- 2.2 This method is based in part on USEPA Methods 8000 and 8100, SW-846, "Test Methods for Evaluating Solid Waste," 3rd Edition [1], Method OA-2 [2], and work by the EPA Total Petroleum Hydrocarbons Methods Committee [3].

3. DEFINITIONS

- 3.1 Diesel Range Organics (DRO): All chromatographic peaks eluting between decane ($n\text{-C}_{10}$) and octacosane ($n\text{-C}_{28}$). Quantification is based on direct comparison of the area within this range to the total area of the ten components in the diesel component standard.
- 3.2 Diesel Component Standard: A ten-component blend of typical diesel compounds (Table 1). This standard serves as a calibration standard and a retention time window defining mix for diesel range organics. A commercial diesel or fuel oil may be used as the calibration standard.
- 3.3 Surrogate Control Sample: A reagent water or method blank sample spiked with the surrogate compound used in the method. The surrogate recovery is used as a laboratory control. See 7.4.2.
- 3.4 Laboratory Control Sample: A reagent water or method blank sample spiked with a commercial diesel #2 as a quality control check. The spike recovery is used as a laboratory control and must be greater than 50%. See 7.4.5.
- 3.5 Other terms are as defined in SW-846.

4. INTERFERENCES

- 4.1 Other organic compounds including animal and vegetable oil and grease, chlorinated hydrocarbons, phenols, and phthalate esters are measurable under the conditions of this method. As defined in the method, the DRO results include these compounds. Note: SW-846 [1] Method 3611 (Alumina Column Cleanup) may be used for the separation of sample extracts into aliphatic, aromatic, and polar fractions. Details of this cleanup are not included in this method.
- 4.2 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing it with tap water, methanol, and methylene chloride. Reagent blanks must be analyzed with each batch or for every 20 samples to demonstrate that the samples are free from method interferences.

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- 4.3 High purity reagents such as Burdick and Jackson GC² methylene chloride or Baker capillary grade methylene chloride must be used to minimize interference problems.
- 4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank to check for cross-contamination.

5. SAFETY ISSUES

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, 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. 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 references to laboratory safety should be available and should be identified for use by the analyst.

6. APPARATUS

6.1 Glassware

- 6.1.1 All specifications are suggested only.
- 6.1.2 4 oz. amber glass, wide-mouth jars.
- 6.1.3 Separatory Funnel: 2000 mL with Teflon stopcock.
- 6.1.4 Continuous Liquid-Liquid Extractor: Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, New Jersey, P/N6841-10, or equivalent).
- 6.1.5 Concentrator Tube, Kuderna-Danish: 10 mL graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.
- 6.1.6 Evaporative Flask, Kuderna-Danish: 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.
- 6.1.7 Snyder Column, Kuderna-Danish: Three ball macro (Kontes K-503000-0121 or equivalent). Rotary evaporation set-up may also be used alternatively.

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- 6.1.8 Vials: Amber glass, 10 to 15 mL capacity, with Teflon-lined screwcap. Two mL glass vials with Teflon-lined cap.
- 6.1.9 Disposable Pipets: Pasteur.
- 6.2 Boiling Chips: Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.
- 6.3 Microsyringes: 1 μ L, 5 μ L, 10 μ L, 25 μ L, and 100 μ L.
- 6.4 Water Bath: Heated with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.
- 6.5 An analytical balance capable of accurately weighing 0.0001 g should be used for standards. A top-loading balance capable of weighing to the nearest 0.1 g should be used for sample analysis.
- 6.6 Gas Chromatography
- 6.6.1 Gas Chromatograph: Analytical system complete with gas and all required accessories, including a flame ionization detector, column supplies, gases, and syringes. A data system capable of determining peak areas using a forced baseline and baseline projection is required. A data system capable of storing and reintegrating chromatographic data is also recommended.
- Note: A FID must be used for the measurement of hydrocarbons as described in this method. FID response is essentially the same for all hydrocarbons; other detectors will not produce accurate results.
- 6.6.2 Columns
- 6.6.2.1 Column 1: 25 M x 0.25 mm Quadrex 007 5% methyl phenyl 0.5 micron film thickness.
- 6.6.2.2 Alternate Column: 30 M x 0.53 mm ID Restek RTX-5, 1.5 micron film thickness.
- 6.6.2.3 Other columns may be used; capillary columns are required. See 9.2.2 for GC criteria.
- 6.7 Sonication
- 6.7.1 Ultrasonic Cell Disrupter: A horn-type sonicator equipped with a titanium tip should be used. A Heat Systems - Ultrasonics, Inc. Model W-385 (475 Watt) sonicator or equivalent (power wattage must be a minimum of 375 with pulsing capability and No. 200 1/2" Tapped Disrupter Horn)

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plus No. 207 3/4" Tapped Disrupter Horn, and No. 419 1/8" Standard tapered Microtip probe.

- 6.7.2 A Sonabox is recommended with the above disrupter for decreasing sound (Heat Systems-Ultrasonics, Inc., Model 432 13 or equivalent).

6.8 Soxhlet extraction apparatus is described in Method 3540. [1]

6.9 Nitrogen evaporator with high purity nitrogen gas source.

7. REAGENTS AND STANDARDS

7.1 Reagent Water: Carbon filtered deionized water.

7.2 Methylene Chloride, Hexane, Acetone: Pesticide grade or equivalent.

7.3 Sodium Sulfate: (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

7.4 Stock Standard Solution: Prepare the following stock standards. Unless noted, all are prepared in the methylene chloride listed in 7.2 above. Standard preparation should follow guidelines in Method 8000.

7.4.1 Optional Stock Internal Standard: 1000 µg/mL 5α-androstane.

7.4.2 Recommended Surrogate Standard: 2000 µg/mL *ortho*-terphenyl (OTP). A working solution is made at 20 µg/mL in acetone (a water soluble solvent).

7.4.3 Individual stock solutions of C₁₀ - C₂₈ even normal alkanes at a level of at least 2000 µg/mL. For solubility reasons, it may be necessary to prepare stock solutions of n-alkanes in other solvents such as hexane or chloroform. Some of the n-alkanes are available in solution in chloroform from Supelco (Cat. #4-7103M and 4-7104M).

7.4.4 Diesel Component Standard: C₁₀ - C₂₈ even normal alkane standard + OTP with each component at 50 µg/mL. Suggested calibration running levels are 1, 5, 10, 20, and 50 µg/mL. See Table 1. Calibration standards may be prepared using a commercial diesel or fuel oil.

7.4.5 Stock Laboratory Control Sample - 2500 µg/mL diesel #2 or fuel oil #2. A working solution is made at 500 µg/mL in acetone (a water soluble solvent).

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8. SAMPLE COLLECTION, PRESERVATION, CONTAINERS, AND HOLDING TIMES

Water samples are collected in a one liter glass container and acidified to pH 2. Soils are collected in a core tube or glass jar. The samples are stored at 4°C from the time of collection until extraction. Extraction must be performed on waters within seven days and soils within 14 days. All analyses must take place within 40 days.

9. PROCEDURE

9.1 Sample Preparation

9.1.1 Waters are extracted according to SW-846 Method 3510 (Separatory Funnel Liquid-Liquid Extraction) or Method 3520 (Continuous Liquid-Liquid Extraction). Soil samples are extracted using Method 3550 (Sonication). Method 3540 (Soxhlet Extraction) may also be used.

9.1.2 Water Extraction - Separatory Funnel

9.1.2.1 Measure a 1-L portion of the sample and transfer to the 2-L separatory funnel. If the sample is in a 1 liter or smaller bottle, mark the water meniscus on the side of the sample bottle for later determination of the sample volume. If the sample is in a larger bottle, use a 1 liter graduated cylinder. Pour the sample into a 2 liter separatory funnel. For blanks and quality control standards, pour 1 liter of carbon filtered water into the separatory funnel.

9.1.2.2 Check and note the initial pH.

9.1.2.3 Add 1 mL of *ortho*-terphenyl surrogate standard at 20 µg/mL.

9.1.2.4 For every batch or 20 samples extracted, prepare duplicate laboratory control samples by adding 1 mL of 500 µg/mL diesel #2 (laboratory control standard) to each of two blank matrices. Daily or for every 20 samples, prepare a blank/surrogate control standard using 1 L of carbon-filtered water.

9.1.2.5 For samples that were mixed before extraction, add 60 mL CH₂Cl₂ to the sample bottle to rinse the inner walls. Do NOT cap and shake the bottle, rinse the glass only; transfer the solvent to the separatory funnel. Extract the sample by shaking it for two minutes with frequent ventilation.

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- 9.1.2.6 Allow the layers to separate. If there is an emulsion, break it. If the emulsion cannot be broken (recovery of <80% of the methylene chloride, corrected for water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in 9.1.3.
- 9.1.2.7 Drain the bottom layer (CH_2Cl_2) into a 250 mL beaker.
- 9.1.2.8 Repeat the extraction twice more using a 60 mL aliquot of CH_2Cl_2 each time. Collect the solvent in the same beaker described in 9.1.2.7. Record the volume recovered.
- 9.1.2.9 Put a plug of glass wool in a funnel and fill about 2/3 full with Na_2SO_4 . Rinse the funnel and Na_2SO_4 with 30-40 mL of CH_2Cl_2 , discard. Pour the extract through the Na_2SO_4 into a 500 mL Kuderna-Danish (K-D) evaporative concentrator. Rinse the beaker then the Na_2SO_4 with small amounts of CH_2Cl_2 . Add these rinses to the K-D.
- 9.1.2.10 Add a boiling chip to the K-D and attach a 3 ball Snyder to the top. Pre-wet the column by adding about 1 mL of CH_2Cl_2 to the top.
- NOTE: The concentration step is critical; losses can occur if care is not taken.
- 9.1.2.11 Place the K-D in a heated water bath set at 95°C so that the receiver tube is immersed in hot water and the entire lower rounded surface is bathed in steam. At a proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume reaches 5-10 mL, remove the K-D from the bath and allow it to cool completely.
- 9.1.2.12 If the extract is highly colored or a precipitate forms during concentration, the final volume should be higher (5-10 mL).
- 9.1.2.13 After the K-D has cooled, rinse the Snyder column and middle flask with a small amount of CH_2Cl_2 . Transfer the extract to a calibrated 15 mL centrifuge tube, rinsing with a small amount of CH_2Cl_2 . Be sure to rinse all of the ground glass

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joints well, as compounds collect on the ground glass.

9.1.2.14 Carefully concentrate the extract to 1.0 mL under a gentle stream of nitrogen using the N-evap apparatus. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher (5-10 mL). Transfer to a labeled 2 mL (or 12 mL) vial with Teflon-lined cap, mark the meniscus.

9.1.2.15 Record the prep information for the extraction and concentration steps. The sample extract is ready for analysis (See Section 9.2 through 9.6).

9.1.3 Water Extraction - Continuous Liquid Liquid Extraction

9.1.3.1 Mount the continuous extractor on appropriate racks.

9.1.3.2 Put 250 mL CH_2Cl_2 in a round bottom flask, add a few boiling chips. Add 300 mL of CH_2Cl_2 to the extractor flask.

9.1.3.3 When pouring water into the extractor, minimize the disturbance of the solvent layer and avoid getting water into either sidearm by pouring the water down the back of the extractor.

9.1.3.4 Check and note the pH. Prepare surrogate and laboratory control standards as in 9.1.2.3 and 9.1.2.4.

9.1.3.5 For samples in 1 liter or smaller bottles, mark the meniscus on the side of the sample bottle and pour approximately 1 liter of the sample into the extractor flask. Measure the exact volume by adding tap water to the bottle to the marked level and measuring the volume with a graduated cylinder. For samples in bottles larger than 1 liter, measure 1 liter of the sample in a graduated cylinder. Record the volume.

9.1.3.6 Add enough carbon-filtered water to the extractor flask to allow the solvent in the removable sidearm to just begin to drip into the round bottom flask. Record the total volume carbon-filtered water that was added on the prep sheet.

9.1.3.7 Remove the condenser from the rack and wipe the lower joint and lip with a tissue soaked with

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solvent. Place the condenser on the top of the extractor. Turn on the cool water supply and check the flow indicators.

- 9.1.3.8 Turn on the heating mantle. Record the starting time on the prep sheet. Check after 15 minutes to be sure that the solvent in the round bottom flask is boiling, that solvent is dripping from the lip on the condenser, and that the volume of the solvent in the round bottom flask is still about 240 mL.
- 9.1.3.9 Check all extractor joints for leaks with a Kimwipe. Allow the extraction to proceed for 18-24 hours.
- 9.1.3.10 Turn off the heating mantle and allow the apparatus to cool (30-60 minutes) with water flowing through the condenser.
- 9.1.3.11 The solvent contained in the round bottom flask is the extract. Transfer the extract to a 400 mL beaker, rinsing with a small amount of CH_2Cl_2 . If the volume of solvent is less than about 250 mL, record the solvent volume.
- 9.1.3.12 Go to 9.1.2.9 and proceed with the prep.

9.1.4 Soil Preparation - Sonication

- 9.1.4.1 Decant any water layer on a sediment sample. Mix the sample well to ensure a representative sample. Note any anomalies observed in the sample (presence of foreign materials, variable particle size, presence of oil or aqueous phases, etc.).
- 9.1.4.2 Weigh 25 g of the original sample into a 250 mL centrifuge bottle. Add 25 g of dried Na_2SO_4 and stir the mixture well with a steel spatula. The sample should have a grainy texture; if it forms a large clump, add more Na_2SO_4 and note this.
- 9.1.4.3 Add 100 mL of CH_2Cl_2 to all samples.
- 9.1.4.4 Add 1 mL of 20 $\mu\text{g/mL}$ *ortho*-terphenyl to all samples and standards. Mix the samples immediately.
- 9.1.4.5 Add one mL of 500 $\mu\text{g/mL}$ fuel oil #2 (laboratory control standard) to the duplicate laboratory

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control standards. These standards should contain 25 g of Ottawa Sand. In addition, prepare a reagent blank/surrogate control standard containing 1 mL of 20 $\mu\text{g/mL}$ *ortho*-terphenyl.

- 9.1.4.6 Sonicate the samples for 1.5 minutes at an output setting of 10 with the 3/4 inch sonicator horn 1/2 inch below the surface of the solvent. The sonicator should be in the 1 second pulse mode, with the duty cycle set at 50%.
- 9.1.4.7 Decant and filter the extracts through Whatman No. 41 filter paper using vacuum or pressure filtration into a rinsed 400 mL beaker. Alternately, the extracts may be centrifuged and decanted.
- 9.1.4.8 Repeat the extraction twice more using 100 mL aliquots of CH_2Cl_2 each time. Collect these extracts in the same beaker described in 9.1.4.7.
- 9.1.4.9 Record the total volume of the solvent that is recovered.
- 9.1.4.10 Go to 9.1.2.9 and proceed with the prep.

9.1.5 Dilution Technique

- 9.1.5.1 This is used for product or waste samples that are soluble in methylene chloride.
- 9.1.5.2 Weigh 1 g of sample into a 10 mL volumetric flask. Dilute to 10 mL with methylene chloride. Store in a 12 mL vial.

9.2 Gas Chromatography

- 9.2.1 Conditions (Recommended): Set helium column pressure to 20#. Set column temperature to 40° C for 2 minutes, then 12° C/min to 320°C and hold for 15 min. (run time = 36 minutes). Set FID Detector to 320°C and injector to 280°C.
- 9.2.2 Performance Criteria: GC run conditions and columns must be chosen to meet the following criteria:
 - 9.2.2.1 Resolution from the solvent front of C_{10} .
 - 9.2.2.2 Area of C_{28} within 15% of area of C_{20} . (Mass discrimination check).

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- 9.2.2.3 The column must be capable of separating typical diesel components from the surrogate and internal standards. In particular, there are potential problems with the resolution of n-C₁₉/ortho-terphenyl and n-C₂₁/5 α -androstane at varying relative concentrations.

9.3 Calibration

- 9.3.1 Calibrate the GC with an initial five point calibration using the diesel component standard (7.4.4.). Tabulate the area response of the ten components against mass injected. The ratio of the response to the amount injected, defined as the response factor (RF), can be calculated for the standard at each concentration. If the percent relative standard deviation (% RSD) is less than 25% over the working range, linearity through the origin can be assumed, and the continuing calibration response factor can be used in place of a calibration curve.

$$\text{Response Factor} = \frac{\text{Total area of 10 diesel components} \times \text{I.S. amount (mg/mL)}}{\text{Total Diesel standard amount (mg/mL)} \times \text{I.S. area}}$$

Note: I.S. = Internal Standard

Alternately, external standard calibration may be used (see Method 8000).

Note: It is recommended that area response from calibration standards be acquired in the same manner as samples (see 9.5).

- 9.3.2 The working response factor or calibration curve must be verified on each working day by the injection of a continuing calibration standard (CCS) (20 $\mu\text{g/mL}$ mid-point). If the response for this standard varies from the predicted response by more than $\pm 25\%$, a new calibration curve must be prepared.

$$\text{Percent Difference} = \frac{R1 - R2}{R_{\text{avg}}} \times 100$$

where:

R1 = Average RF from the calibration curve

R2 = Response Factor from CCS

R_{avg} = (R1 + R2)/2

9.4 Retention Time Window Definition

- 9.4.1 Before establishing windows, be certain that the GC system is within optimum operating conditions. Make three injections of the method standard throughout the course of a 72-hour