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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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

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 C_6-C_{10} 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 C_{10}-C_{28} hydrocarbons, and a

petroleum hydrocarbons (PHC) method to measure C_6-C_{28} 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 C_{10} and C_{28} alkanes. Calibration is based on a synthetic blend that contains ten even n-alkanes (n-C_{10} through n-C_{28}). 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 C_6 and C_{10} 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 C_6 and C_{28} 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
Total	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 ± 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.

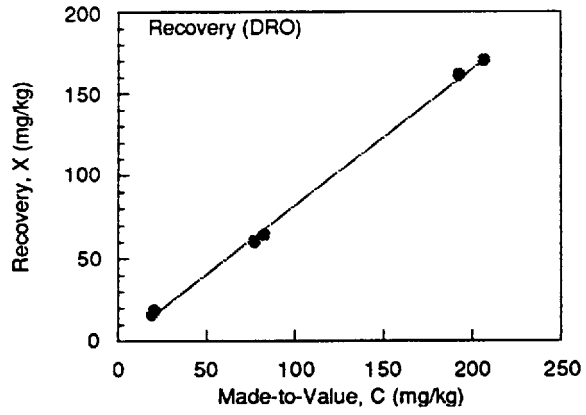
Regression equations were then calculated to describe method performance criteria. These regression equations are summarized in Table 3-1.

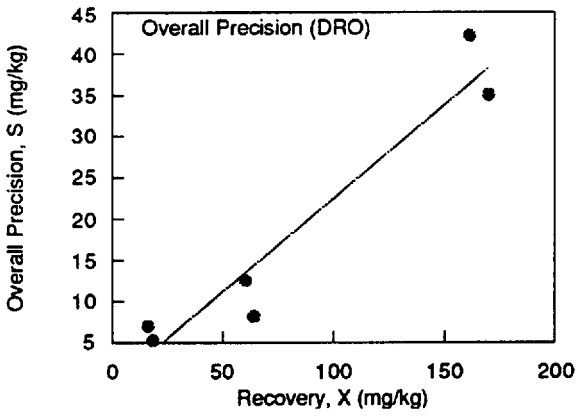
Table 3-1. Regression Equations for Accuracy and Precision

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)	19.3-207	X=0.83C-1.20	S=0.23X-0.03	Sr=0.12X+2.01
Probability*		[<<0.1%]	[2%]	[3%]
Gasoline Range Organics (GRO)	18.5-130	X=0.66C+1.34	S=0.23X+0.39	Sr=0.13X-0.55
Probability*		[<<0.1%]	[2%]	[1%]
Petroleum Hydrocarbons (PHC)	93.6-831	X=0.81C+7.29	S=0.30X+0.45	Sr=0.07X+16.35
Probability*		[<<0.1%]	[<<0.1%]	[51%]

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





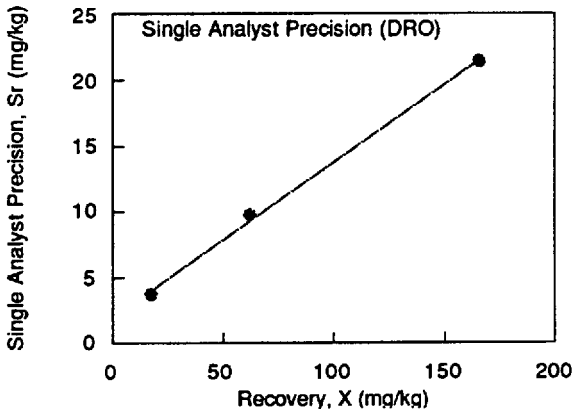
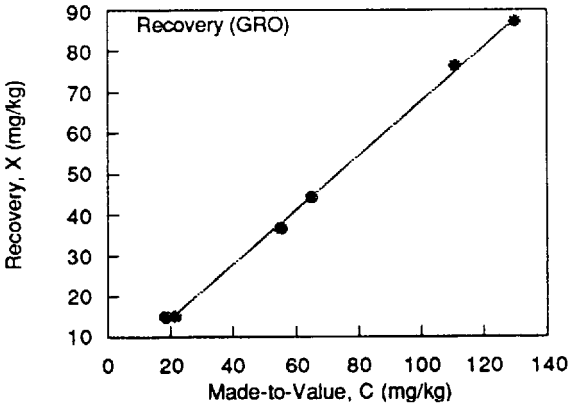
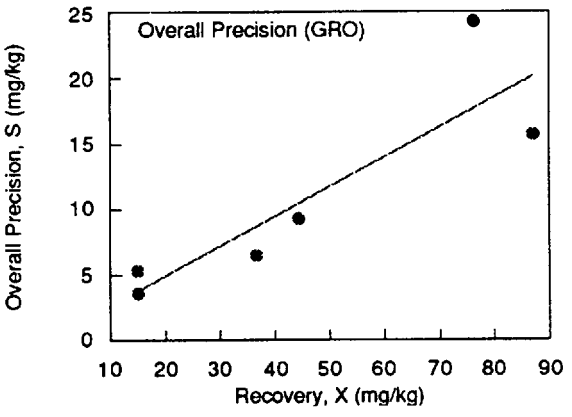


Figure 3-1. DRO Recovery and Precision





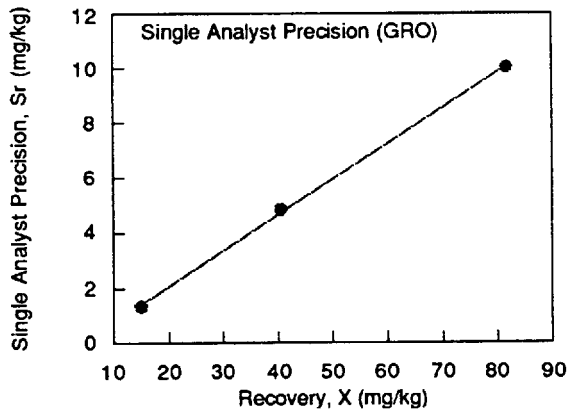


Figure 3-2. GRO Recovery and Precision

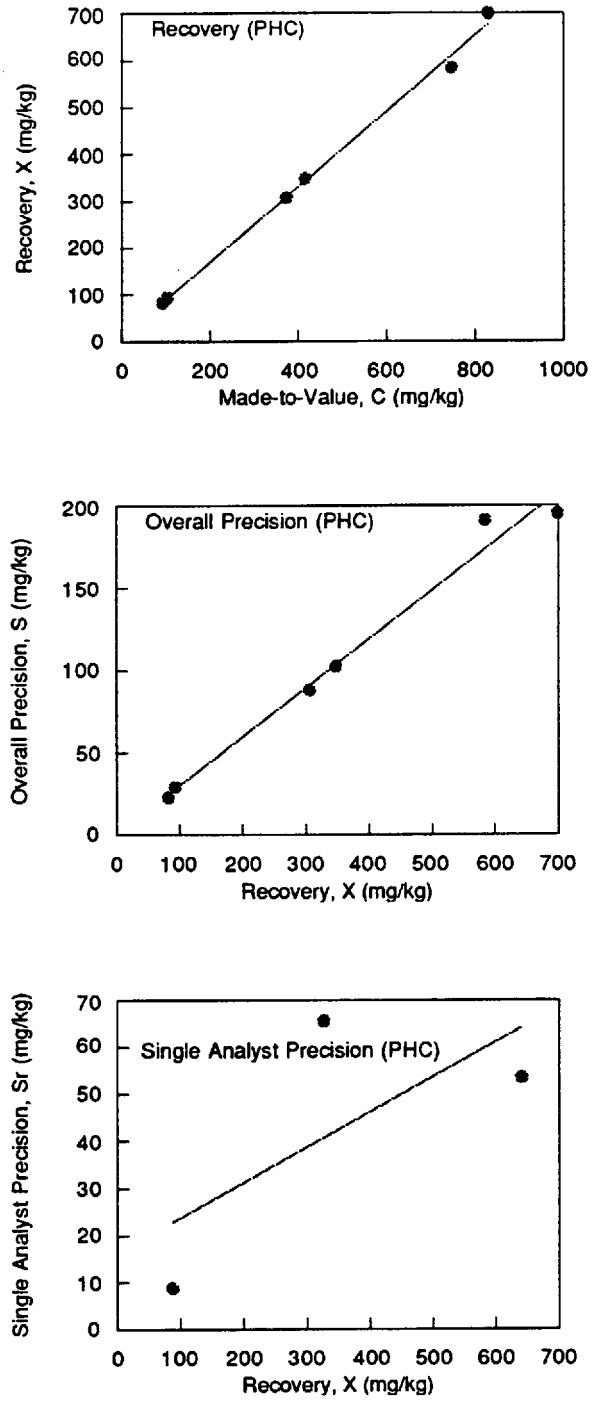


Figure 3-3. PHC Recovery and Precision

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: (standard deviation ÷ mean recovery) x 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% ± 40% rule, and the 95% rule. The 80% ± 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 ± 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%±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% ± 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%

Section 4
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APPENDIX A

METHOD PROTOCOLS

Diesel-Range Organics

REVISION: 4
DATE: 8/18/93

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

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-C_{10} and n-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-C_{10}) and octacosane (n-$_{28}$). 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 (Alumna 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.

4.3 High purity reagents such as Burdick and Jackson GC[2] 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.

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 µL, 5 µl, 10 µl, 25 µl, and 100 µl.

6.4 Water Bath: Heated with concentric ring cover, capable of temperature control (±2°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)

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 C_{10} - C_{28} 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: C_{10} - C_{28} 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).

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 CH_2Cl_2 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.

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

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

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 µg/mL *ortho*-terphenyl to all samples and standards. Mix the samples immediately.

9.1.4.5 Add one mL of 500 µg/mL fuel oil #2 (laboratory control standard) to the duplicate laboratory

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 μg/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).

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-C_{19}/*ortho*-terphenyl and n-C_{21}/5α-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.

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

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 μg/mL mid-point). If the response for this standard varies from the predicted response by more than ± 25%, a new calibration curve must be prepared.

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

where:
R1 = Average RF from the calibration curve
R2 = Response Factor from CCS
Ravg = (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

period. Serial injections over less than a 72-hour period result in retention time windows that are too tight.

9.4.2 Calculate the standard deviation of the three absolute retention times for the surrogate and/or internal standard.

9.4.2.1 The retention time window for individual peaks is defined as plus or minus three times the standard deviation of the absolute retention time for each component.

9.4.2.2 In those cases where the standard deviation for a particular analyte is zero, the laboratory should use ±0.05 min as a retention time window.

9.4.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

9.4.4 Some additional information on hydrocarbon pattern interpretation is included in references 6, 7, 8, and 9.

9.5 Gas Chromatograph Analysis

9.5.1 Samples are analyzed by GC/FID. Suggested injection volumes are 2 µl using the conditions established in 9.2.

9.5.2 For internal standard calibration, 5α-androstane internal standard is spiked into each sample and standard at a concentration of 20 µg/mL of sample extract. 20 µl of 5α-androstane stock at 1000 µg/mL may be spiked into the 1 mL final volume or a corresponding amount may be added to an aliquot of the final extract. Note: Diesel range organic values >2000 µg/mL may lead to measurement bias due to coelution with the internal standard.

9.5.3 If initial calibration (9.3.1) has been performed, verify the calibration by analysis of a mid-point CCS (9.3.2).

The midpoint standard must also be run once every ten runs and at the end of each sequence.

9.5.4 Calculate the percent difference of the response factor from the mean response factor as in 9.3.2. If the response factors have a percent difference >± 25%, the instrument must be recalibrated. (9.3.1)

9.5.5 Forward baseline project must be used to generate the area for DRO calculation. (Valley-to-valley integration disregards the unresolvable area of the chromatogram, which may contribute significantly to the DRO area.) Valley-to-

valley integration must be used to generate areas for the internal standard and surrogate standard. See Figure 2 for an example of integration.

9.5.6 A methylene chloride blank must be run in every sequence to determine the area generated on normal baseline bleed under the conditions prevailing in the 24-hour period. This area is generated by projecting a horizontal baseline between the retention times observed for C_{10} and C_{28}. This area is subtracted from the DRO area generated in the same manner for the samples. (Refer to reference 4.)

Methylene chloride blanks should also be run after samples suspected of being highly concentrated to prevent carryover.

9.5.7 If the product concentration exceeds the linear range of the method in the final extract, the extract must be diluted and reanalyzed. 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. Due to potential measurement bias, internal standard calibration should not be used when DRO exceeds 2000 µg/mL in the final extract. The sample should be diluted or external standard calibration should be used.

9.6 Calculations

9.6.1 Internal Standard Calibration: The concentration of Diesel Range Organics in the sample is determined by calculating the absolute weight of analyte chromatographed from a summation of peak response for all chromatographic peaks eluting between *n*-decane and *n*-octacosane, using the calibration curve or the response factor determined in Section 9.3.2. Refer to Section 9.4 (Retention Time Window Definition). The concentration of Diesel Range Organics is calculated as follows:

Aqueous/Soil samples:

$$Cs = \frac{Ax}{As} \times \frac{Cis}{RF} \times \frac{Vt}{Vs} \times D$$

Where:

Cs = Concentration of Diesel Range Organics (mg/L or mg/kg).

Ax = Response for the Diesel Range Organics in the sample, units in area.

RF = Response Factor from continuing calibration (see 9.3.1).

As = Response for the internal standard, units same as for Ax.

Cis = Concentration of Internal Standard (mg/mL).

Vt = Volume of Final extract (mL).

D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

Vs = Volume of sample extracted in L or kg.

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

10. QUALITY CONTROL

10.1 The laboratory must establish the ability to generate acceptable accuracy and precision. This should include the analysis of QC check samples plus the calculation of average recovery and the standard deviation of the recovery as outlined in Method 8000, Section 8.0.

10.2 The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control.

10.3 After successful calibration (Section 9.3), analyze a Surrogate Control Sample. This standard is also the reagent blank sample and is analyzed with every analytical batch or sequence. The surrogate recovery should be within established limits (Table 2) and the sample should not have Diesel Range Organics above the practical quantitation limit.

10.4 Every batch or 20 samples, duplicate Laboratory Control Samples must be analyzed. The accuracy and precision of the duplicate standards must be within established limits (Table 2).

10.5 Each laboratory should generate control limits based on the average recovery +/- 3 standard deviations.

10.6 If any of the criteria in 10.3 and 10.4 are not met, the problem must be corrected before samples are analyzed.

10.7 Calculate the surrogate standard recovery in each sample. If recoveries are outside established limits, verify calculations, dilutions and standard solutions. Verify instrument performance.

10.7.1 High recoveries may be due to a coeluting matrix interference; examine the sample chromatogram.

10.7.2 Low recoveries may be due to the sample matrix.

10.8 Field blanks, duplicates, and matrix spikes are recommended for specific sampling programs. Matrix spikes should use the spike levels specified for laboratory control samples.

11. METHOD PERFORMANCE

11.1 Single-lab method performance data method is presented in Table 3. Chromatograms for a normal alkane standard and commercial diesel are in Figures 1 and 2.

11.2 The method detection limit for soil calculated according to 40 CFR, Part 136, Appendix B was 1.6 mg/kg (external standard calibration). A recommended practical quantitation limit is 4 mg/kg for soil and 0.1 mg/L for water.

11.3 This method was tested by 13 laboratories [10]. Single operator precision, overall precision, and method accuracy were determined. These results are summarized in Table 4. Linear regression equation to describe these relationships is presented in Table 4. The results from this interlaboratory study were also used to evaluate the stated PQL. The results of this evaluation are presented in Table 4.

12. REFERENCES

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3. "Method for Determination of Extractable Petroleum Hydrocarbons (EPH) in Soil and Water," Draft - February 28, 1990, Prepared for Total Petroleum Hydrocarbons Method Committee by Midwest Research Institute.

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5. "Leaking Underground Fuel Tank (LUFT) Field Manual," State Water Resources Control Board, State of California, Sacramento, CA, May 1988.

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7. Senn, R.B., and M.S. Johnson, "Interpretation of Gas Chromatographic Data in Subsurface Hydrocarbon Investigations," Ground Water Monitoring Review, 1987.

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9. ASTM "Standard Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography," pp. 3328-78.

10. "Interlaboratory Study of Three Methods for Petroleum Hydrocarbons in Soil," American Petroleum Institute Publication, August 1993.

TABLE 1
DIESEL RANGE COMPONENT STANDARD

Component	Midpoint Concentration
Decane	20
Dodecane	20
Tetradecane	20
Hexadecane	20
Octadecane	20
Eicosane	20
Decosane	20
Tetracosane	20
Hexacosane	20
Octacosane	20

TABLE 2
ACCEPTANCE CRITERIA FOR LCS AND SCS

Laboratory Control Sample	Water mg/L	Soil mg/kg	% Recovery	Relative % Difference
Diesel Range Organics	0.5	20	60-120	20
Surrogate Control Standard				
ortho-Terphenyl	0.02	0.8	50-150	

TABLE 3

CALIBRATION BIAS

True Concentration mg/kg	Measured Concentration, mg/kg (Percent Recovery)			
	DRO Standard		Fuel Oil #2 Standard	
	Internal Standard	External Standard	Internal Standard	External Standard
8	8.83 (110)	8.10 (101)	9.78 (122)	8.03 (100)
8	7.59 (95)	7.43 (93)	8.11 (101)	7.01 (88)
80	54.1 (68)	63.9 (80)	64.5 (81)	63.4 (79)
80	59.2 (74)	62.7 (78)	62.4 (78)	64.2 (80)
200	112 (56)	160 (80)	139 (70)	166 (83)
200	114 (57)	161 (80)	137 (68)	160 (80)
0	0.87	0.82	0.95	0.83

Note: Internal Standard results in low bias at high concentrations. DRO vs. Fuel Oil Standards are statistically equivalent.

PETROLEUM PRODUCT BIAS

	Amount Spiked, mg/kg	Amount Measured, mg/kg		Percent Recovery	
		Internal Standard	External Standard	Internal Standard	External Standard
Jet-A	100	76	68	76	68
JP-4	100	88	89	88	89
Diesel #4	100	32	41	32	41
Motor Oil	100	21	26	21	26

TABLE 3
Continued

MATRIX EFFECTS

Soil Type		Amount Spiked, mg/kg	Amount Measured, mg/kg: Internal Standard	Amount Measured, mg/kg: External Standard	Percent Recovery: Internal Standard	Percent Recovery: External Standard
Pedina Sand	(1)	16.7	13.2	6.3	79	38
	(2)	16.7	12.2	11.8	73	71
Norwood Loam	(1)	16.7	13.2	13.3	79	80
	(2)	16.7	12.3	13.6	74	81
Houston Black Clay	(1)	16.7	16.1	15.4	96	92
	(2)	16.7	17.1	16.6	102	99

Note: The recovery in the clay is biased high. External standard recovery from Pedina Sand (1) is biased low. Recoveries in other matrices are comparable to calibration results.

TABLE 4
INTERLABORATORY STUDY RESULTS FOR DRO

Average Performance: Accuracy and Precision

Average Accuracy	Average Single Analyst Precision, RSD	Average Overall Precision, RSD
82%	17%	25%

Regression Equation for Accuracy and Precision

Range for Equation (mg/kg)	Accuracy as Recovery X (mg/kg)	Overall Precision S (mg/kg)	Single Analyst Precision Sr (mg/kg)
19.3-207	X=0.83C-1.20	S=0.23X-0.03	Sr=0.12X+2.01

Method PQLs

PQL Stated in Method (mg/kg)	PQL by 80% + 40% Rule (mg/kg)	PQL by 95% Rule (mg/kg)
4	20	12

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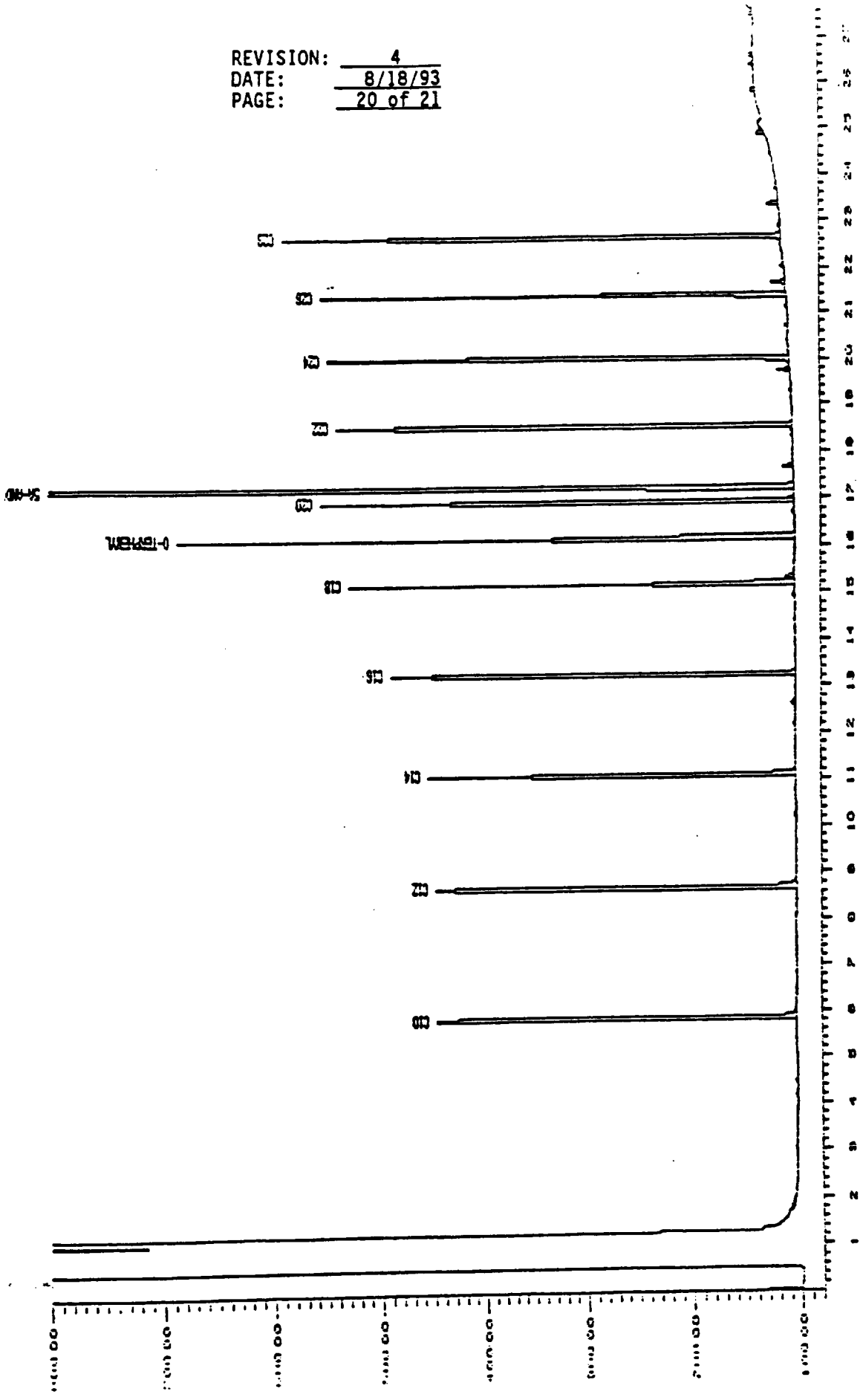

Figure 1. Diesel Component Standard, 500 ug/mL

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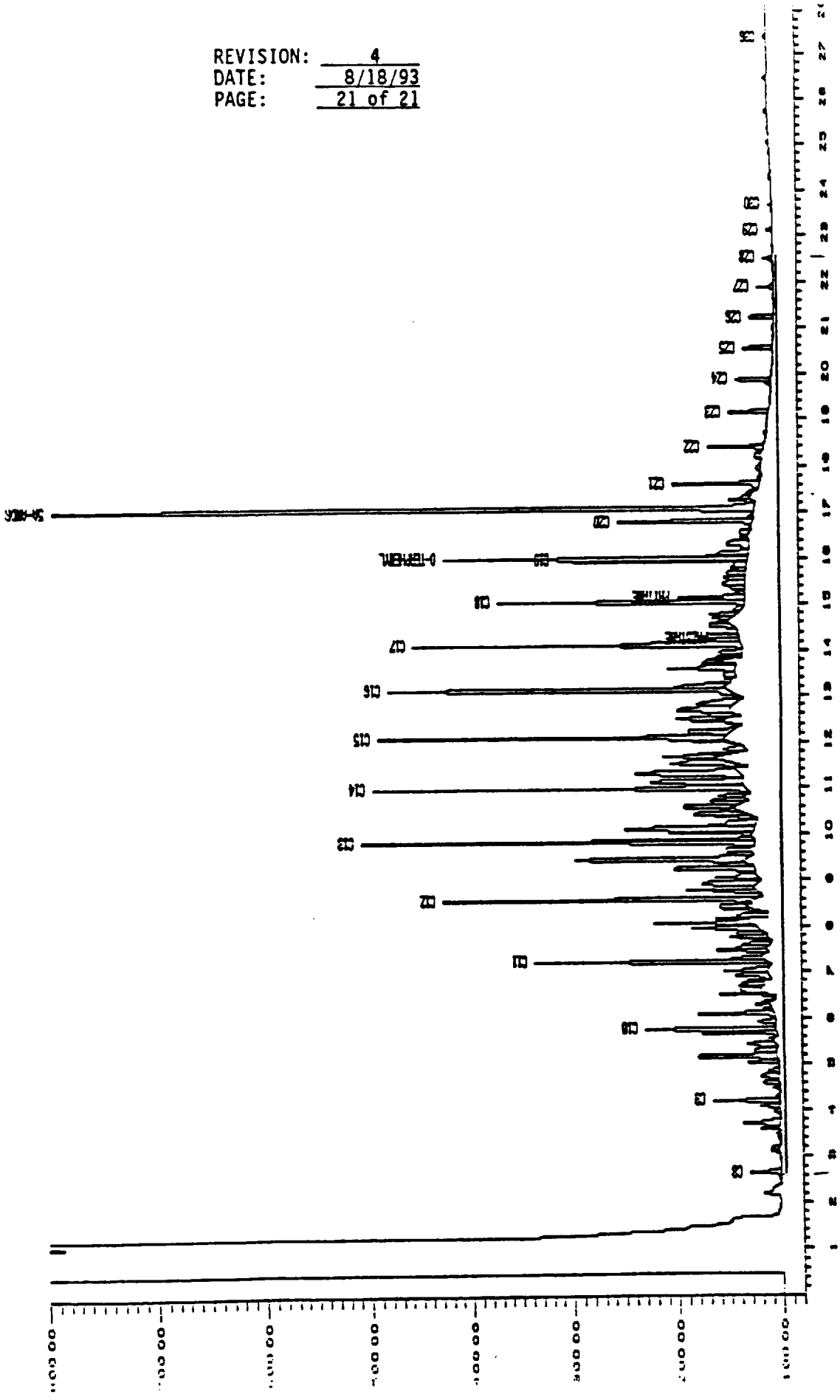

Figure 2. Fuel Oil #2, 500 ug/mL

Gasoline-Range Organics

METHOD FOR DETERMINATION OF GASOLINE RANGE ORGANICS

1. SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of gasoline range organics in water and soil. This corresponds to an alkane range of C_6 - C_{10} and a boiling point range between approximately 60°C and 170°C. Gasoline or other specific petroleum products may be identified by the use of pattern recognition techniques.

1.2 The practical quantification limit (PQL) of this method for gasoline range organics is approximately 5 mg/kg for soils and 0.1 mg/L for water.

1.3 This method is based on a purge-and-trap, gas chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.4 With the optional photoionization detector (PID), this method can be extended for the specific determination of volatile aromatics (BTEX) as specified in EPA Method 8020.

2. SUMMARY OF METHOD

2.1 This method provides gas chromatographic conditions for the detection of certain volatile petroleum fractions such as gasoline. Samples are analyzed utilizing purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID) or FID with photoionization detector (PID) in series (photoionization detector first in the series). Quantification is based on FID detector response to a gasoline component standard or a commercial gasoline.

2.2 This method is suitable for the analysis of waters, soils, or wastes. Water samples can be analyzed directly for gasoline range organics by purge-and-trap extraction and gas chromatography. Soil or waste samples are dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is analyzed by purge-and-trap GC following the normal water method.

2.3 Special field sampling techniques are recommended to minimize the loss of volatiles from soil by using conventional sampling and sample handling techniques. Collection of small volume soil core samples in methanol is considered to be the more reliable means of minimizing VOC losses from the samples when compared to placing soil in larger jars, which require later subsampling and which will be subject to the resultant volatile losses during handling. See 8.2.

2.4 This method is based on USEPA SW-846 [1] Methods 5030, 8000, 8015, 8020, a single laboratory method evaluation study conducted by the American Petroleum Institute [2], and work by the EPA Total Petroleum Hydrocarbons Methods Committee [3].

3. DEFINITIONS

3.1 Gasoline Range Organics (GRO): All chromatographic peaks eluting between 2-methylpentane and 1,2,4-trimethylbenzene. Quantification is based on a direct comparison of the area within this range to the total area of the calibration standard within this range.

3.2 Gasoline Component Standard: A ten-component blend of typical gasoline compounds (Table 4). This standard serves as a calibration standard and a retention time window-defining mix for gasoline range organics. It may also be used as the PID calibration standard for the optional determination of BTEX by Method 8020. A commercial gasoline may be used as the calibration standard for GRO.

3.3 Gasoline Control Standard: A commercial gasoline used by the laboratory as a quality control check. See 7.2.

3.4 Surrogate Control Sample: A reagent water or method blank sample spiked with the surrogate compounds used in the method. The surrogate recovery is used to evaluate method control. See 7.8.

3.5 Laboratory Control Sample: A reagent water or method blank sample spiked with the gasoline control standard. The spike recovery is used to evaluate method control and must be greater than 50%.

3.6 Pattern Recognition Standards: Various commercial gasolines and other petroleum products used by the laboratory to identify petroleum products.

3.7 Other terms are as defined in SW-846.

4. INTERFERENCES

4.1 High levels of heavier petroleum products such as diesel fuel may contain some volatile components producing a response within the retention time range for gasoline. Other organic compounds, including chlorinated solvents, ketones, and ethers, are measurable. As defined in the method, the GRO results include these compounds.

4.2 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. A trip blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank of reagent water to check for cross contamination. For volatile samples containing high concentrations of water-soluble materials, suspended solids, high boiling compounds or organohalides, it may be necessary to wash the syringe or purging device with a detergent solution, rinse with distilled water, and then dry in a 105°C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation.

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 AND MATERIALS

6.1 Gas Chromatograph

6.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system capable of determining peak areas is recommended.

6.1.2 Columns:

6.1.2.1 Column 1: 105 M x 0.53 mm I.D. Restek RTX 502.2 0.3 micron film thickness, or equivalent.

6.1.2.2 Other columns such as a 30 M x 0.53 mm DB-5 may be used; capillary columns are recommended to achieve necessary resolution. At a minimum, the column should resolve 2-methylpentane from the methanol solvent front in a 25 mg/kg LCS standard and should resolve ethylbenzene from *m/p*-xylene. Some

columns may require subambient cooling to achieve these guidelines.

6.1.3 Detector: Flame ionization (FID) or FID in series with a photoionization detector (PID). The optional PID is to be used only for the measurement of volatile aromatics.

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.

6.2 Syringes: 5 mL Luerlock glass hypodermic and a 5 mL gas-tight syringe with shutoff valve.

6.2.1 For purging large sample volumes for low detection limit analysis of aqueous samples for petroleum products, 25 or 50 mL syringes may be used. Subsequently, substitute the appropriate volume in the method wherever 5 mL is stated when low detection limits are required.

6.3 Volumetric Flask: 10 mL, 50 mL, 100 mL, 500 mL, and 1,000 mL with a ground-glass stopper.

6.4 Microsyringes: 1 μl, 5 μl, 10 μl, 25 μl, 100 μl, 250 μl, 500 μl, and 1,000 μl.

6.5 Syringe Valve: Two-way, with luer ends (three each), if applicable to the purging device.

6.6 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g, and a top-loading balance capable of weighing to the nearest 0.1 g.

6.7 Glass Scintillation Vials: 20 mL, with screw-caps/crimp caps and Teflon liners or glass culture tubes with a screw-cap and Teflon liner, or equivalent.

6.8 Spatula: Stainless Steel.

6.9 Disposable Pipets: Pasteur.

6.10 Purge-and-Trap Device: The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

6.10.1 The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a

diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, used in EPA SW-846 Method 5030, meets these design criteria. Alternate sample purge devices may be used provided equivalent performance is demonstrated.

6.10.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must be packed with the following adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap. Since only compounds boiling above 35°C are to be analyzed by this method, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Prior to initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min. at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

6.10.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake-out mode. The desorber described in EPA SW-846 Method 5030 meets these criteria.

6.10.4 Another alternate trap uses 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III (Supelco Cat# 2-0321R). This trap should be desorbed at 240°C and baked to 300°C.

6.10.5 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph.

6.10.6 Trap Packing Materials

6.10.6.1 2,6-Diphenylene Oxide Polymer: 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

6.10.6.2 Methyl Silicone Packing: OV-1 (3%) on chromosorb-W,60/80 mesh or equivalent.

6.10.6.3 Silica Gel: 35/60 mesh, Davison, grade 15 or equivalent.

6.10.6.4 Coconut Charcoal: Prepare from Barnebey Cheney, CA-580-26 lot #M-2649, by crushing through 26 mesh screen.

7. REAGENTS AND STANDARDS

7.1 Reagent Water: Carbon-filtered water purged with helium prior to use.

7.2 Gasoline Control and Calibration Standards: One reference standard is API PS-6 gasoline, a characterized gasoline used in petroleum research. (Major components are listed in Table 3.) Other gasolines of similar composition can be used if they are thoroughly evaluated by the laboratory.

7.3 Gasoline Component Standard: The ten-component calibration standard that also serves as the quantification range (retention time window defining mix) standard. The components and concentration of the 10000 μg/mL stock solution are in Table 4. The standard is prepared by the procedures in 7.4 and 7.5. A commercial gasoline may be used as the calibration standard using similar procedures.

7.4 Stock Standards: Prepare stock standards for the gasoline and individual gasoline component standards in methanol at approximately 20 mg/mL.

7.4.1 Place about 8 mL of methanol in a 10 mL tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min. or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.4.2 Using a 500 μl syringe, immediately add 200-300 μl of gasoline or gasoline component to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

7.4.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micro grams per microliter (μg/μl) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.4.4 Transfer the stock standard solution into a Teflon-sealed screw-cap/crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

7.4.5 Standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.5 Secondary Dilution Standards: Using stock standard solutions, prepare secondary dilution standards in methanol as needed. The gasoline component standard should be prepared at the concentrations shown in Table 4. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 7.6 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.6 Calibration Standards: Calibration standards at a minimum of three concentration levels are prepared in reagent water from the secondary dilution of the stock standards. One of the concentration levels should be at a concentration near the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. See 9.3.2.

7.7 Internal Standard: An internal standard (1-chloro-4-fluorobenzene) is recommended for 602/8020 quantification on the PID detector. Due to potential interferences, the internal standard is not recommended for FID quantification.

7.8 Surrogate Control Standard (SCS): The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogate compounds: bromofluorobenzene or trifluorotoluene. From stock standard solutions prepared as in Section 7.4, prepare a surrogate spiking solution at 50 µg/mL of each surrogate in methanol. Add 5.0 µl of this surrogate spiking solution directly into the 5 mL syringe with every water sample and reference standard analyzed. Surrogate spike solution is added to soil samples during the extraction step (see 9.5.1).

7.9 Laboratory Control Sample (LCS) Standard: From the stock PS-6 gasoline standard or other appropriate gasoline control standards (Section 7.4), prepare a secondary dilution standard at 500 µg/mL in methanol. Addition of the following amounts yields the indicated concentrations:

0.005 mL added to 5 mL water: 0.5 mg/L
0.5 mL added to 10 g soil (methanol extraction): 25 mg/kg

7.10 Methanol: Pesticide quality or equivalent. Store away from other solvents.

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

8.1 Aqueous samples should be collected in triplicate without agitation and without headspace in contaminant-free glass 40 mL vials with Teflon-lined septa in the caps. The Teflon layer must contact the sample. Sample vials should contain 200 μl of 50% HCL as a preservative for aromatic analytes. Refrigerate samples at 4°C after collection.

8.2 Special field sampling techniques are recommended for soil samples to minimize the loss of volatiles during transit from the field to laboratory. Samples for the methanol extraction method should be collected in duplicate tared 40 mL vials that contain 10 mL methanol (includes 0.5 mL of surrogate solution at 50 μg/mL). A reagent methanol blank should be prepared in the same manner as the sample vials. Soil for the vials can be collected using a 10 mL plastic syringe with the end sliced off. A sufficient number of vials (two are recommended) should be collected to provide for backup analyses in the event of breakage. A soil volume of 6-8 mL corresponds to about 10 g. In addition, soil may be collected in a wide-mouth glass jar with a Teflon-lined lid for soil screening analysis and/or supporting tests (e.g., % moisture). The soil should be disturbed as little as possible and the containers filled as full as possible. Refrigerate all samples at 4°C after collection.

8.3 Alternatively, the sampling techniques in SW-846 [1] may be used (samples collected in this manner may represent minimum values). According to SW-846, soils for volatile organic analysis must be held at 4°C and analyzed within 14 days.

8.4 For reference, an API study [2] has indicated that samples sampled (preserved) in methanol can be held for up to 28 days at 4°C with no apparent losses. Samples taken by conventional techniques are subject to volatile losses throughout their storage period. These losses may exceed 90% after 28 days. Additional studies [4, 5] have demonstrated that field addition of methanol yields more accurate results than obtained from standard jar or vial sampling techniques.

9. PROCEDURE

9.1 Volatile compounds are introduced into the gas chromatograph by purge-and-trap. Purge-and-trap may be used directly on ground water samples. Soils and solids should be analyzed by methanol extraction. It is highly recommended that all samples be screened prior to analysis. This screening step may be analysis of a solid sample's methanol extract (diluted), the headspace method (SW-846 Method 3810), or the hexadecane extraction and screening method (SW-846 Method 3820). See Table 2.

9.2 Gas Chromatography Conditions (Recommended)

9.2.1 Column 1: Set helium column pressure to 20#. Set column temperature to 40°C for 1 min, then 5°C/min to 100°C, then 8°C/min to 240°C and hold for 7.5 min. Conditions may be altered to improve resolution of gasoline range organics.

9.2.2 Other Columns: Set GC conditions to meet the criteria in 6.1.2.2.

9.3 Calibration

9.3.1 Prepare final solutions containing required concentrations of calibration standards, including surrogate standards, directly in the 5 mL glass syringe. Add the aliquot of calibration solution directly to the reagent water in the glass syringe by inserting the needle through the syringe end. When discharging the contents of the microsyringe, be sure that the end of the syringe needle is well beneath the surface of the reagent water. Similarly, add 5.0 µl of the surrogate standard solution. Attach the 2-way syringe valve to the syringe and then inject the standard into the purge vessel through the two way valve. Proceed with purge-and-trap analysis procedure.

9.3.2 Run the gasoline component standard at a minimum of three concentration levels above the detection limits and covering the expected range of samples or the linear range of the instrument. The recommended calibration range (and corresponding method amounts are):

GASOLINE COMPONENT STANDARD

Nanograms to Detector	Water mg/L	Soil-MeOH extraction mg/kg
250 (12.5 to 37.5)*	0.05	2.5
1000 (50 to 150)	0.2	10
2500 (125 to 375)	0.5	25

* Nanograms per individual component in parentheses

An additional low point at 0.01 mg/L (0.5 to 1.5 µg/L for individual aromatics) is recommended for the optional PID quantification. For the FID quantification of a multicomponent product like gasoline, the linear range is related to the areas of individual components. Individual components in the method standard are three to five times the concentration of the same components in PS-6 gasoline. Therefore, considering the calibration curve, 0.5 mg/L of the

method standard is the high point on the curve; but gasoline at 2 mg/L (100 mg/kg in soil) is within the range of the calibration curve.

9.3.3 External Standard Calibration

9.3.3.1 For quantification utilizing the method standard response, prepare calibration standards at a minimum of three concentration levels by adding appropriate volumes of the stock standards and surrogate standards to a 5 mL glass syringe. One of the external standards should be at a concentration near the method detection limit. The other concentrations should correspond to the expected range of concentrations found in samples or should define the working range of the detector. Due to potential carry over, do not purge more than 10 μg of gasoline or total gasoline components in 5 mL of water (2 mg/L).

9.3.3.2 Inject each calibration standard utilizing the purge-and-trap. Tabulate area response for the ten components against mass injected. The results can be used to prepare a calibration curve for the detector. Alternatively, the ratio of the amount injected to the response, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (% RSD) of the calibration factor is less than 25% over the working range, linearity through the origin can be assumed; and the calibration factor from the midpoint continuing calibration standard can be used in place of a calibration curve.

$$\text{Calibration Factor} = \frac{\text{Standard Amount (mg) Purged}}{\text{Total Area}}$$

9.3.3.3 The working calibration curve or calibration factor must be verified on each working day by the injection of a midpoint continuing calibration standard. If the response for the method standard varies from the predicted response by more than 25%, a new calibration curve must be prepared.

$$\text{Percent Difference} = \frac{CF1 - CF2}{CF\ avg.} \times 100$$

where:

CF1 = Average calibration from the calibration curve

CF2 = Calibration factor from the midpoint continuing calibration
CFavg. = (CF1+CF2) /2

9.4 Retention Time Window and Pattern Recognition

9.4.1 Before establishing windows, be certain that the GC system is within optimum operating conditions. Make three injections of the gasoline component standard throughout the course of a 72-hour period. Serial injections over less than a 72-hour period result in retention time windows that are too tight.

9.4.2 Calculate the standard deviation of the three absolute retention times for each method standard component.

9.4.2.1 The retention time window for individual peaks is defined as plus or minus three times the standard deviation of the absolute retention time for each component. For multiresponse petroleum products, the analyst may use the retention time window but should primarily rely on pattern recognition.

9.4.2.2 In those cases where the standard deviation for a particular analyte is zero, the laboratory should use $\pm$0.05 min as a retention time window.

9.4.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

9.4.4 The experience of the analyst weighs heavily in the interpretation of the chromatogram. References 6, 7, and 8 contain some background information on hydrocarbon pattern recognition. Environmental samples may contain more than one type of product, and loss of light end components may indicate that the product has been in the subsurface a longer period of time.

9.4.4.1 Other organic compounds, including chlorinated solvents, ketones, and ethers, are measurable by this method and will be reported as gasoline range organics. The presence of interferences should be noted. Other analyses, such as GC/MS, may be used to identify interferences.

9.4.4.2 Note: Although the retention time window definition (2-methylpentane to 1,2,4-trimethylbenzene) introduces a bias (55 to 75% for gasoline in Ottawa Sand), it improves precision and reduces interferences from petroleum products other than gasoline.

9.5 Gas Chromatograph Analysis

9.5.1 Water Samples: Introduce volatile compounds into the gas chromatograph using the purge-and-trap method. Add 5.0 µl of surrogate standard to the sample prior to purging.

9.5.1.1 Adjust the purge gas flow rate (nitrogen or helium) to 25-40 mL/min on the purge-and-trap device.

9.5.1.2 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process destroys the validity of the liquid sample for future analysis; therefore, if there is only one 40 ml vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until the analyst has determined that the first sample has been analyzed properly. Filling one 5 mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

9.5.1.3 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

9.5.1.4 Dilutions may be made in volumetric flasks (10 mL to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.

9.5.1.5 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this volume of reagent water to the flask.

9.5.1.6 Inject the proper aliquot of samples from the syringe prepared in Section 9.5.1.2 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert, and shake

three times. Repeat the above procedure for additional dilutions. Alternatively, the dilutions can be made directly in the glass syringe to avoid further loss of volatiles.

9.5.1.7 Fill a 5 mL syringe with diluted sample as in Section 9.5.1.2.

9.5.1.8 Add 5.0 μl of surrogate spiking solution through the valve bore of the syringe; then close the valve.

9.5.1.9 Attach the syringe-syringe valve assembly to syringe valve on the purging device. Open the syringe valves and inject sample into the purging chamber.

9.5.1.10 Close both valves and purge the sample for 12 min.

9.5.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C and backflushing the trap with inert gas between 20 and 60 mL/min for 4 minutes.

9.5.1.12 While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with minimum of two 5 mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

9.5.1.13 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 sec; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7-35 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

9.5.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the

sample must be reanalyzed at a higher dilution. When a sample is analyzed that has a saturated response from a compound, this analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

9.5.1.15 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

9.5.2 Methanol Extraction for Soil/Sediment: Method is based on extracting the sediment/soil with methanol. The soil sample is either extracted or diluted depending on solubility in methanol. An aliquot of the extract is added to reagent water. This is purged at the temperatures indicated in Table 1. A screening analysis is recommended (see 9.1).

9.5.2.1 If available, obtain the field sample collected in methanol (Section 8.2). Weigh the sample vial to determine the actual weight. Shake for 2 min. Proceed to 9.5.2.4. If the methanol preserved field sample is not available, proceed to 9.5.2.2.

9.5.2.2 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. In order to obtain representative analytical results, gently mix the contents of the sample container with a narrow metal spatula. For sediment/soil and waste that are insoluble in methanol, weigh 10 g (wet weight) of sample into a tared 20 mL vial using a top-loading balance. Note and record the actual weight to 0.1 gram. For waste that is soluble in methanol, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10 mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Calibrate by pipeting 10.0 mL of methanol into the vial and marking the bottom of the meniscus. Discard this solvent.)

9.5.2.3 Quickly add 9.5 mL of methanol; then add 0.5 mL of the surrogate spiking solution (50 µg/mL) to the vial. Cap and shake for 2 min.

Note: Steps 9.5.2.2 and 9.5.2.3 must be performed rapidly and without interruption to avoid loss of

volatile organics. These steps must be performed in a laboratory free from solvent fumes.

9.5.2.4 Allow sediment to settle, centrifuge if necessary. Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed. If not analyzed immediately, these extracts must be stored at 4°C in the dark.

9.5.2.5 The GC system should be set up as in Section 6. This should be performed prior to the addition of the methanol extract to reagent water.

9.5.2.6 Table 2 can be used to determine the volume of methanol extract to add to 5 mL of reagent water for analysis. If a screening procedure was followed, use the estimated concentration to determine the appropriate volume. The maximum volume of methanol is 100 μl. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

9.5.2.7 Remove the plunger from a 5.0 mL Luerlock-type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger to 5.0 mL to allow volume for the addition of the sample extract and of surrogate standard. Add the volume of methanol extract determined from screening and a volume of methanol solvent to total 100 μl (excluding methanol in standards).

9.5.2.8 Attach syringe valve assembly to syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.5.2.9 Proceed with the analysis as in 9.5.1.10-9.5.1.15. Analyze all reagent blanks on the same instrument as that used for the samples. The reagent blank should contain 100 μl of the methanol used to extract the samples.

9.5.3 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with continuing calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

9.5.4 If the responses exceed the linear range of the system, use a smaller amount of sample.

9.5.5 The calibration factor for each analyte to be quantitated must not exceed ± 25% when compared to the initial standard of the analysis sequence. When this criteria is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary prior to recalibration and proceeding with sample analysis. All samples that were injected following the sample exceeding QC criteria must be reanalyzed.

9.6 Calculations

9.6.1 External Standard Calibration: The concentration of gasoline range organics in the sample is determined by calculating the absolute weight of analyte purged from a summation of peak response for all chromatographic peaks eluting between 2-methylpentane and 1,2,4-trimethylbenzene using the calibration curve or the calibration factor determined in Section 9.3.3. Refer to Section 9.4 (Retention Time Window and Pattern Recognition). The concentration of gasoline range organics is calculated as follows:

Aqueous samples:

$$Cs\ (mg/L) = \frac{Ax}{Vs} \times CF \times D$$

Where: Cs = Concentration of gasoline range organics

Ax = Response for the gasoline range organics in the sample, units in area.

CF = Calibration factor from continuing calibration, units = mg/area

D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

Vs = Volume of sample purged, L.

Non-aqueous Samples(methanol extraction):

$$Cs\ (mg/kg) = \frac{Ax}{W} \times \frac{Vt}{Vi} \times CF \times D$$

Where:

Vt = Volume of total extract (μl) (use 10000 μl or a factor of this when dilutions are made).

Vi = Volume of extract added for purging (μl)

W = Weight of sample extracted, kg. The wet weight is used.

Ax, CF, and D have the same definition as for aqueous samples.

10. QUALITY CONTROL

10.1 The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control. This should include the analysis of QC check samples plus the calculation of average recovery and the standard deviation of the recovery as outlined in Method 8000, Section 8.0.

10.2 After successful calibration (Section 9.3), analyze a surrogate control sample. This standard is also the reagent blank sample and is analyzed with every analytical batch or sequence. The surrogate recovery should be within established limits (Table 5) and the sample should not have gasoline range organics above the practical quantification limit.

10.3 Every batch or 20 samples, duplicate Laboratory Control Samples must be analyzed. The accuracy and precision of the duplicate standards must be within established limits (Table 5).

10.4 If any of the criteria in 10.2 and 10.3 are not met, the problem must be corrected before samples are analyzed.

10.5 Calculate the surrogate standard recovery in each sample. If recoveries are outside established limits, verify calculations, dilutions, and standard solutions. Verify instrument performance.

10.5.1 High recoveries may be due to a coeluting matrix interference; examine the sample chromatogram.

10.5.2 Low recoveries may be due to the sample matrix.

10.5.3 Low recoveries may be due to a poor purge (clogged purge tube). If this is suspected, reanalyze the sample while observing the purge tube.

10.6 Field blanks, duplicates, and matrix spikes are recommended for specific sampling programs.

11. METHOD PERFORMANCE

11.1 Single-lab method performance data for the methanol extraction method in Ottawa Sand and other soil types is presented below. Chromatograms for the method standard and PS-6 gasoline are in Figures 6 and 7.

11.2 Results for PS-6 spikes (methanol extraction purge-and-trap)

Spike	PS-6 Spike Amount mg/kg	Percent Recovery
Ottawa Sand	50	70
Ottawa Sand	500	78
Houston Black Clay	50	68
Houston Black Clay	50	66
Norwood Loam	50	60
Norwood Loam	50	57

11.3 The method detection limit calculated according to 40 CFR, Part 136, Appendix B was 0.5 mg/kg gasoline for the methanol extraction of soils. The recommended practical quantification limit (PQL) is 5 mg/kg for soil and 0.1 mg/L for water.

11.4 This method was tested by 11 laboratories. [10] Single operator precision, overall precision, and method accuracy were determined. These results are summarized in Table 6. Linear regression equation to describe these relationships is presented in Table 6. The results from this interlaboratory study were also used to evaluate the stated PQL. The results of this evaluation are presented in Table 6.

12. REFERENCES

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4. Urban, M.J., J.S. Smith, E.K. Schultz, R.K. Dickson, "Volatile Organic Analysis for a Soil, Sediment or Waste Sample," Fifth Annual Waste Testing and Quality Assurance Symposium, USEPA, July 24-28, 1989.

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9. "Laboratory Study on Solubilities of Petroleum Hydrocarbons in Groundwater," American Petroleum Institute Pub. 4395, August 1985.

10. "Interlaboratory Study of Three Methods for Petroleum Hydrocarbons in Soil," American Petroleum Institute Pub., August 1993.

13. ADDITIONAL REFERENCES

"Leaking Underground Fuel Tank (LUFT) Field Manual," State Water Resources Control Board, State of California, Sacramento, CA, May, 1988.

Parr, J.L., G. Walters, and M. Hoffman, "Sampling and Analysis of Soils for Gasoline Range Organics" presented at First Annual West Coast Conference Hydrocarbon Contaminated Soils and Groundwater, February 21, 1990.

TABLE 1
PURGE-AND-TRAP OPERATING PARAMETERS

	Analysis Method 8020
Purge gas	Nitrogen or Helium
Purge gas flow rate (mL/min)	40
Purge time (min)	12.0 ± 0.1
Purge temperature	Ambient
Desorb temperature (°C)	180
Backflush inert gas flow (mL/min)	20-60
Desorb time	4

TABLE 2
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF SOILS/SEDIMENTS

Approximate Concentration, GRO	Volume of Methanol Extract[a]
5-100 µg/g	100 µl
200 µg/g	50 µl
1000 µg/g	10 µl
5000 µg/g	100 µl of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 µl added to the syringe.

[b] Dilute an aliquot of the methanol extract and then take 100 µl for analysis.

TABLE 3
MAJOR COMPONENTS OF API PS-6 GASOLINE

Compound	Percent Weight
2-Methylbutane	8.72
m-Xylene	5.66
2,2,4-Trimethylpentane	5.22
Toluene	4.73
2-Methylpentane	3.93
n-Butane	3.83
1,2,4-Trimethylbenzene	3.26
n-Pentane	3.11
2,3,4-Trimethylpentane	2.99
2,3,3-Trimethylpentane	2.85
3-Methylpentane	2.36
o-Xylene	2.27
Ethylbenzene	2.00
Benzene	1.94
p-Xylene	1.72
2,3-Dimethylbutane	1.66
n-Hexane	1.58
1-Methyl, 3-ethylbenzene	1.54
1-Methyl, 4-ethylbenzene	1.54
3-Methylhexane	1.30

Reference [9]

TABLE 4
GASOLINE COMPONENT STANDARD AND CONCENTRATIONS

Component	Concentration, µg/mL
2-Methylpentane	1500
2,2,4-Trimethylpentane	1500
Heptane	500
Benzene	500
Toluene	1500
Ethylbenzene	500
m-Xylene	1000
p-Xylene	1000
o-Xylene	1000
1,2,4-Trimethylbenzene	1000
	10000 ug/mL Total

TABLE 5
ACCEPTANCE CRITERIA FOR LABORATORY QUALITY CONTROL CHECKS

Analyte	Spike Concentration		Control Limits	
Laboratory Control Sample	Water mg/L	Soil mg/kg	%Recovery	Relative %Difference
Gasoline Range Organics	0.5	25	50-100	20
Surrogate Control Sample				
Trifluorotoluene	0.05	2.5	50-150	

TABLE 6
INTERLABORATORY STUDY RESULTS FOR GRO

Average Performance: Accuracy and Precision

Average Accuracy	Average Single Analyst Precision, RSD	Average Overall Precision, RSD
70%	11%	25%

Regression Equation for Accuracy and Precision

Range for Equation (mg/kg)	Accuracy as Recovery X (mg/kg)	Overall Precision S (mg/kg)	Single Analyst Precision Sr (mg/kg)
18.5-130	X=0.66C+1.34	S=0.23X+0.39	Sr=0.13X-0.55

Method PQLs

PQL Stated in Method (mg/kg)	PQL by 80% + 40% Rule (mg/kg)	PQL by 95% Rule (mg/kg)
5	130	17

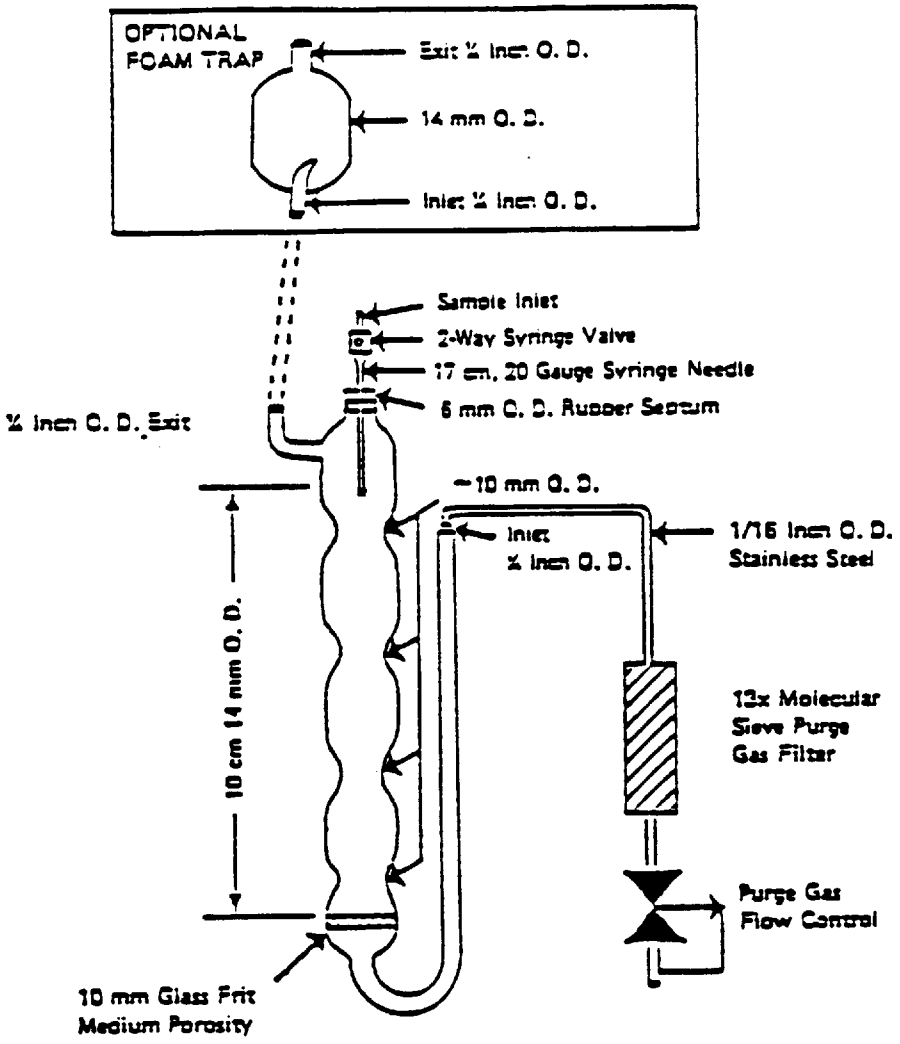

Figure 1 Purging chamber.

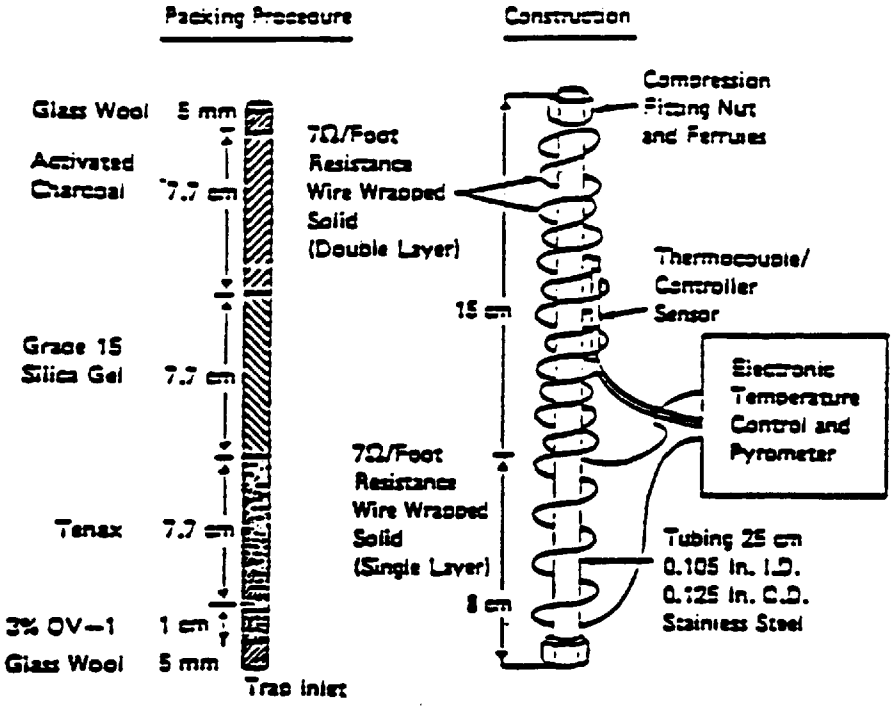

Figure 2 Trap packings and construction

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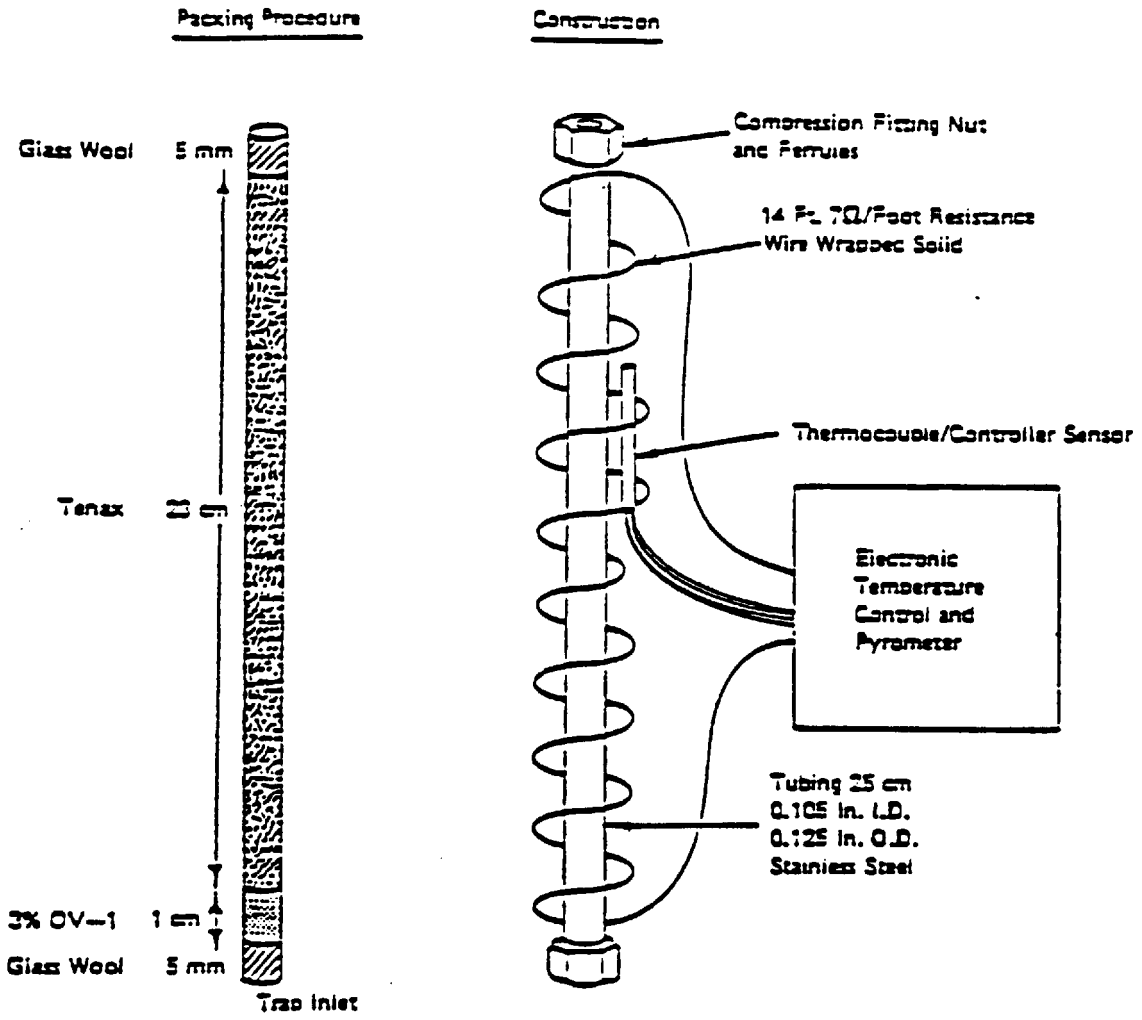

Figure 3 Trap packing and construction

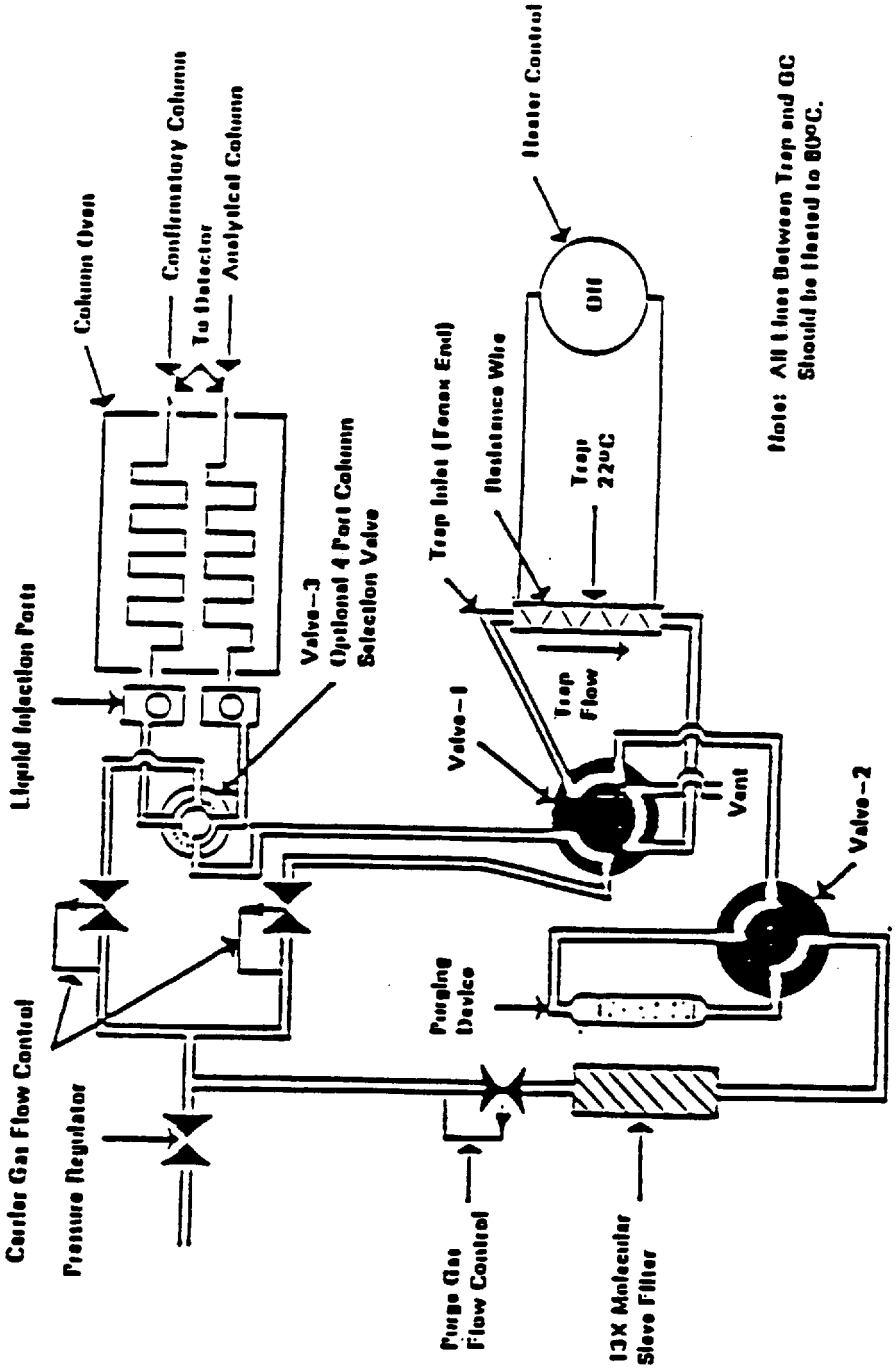

Figure 4 Purge-and-trap system, purge mode

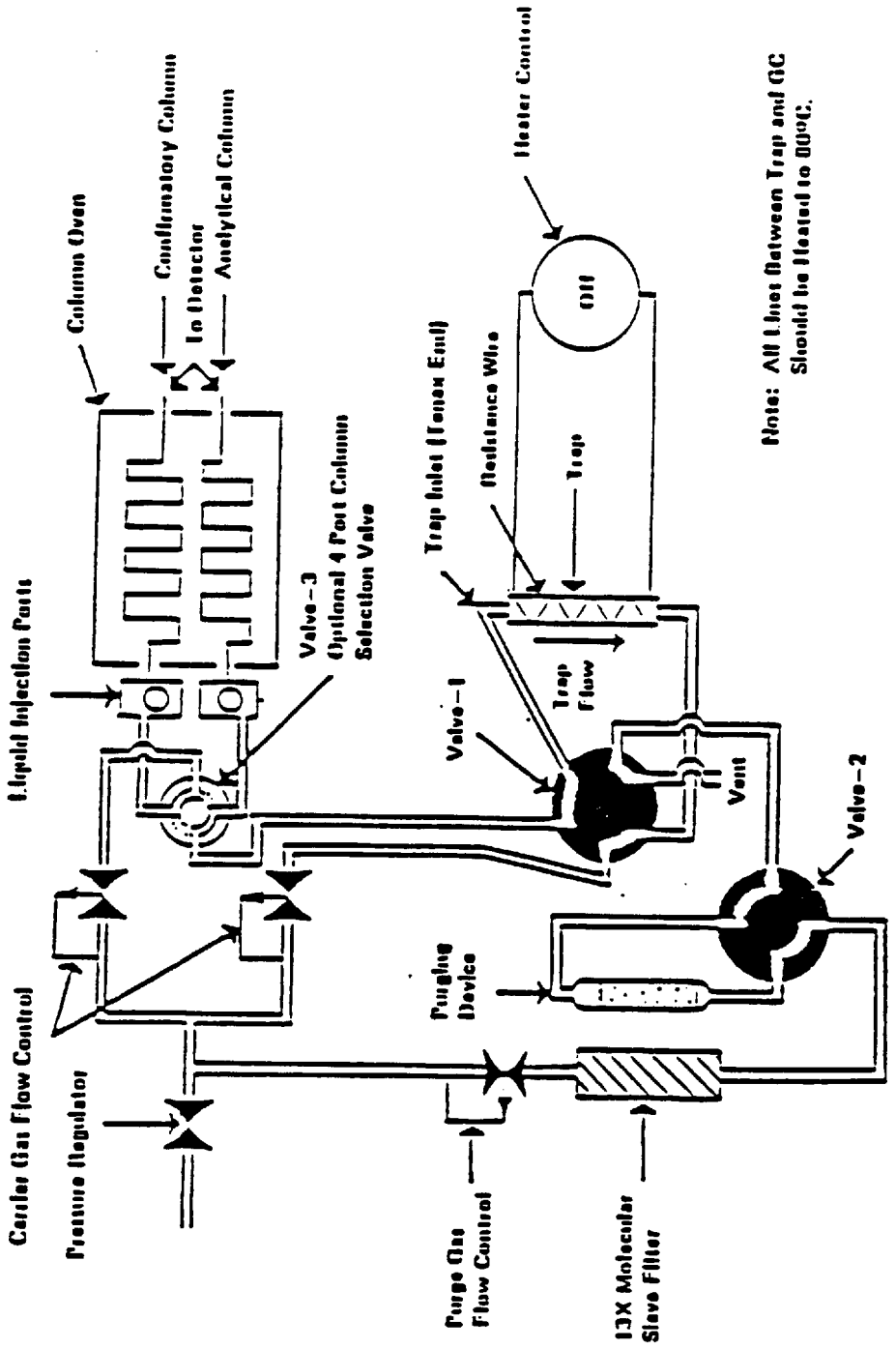

Figure 5 Purge-and-trap system, dasorb mode.

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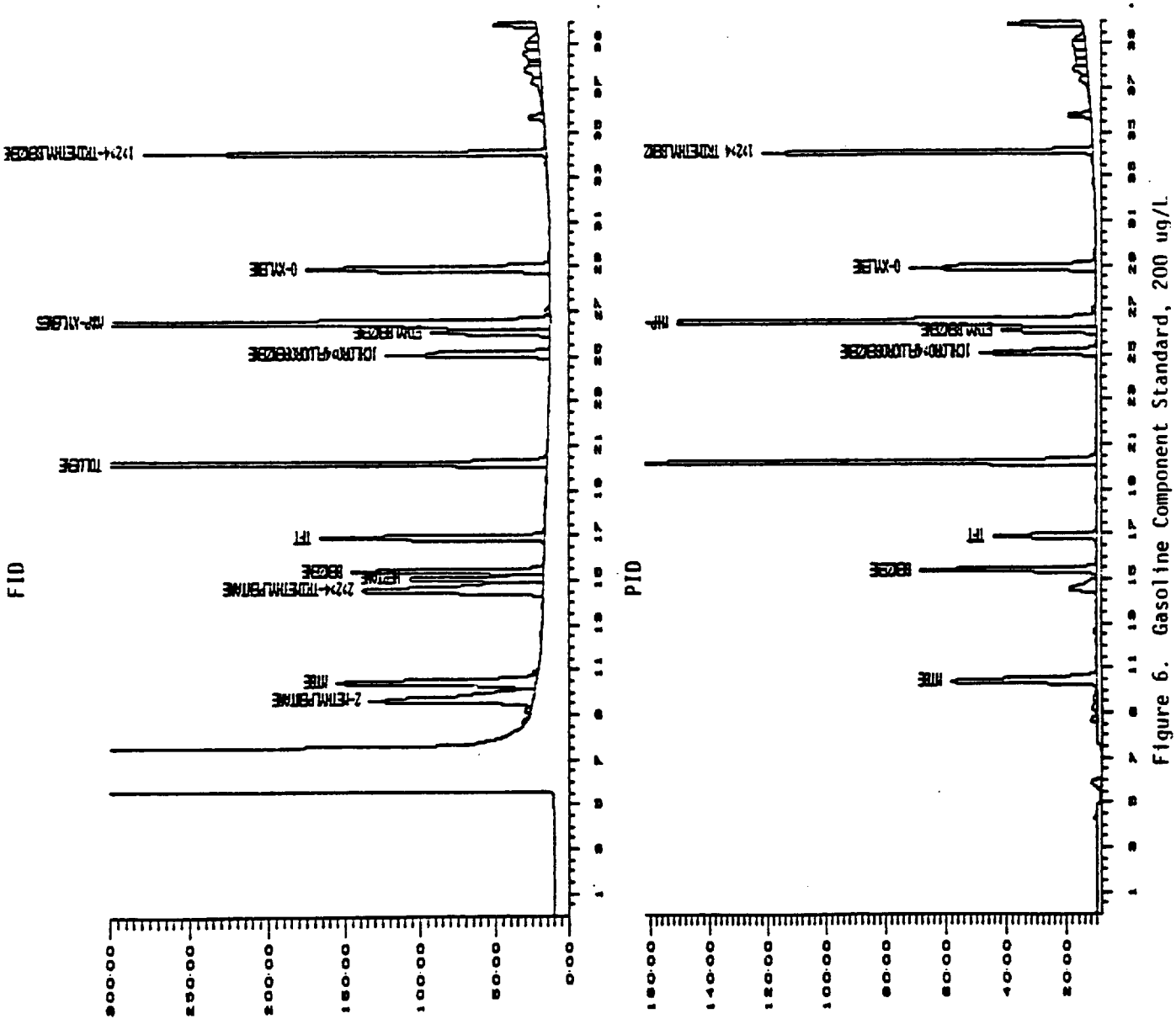

Figure 6. Gasoline Component Standard, 200 ug/L

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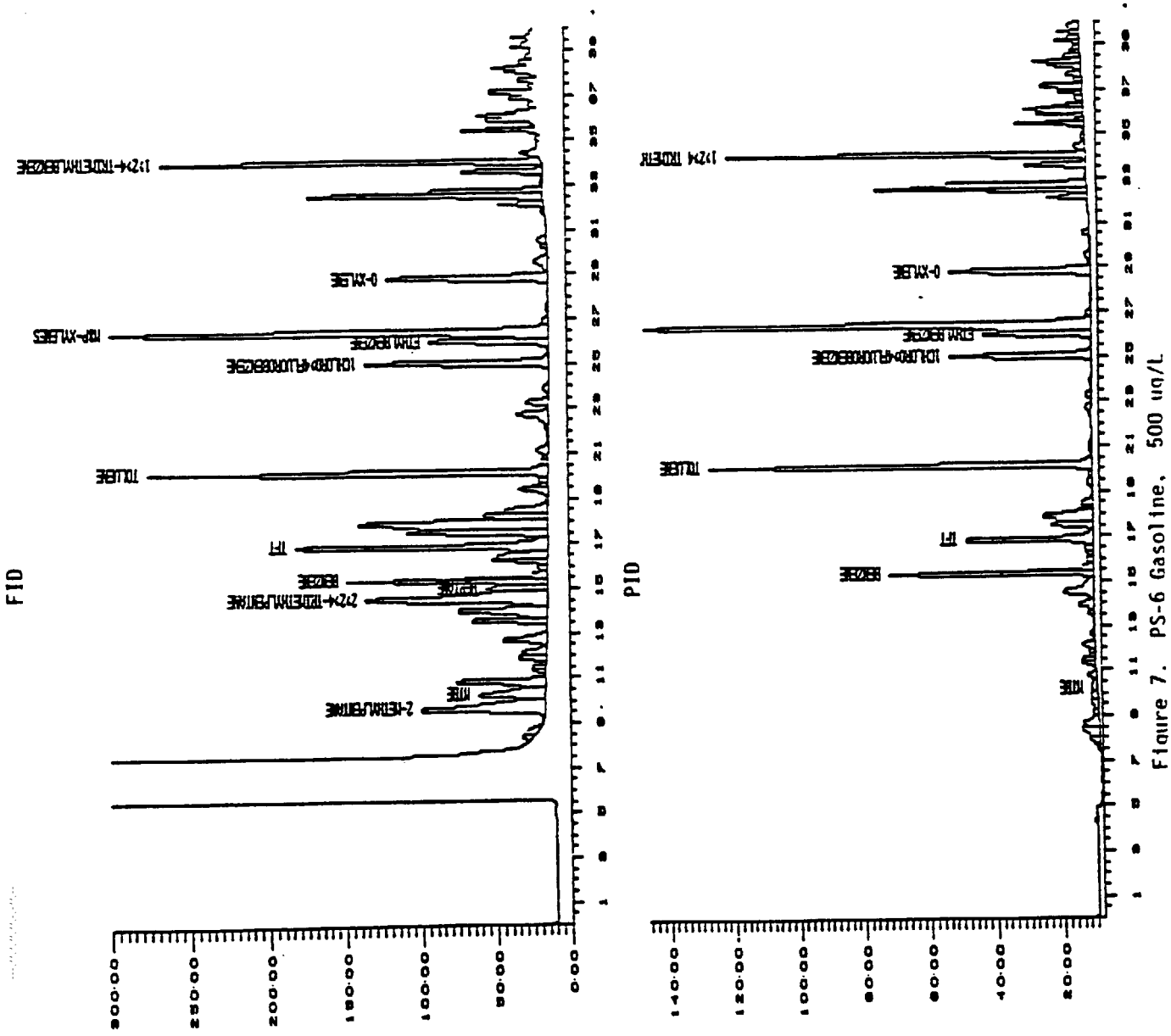

Figure 7. PS-6 Gasoline, 500 ug/L

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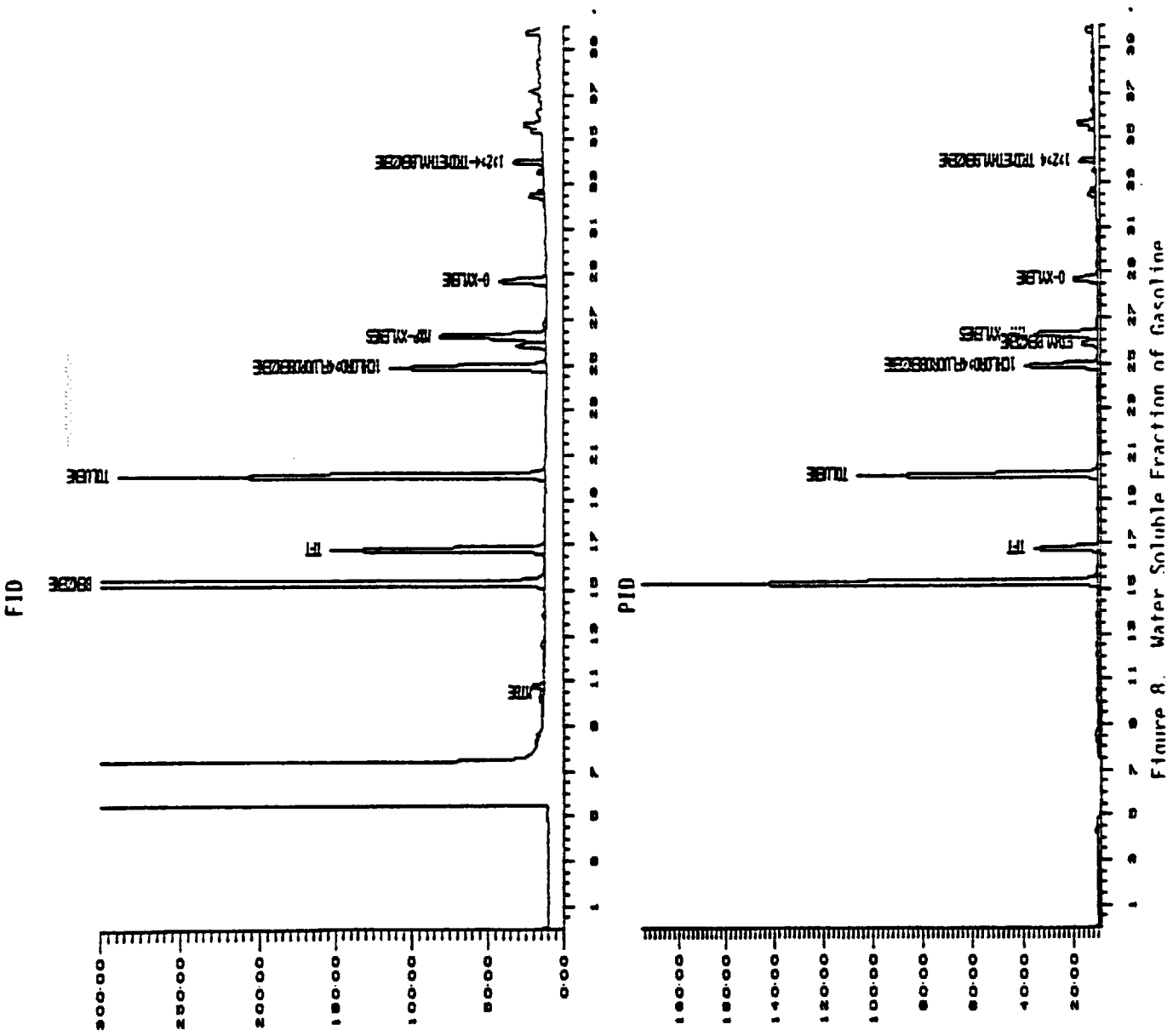

Figure 8. Water Soluble Fraction of Gasoline

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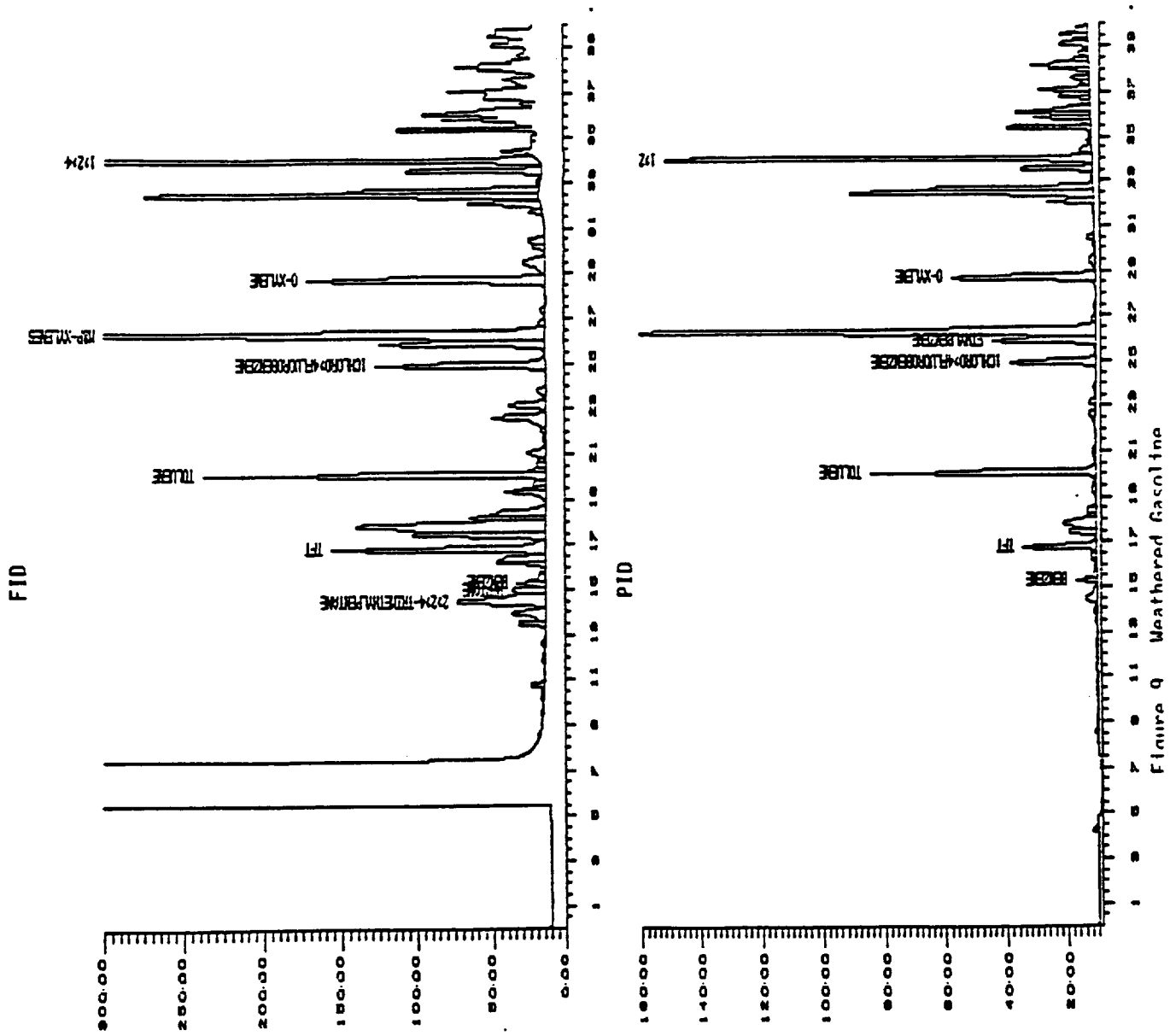

Figure Q Weathered Gasoline

Petroleum Hydrocarbons

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METHOD FOR CHARACTERIZATION OF PETROLEUM HYDROCARBONS IN SOIL

1. SCOPE AND APPLICATION

1.1 Analytes

1.1.1 This method is designed to measure the concentration of gasoline and diesel range petroleum hydrocarbons in soil. This corresponds to an alkane range of C_6 - C_{28} and a boiling point range between approximately 70°C and 400°C.

1.1.2 As a method option, selected components (e.g., benzene, toluene, ethyl benzene, xylenes, *n*-alkanes, naphthalene) may be measured and reported individually. Refer to 9.3.4.

1.1.3 As a method option, approximate boiling point distribution similar to those obtained from simulated distillation or true boiling point types of analysis can be obtained. Refer to Table 1. Typically, a detailed boiling point distribution is needed only for the gasoline range to assist in the selection of suitable remediation technology (e.g., soil venting).

1.2 Dynamic Range

1.2.1 The linear range of the method is approximately equivalent to 50 mg/kg to 10000 mg/kg of petroleum hydrocarbons in soil.

1.3 Experience

1.3.1 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 chromatography. The analysts should be skilled in the interpretation of capillary gas chromatograms and their use as a quantitative tool.

1.4 Limitations

1.4.1 The practical quantitation level of this method is 50-100 mg/kg. This level is compatible with clean-up standards for many states. [1] If data quality objectives require lower detection levels, alternate methods should be used. See Figure 1.

1.4.2 The method is designed to measure petroleum products such as gasoline and diesel or fuel oil. Components greater than C_{28} present in products such as motor oils or lubricating oils may be detectable under the conditions of the method. However, due to elevated column phase bleed and solubility limitations, the quantitation of hydrocarbons $>C_{28}$ by this

method is not recommended. Performance of this method for products other than gasoline, diesel or fuel oil must be demonstrated.

1.4.3 The method contains options regarding choices of calibration standards. While these options produce similar results, the laboratory and data user must be aware of the significance of these choices. Refer to 9.3.

1.4.4 For certain data quality objectives, alternative extraction solvents may be necessary. The laboratory should satisfy the criteria in Section 10 if alternative solvents are used. The laboratory and data user must realize that alternative solvents may not produce equivalent results to those obtained with this method. Some alternate solvents are:

A. Methanol (for soils) - is somewhat less efficient than methylene chloride for extraction of diesel range material. However, methanol soil extracts can be further analyzed by purge-and-trap for the volatile/gasoline range.

B. Tetradecane (for soils) - allows estimation of the boiling point range from C_1 to C_{12}. This may be used for a fresh gasoline spill or where information is needed below C_6. [2]

2. METHOD SUMMARY

2.1 Ten grams of soil are extracted with 10 mL methylene chloride or alternate solvents. One to five μl of 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 after the solvent peak up to n-C_{28} with calibration standards.

2.2 This method is based in part on USEPA Methods 8000, 8015, and 8100, SW-846, "Test Methods for Evaluating Solid Waste", 3rd Edition [3], and work by Rhodes, et al. [2, 4] It is similar to Washington State's WTPH-HCID [5].

3. DEFINITIONS

3.1 Petroleum Hydrocarbons (PHC): All chromatographic peaks eluting between the solvent front and octacosane (n-C_{28}). Quantitation is based on direct comparison of the total area within this range to the total area (within the same range) of calibration standards used to generate a calibration curve or average response factor.

3.2 Laboratory Control Sample: A method blank sample spiked with commercial gasoline and diesel #2 as a quality control check. The

spike recovery is used as a laboratory control and must be between 70-130%. See 7.3.6.

3.3 Other terms are as defined in SW-846.

4. INTERFERENCES

4.1 Other organic compounds including vegetable and animal oils and greases, organic acids, chlorinated hydrocarbons, phenols, and phthalate esters are measurable under the conditions of this method. As defined in the method, the PHC results include these compounds. However, characteristic fuel pattern will be altered.

4.2 Method interferences are essentially eliminated by the use of disposable glassware. Reagent blanks must be analyzed with each batch or for every 20 samples to demonstrate that the samples are free from contamination.

4.3 High purity reagents such as Burdick and Jackson GC[2] methylene chloride or Baker capillary grade methylene chloride should be used to minimize contamination 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 blanks 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 Vials - 40 mL glass vials with Teflon-lined screwcaps. GC autosampler vials.

6.1.4 Disposable Pipets: Pasteur.

6.2 Microsyringes: 5 µl, 10 µl, 25 µl, and 100 µl.

6.3 An analytical balance capable of accurately weighing 0.0001 g should be used for preparation of standards. A top-loading balance capable of weighing to the nearest 0.1 g should be used for obtaining sample weights.

6.4 Vortex Mixer

6.5 Ultrasonic Bath

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 required.

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 MS-007, 1.0 micron film thickness.

6.6.2.2 Other columns may be used; boiling point capillary columns are recommended. See 9.2.2 for GC performance criteria.

7. REAGENTS AND STANDARDS

7.1 Methylene chloride, methanol, tetradecane: Pesticide grade or equivalent.

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

7.3 Stock Standard Solution: Prepare the following stock standards. Unless noted, all are prepared in the methylene chloride listed in 7.1 above. Standard preparation should follow guidelines in Method 8000.

7.3.1 Calibration Standards: Prepared using gasoline and diesel #2 in a 1:1 ratio in the extraction solvent. If only the gasoline range or diesel range are of interest, the calibration standards should be prepared with either gasoline or diesel. Typical working concentration ranges are 50 to 10000 µg/mL. Calibration standards may be prepared from a blend of selected hydrocarbons (as in 7.3.5). See 9.3.

7.3.2 Optional Boiling Point Distribution Reference Standard: A solution containing approximately 200 ppm each of *n*-alkanes (*n*-hexane through octacosane) can be used for determination of retention times corresponding to the different boiling point fractions. Table 1 lists the boiling points of the *n*-alkanes and retention times for reference (using GC conditions in 9.2.1). Actual retention times must be determined by the laboratory.

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

7.3.4 Optional Surrogate Standard: 2000 µg/mL *ortho*-terphenyl (OTP). A working solution is made at 20 µg/mL.

7.3.5 Gasoline and Diesel Component Standard: A blend of typical gasoline and diesel compounds may be used as a calibration standard. Suggested running levels (total PHC) are 50, 100, 400, 2500, and 10000 µg/mL. See Table 3. Other components may be used as shown in Figure 2.

7.3.6 Stock Laboratory Control Standard: 10000 µg/mL gasoline and diesel #2 (prepared from a different source than the calibration standard in 7.3.1).

7.3.6.1 A working solution of the stock laboratory control standard is made at 5000 µg/mL in CH_2CL_2.

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

Soils are collected in wide-mouth glass jars with minimal head space. The samples are stored at 4°C from the time of collection until extraction. Extraction and analysis should be performed on soils within 14 days. Depending on analytes of interest and data quality objectives, other holding times may be applicable.

9. PROCEDURE

9.1 Soil samples are extracted by using either a mixer/shaker technique or by a sonic bath technique.

9.1.1 Soil Extraction

9.1.1.1 Weigh 10 g of sample in a 40 mL vial with Teflon cap. Add 5 g of sodium sulfate and 10 mL of methylene chloride. The sample should be free flowing prior to addition of methylene chloride; if necessary, add additional sodium sulfate in 1 g increments until the sample is free flowing.

9.1.1.1.1 For laboratory control samples and matrix spikes, add 1 mL of 5000 µg/mL (in CH_2CL_2) LCS solution (see 7.3.6.1). Use 10 g of Ottawa sand or other standard soil for lab control sample. Reduce solvent addition to 9 mL.

9.1.1.1.2 Prepare a reagent blank sample daily or for each batch of 20 samples.

9.1.1.2 Extract for 1 minute using a vortex mixer and shake with a horizontal or wrist-action shaker for 1-4 hours. Alternatively, the vials can be placed in a sonic bath for 5 minutes, shaken well, and returned to the sonic bath for 5 more minutes.

9.1.1.3 Samples can be centrifuged if necessary, and the extract then transferred to autosampler vials or storage vials with teflon caps. Extracts should be stored at 4°C.

9.2 Gas Chromatography

9.2.1 Conditions (Recommended): Set helium column pressure to 15#. Nitrogen make up gas at 30 mL/min is necessary to enhance sensitivity. Set column temperature to 40°C for 4 minutes, then 10°C/minute to 280°C and hold for 15 minutes (run time = 37 minutes). Set FID to 350°C and injector to 325°C. A 30:1 split injection is recommended. A splitless injection may be used for the diesel range; however, splitless injection is generally not effective for the gasoline range due to peak broadening. Other columns, conditions, and injection techniques may be used if criteria in Section 9.2.2 can be achieved.

9.2.2 Performance Criteria: GC run conditions and columns should be chosen to produce chromatograms similar to Figures 2-5. Response factors relative to *n*-heptane should be similar to Table 2.

9.2.3 If optional surrogate and internal standards are used, the column must be capable of separating these standards from

typical diesel components. If using internal standards, elevated levels of hydrocarbons may interfere with the internal standard and bias the results.

9.3 Calibration

9.3.1 The method takes advantage of the fact that the response of the flame ionization detector is essentially the same for all hydrocarbons (on a weight basis) and based primarily on effective carbon number as shown in Table 2. Only methyl *tert*-butyl ether (MTBE) is significantly different. Similar data are available for other hydrocarbons. [6] It is therefore not essential that calibration be performed using material similar to the material in the samples. For example, any gasoline, diesel, synthetic mixture, or single hydrocarbon can be used for calibration and calculation of TPH in samples with any type of petroleum hydrocarbon contamination. This is essentially true. However, because products such as gasoline or diesel are composed of more than 300 individual components, at low concentration of total product, many of the individual components are simply too small to be detected and cannot contribute to the total signal detected and thus linearity falls off. Conversely, when synthetic standards are used, typically no more than 10-20 components are used and thus the TPH is distributed among a few peaks that can be all detected for all concentrations of the standards above the stated practical quantitation limits. The use of synthetic standards always results in underestimation of the TPH present in the samples.

In addition, by using extraction solvents that are in the gasoline range ($<C_6$), a portion of gasoline range material cannot be measured, thus adding an additional bias to the method. This bias can be somewhat corrected by using gasoline standards for calibration of samples containing gasoline range materials.

9.3.2 Calibrate the GC with an initial five-point calibration using the calibration standards (7.3.1) from 50 to 10,000 µg/mL. A quadratic calibration fit is recommended for the calculation of sample results. Alternatively, 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, the average response factor can be used in place of a calibration curve.

$$\text{Response Factor} = \frac{\text{Total area of calibration standard}}{\text{Total diesel standard amount (mg/mL)}}$$

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

9.3.3 The working response factor or calibration curve must be verified on each working day by the injection of a low point and mid-point continuing calibration standard (CCS). If the concentration or response for these standards varies from the standard value or predicted response by more than ± 25%, a new calibration curve must be prepared. It is advisable to check instrument performance and reanalyze the CCS prior to analyzing a new calibration curve.

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

where: R1 = Standard value or average RF
R2 = Calculated value or RF from CCS
Ravg = (R1 + R2)/2

9.3.4 Calibration of Selected Target Analytes: Selected components (volatile aromatics and *n*-alkanes) can be measured individually if desired. Assuming an equivalent response factor, the calibration curve or response factor developed above can be used for target analytes.

9.4 Product Type Identification

9.4.1 Chromatographic peaks with characteristic fuel fingerprints eluting between the solvent front and C_{10} indicate the presence of gasoline range compounds. Peaks between C_{10} and C_{25} indicate the presence of diesel range compounds. Patterns that do not resemble either product should be noted.

9.4.2 Product type can be determined by visual inspection of the chromatograms. The "fingerprints" of gasoline, diesel, and mixtures of these two petroleum hydrocarbon ranges are shown in Figures 3-6. The chromatogram can become more complicated if crude oil, jet range material, or other refined products are also present. However, it may still be possible to determine that the contamination is due to some sort of fuel oil. Industrial solvents can interfere in the analysis; however, the chromatographic fingerprints would be noticeably different. The best approach to maximize the probability of a correct identification is to analyze reference fuels, from the sample location, along with the sample. These reference fuels can be used as calibration standards.

9.4.3 As with any gas chromatographic procedure using non-selective flame ionization detection, interferences are possible from

coelution of gasoline components with other soil contaminants of other sources. Potentially, any compound with similar boiling point and polarity as the hydrocarbons of gasoline-to-diesel range may have retention times within the range of interest and may result in over estimation of the TPH concentration. For example, volatile industrial solvents, cleaners, and naturally occurring compounds not of petroleum origin may interface with this analysis. It is often possible to assess the presence of solvents and cleaners since the characteristic fingerprint of gasoline, kerosene, diesel, and heavier materials is altered.

9.4.4 Decisions must be made by the analyst in determination of cutoff points for quantitation of different product ranges when contamination is caused by a combination of sources. For example, if soils are contaminated with gasoline range and diesel range materials, there is an area of overlap where certain components are common to both types of petroleum fractions. A compromise cutoff for mixtures of gasoline with diesel fuel range material is C_{10}. There is no appropriate cutoff for a mixture of jet fuel or kerosene and diesel fuel since there is a great deal of overlap. Crude oil contamination also contains a wide range of materials. In cases where mixed products are present, it is perhaps best not to quantitate how much is due to what type of product but to simply quantitate total hydrocarbons.

In order to minimize quantitation problems due to column bleed, the method is best suited for analysis of materials up to diesel range. Heavier materials can be detected with a qualitative identification of product mix but not quantitated effectively.

9.4.5 Some additional information on hydrocarbon pattern interpretation is included in references 7, 8, 9, and 10.

9.5 Gas Chromatographic Analysis

9.5.1 Samples are analyzed by GC/FID. Suggested injection volumes are 1 to 5 μl using the conditions established in 9.2.

9.5.2 For optional internal standard calibration, 5α-androstane internal standard is spiked into each sample and standard at a concentration of 20 μg/mL of sample extract. 20 μl of 5α-androstane stock at 1000 μg/mL may be spiked into a 1 mL final volume or a corresponding amount may be added to an aliquot of the final extract. Note: PHC values > 2000 μg/mL (in the solvent extract) may lead to measurement bias due to coelution with the internal standard.

9.5.3 After initial calibration (9.3.2) has been performed, verify the calibration by analysis of a low point and medium point CCS at the start of a new analytical sequence using the criteria in 9.3.3.

The low point standard must also be run once every ten runs and at the end of each sequence.

9.5.4 For samples that contain unresolved hydrocarbons (elevated baseline), baseline projection must be used to generate the area for PHC calculation. The GC conditions used for this method produce minimal column bleed up to C_{28}, so baseline subtraction of column bleed should not be necessary.

9.5.5 Alternatively, if peak resolution is adequate, valley-to-valley integration may be used to generate peak areas. The analyst should avoid discarding chromatographic area related to unresolved hydrocarbons.

9.5.6 If the product concentration exceeds the linear range of the method in the final extract, the extract must be diluted and reanalyzed. The linear range tested is approximately equivalent to 50 µg/mL to 10000 µg/mL of petroleum hydrocarbons in the extract. Linearity beyond this range must be verified.

9.6 Calculations

9.6.1 External Standard Calibration: The concentration of petroleum hydrocarbons in the sample is determined by calculating the absolute weight of analyte chromatographed from a summation of peak response for all chromatographic peaks eluting between the solvent front and n-C_{28}, using the quadratic calibration curve or the response factor determined in paragraph 9.3.2. Refer to Sections 9.4 and 9.5. The concentration of petroleum hydrocarbons is calculated as follows:

Soil samples:

$$Cs = Cc \times \frac{Vt}{Ms} \times D \times \frac{1\ mg}{1000\ \mu g}$$

Where:

Cs = Concentration of petroleum hydrocarbons (mg/kg).

Cc = Concentration from calibration curve in µg/mL. (If average RF is used for calculations, this value is area response/average RF).

Vt = Volume of final extract (mL).

D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

Ms = Mass of sample extracted in kg.

9.6.2 Alternatively, internal standard calibration may be used (see Method 8000).

9.6.3 The peak areas may be divided at C_{10} (see 9.4) and reported as gasoline PHC and diesel PHC. Patterns that do not resemble either product should be noted.

9.7 Calculation of Approximate Boiling Point Distribution: The approximate boiling point distribution is calculated by normalization of sums of peak areas of portions of the chromatograms eluting between preselected retention times as indicated in Table 1. Actual retention times must be verified in the laboratory. These retention times correspond to known boiling points selected as references. The chromatographic column used in this method is essentially a boiling point non-polar column and compound separation is achieved by boiling point differences. A homologous series of *n*-alkanes is used as approximate boiling point references. The cumulative boiling point distribution is graphically displayed by plotting the cumulative area percents versus boiling points of the *n*-alkanes. The plots are similar to those obtained from simulated distillation or true boiling point gas chromatographic analyses. Figure 7 includes several approximate boiling point distribution plots.

10. QUALITY CONTROL

10.1 The laboratory must establish the ability to generate acceptable accuracy and precision. This should include the analysis of QC check samples plus the calculation of average recovery and the standard deviation of the recovery as outlined in Method 8000, Section 8.0.

10.2 The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control.

10.3 After successful calibration (Section 9.3), analyze a reagent blank sample with every analytical batch or sequence. The sample should not have petroleum hydrocarbons above the practical quantitation limit.

10.4 Every batch or 20 samples, duplicate Laboratory Control Samples must be analyzed. The accuracy and precision of the duplicate standards must be within recommended limits (Table 4) or laboratory control limits (10.5).

10.5 Each laboratory should generate control limits based on the average recovery +/- 3 standard deviations.

10.6 If any of the criteria in 10.3 and 10.4 are not met, the problem must be corrected before samples are analyzed.

10.7 Field blanks, duplicates, and matrix spikes are recommended for specific sampling programs. Matrix spikes should use the spike levels specified for laboratory control samples.

11. METHOD PERFORMANCE

11.1 Single-lab method performance data for this method is presented below. Chromatograms for synthetic standards, gasoline, and diesel are in Figures 2-6.

11.2 The average recovery of various soils spiked with gasoline, diesel, and mixtures was 87% with a relative standard deviation of 8% [3]. Results are in Table 5.

11.3 This method was tested by 12 laboratories [11]. Single operator precision, overall precision, and method accuracy were determined. These results are summarized in Table 6. Linear regression equation to describe these relationships is also presented in Table 6. The results from this interlaboratory study were also used to evaluate the stated PQL. The results of this evaluation are presented in Table 6.

12. REFERENCES

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3. USEPA "SW-846 Test Methods for Evaluating Solid Waste," 3rd Edition, Methods 8000, 8015, and 8100.

4. Rhodes, I.A.L., R.Z. Olvera, J.A. Leon, and E.M. Hinojosa, "Determination of Total Petroleum Hydrocarbons by Capillary Gas Chromatography," presented at the 14th Annual Analytical Symposium, U.S. EPA Office of Water, Industrial Technology Division, May, 1991.

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8. Senn, R.B., and M.S. Johnson, "Interpretation of Gas Chromatographic Data in Subsurface Hydrocarbon Investigations," Ground Water Monitoring Review, 1987.

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10. ASTM "Standard Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography," pp. 3328-78.

11. "Interlaboratory Study of Three Methods for Petroleum Hydrocarbons in Soil," American Petroleum Institute Publication, August 1993.

TABLE 1

Retention times and boiling points of *n*-alkanes for determination of boiling point distribution of gasoline to diesel range hydrocarbons in soil using designated instrumental parameters. Actual retention times must be verified.

	BP °C	Retention Time (min)	Alkane Marker
GASOLINE RANGE	36	2.15	*n*-C5
	69	4.09	*n*-C6
	98	6.85	*n*-C7
	126	9.55	*n*-C8
	151	11.93	*n*-C9
	174	14.03	*n*-C10
	196	15.92	*n*-C11
	216	17.65	*n*-C12
	236	19.26	*n*-C13
	253	20.76	*n*-C14
	270	22.18	*n*-C15
	287	23.51	*n*-C16
	302	24.77	*n*-C17
	316	25.98	*n*-C18
	329	27.11	*n*-C19
	343	28.20	*n*-C20
	402	35.99	*n*-C25

TABLE 2

RELATIVE RESPONSE FACTORS OF SELECTED GASOLINE RANGE COMPONENTS USING GC-FID. (NORMALIZED WITH RESPECT TO *n*-HEPTANE)

Methyl *tert*-butyl ether	0.70
n-Butane	1.00
Isopentane	1.00
2-Methylbutene-1	0.96
n-Pentane	1.00
Cyclopentane	0.96
2-Methylpentane	1.00
n-Hexane	1.00
Methylcyclopentane	0.97
2,4-Dimethylpentane	1.00
Benzene	0.92
Cyclohexane	0.99
Cyclohexene	0.98
2-Methylhexane	1.00
3-Methylhexane	1.00
trans-1,3-Dimethylcyclopentane	1.00
trans-1,2-Dimethylcyclopentane	1.00
3-Ethylpentane	1.00
2,2,4-Trimethylpentane	1.00
n-Heptane	1.00
Methylcyclohexane	0.98
Ethylcyclopentane	0.98
2,4-Dimethylhexane	1.00
2,3,4-Trimethylpentane	1.00
Toluene	0.93
2-Methylheptane	1.00
3-Methylheptane	1.00
trans-1,3- & *cis*-1,4-Dimethylcyclohexane	0.99
n-Octane	1.00
n-Propylcyclopentane	0.99
Ethylbenzene	0.96
m-Xylene	0.96
p-Xylene	0.96
o-Xylene + 3-Methyloctane	0.98
n-Nonane	1.00
Isopropylbenzene	0.98
2,6-Dimethyloctane + *n*-Propylbenzene	0.98
1-Methyl-4-ethylbenzene	0.98
1,3,5-Trimethylbenzene	0.98
1-Methyl-2-ethylbenzene	0.98
4-Methylnonane	1.00
trans-Butylbenzene + 1,2,4-Trimethylbenzene	0.99
n-Decane + 1,2,3-Trimethylbenzene	0.98
Indan	1.00
1,2,3,5-Trimethylbenzene	0.99
Naphthalene	0.96
n-Dodecane	1.00
AVERAGE RESPONSE FACTOR	0.98

TABLE 3

DIESEL RANGE COMPONENT STANDARD

Component	Midpoint Concentration
Decane	25
Dodecane	25
Tetradecane	25
Hexadecane	25
Octadecane	25
Eicosane	25
Decosane	25
Tetracosane	25
	200 µg/mL Total

GASOLINE COMPONENT STANDARD

Component	Midpoint Concentration
2-Methylpentane	30
2,2,4-Trimethylpentane	30
Heptane	10
Benzene	10
Toluene	30
Ethylbenzene	10
m-Xylene	20
p-Xylene	20
o-Xylene	20
1,2,4-Trimethylbenzene	20
	200 µg/mL Total

TABLE 4

ACCEPTANCE CRITERIA FOR LCS AND SCS

Laboratory Control Sample	% Recovery	Relative % Difference
Petroleum Hydrocarbons	70-130	20

TABLE 5: SUMMARY OF TPH RESULTS FOR SPIKED SOILS

RESULTS CALCULATED WITH RESPECT TO GASOLINE STANDARDS, GASOLINE AND DIESEL STANDARDS, DIESEL STANDARDS AND SYNTHETIC MIXTURE STANDARDS AS INDICATED.

PRODUCT TYPE	TARGET VALUE PPM	GAS STD PPM	G•D STD PPM	DIES STD PPM	SYN STD PPM	AVE PPM	ACC AVG %
GASOLINE	57	43	55	77	43	55	96
		46	61	62	23	48	84
GASOLINE	113	85	110	125	77	99	88
		96	110	120	60	97	85
GASOLINE	2300	1980	2530	2210	1670	2098	91
		2000	2040	2400	1470	1978	86
GASOLINE	4770	4580	5500	4750	3740	4643	97
		4600	4680	5400	3800	4620	97
GAS•DIES	58	36	48	71	44	50	87
		67	51	69	24	53	91
GAS•DIES	117	91	120	130	83	106	91
		65	78	102	44	77	66
GAS•DIES	2230	1680	2150	1900	1410	1785	80
		2250	2180	2630	1620	2170	97
GAS•DIES	4140	3300	4120	3580	2760	3440	83
		4110	4010	4730	2990	3960	96
DIESEL	52	40	50	73	39	51	97
		46	62	62	20	48	91
DIESEL	104	74	96	110	68	87	83
		62	86	94	35	69	67
DIESEL	2770	2140	2730	2390	1800	2265	82
		2400	2450	3000	1770	2405	87
DIESEL	6660	5310	6440	5540	4420	5428	81
		6100	6240	7000	4560	5975	90

ACCURACY AVERAGE % (PER CONCENTRATION LEVEL): 87
RELATIVE STANDARD DEVIATION ("): 8

OVERALL ACCURACY AVERAGE PERCENT LIMITS:

GASOLINE:	92±20
GASOLINE•DIESEL:	86±21
DIESEL:	85±22

EXTRACTS ANALYZED USING 2 DIFFERENT GAS CHROMATOGRAPHS

TABLE 6
INTERLABORATORY STUDY RESULTS FOR PHC

Average Performance: Accuracy and Precision

Average Accuracy	Average Single Analyst Precision, RSD	Average Overall Precision, RSD
84%	13%	30%

Regression Equation for Accuracy and Precision

Range for Equation (mg/kg)	Accuracy as Recovery X (mg/kg)	Overall Precision S (mg/kg)	Single Analyst Precision Sr (mg/kg)
93.6-831	X=0.81C+7.29	S=0.30X+0.45	Sr=0.07X+16.35

Method PQLs

PQL Stated in Method (mg/kg)	PQL by 80% + 40% Rule (mg/kg)	PQL by 95% Rule (mg/kg)
50-100	104	50

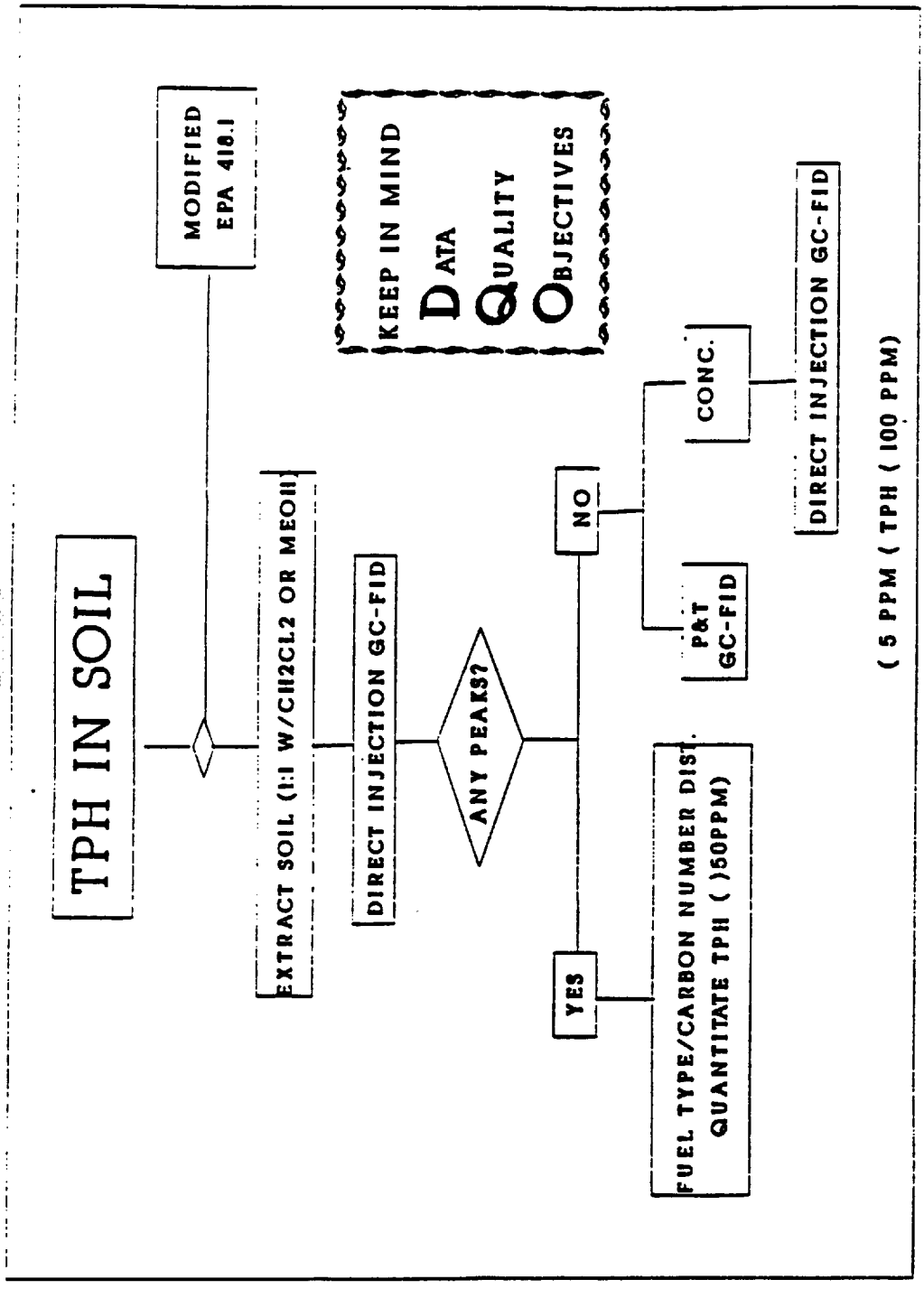

FIGURE 1: RECOMMENDED APPROACH TO DETERMINATION OF TPH IN SOILS.

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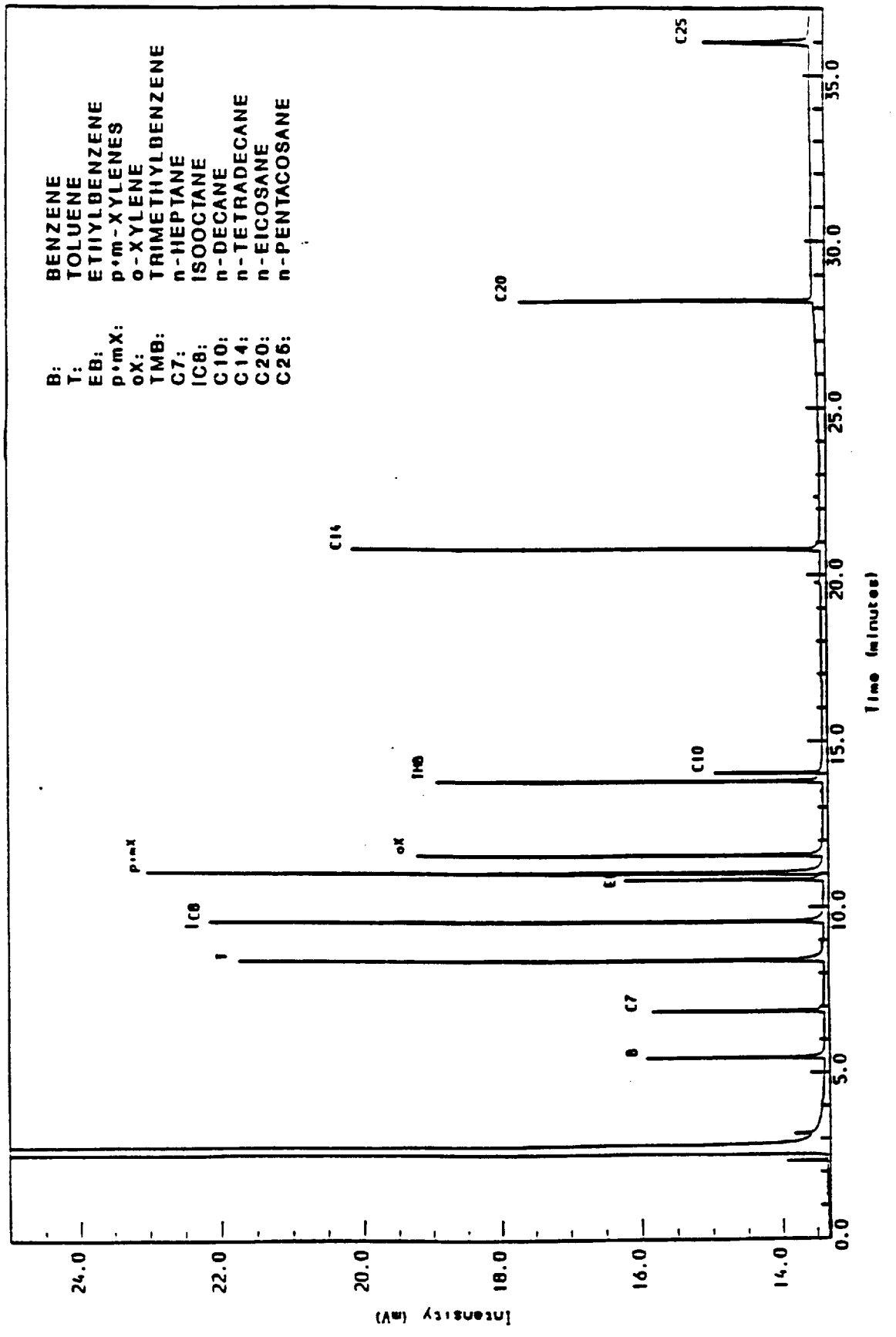

FIGURE 2: CHROMATOGRAM OF 1000 PPM SYNTHETIC MIX STANDARD

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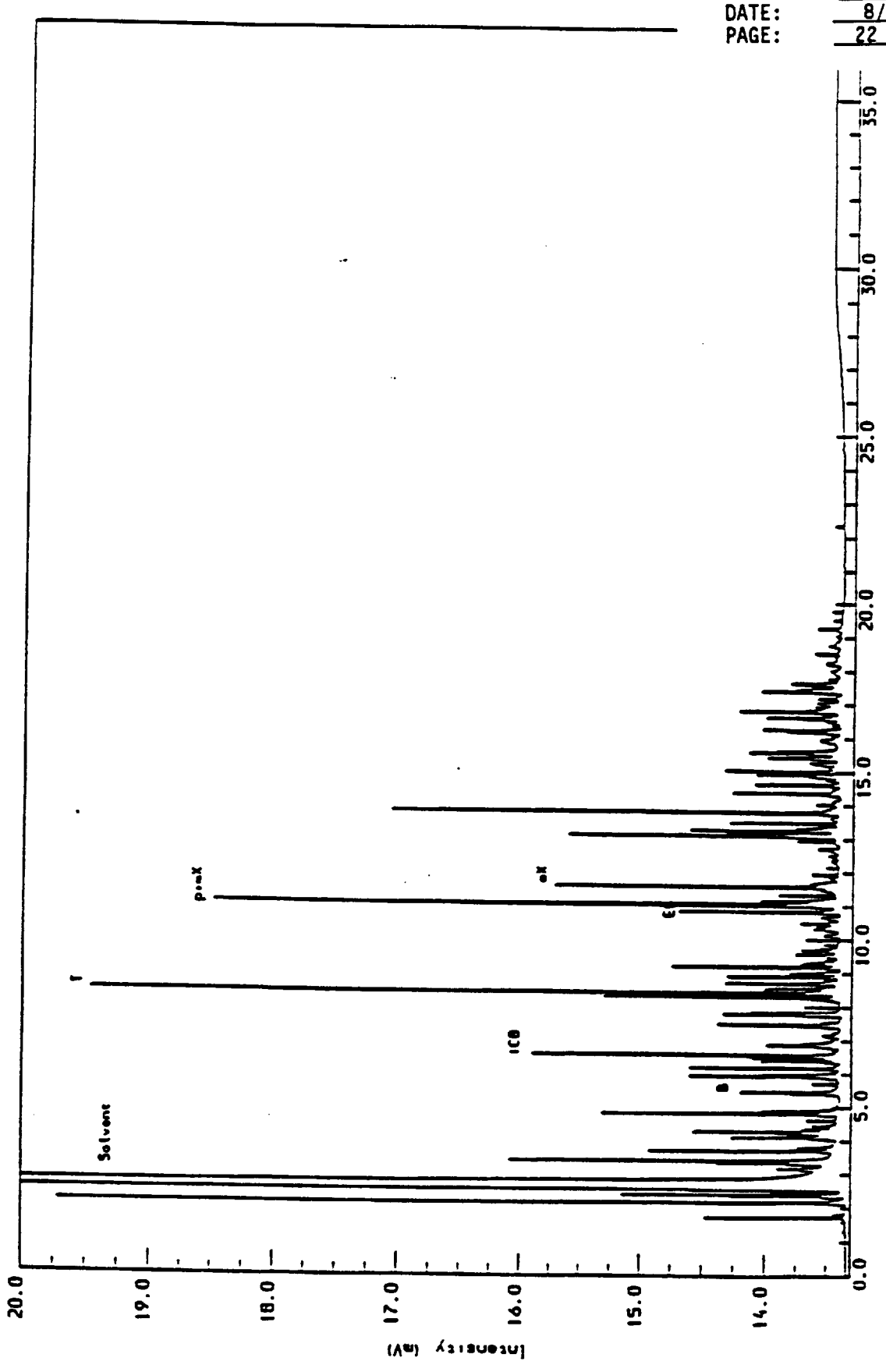

FIGURE 3: CHROMATOGRAM OF EXTRACT FROM SPIKED SOIL. 2300 PPM GASOLINE IN SOIL.

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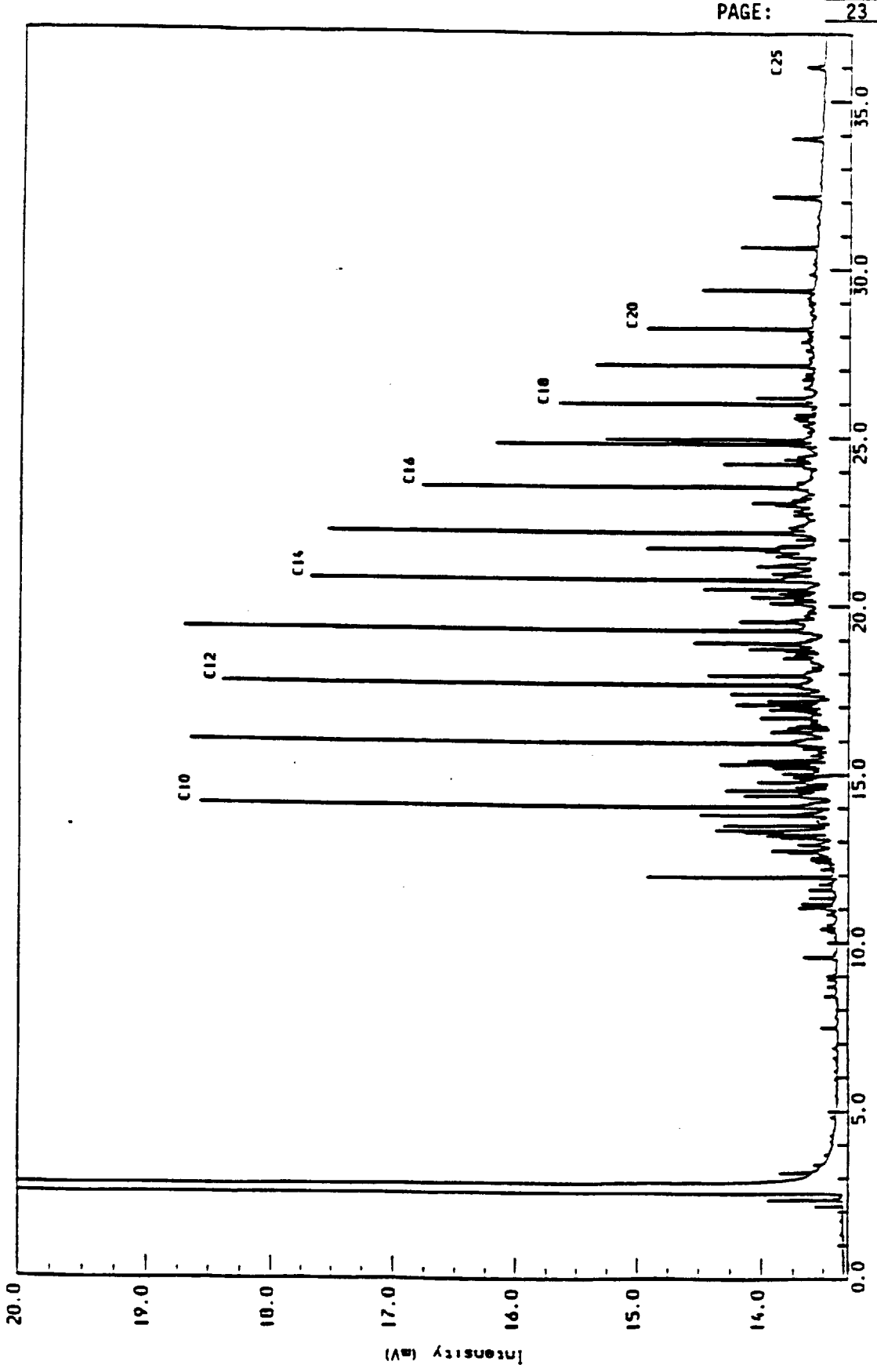

FIGURE 4: CHROMATOGRAM OF EXTRACT FROM SPIKED SOIL. 2700 PPM DIESEL IN SOIL.

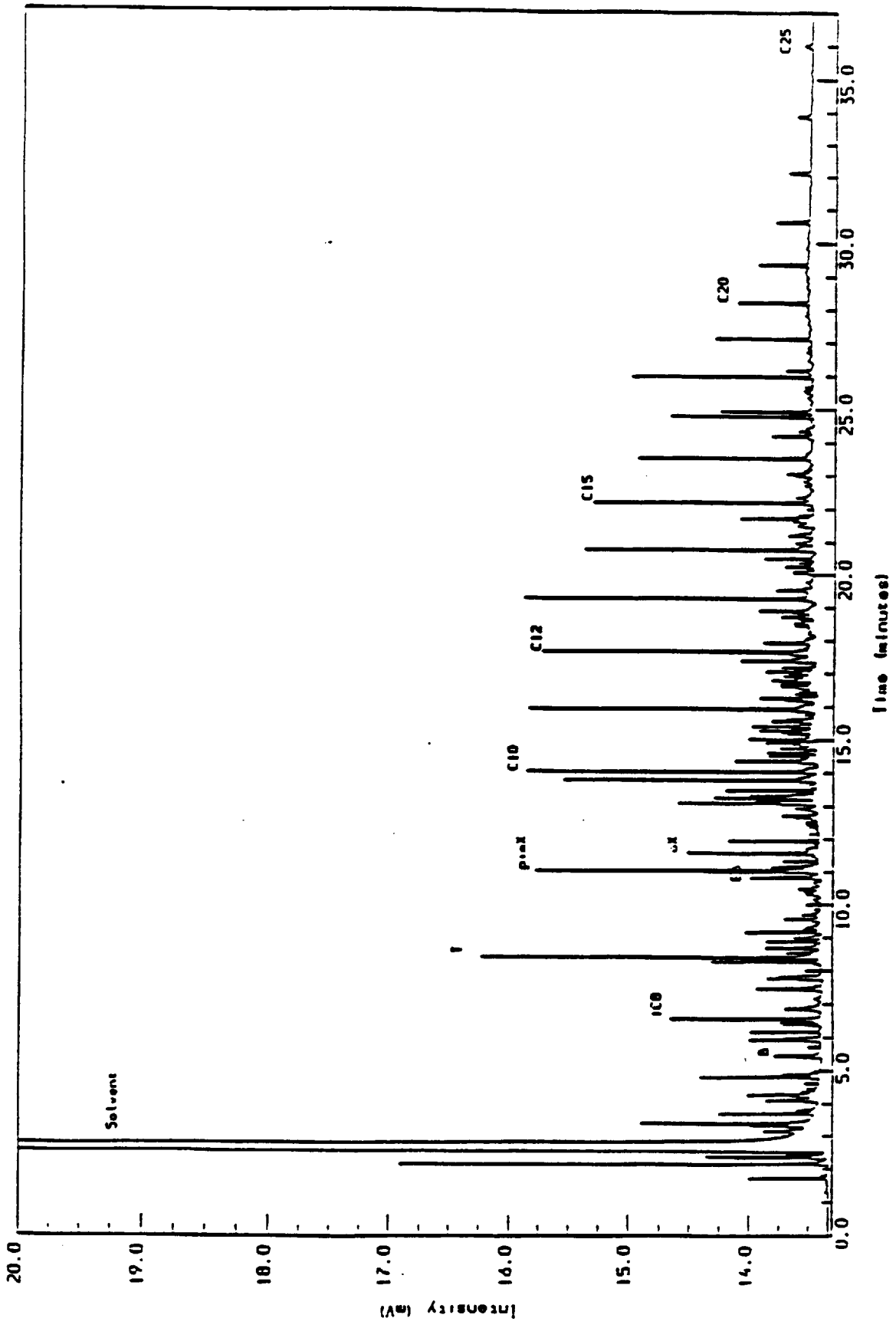

FIGURE 5: CHROMATOGRAM OF EXTRACT FROM SPIKED SOIL.
2200 PPM GASOLINE PLUS DIESEL (~1:1)

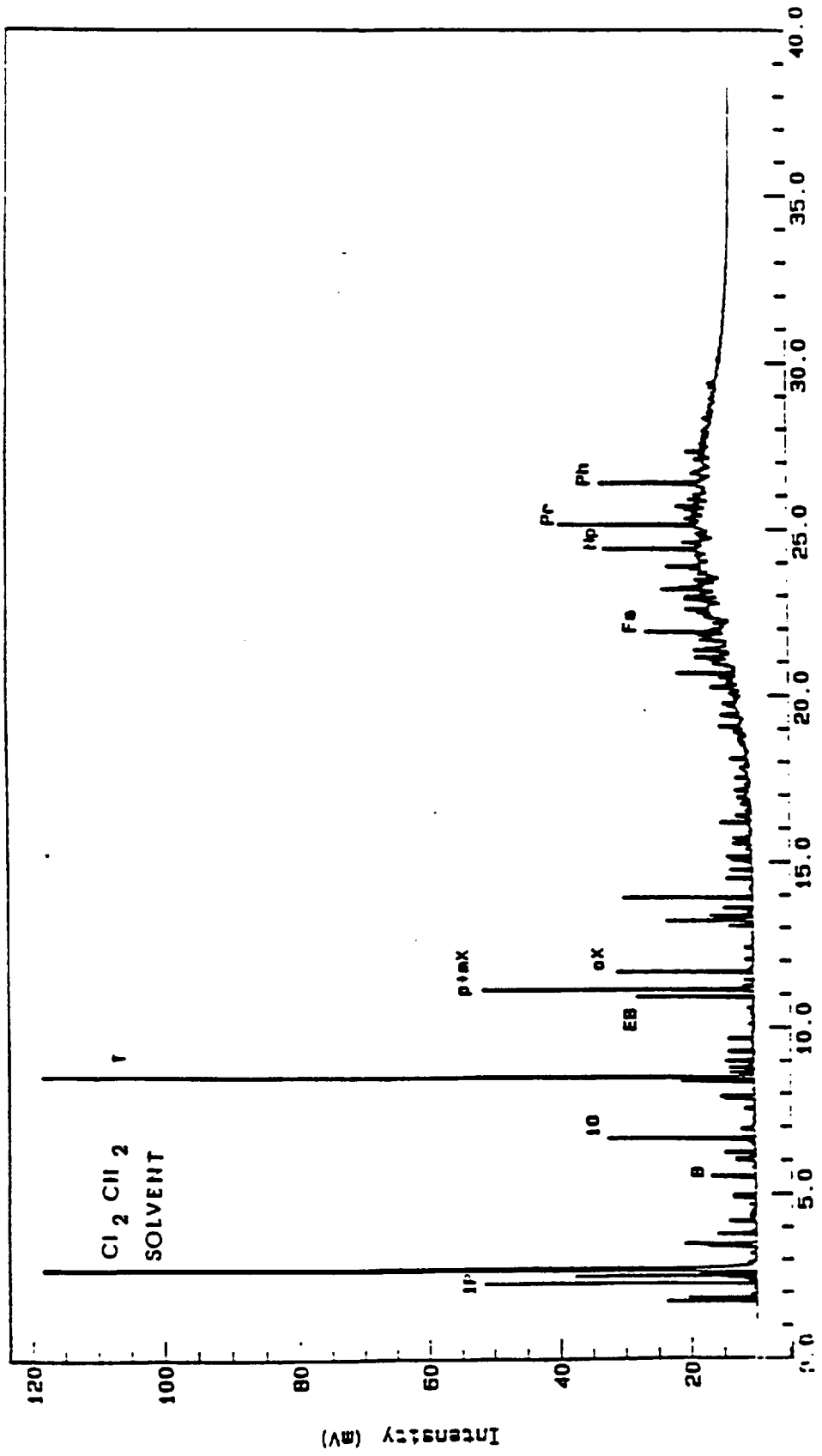

FIGURE 6: CHROMATOGRAM OF EXTRACT FROM A SOIL SAMPLE CONTAINING GASOLINE AND EXTREMELY WEATHERED DIESEL RANGE MATERIAL

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DATE: 8/18/93
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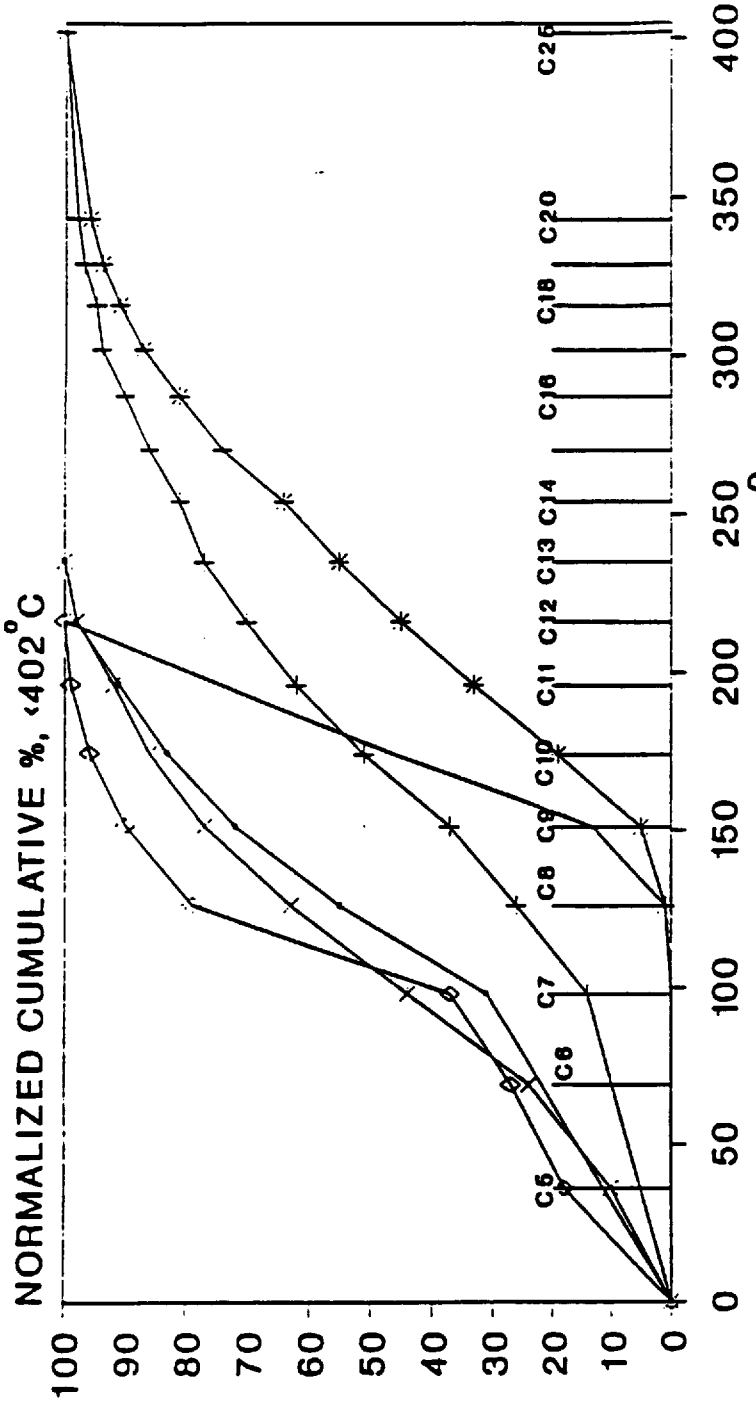

FIGURE 7: APPROXIMATE BOILING POINT DISTRIBUTION PLOTS.

APPENDIX B

VERIFICATION OF PREPARED CONCENTRATIONS

5540 MARSHALL STREET
ARVADA, COLORADO 80002
303 431-8454
1-800-ERA-0122
FAX 303 421-0159

June 26, 1992

Roger Claff
American Petroleum Institute
1220 L Street, N.W.
Washington, DC 20005

ONMENTAL
RCE ASSOCIATES

Dear Roger,

The Interlaboratory Study of API Methods for Petroleum Hydrocarbon samples were shipped to the fifteen laboratories on June 12th, 1992. The letter sent with the samples is attached. We requested that the laboratories complete the analyses and return all data within six weeks. The certified values and verification data for the twenty-four samples are summarized in the attached table.

The analytical verification of the standards was completed by ERA. The method used consisted of a methanol extraction followed by GC/FID. Accuracy and precision were calculated by comparing the results obtained with the gasoline and diesel stocks used to spike the study standards. Overall the recoveries for the PHC and DRO samples were quite good. The GRO sample recoveries were slightly lower than the DRO and PHC samples. For all three standard types, precision was less than 8.5% relative standard deviation. The higher %RSD's are from the lower level samples, where the analytical method is less precise. All results fit well within the Class C guidelines presented in the work plan.

The raw materials used for the three methods were a weathered API gasoline (Lot EPL 470 91-01) and a no. 2 diesel fuel from a local gas station (ERA Lot 091691). The API gasoline was weathered by volume to 50% under a constant stream of helium in a 60°C water bath. The PHC stock consisted of a mixture of 50.4% gasoline and 49.6% diesel (w/w).

Thank you for the opportunity to work with API on this project. If you have any questions, please feel free to call.

Sincerely,

Jeff Lowry
Senior Chemist

Interlaboratory Study of API Methods of Petroleum Hydrocarbons - Certified Values

Sample Number	Certified Value (mg/Kg)	Average Result (mg/Kg)	Std Dev. (mg/Kg)	Ave. % Rec.
GRO-1	5.02	--		
GRO-2	55.4	39.1	1.4	70.6
GRO-3	130	107	6.4	82.3
GRO-4	21.6	17.2	0.72	79.6
GRO-5	Blank	--		
GRO-6	65.2	57.4	0.66	88.0
GRO-7	18.5	15.8	1.3	85.4
GRO-8	111	86.8	3.1	78.2
PHC-1	748	765	23	102
PHC-2	104	96.8	5.2	93.1
PHC-3	50.4	--		
PHC-4	416	384	15	92.3
PHC-5	374	339	21	90.6
PHC-6	831	830	34	99.9
PHC-7	Blank	--		
PHC-8	93.6	78.8	3.1	84.2
DRO-1	77.1	76.8	1.2	99.6
DRO-2	Blank	--		
DRO-3[1]	207	211	7.8	102
DRO-4[1]	193	170	4.3	88.1
DRO-5	19.3	18.8	2.2	97.4
DRO-6	4.99	--		
DRO-7	82.6	84.9	0.76	103
DRO-8	20.7	20.6	0.79	99.5

All data generated from three randomly selected vials within the lot.

1. Data generated with six data points. Two samples taken from each of three vials.

APPENDIX C

DATA AND CALCULATIONS

Summary of Laboratory Results

Summary of Laboratory Results
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
Diesel Range Organics (DRO)

Sample ID	DRO-1	DRO-2	DRO-3	DRO-4 (mg/kg)	DRO-5	DRO-6	DRO-7	DRO-8
Made-to Values	77.1	blank	207	193	19.3	4.99	82.6	20.7
Interlaboratory Results								
Laboratory ID								
API-01	68.6	5.88	151	111	18.7	10.3	70.9	18.6
API-02	—	—	—	—	—	—	—	—
API-03	61	3	180	170	12	7.6	69	22
API-04	85	22	200	234	26	19	54	20
API-05	48	6	190	160	13	5	55	13
API-07	69	9.8	200	180	26	13	78	28
API-08	47	6	130	110	18	9	58	18
API-09	52	1.4	130	180	5.9	17	69	17
API-10	79.1	6.07	213	187	26.3	13	87.6	28.8
API-13	89.7	13.1	236	188	23.8	13.8	77.7	30.2
API-14	49.4	7.99	132	116	18	9.88	58.3	19.9
API-15	62	18.6	220	193	8.6	ND	64.4	9.2
API-16	16	0.4	40	39	3.9	1.4	16	3.8
API-17	—	—	—	—	—	—	—	—
API-18	29	<4	65	70	8.5	<4	30	7.4

— No data submitted
ND Reported as nondetect

Summary of Laboratory Results
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
Gasoline Range Organics (GRO)

Sample ID	GRO-1	GRO-2	GRO-3	GRO-4 (mg/kg)	GRO-5	GRO-6	GRO-7	GRO-8
Made-to Values	5.02	55.4	130	21.6	blank	65.2	18.5	111
Interlaboratory Results								
Laboratory ID								
API-01	—	—	—	—	—	—	—	—
API-02	2.8	34	85	14	<DL	38	10	82
API-03	—	—	—	—	—	—	—	—
API-04	†3198	†6562	SB	†5242	SB	†8696	†4050	†7368
API-05	13	47	120	36	6	42	23	100
API-07	2	43	84	16	2	56	16	41
API-08	19	35	64	15	10	41	15	66
API-09	10.3	104	285	41.3	4.91	134	29.8	209
API-10	3.2	29.3	82.9	12.5	ND	38.4	11.2	65
API-13	3.04	32.2	82	15	0.42	41.3	12	70.7
API-14	ND	33.9	84.7	14.4	ND	48.3	10.1	71.3
API-15	3.7	44.8	176	23.1	ND	61.8	22.8	126
API-16	—	—	—	—	—	—	—	—
API-17	—	—	—	—	—	—	—	—
API-18	<10	31	94	11	<10	33	<10	66

† Data deleted before any analysis, including outlier statistics
SB Sample broken
— No data submitted
ND Reported as nondetect
DL Detection limit

Appendix C
Gasoline Range Organics (GRO)

Summary of Laboratory Results
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
BTEX—Benzene (GRO/PID)

Concentration Level	GRO-1 PQL	GRO-2 MED	GRO-3 HI	GRO-4 LO	GRO-5 blank	GRO-6 MED	GRO-7 LO	GRO-8 HI	
Laboratory ID									
API-01	—	—	—	—	—	—	—	—	
API-02	<0.2	<0.2	0.24	<0.2	<0.2	<0.2	<0.2	0.26	
API-03	—	—	—	—	—	—	—	—	
API-04	15*	25.6*	—	23.1*	—	34.4*	19.4*	36.4*	
API-05	—	—	—	—	—	—	—	—	
API-07	0.05u	0.09	0.17	0.12	0.05u	0.14	0.06	0.05u	
API-08	—	—	—	—	—	—	—	—	
API-09	—	—	—	—	—	—	—	—	
API-10	—	—	—	—	—	—	—	—	
API-13	0.0218J	0.164	0.431	0.0984	0.0037J	0.257	0.0766	0.406	
API-14	—	—	—	—	—	—	—	—	
API-15	ND	0.124	0.378	0.06	ND	0.191	0.057	0.338	
API-16	—	—	—	—	—	—	—	—	
API-17	—	—	—	—	—	—	—	—	
API-18	0.18	0.12	0.39	<0.1	<0.1	0.11	<0.1	0.36	
Average		0.1245	0.3218	0.0928		0.1745	0.0645	0.341	Ave
RSD%		24%	35%	33%		37%	16%	18%	27%

— No data submitted
* Assumed outlier
Note: Any outlier, ND (nondetect), less-than value, or value qualified with a "J" or "u" were not included in average and RSD.

Appendix C
BTEX (GRO)

Summary of Laboratory Results
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
BTEX—Toluene (GRO/PID)

Concentration Level	GRO-1 PQL	GRO-2 MED	GRO-3 HI	GRO-4 LO	GRO-5 blank	GRO-6 MED	GRO-7 LO	GRO-8 HI	
Laboratory ID									
API-01	—	—	—	—	—	—	—	—	
API-02	0.24	3.6	7.7	1.4	<0.2	3.6	1	7.2	
API-03	—	—	—	—	—	—	—	—	
API-04	68*	330*	—	286*	—	460*	264*	542*	
API-05	—	—	—	—	—	—	—	—	
API-07	0.37	2.7	5.5	1.5	0.09	3.6	1.2	0.8	
API-08	—	—	—	—	—	—	—	—	
API-09	—	—	—	—	—	—	—	—	
API-10	—	—	—	—	—	—	—	—	
API-13	0.348	3.58	8.84	1.8	0.0189J	4.65	1.37	8.32	
API-14	—	—	—	—	—	—	—	—	
API-15	0.196	2.85	7.57	1.37	nd	4.05	1.16	6.48	
API-16	—	—	—	—	—	—	—	—	
API-17	—	—	—	—	—	—	—	—	
API-18	0.38	3.3	8.3	1.5	<0.1	3.8	0.96	7.6	
Average		3.206	7.582	1.514		3.94	1.138	6.08	Ave
RSD%		13%	17%	11%		11%	14%	50%	19%

— No data submitted
* Assumed outlier
Note: Any outlier, ND (nondetect), less-than value, or value qualified with a "J" or "u" were not included in average and RSD.

Appendix C
BTEX (GRO)

Summary of Laboratory Results
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
BTEX—Ethylbenzene (GRO/PID)

Concentration Level	GRO-1 PQL	GRO-2 MED	GRO-3 HI	GRO-4 LO	GRO-5 blank	GRO-6 MED	GRO-7 LO	GRO-8 HI	
Laboratory ID									
API-01	—	—	—	—	—	—	—	—	
API-02	<0.2	2	5.1	0.9	<0.2	2.3	0.66	4.6	
API-03	—	—	—	—	—	—	—	—	
API-04	62*	306*	—	256*	—	488*	226*	568*	
API-05	—	—	—	—	—	—	—	—	
API-07	0.19	2.1	4.1	0.96	0.05u	2.6	0.79	2	
API-08	—	—	—	—	—	—	—	—	
API-09	—	—	—	—	—	—	—	—	
API-10	—	—	—	—	—	—	—	—	
API-13	0.231	2.5	6.02	1.18	0.0044J	3.1	0.881	5.74	
API-14	—	—	—	—	—	—	—	—	
API-15	0.298	4.39	10.8	1.8	nd	5.38	1.43	8.25	
API-16	—	—	—	—	—	—	—	—	
API-17	—	—	—	—	—	—	—	—	
API-18	0.25	<0.1	5.8	1	<0.1	2.9	0.72	0.13	
Average		2.7475	6.364	1.168		3.256	0.8962	4.144	Ave
RSD%		41%	41%	32%		38%	35%	77%	44%

— No data submitted
* Assumed outlier
Note: Any outlier, ND (nondetect), less-than value, or value qualified with a "J" or "u" were not included in average and RSD.

Appendix C
BTEX (GRO)

Summary of Laboratory Results
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
BTEX—Total Xylenes (GRO/PID)

Concentration Level	GRO-1 PQL	GRO-2 MED	GRO-3 HI	GRO-4 LO	GRO-5 blank	GRO-6 MED	GRO-7 LO	GRO-8 HI	
Laboratory ID									
API-01	—	—	—	—	—	—	—	—	
API-02	0.57	7.2	18	3.1	<0.2	8.2	2.1	17	
API-03	—	—	—	—	—	—	—	—	
API-04	122*	600*	—	722*	—	760*	574*	872*	
API-05	—	—	—	—	—	—	—	—	
API-07	0.69	6.4	13	3.1	0.05u	9.2	2.5	6.8	
API-08	—	—	—	—	—	—	—	—	
API-09	—	—	—	—	—	—	—	—	
API-10	—	—	—	—	—	—	—	—	
API-13	0.71	7.73	18.5	3.67	0.0144J	9.52	2.72	17.7	
API-14	—	—	—	—	—	—	—	—	
API-15	0.542	7.1	17.09	3.05	nd	8.58	2.94	14.89	
API-16	—	—	—	—	—	—	—	—	
API-17	—	—	—	—	—	—	—	—	
API-18	0.66	9.7	18	3.2	<0.3	9.2	2.2	20	
Average		7.626	16.918	3.224		8.94	2.492	15.278	Ave
RSD%		16%	13%	8%		6%	14%	33%	15%

— No data submitted
* Assumed outlier
Note: Any outlier, ND (nondetect), less-than value, or value qualified with a "J" or "u" were not included in average and RSD.

Appendix C
BTEX (GRO)

Summary of Laboratory Results
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
Petroleum Hydrocarbons (PHC)

Sample ID	PHC-1	PHC-2	PHC-3	PHC-4 (mg/kg)	PHC-5	PHC-6	PHC-7	PHC-8
Made-to Values	748	104	50.4	416	374	831	blank	93.6
Interlaboratory Results								
Laboratory ID								
API-01	660	104	54.8	521	345	739	5.13	98.8
API-02	1500	109	52	474	335	995	60	<DL
API-03	370	82	15	280	440	550	110	220
API-04	387	80.5	50	245	205	414	ND	86
API-05	510	150	65	370	230	590	<50	120
API-07	1500	170	230	1200	690	1000	50	95
API-08	900	110	46	430	430	990	<40	89
API-09	410	64	30	260	220	510	ND	52
API-10	846	112	58	422	349	839	<50	98.1
API-13	—	—	—	—	—	—	—	—
API-14	477	54.2	11.9	238	212	533	ND	54.4
API-15	—	—	—	—	—	—	—	—
API-16	550	53	15	240	240	790	ND	59
API-17	732	102	39	354	371	744	<25	83
API-18	—	—	—	—	—	—	—	—

— No data submitted
ND Reported as nondetect
DL Detection limit

Appendix C
Petroleum Hydrocarbons (PHC)

Youden Laboratory Ranking Test

Youden Laboratory Ranking Test
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
Diesel Range Organics (DRO)

Sample ID	DRO-1	DRO-2	DRO-3	DRO-4	DRO-5	DRO-6	DRO-7	DRO-8
				(mg/kg)				
Made-to Values	77.1	blank	207	193	19.3	4.99	82.6	20.7

Laboratory Rank

Rank 1 is assigned to the highest value, rank 2 to the next largest, etc.

Laboratory ID							Total	Allowable Range: 16-68
API-01	5	8	10	5	4	7	39	okay
API-02	—	—	—	—	—	—	—	—
API-03	7	7	7	9	5.5	4	39.5	okay
API-04	2	4.5	1	2.5	11	5	26	okay
API-05	10	6	8	8	10	10	52	okay
API-07	4	4.5	5.5	2.5	2	3	21.5	okay
API-08	11	10.5	11	6.5	9	8	56	okay
API-09	8	10.5	5.5	12	5.5	9	50.5	okay
API-10	3	3	4	1	1	2	14	outlier
API-13	1	1	3	4	3	1	13	outlier
API-14	9	9	9	6.5	8	6	47.5	okay
API-15	6	2	2	10	7	11	38	okay
API-16	13	13	13	13	13	13	78	outlier
API-17	—	—	—	—	—	—	—	—
API-18	12	12	12	11	12	12	71	outlier
Rank Sums	91	91	91	91	91	91		

— No data submitted

Appendix C
Diesel Range Organics (DRO)

Youden Laboratory Ranking Test

Interlaboratory Study of API Methods for Petroleum Hydrocarbons

Gasoline Range Organics (GRO)

Sample ID	GRO-1	GRO-2	GRO-3	GRO-4 (mg/kg)	GRO-5	GRO-6	GRO-7	GRO-8
Made-to Values	5.02	55.4	130	21.6	blank	65.2	18.5	111

Laboratory Rank

Rank 1 is assigned to the highest value, rank 2 to the next highest, etc.

Laboratory ID							Total	Allowable Range: 14-52
API-01	—	—	—	—	—	—	—	—
API-02	6	5	8	9	9	4	41	okay
API-03	—	—	—	—	—	—	—	—
API-04	†	†	†	†	†	†	†	†
API-05	2	3	2	5	2	3	17	okay
API-07	4	7	4	3	4	10	32	okay
API-08	5	10	5.5	7	5	7.5	40	okay
API-09	1	1	1	1	1	1	6	outlier
API-10	10	8	9	8	7	9	51	okay
API-13	8	9	5.5	6	6	6	40.5	okay
API-14	7	6	7	4	8	5	37	okay
API-15	3	2	3	2	3	2	15	okay
API-16	—	—	—	—	—	—	—	—
API-17	—	—	—	—	—	—	—	—
API-18	9	4	10	10	10	7.5	50.5	okay
Rank Sums	55	55	55	55	55	55		

† Data deleted before any analysis, including outlier statistics

— No data submitted

Appendix C
Gasoline Range Organics (GRO)

Youden Laboratory Ranking Test
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
Petroleum Hydrocarbons (PHC)

Sample ID	PHC-1	PHC-2	PHC-3	PHC-4 (mg/kg)	PHC-5	PHC-6	PHC-7	PHC-8
Made-to Values	748	104	50.4	416	374	831	blank	93.6

Laboratory Rank
Rank 1 is assigned to the highest value, rank 2 to the next largest, etc.

Laboratory ID						Total	Allowable Range: 15-63
API-01	6	6	2	6	7	3	30 okay
API-02	1.5	5	3	7	2	12	30.5 okay
API-03	12	8	8	2	9	1	40 okay
API-04	11	9	10	12	12	7	61 okay
API-05	8	2	6	9	8	2	35 okay
API-07	1.5	1	1	1	1	5	10.5 outlier
API-08	3	4	4	3	3	6	23 okay
API-09	10	10	9	10	11	11	61 okay
API-10	4	3	5	5	4	4	25 okay
API-13	—	—	—	—	—	—	— —
API-14	9	11	12	11	10	10	63 okay
API-15	—	—	—	—	—	—	— —
API-16	7	12	11	8	5	9	52 okay
API-17	5	7	7	4	6	8	37 okay
API-18	—	—	—	—	—	—	— —
Rank Sums	78	78	78	78	78	78	

— No data submitted

Appendix C
Petroleum Hydrocarbons (PHC)

Grubbs Outlier Test

Grubbs Outlier Test
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
Diesel Range Organics (DRO)

Sample ID	DRO-1	DRO-2	DRO-3	DRO-4 (mg/kg)	DRO-5	DRO-6	DRO-7	DRO-8
Made-to Values	77.1	blank	207	193	19.3	4.99	82.6	20.7

Grubbs test performed on laboratories remaining after Youden rank test.
"Okay" means the laboratory result was within the lower and upper limits; "outlier" means the result was outside the limits.

Laboratory ID						
API-01	okay	okay	okay	okay	okay	okay
API-02	—	—	—	—	—	—
API-03	okay	okay	okay	okay	okay	okay
API-04	okay	okay	okay	okay	okay	okay
API-05	okay	okay	okay	okay	okay	okay
API-07	okay	okay	okay	okay	okay	okay
API-08	okay	okay	okay	okay	okay	okay
API-09	okay	okay	okay	okay	okay	okay
API-10	•	•	•	•	•	•
API-13	•	•	•	•	•	•
API-14	okay	okay	okay	okay	okay	okay
API-15	okay	okay	okay	okay	okay	okay
API-16	•	•	•	•	•	•
API-17	—	—	—	—	—	—
API-18	•	•	•	•	•	•
Grubbs Statistics						
n	9	9	9	9	9	9
Average	60.22	170.3	161.6	16.24	64.07	18.41
Standard Deviation	12.62	35.01	42.25	7.04	8.24	5.31
t-value	2.215	2.215	2.215	2.215	2.215	2.215
Upper Limit	88.17	247.9	255.1	31.84	82.32	30.18
Lower Limit	32.27	92.79	67.97	0.65	45.81	6.64

— No data submitted
• Outlier identified by Youden rank test

Appendix C
Diesel Range Organics (DRO)

Grubbs Outlier Test

Interlaboratory Study of API Methods for Petroleum Hydrocarbons

Gasoline Range Organics (GRO)

Sample ID	GRO-1	GRO-2	GRO-3	GRO-4 (mg/kg)	GRO-5	GRO-6	GRO-7	GRO-8
Made-to Values	5.02	55.4	130	21.6	blank	65.2	18.5	111

Grubbs test performed on laboratories remaining after Youden rank test.
"Okay" means the laboratory result was within the lower and upper limits; "outlier" means the result was outside the limits.

Laboratory ID						
API-01	—	—	—	—	—	—
API-02	okay	okay	okay	okay	okay	okay
API-03	—	—	—	—	—	—
API-04	†	†	†	†	†	†
API-05	okay	okay	outlier	okay	okay	okay
API-07	okay	okay	okay	okay	okay	okay
API-08	okay	okay	okay	okay	okay	okay
API-09	•	•	•	•	•	•
API-10	okay	okay	okay	okay	okay	okay
API-13	okay	okay	okay	okay	okay	okay
API-14	okay	okay	okay	okay	okay	okay
API-15	okay	outlier	okay	okay	okay	okay
API-16	—	—	—	—	—	—
API-17	—	—	—	—	—	—
API-18	okay	okay	okay	okay	<DL	okay
Grubbs Statistics						
n	9	9	9	9	8	9
Average	36.689	96.956	17.444	44.422	15.013	76.444
Standard Deviation	6.49	33.08	7.73	9.26	5.32	24.25
t-value	2.215	2.215	2.215	2.215	2.126	2.215
Upper Limit	51.1	170.2	34.6	64.9	26.3	130.2
Lower Limit	22.31	23.68	0.33	23.91	3.70	22.72

† Data deleted before any analysis, including outlier statistics
— No data submitted
• Outlier identified by Youden rank test
DL Detection limit

Appendix C
Gasoline Range Organics (GRO)

Grubbs Outlier Test
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
Petroleum Hydrocarbons (PHC)

Sample ID	PHC-1	PHC-2	PHC-3	PHC-4	PHC-5	PHC-6	PHC-7	PHC-8
				(mg/kg)				
Made-to Values	748	104	50.4	416	374	831	blank	93.6

Grubbs test performed on laboratories remaining after Youden rank test.

"Okay" means the laboratory result was within the lower and upper limits; "outlier" means the result was outside the limits.

Laboratory ID						
API-01	okay	okay	okay	okay	okay	okay
API-02	outlier	okay	okay	okay	okay	<DL
API-03	okay	okay	okay	okay	okay	outlier
API-04	okay	okay	okay	okay	okay	okay
API-05	okay	okay	okay	okay	okay	okay
API-07	•	•	•	•	•	•
API-08	okay	okay	okay	okay	okay	okay
API-09	okay	okay	okay	okay	okay	okay
API-10	okay	okay	okay	okay	okay	okay
API-13	—	—	—	—	—	—
API-14	okay	okay	okay	okay	okay	okay
API-15	—	—	—	—	—	—
API-16	okay	okay	okay	okay	okay	okay
API-17	okay	okay	okay	okay	okay	okay
API-18	—	—	—	—	—	—
Grubbs Statistics						
n	11	11	11	11	11	10
Average	667.45	92.791	348.55	307	699.45	96.03
Standard Deviation	330.39	29.29	102.60	88.50	195.55	48.67
t-value	2.355	2.355	2.355	2.355	2.355	2.29
Upper Limit	1445.5	161.8	590.2	515.4	1160.0	207.5
Lower Limit	-110.62	23.81	106.93	98.58	238.94	-15.42

— No data submitted
DL Detection Limit
• Outlier identified by Youden rank test

Appendix C
Petroleum Hydrocarbons (PHC)

Recovery and Interlaboratory (Overall) Precision

Recovery and Interlaboratory (Overall) Precision
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
Diesel Range Organics (DRO)

Sample ID	DRO-1	DRO-2	DRO-3	DRO-4	DRO-5	DRO-6	DRO-7	DRO-8
				(mg/kg)				
Made-to Values	77.1	blank	207	193	19.3	4.99	82.6	20.7

Recovery is calculated is the analytical value divided by the made-to value times 100%.

Laboratory ID			(%)				
API-01	89	73	58	97	86	90	
API-02	—	—	—	—	—	—	
API-03	79	87	88	62	84	106	
API-04	110	97	121	135	65	97	
API-05	62	92	83	67	67	63	
API-07	89	97	93	135	94	135	
API-08	61	63	57	93	70	87	
API-09	67	63	93	31	84	82	
API-10	*	*	*	*	*	*	
API-13	*	*	*	*	*	*	
API-14	64	64	60	93	71	96	
API-15	80	106	100	45	78	44	
API-16	*	*	*	*	*	*	
API-17	—	—	—	—	—	—	
API-18	*	*	*	*	*	*	
							Ave
Average (%)	78	82	84	84	78	89	82
Ave Conc (mg/kg)	60.2	170.3	161.6	16.2	64.1	18.4	
Stdev (mg/kg)	12.6	35.0	42.2	7.0	8.2	5.3	
%RSD	21%	21%	26%	43%	13%	29%	25%

Regression-Accuracy	C	X	Slope	0.8305	-1.205	Intercept
DRO-1	77.1	60.2	SEn	0.0154	1.9248	SEb
DRO-3	207	170.3	r2	0.9986	2.8291	SEy
DRO-4	193	161.6	F	2906.5	4	df
DRO-5	19.3	16.2	SSreg	23263	32.015	SSresid
DRO-7	82.6	64.1				
DRO-8	20.7	18.4		Eqn: X=mX+b		
				X=0.83C+-1.20	p=0.000001	

Regression-Overall Precision	X	S	Slope	0.2254	-0.03	Intercept
DRO-1	60.2	12.6	SEn	0.0324	3.3287	SEb
DRO-3	170.3	35.0	r2	0.9238	4.9405	SEy
DRO-4	161.6	42.2	F	48.503	4	df
DRO-5	16.2	7.0	SSreg	1183.9	97.635	SSresid
DRO-7	64.1	8.2				
DRO-8	18.4	5.3		Eqn: S=mX+b		
				S=0.23X+-0.03	p=0.002	

— No data submitted
* Outlier identified by Youden rank test

Recovery and Interlaboratory (Overall) Precision
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
Gasoline Range Organics (GRO)

Sample ID	GRO-1	GRO-2	GRO-3	GRO-4	GRO-5	GRO-6	GRO-7	GRO-8
				(mg/kg)				
Made-to Values	5.02	55.4	130	21.6	blank	65.2	18.5	111

Recovery is calculated as the analytical value divided by the made-to value times 100%.

Laboratory ID			(%)				
API-01	—	—	—		—	—	—
API-02	61	65	65		58	54	74
API-03	—	—	—		—	—	—
API-04	†	†	†		†	†	†
API-05	85	92	**		64	124	90
API-07	78	65	74		86	86	37
API-08	63	49	69		63	81	59
API-09	*	*	*		*	*	*
API-10	53	64	58		59	61	59
API-13	58	63	69		63	65	64
API-14	61	65	67		74	55	64
API-15	81	**	107		95	123	114
API-16	—	—	—		—	—	—
API-17	—	—	—		—	—	—
API-18	56	72	51		51	<DL	59
							Ave
Average %	66	67	70		68	81	69	70
Ave Conc (mg/kg)	36.7	87.1	15.1		44.4	15.0	76.4	
Stdev (mg/kg)	6.5	15.7	3.6		9.3	5.3	24.3	
%RSD	18%	18%	24%		21%	35%	32%	25%

Regression-Accuracy	C	X	Slope	0.664	1.3413	Intercept
GRO-2	55.4	36.7	SEn	0.0126	0.9949	SEb
GRO-3	130	87.1	r2	0.9986	1.2894	SEy
GRO-4	21.6	15.1	F	2772.6	4	df
GRO-6	65.2	44.4	SSreg	4609.8	6.6506	SSresid
GRO-7	18.5	15.0				
GRO-8	111	76.4		Eqn: X=mC+b		
				X=0.66C+1.34		p=0.000001

Regression-Overall Precision	X	S	Slope	0.2266	0.3931	Intercept
GRO-2	36.7	6.5	SEn	0.062	3.3201	SEb
GRO-3	87.1	15.7	r2	0.7695	4.2133	SEy
GRO-4	15.1	3.6	F	13.354	4	df
GRO-6	44.4	9.3	SSreg	237.07	71.009	SSresid
GRO-7	15.0	5.3				
GRO-8	76.4	24.3		Eqn: S=mX+b		
				S=0.23X+0.39		p=0.022

† Data deleted before any analysis, including outlier statistics
— No data submitted
* Outlier identified by Youden rank test
** Outlier identified by Grubbs test
DL Detection limit

Appendix C
Gasoline Range Organics (GRO)

Recovery and Interlaboratory (Overall) Precision
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
Petroleum Hydrocarbons (PHC)

Sample ID	PHC-1	PHC-2	PHC-3	PHC-4 (mg/kg)	PHC-5	PHC-6	PHC-7	PHC-8
Made-to Values	748	104	50.4	416	374	831	blank	93.6

Recovery is calculated is the analytical value divided by the made-to value times 100%.

Laboratory ID				(%)					
API-01	88	100		125	92	89		106	
API-02	**	105		114	90	120		<DL	
API-03	49	79		67	118	66		**	
API-04	52	77		59	55	50		92	
API-05	68	144		89	61	71		128	
API-07	*	*		*	*	*		*	
API-08	120	106		103	115	119		95	
API-09	55	62		63	59	61		56	
API-10	113	108		101	93	101		105	
API-13	—	—		—	—	—		—	
API-14	64	52		57	57	64		58	
API-15	—	—		—	—	—		—	
API-16	74	51		58	64	95		63	
API-17	98	98		85	99	90		89	
API-18	—	—		—	—	—		—	
									Ave
Average %	78	89		84	82	84		88	84
Ave Conc (mg/kg)	584.2	92.8		348.5	307.0	699.5		82.3	
Stdev (mg/kg)	191.2	29.3		102.6	88.5	195.5		23.0	
%RSD	33%	32%		29%	29%	28%		28%	30%

Regression-Accuracy	C	X	Slope	0.8067	7.2909	Intercept
PHC-1	748	584.2	SEn	0.025	12.865	SEb
PHC-2	104	92.8	r2	0.9962	17.439	SEy
PHC-4	416	348.5	F	1037.2	4	df
PHC-5	374	307.0	SSreg	315413	1216.4	SSresid
PHC-6	831	699.5				
PHC-8	93.6	82.3		Eqn: X=mC+b		
				X=0.81C+7.29	p=0.000006	

Regression-Overall Precision	X	S	Slope	0.2968	0.4524	Intercept
PHC-1	584.2	191.2	SEn	0.0194	8.1468	SEb
PHC-2	92.8	29.3	r2	0.9833	10.898	SEy
PHC-4	348.5	102.6	F	234.83	4	df
PHC-5	307.0	88.5	SSreg	27890	475.07	SSresid
PHC-6	699.5	195.5				
PHC-8	82.3	23.0		Eqn: S=mX+b		
				S=0.30x+0.45	p=0.00011	

— No data submitted
DL Detection Limit
* Outlier identified by Youden rank test
** Outlier identified by Grubbs test

Intralaboratory (Single Analyst) Precision

Intralaboratory (Single Analyst) Precision
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
Diesel Range Organics (DRO)

Sample ID	DRO-1	DRO-2	DRO-3	DRO-4 (mg/kg)	DRO-5	DRO-6	DRO-7	DRO-8
Made-to Values	77.1	blank	207	193	19.3	4.99	82.6	20.7

	Difference in Sample Pairs		
	Low Conc	Med Conc	Hi Conc
Laboratory ID	S5&S8	S1&S7	S3&S4
API-01	0.1	-2.3	40
API-02	—	—	—
API-03	-10	-8	10
API-04	6	31	-34
API-05	0	-7	30
API-07	-2	-9	20
API-08	0	-11	20
API-09	-11.1	-17	-50
API-10	•	•	•
API-13	•	•	•
API-14	-1.9	-8.9	16
API-15	-0.6	-2.4	27
API-16	•	•	•
API-17	—	—	—
API-18	•	•	•

Average D	-2.167	-3.844	8.7778		
Sr	3.7495	9.754	21.429		
Average Conc	17.328	62.144	165.94	Ave	
%RSD	21.639	15.696	12.914	16.749	

Regression	X	Sr	Slope	0.1178	2.0056	Intercept
Low	17.328	3.7495	SEn	0.005	0.5106	SEb
Med	62.144	9.754	r2	0.9982	0.5356	SEy
Hi	165.94	21.429	F	562.58	1	df
			SSreg	161.36	0.2868	SSresid

Eqn: Sr=mX+b
Sr=0.12X+2.01 p=0.027

— No data submitted
• Outlier identified by Youden rank test

Appendix C
Diesel Range Organics (DRO)

Intralaboratory (Single Analyst) Precision
Interlaboratory Study of API Methods for Petroleum Hydrocarbons
Gasoline Range Organics (GRO)

Sample ID	GRO-1	GRO-2	GRO-3	GRO-4	GRO-5	GRO-6	GRO-7	GRO-8
				(mg/kg)				
Made-to Values	5.02	55.4	130	21.6	blank	65.2	18.5	111

	Difference in Sample Pairs		
	Low Conc	Med Conc	Hi Conc
Laboratory ID	S4&S7	S2&S6	S3&S8
API-01	—	—	—
API-02	4	-4	3
API-03	—	—	—
API-04	†	†	†
API-05	••	5	20
API-07	0	-13	43
API-08	0	-6	-2
API-09	•	•	•
API-10	1.3	-9.1	17.9
API-13	3	-9.1	11.3
API-14	4.3	-14.4	13.4
API-15	0.3	-17	••
API-16	—	—	—
API-17	—	—	—
API-18	<DL	-2	28

Average D	1.8429		-7.733		16.825	
Sr	1.3384		4.8331		10.032	
Average Conc	15.069		40.556		81.76	Ave
%RSD	8.8822		11.917		12.27	11.023
Regression	X	Sr	Slope	0.13	-0.55	Intercept
Low	15.1	1.3	SEn	0.0029	0.1564	SEb
Med	40.6	4.8	r2	0.9995	0.1393	SEy
Hi	81.8	10.0	F	1970.1	1	df
			SSreg	38.255	0.0194	SSresid

Eqn: Sr=mX+b
Sr=0.13X+-0.55 p=0.014

† Data deleted before any analysis, including outlier statistics
— No data submitted
• Outlier identified by Youden rank test
•• Outlier identified by Grubbs test
DL Detection limit

Appendix C
Gasoline Range Organics (GRO)

Intralaboratory (Single Analyst) Precision

Interlaboratory Study of API Methods for Petroleum Hydrocarbons
Petroleum Hydrocarbons (PHC)

Sample ID	PHC-1	PHC-2	PHC-3	PHC-4	PHC-5	PHC-6	PHC-7	PHC-8
				(mg/kg)				
Made-to Values	748	104	50.4	416	374	831	blank	93.6

	Difference in Sample Pairs		
	Low Conc	Med Conc	Hi Conc
Laboratory ID	S2&S8	S4&S5	S1&S6
API-01	5.2	176	-79
API-02	<DL	139	**
API-03	**	-160	-180
API-04	-5.5	40	-27
API-05	30	140	-80
API-07	*	*	*
API-08	21	0	-90
API-09	12	40	-100
API-10	13.9	73	7
API-13	*	*	*
API-14	-0.2	26	-56
API-15	*	*	*
API-16	-6	0	-240
API-17	19	-17	-12
API-18	*	*	*
Average D	9.93	41.55	-85.70
Sr	8.819	65.576	53.414
Average Conc	87.52	327.8	641.8 Average
%RSD	10.077	20.007	8.3221 12.802

Regression	X	Sr	Slope	0.0745	16.354	Intercept
Low	87.5	8.8	SEn	0.0775	32.488	SEb
Med	327.8	65.6	r2	0.4801	30.47	SEy
Hi	641.8	53.4	F	0.9236	1	df
			SSreg	857.52	928.45	SSresid

Eqn: Sr=mX+b
Sr=0.07x+16.35 p=0.513

— No data submitted
DL Detection Limit
* Outlier identified by Youden rank test
** Outlier identified by Grubbs test

Appendix C
Petroleum Hydrocarbons (PHC)

F-tests on EPA Regression Equations

F-tests on Regression Equations From EPA 600 Series Analytical Methods
Reference Source for Data: Table 7, EPA Method Study 29,
Method 624—Purgeables, EPA-600/4-84-054.

Benzene: Method 624, Distilled Water

Accuracy

1/C	X/C				
		Slope	2.0069	0.9269	Intercept
0.09259	1.07407	SEn	0.9398	0.048	SEb
0.08333	1.125	r2	0.5328	0.09	SEy
0.00877	1.04386	F	4.5608	4	df
0.00833	1.00083	SSreg	0.037	0.0324	SSresid
0.00208	0.91042				
0.00231	0.80347				

Eqn: X/C=m+b/C
X=0.93C+2.01 p=0.0996

Overall Precision

1/X	S/X				
		Slope	-1.291	0.2537	Intercept
0.08621	0.13793	SEn	0.6184	0.0289	SEb
0.07407	0.16296	r2	0.5215	0.0537	SEy
0.0084	0.32017	F	4.3586	4	df
0.00833	0.16903	SSreg	0.0126	0.0115	SSresid
0.00229	0.24439				
0.00288	0.25266				
Ave	21%				

Eqn: S/X=m+b/X
S=0.25X+-1.29 p=0.1051

Single Analyst Precision

1/X	Sr/X				
		Slope	-1.7138	0.2582	Intercept
0.07968	0.11952	SEn	0.6462	0.0299	SEb
0.00836	0.27269	r2	0.8755	0.0393	SEy
0.00255	0.22727	F	7.0328	1	df
Ave	21%	SSreg	0.0108	0.0015	SSresid

Eqn: Sr/X=m+b/X
Sr=0.26X+-1.71 p=0.230

F-tests on Regression Equations From EPA 600 Series Analytical Methods
Reference Source for Data: Table 7, EPA Method Study 29,
Method 624—Purgeables, EPA-600/4-84-054.

Toluene: Method 624, Distilled Water

Accuracy

1/C	X/C
0.07407	1.1037
0.06667	1.12667
0.00704	1.07676
0.00667	1.05067
0.00167	0.86117
0.00185	0.96352

Slope	2.0265	0.9771	Intercept
SEn	1.056	0.0432	SEb
r2	0.4794	0.0809	SEy
F	3.6828	4	df
SSreg	0.0241	0.0262	SSresid

Eqn: X/C=m+b/C
X=0.98C+2.03 p=0.1274

Overall Precision

1/X	S/X
0.06711	0.11409
0.05917	0.10059
0.00654	0.2034
0.00635	0.19289
0.00194	0.3085
0.00192	0.13781
Ave	18%

Slope	-1.745	0.2178	Intercept
SEn	0.9034	0.0332	SEb
r2	0.4826	0.0618	SEy
F	3.7312	4	df
SSreg	0.0143	0.0153	SSresid

Eqn: S/X=m+b/X
S=0.22X+-1.74 p=0.1256

Single Analyst Precision

1/X	Sr/X
0.06289	0.11321
0.00644	0.0818
0.00193	0.21234
Ave	14%

Slope	-0.7019	0.1525	Intercept
SEn	1.8789	0.0686	SEb
r2	0.1225	0.0903	SEy
F	0.1396	1	df
SSreg	0.0011	0.0081	SSresid

Eqn: Sr/X=m+b/X
Sr=0.15X+-0.70 p=0.772

Appendix C
F-tests on EPA Regression Equations

F-tests on Regression Equations From EPA 600 Series Analytical Methods
Reference Source for Data: Table 8, EPA Method Study 30, Method 625—Base/Neutrals, Acids and Pesticides, EPA-600/4-84-053.

Naphthalene: Method 625, Distilled Water

Accuracy

1/C	X/C
0.16667	1.08333
0.14286	0.91429
0.00952	0.74667
0.01064	0.87553
0.00159	0.76397
0.00143	0.70714

Slope	1.5869	0.7605	Intercept
SEn	0.4314	0.0387	SEb
r2	0.7719	0.0746	SEy
F	13.535	4	df
SSreg	0.0754	0.0223	SSresid

Eqn: X/C=m+b/C
X=0.76C+1.59 p=0.0212

Overall Precision

1/X	S/X
0.15385	0.21538
0.15625	0.17188
0.01276	0.46046
0.01215	0.1932
0.00208	0.32516
0.00202	0.2202
Ave	26%

Slope	-0.695	0.3037	Intercept
SEn	0.6272	0.0563	SEb
r2	0.2349	0.1072	SEy
F	1.2279	4	df
SSreg	0.0141	0.046	SSresid

Eqn: S/X=m+b/X
S=0.30X+-0.69 p=0.3299

Single Analyst Precision

1/X	Sr/X
0.15504	0.13953
0.01245	0.229
0.00205	0.18089
Ave	18%

Slope	-0.4238	0.2071	Intercept
SEn	0.3077	0.0276	SEb
r2	0.6548	0.0372	SEy
F	1.8967	1	df
SSreg	0.0026	0.0014	SSresid

Eqn: Sr/X=m+b/X
Sr=0.21X+-0.42 p=0.400

Order No. 841-45990

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