



# Innovative Technology Verification Report

## Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil

### Horiba Instruments Incorporated OCMA-350 Oil Content Analyzer



# **Innovative Technology Verification Report**

## **Horiba Instruments Incorporated OCMA-350 Oil Content Analyzer**

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## **Notice**

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## ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM VERIFICATION STATEMENT

TECHNOLOGY TYPE:	<b>FIELD MEASUREMENT DEVICE</b>
APPLICATION:	<b>MEASUREMENT OF TOTAL PETROLEUM HYDROCARBONS</b>
TECHNOLOGY NAME:	<b>OCMA-350 OIL CONTENT ANALYZER</b>
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### VERIFICATION PROGRAM DESCRIPTION

The U.S. Environmental Protection Agency (EPA) created the Superfund Innovative Technology Evaluation (SITE) and Environmental Technology Verification (ETV) Programs to facilitate deployment of innovative technologies through performance verification and information dissemination. The goal of these programs is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. These programs assist and inform those involved in design, distribution, permitting, and purchase of environmental technologies. This document summarizes results of a demonstration of the OCMA-350 Oil Content Analyzer (OCMA-350) developed by Horiba Instruments Incorporated (Horiba).

### PROGRAM OPERATION

Under the SITE and ETV Programs, with the full participation of the technology developers, the EPA evaluates and documents the performance of innovative technologies by developing demonstration plans, conducting field tests, collecting and analyzing demonstration data, and preparing reports. The technologies are evaluated under rigorous quality assurance (QA) protocols to produce well-documented data of known quality. The EPA National Exposure Research Laboratory, which demonstrates field sampling, monitoring, and measurement technologies, selected Tetra Tech EM Inc. as the verification organization to assist in field testing seven field measurement devices for total petroleum hydrocarbons (TPH) in soil. This demonstration was funded by the SITE Program.

### DEMONSTRATION DESCRIPTION

In June 2000, the EPA conducted a field demonstration of the OCMA-350 and six other field measurement devices for TPH in soil. This verification statement focuses on the OCMA-350; a similar statement has been prepared for each of the other six devices. The performance and cost of the OCMA-350 were compared to those of an off-site laboratory reference method, "Test Methods for Evaluating Solid Waste" (SW-846) Method 8015B (modified). To verify a wide range of performance attributes, the demonstration had both primary and secondary objectives. The primary objectives included (1) determining the method detection limit, (2) evaluating the accuracy and precision of TPH measurement, (3) evaluating the effect of interferences, and (4) evaluating the effect of moisture content on TPH measurement for each device. Additional primary objectives were to measure sample throughput and estimate TPH measurement costs. Secondary objectives included (1) documenting the skills and training required to properly operate the device, (2) documenting the portability of the device, (3) evaluating the device's durability, and (4) documenting the availability of the device and associated spare parts.

The OCMA-350 was demonstrated by using it to analyze 74 soil environmental samples, 89 soil performance evaluation (PE) samples, and 36 liquid PE samples. In addition to these 199 samples, 9 extract duplicates prepared using the environmental samples were analyzed. The environmental samples were collected in five areas contaminated with gasoline, diesel, lubricating oil, or other petroleum products, and the PE samples were obtained from a commercial provider.

Collectively, the environmental and PE samples provided the different matrix types and the different levels and types of petroleum hydrocarbon contamination needed to perform a comprehensive evaluation of the OCMA-350. A complete description of the demonstration and a summary of its results are available in the “Innovative Technology Verification Report: Field Measurement Devices for Total Petroleum Hydrocarbons in Soil—Horiba Instruments Incorporated OCMA-350 Oil Content Analyzer” (EPA/600/R-01/089).

## TECHNOLOGY DESCRIPTION

The OCMA-350 developed by Horiba is based on infrared analysis. The OCMA-350 includes a single-beam, fixed-wavelength, nondispersive infrared filter-based spectrophotometer. Infrared radiation from a tungsten lamp is transmitted through a cylindrical, quartz cuvette containing a sample extract. The radiation that has passed through the extract enters a detector containing a filter that isolates analytical wavelengths in the 3,400- to 3,500-nanometer range.

During the demonstration, Horiba dried soil by adding anhydrous sodium sulfate. Extraction of petroleum hydrocarbons in a given soil sample was typically performed by adding 20 milliliters of Horiba’s proprietary S-316 extraction solvent to 5 grams of the sample. The mixture was agitated using an ultrasonic mixer. The sample extract was decanted into a beaker through a filter-lined funnel, and then the filtrate was poured into a quartz cuvette. The cuvette was placed in the spectrophotometer, and the TPH concentration in milligrams per kilogram was read on the digital display. Periodically, Horiba recycled the extraction solvent using its Model SR-300 solvent reclaimer.

## VERIFICATION OF PERFORMANCE

To ensure data usability, data quality indicators for accuracy, precision, representativeness, completeness, and comparability were assessed for the reference method based on project-specific QA objectives. Although the reference method results generally exhibited a negative bias, based on the results for the data quality indicators, the reference method results were considered to be of adequate quality. The bias was considered to be significant primarily for low- and medium-concentration-range soil samples containing diesel, which made up only 13 percent of the total number of samples analyzed during the demonstration. The reference method recoveries observed during the demonstration were typical of the recoveries obtained by most organic analytical methods for environmental samples. In general, the user should exercise caution when evaluating the accuracy of a field measurement device by comparing it to reference methods because the reference methods themselves may have limitations. Key demonstration findings are summarized below for the primary objectives.

**Method Detection Limit:** Based on the TPH results for seven low-concentration-range diesel soil PE samples, the method detection limits were determined to be 15.2 and 4.79 milligrams per kilogram for the OCMA-350 and reference method, respectively.

**Accuracy and Precision:** Seventy-eight of 107 OCMA-350 results (73 percent) used to draw conclusions regarding whether the TPH concentration in a given sampling area or sample type exceeded a specified action level agreed with those of the reference method; 6 OCMA-350 conclusions were false positives, and 23 were false negatives.

Of 102 OCMA-350 results used to assess measurement bias, 36 were within 30 percent, 16 were within 30 to 50 percent, and 50 were not within 50 percent of the reference method results; 64 OCMA-350 results were biased low, and 38 were biased high.

For soil environmental samples, the OCMA-350 results were statistically (1) the same as the reference method results for four of the five sampling areas and (2) different from the reference method results for one sampling area. For soil PE samples, the OCMA-350 results were statistically (1) the same as the reference method results for blank samples and (2) different from the reference method results for medium- and high-concentration-range weathered gasoline samples and low-, medium-, and high-concentration-range diesel samples. For liquid PE samples, the OCMA-350 results were statistically (1) the same as the reference method results for weathered gasoline samples and (2) different from the reference method results for diesel samples.

The OCMA-350 results correlated highly with the reference method results for three of the five sampling areas (the square of the correlation coefficient [ $R^2$ ] values were greater than or equal to 0.90, and F-test probability values were less than 5 percent). The OCMA-350 results correlated moderately with the reference method results for diesel soil PE samples (the  $R^2$  value was 0.68, and the F-test probability value was less than 5 percent). The OCMA-350 results correlated weakly with the reference method results for two sampling areas and for weathered gasoline soil PE samples ( $R^2$  values ranged from 0.19 to 0.53, and F-test probability values ranged from 22.58 to 62.68 percent).

Comparison of the OCMA-350 and reference method median relative standard deviations (RSD) showed that the OCMA-350 and the reference method exhibited similar overall precision. Specifically, the median RSD ranges were 1.5 to 20 percent and 5.5 to 18 percent for the OCMA-350 and reference method, respectively. The analytical precision for the OCMA-350 (a median relative percent difference of 1) was better than that for the reference method (a median relative percent difference of 4).

**Effect of Interferents:** The OCMA-350 showed no response to neat tetrachloroethene (PCE); neat 1,2,4-trichlorobenzene; or soil spiked with humic acid. The device's mean responses for neat methyl-tert-butyl ether (MTBE), Stoddard solvent, and turpentine were 72.5, 86, and 85 percent, respectively. The reference method showed varying mean responses for MTBE (39 percent); PCE (17.5 percent); Stoddard solvent (85 percent); turpentine (52 percent); 1,2,4-trichlorobenzene (50 percent); and humic acid (0 percent). For the demonstration, MTBE and Stoddard solvent were included in the definition of TPH.

**Effect of Moisture Content:** The OCMA-350 showed a three-fold increase in TPH results when the soil moisture content was increased from 9 to 16 percent for weathered gasoline soil PE samples. However, the device showed a three-fold decrease in TPH results when the soil moisture content was increased from less than 1 percent to 9 percent for diesel soil PE samples. The reference method TPH results were unaffected when the soil moisture content was increased.

**Measurement Time:** From the time of sample receipt, Horiba required 46 hours, 15 minutes, to prepare a draft data package containing TPH results for 199 samples and 9 extract duplicates compared to 30 days for the reference method, which was used to analyze 4 additional extract duplicates.

**Measurement Costs:** The TPH measurement cost for 199 samples and 9 extract duplicates was estimated to be \$15,750, including the capital equipment purchase cost of \$6,500, for the OCMA-350 compared to \$42,050 for the reference method.

Key demonstration findings are summarized below for the secondary objectives.

**Skill and Training Requirements:** The OCMA-350 can be operated by one person with basic wet chemistry skills. The sample analysis procedure for the device can be learned in the field with a few practice attempts. During the demonstration, some of the items in the OCMA-350, including the narrow-mouth vials used for weighing and extracting soil samples and the gravity filtration setup, made the TPH measurement procedure less simple and more time-consuming.

**Portability:** The OCMA-350 can be easily moved between sampling areas in the field, if necessary. It can be operated using a 110-volt alternating current power source or a direct current power source such as a 12-volt power outlet in an automobile.

**Durability and Availability of the Device:** During a 1-year warranty period, Horiba will repair any malfunctioning items of the device at no cost. During the demonstration, none of the device's reusable items malfunctioned or was damaged. Horiba does not supply some items necessary for TPH measurement using the device, including a test tube rack, a funnel rack and stand, a digital balance, and miscellaneous glassware and laboratory supplies; the availability of replacement or spare parts not supplied by Horiba depends on their manufacturer or distributor.

In summary, during the demonstration, the OCMA-350 exhibited the following desirable characteristics of a field TPH measurement device: (1) good precision, (2) sensitivity to interferents that are petroleum hydrocarbons, and (3) high sample throughput. In addition, the OCMA-350 exhibited moderate measurement costs. In general, however, the OCMA-350 TPH results for the PE samples did not compare well with the reference method results. The device results were significantly impacted by soil moisture content and by turpentine, an interferent that is not a petroleum hydrocarbon. Collectively, the demonstration findings indicated that the OCMA-350 may be considered for TPH screening purposes; however, the user should exercise caution when considering the device for a field TPH measurement application requiring definitive results.

Original  
signed by

Gary J. Foley, Ph.D.  
Director  
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Office of Research and Development

**NOTICE:** EPA verifications are based on an evaluation of technology performance under specific, predetermined criteria and appropriate quality assurance procedures. The EPA makes no expressed or implied warranties as to the performance of the technology and does not certify that a technology will always operate as verified. The end user is solely responsible for complying with any and all applicable federal, state, and local requirements.

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## Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's natural resources. Under the mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and scientific support that can be used to solve environmental problems, build the scientific knowledge base needed to manage ecological resources wisely, understand how pollutants affect public health, and prevent or reduce environmental risks.

The National Exposure Research Laboratory (NERL) is the agency's center for investigation of technical and management approaches for identifying and quantifying risks to human health and the environment. Goals of the laboratory's research program are to (1) develop and evaluate methods and technologies for characterizing and monitoring air, soil, and water; (2) support regulatory and policy decisions; and (3) provide the scientific support needed to ensure effective implementation of environmental regulations and strategies.

The EPA's Superfund Innovative Technology Evaluation (SITE) Program evaluates technologies designed for characterization and remediation of contaminated Superfund and Resource Conservation and Recovery Act sites. The SITE Program was created to provide reliable cost and performance data in order to speed acceptance and use of innovative remediation, characterization, and monitoring technologies by the regulatory and user community.

Effective measurement and monitoring technologies are needed to assess the degree of contamination at a site, provide data that can be used to determine the risk to public health or the environment, supply the necessary cost and performance data to select the most appropriate technology, and monitor the success or failure of a remediation process. One component of the EPA SITE Program, the Monitoring and Measurement Technology (MMT) Program, demonstrates and evaluates innovative technologies to meet these needs.

Candidate technologies can originate within the federal government or the private sector. Through the SITE Program, developers are given the opportunity to conduct a rigorous demonstration of their technologies under actual field conditions. By completing the demonstration and distributing the results, the agency establishes a baseline for acceptance and use of these technologies. The MMT Program is administered by the Environmental Sciences Division of NERL in Las Vegas, Nevada.

Gary J. Foley, Ph.D.  
Director  
National Exposure Research Laboratory  
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## Abstract

The OCMA-350 Oil Content Analyzer (OCMA-350) developed by Horiba Instruments Incorporated (Horiba), was demonstrated under the U.S. Environmental Protection Agency Superfund Innovative Technology Evaluation Program in June 2000 at the Navy Base Ventura County site in Port Hueneme, California. The purpose of the demonstration was to collect reliable performance and cost data for the OCMA-350 and six other field measurement devices for total petroleum hydrocarbons (TPH) in soil. In addition to assessing ease of device operation, the key objectives of the demonstration included determining the (1) method detection limit, (2) accuracy and precision, (3) effects of interferents and soil moisture content on TPH measurement, (4) sample throughput, and (5) TPH measurement costs for each device. The demonstration involved analysis of both performance evaluation samples and environmental samples collected in five areas contaminated with gasoline, diesel, lubricating oil, or other petroleum products. The performance and cost results for a given field measurement device were compared to those for an off-site laboratory reference method, "Test Methods for Evaluating Solid Waste" (SW-846) Method 8015B (modified). During the demonstration, Horiba required 46 hours, 15 minutes, for TPH measurement of 199 samples and 9 extract duplicates. The TPH measurement costs for these samples were estimated to be \$15,750 for the OCMA-350 compared to \$42,050 for the reference method. The method detection limits were determined to be 15.2 and 4.79 milligrams per kilogram for the OCMA-350 and reference method, respectively. During the demonstration, the OCMA-350 exhibited good precision and sensitivity to interferents that are petroleum hydrocarbons (methyl-tert-butyl ether and Stoddard solvent). However, the OCMA-350 TPH results (1) did not compare well with the reference method results for the performance evaluation samples and (2) were significantly impacted by soil moisture content and by turpentine, an interferent that is not a petroleum hydrocarbon. In addition, some of the items in the OCMA-350 made the TPH measurement procedure less simple and more time-consuming during the demonstration. Collectively, the demonstration findings indicated that the OCMA-350 may be considered for TPH screening purposes; however, the user should exercise caution when considering the device for a field TPH measurement application requiring definitive results.



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## Contents

<u>Chapter</u>	<u>Page</u>
Notice .....	ii
Verification Statement .....	iii
Foreword .....	vi
Abstract .....	vii
Figures .....	xi
Tables .....	xii
Abbreviations, Acronyms, and Symbols .....	xiv
Acknowledgments .....	xvi
1 Introduction .....	1
1.1 Description of SITE Program .....	1
1.2 Scope of Demonstration .....	4
1.3 Components and Definition of TPH .....	4
1.3.1 Composition of Petroleum and Its Products .....	4
1.3.1.1 Gasoline .....	6
1.3.1.2 Naphthas .....	6
1.3.1.3 Kerosene .....	6
1.3.1.4 Jet Fuels .....	6
1.3.1.5 Fuel Oils .....	7
1.3.1.6 Diesel .....	7
1.3.1.7 Lubricating Oils .....	7
1.3.2 Measurement of TPH .....	7
1.3.2.1 Historical Perspective .....	7
1.3.2.2 Current Options for TPH Measurement in Soil .....	8
1.3.2.3 Definition of TPH .....	9
2 Description of Infrared Analysis and the OCMA-350 .....	11
2.1 Description of Infrared Analysis .....	11
2.2 Description of OCMA-350 .....	13
2.2.1 Device Description .....	13
2.2.2 Operating Procedure .....	15

---

## Contents (Continued)

<u>Chapter</u>		<u>Page</u>
2.3	Developer Contact Information .....	15
3	Demonstration Site Descriptions .....	16
3.1	Navy Base Ventura County Site .....	17
3.1.1	Fuel Farm Area .....	17
3.1.2	Naval Exchange Service Station Area .....	18
3.1.3	Phytoremediation Area .....	18
3.2	Kelly Air Force Base Site .....	19
3.3	Petroleum Company Site .....	19
4	Demonstration Approach .....	21
4.1	Demonstration Objectives .....	21
4.2	Demonstration Design .....	21
4.2.1	Approach for Addressing Primary Objectives .....	22
4.2.2	Approach for Addressing Secondary Objectives .....	26
4.3	Sample Preparation and Management .....	30
4.3.1	Sample Preparation .....	30
4.3.2	Sample Management .....	32
5	Confirmatory Process .....	36
5.1	Reference Method Selection .....	36
5.2	Reference Laboratory Selection .....	38
5.3	Summary of Reference Method .....	38
6	Assessment of Reference Method Data Quality .....	47
6.1	Quality Control Check Results .....	47
6.1.1	GRO Analysis .....	47
6.1.2	EDRO Analysis .....	50
6.2	Selected Performance Evaluation Sample Results .....	56
6.3	Data Quality .....	59
7	Performance of the OCMA-350 .....	60
7.1	Primary Objectives .....	60
7.1.1	Primary Objective P1: Method Detection Limit .....	62
7.1.2	Primary Objective P2: Accuracy and Precision .....	62
7.1.2.1	Accuracy .....	63
7.1.2.2	Precision .....	72
7.1.3	Primary Objective P3: Effect of Interferents .....	77
7.1.3.1	Interferent Sample Results .....	77
7.1.3.2	Effects of Interferents on TPH Results for Soil Samples .....	77
7.1.4	Primary Objective P4: Effect of Soil Moisture Content .....	85
7.1.5	Primary Objective P5: Time Required for TPH Measurement .....	87
7.2	Secondary Objectives .....	89
7.2.1	Skill and Training Requirements for Proper Device Operation .....	89
7.2.2	Health and Safety Concerns Associated with Device Operation .....	90

---

## Contents (Continued)

<u>Chapter</u>		<u>Page</u>
	7.2.3 Portability of the Device .....	90
	7.2.4 Durability of the Device .....	90
	7.2.5 Availability of the Device and Spare Parts .....	91
8	Economic Analysis .....	92
8.1	Issues and Assumptions .....	92
8.1.1	Capital Equipment Cost .....	92
8.1.2	Cost of Supplies .....	92
8.1.3	Support Equipment Cost .....	93
8.1.4	Labor Cost .....	93
8.1.5	Investigation-Derived Waste Disposal Cost .....	93
8.1.6	Costs Not Included .....	93
8.2	OCMA-350 Costs .....	94
8.2.1	Capital Equipment Cost .....	94
8.2.2	Cost of Supplies .....	94
8.2.3	Support Equipment Cost .....	94
8.2.4	Labor Cost .....	94
8.2.5	Investigation-Derived Waste Disposal Cost .....	96
8.2.6	Summary of OCMA-350 Costs .....	96
8.3	Reference Method Costs .....	96
8.4	Comparison of Economic Analysis Results .....	96
9	Summary of Demonstration Results .....	98
10	References .....	103
Appendix	Supplemental Information Provided by the Developer .....	105

---

## Figures

<b><u>Figure</u></b>	<b><u>Page</u></b>
1-1. Distribution of various petroleum hydrocarbon types throughout boiling point range of crude oil .....	5
5-1. Reference method selection process .....	37
7-1. Summary of statistical analysis of TPH results .....	61
7-2. Measurement bias for environmental samples .....	65
7-3. Measurement bias for soil performance evaluation samples .....	66
7-4. Linear regression plots for environmental samples .....	71
7-5. Linear regression plots for soil performance evaluation samples .....	72

---

## Tables

<u>Table</u>	<u>Page</u>
1-1. Summary of Calibration Information for Infrared Analytical Method . . . . .	8
1-2. Current Technologies for TPH Measurement . . . . .	9
2-1. Infrared Absorbance Values of CH, CH <sub>2</sub> , and CH <sub>3</sub> Groups . . . . .	12
2-2. OCMA-350 Components and Supplies . . . . .	14
3-1. Summary of Site Characteristics . . . . .	17
4-1. Action Levels Used to Evaluate Analytical Accuracy . . . . .	23
4-2. Demonstration Approach . . . . .	27
4-3. Environmental Samples . . . . .	31
4-4. Performance Evaluation Samples . . . . .	33
4-5. Sample Container, Preservation, and Holding Time Requirements . . . . .	35
5-1. Laboratory Sample Preparation and Analytical Methods . . . . .	38
5-2. Summary of Project-Specific Procedures for GRO Analysis . . . . .	40
5-3. Summary of Project-Specific Procedures for EDRO Analysis . . . . .	44
6-1. Summary of Quality Control Check Results for GRO Analysis . . . . .	51
6-2. Summary of Quality Control Check Results for EDRO Analysis . . . . .	55
6-3. Comparison of Soil and Liquid Performance Evaluation Sample Results . . . . .	57
6-4. Comparison of Environmental Resource Associates Historical Results to Reference Method Results . . . . .	58
7-1. TPH Results for Low-Concentration-Range Diesel Soil Performance Evaluation Samples . . . . .	62
7-2. Action Level Conclusions . . . . .	64
7-3. Statistical Comparison of OCMA-350 and Reference Method TPH Results for Environmental Samples . . . . .	68
7-4. Statistical Comparison of OCMA-350 and Reference Method TPH Results for Performance Evaluation Samples . . . . .	70
7-5. Summary of Linear Regression Analysis Results . . . . .	73
7-6. Summary of OCMA-350 and Reference Method Precision for Field Triplicates of Environmental Samples . . . . .	74

---

## Tables (Continued)

<b><u>Table</u></b>		<b><u>Page</u></b>
7-7.	Summary of OCMA-350 and Reference Method Precision for Extract Duplicates . . . .	75
7-8.	Comparison of OCMA-350 and Reference Method Precision for Replicate Performance Evaluation Samples . . . . .	76
7-9.	Comparison of OCMA-350 and Reference Method Results for Interferent Samples . . . . .	78
7-10.	Comparison of OCMA-350 and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents . . . . .	80
7-11.	Comparison of Results for Soil Performance Evaluation Samples at Different Moisture Levels . . . . .	86
7-12.	Time Required to Complete TPH Measurement Activities Using the OCMA-350 . . . .	88
8-1.	OCMA-350 Cost Summary . . . . .	95
8-2.	Reference Method Cost Summary . . . . .	97
9-1.	Summary of OCMA-350 Results for the Primary Objectives . . . . .	99
9-2.	Summary of OCMA-350 Results for the Secondary Objectives . . . . .	102

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## Abbreviations, Acronyms, and Symbols

>	Greater than
#	Less than or equal to
±	Plus or minus
µg	Microgram
µL	Microliter
µm	Micrometer
AC	Alternating current
AEHS	Association for Environmental Health and Sciences
AFB	Air Force Base
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
bgs	Below ground surface
BTEX	Benzene, toluene, ethylbenzene, and xylene
BVC	Base Ventura County
CCV	Continuing calibration verification
CFC	Chlorofluorocarbon
CFR	<i>Code of Federal Regulations</i>
cm	Centimeter
DC	Direct current
DER	Data evaluation report
DRO	Diesel range organics
EDRO	Extended diesel range organics
EPA	U.S. Environmental Protection Agency
EPH	Extractable petroleum hydrocarbon
ERA	Environmental Resource Associates
FFA	Fuel Farm Area
FID	Flame ionization detector
GC	Gas chromatograph
GRO	Gasoline range organics
Horiba	Horiba Instruments Incorporated
HPLC	High-performance liquid chromatography
ICV	Initial calibration verification
IDW	Investigation-derived waste
ITVR	Innovative technology verification report
kg	Kilogram
L	Liter
LCS	Laboratory control sample
LCSD	Laboratory control sample duplicate
MCAWW	“Methods for Chemical Analysis of Water and Wastes”
MDL	Method detection limit

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## Abbreviations, Acronyms, and Symbols (Continued)

Means	R.S. Means Company
mg	Milligram
min	Minute
mL	Milliliter
mm	Millimeter
MMT	Monitoring and Measurement Technology
MS	Matrix spike
MSD	Matrix spike duplicate
MTBE	Methyl-tert-butyl ether
n-C <sub>x</sub>	Alkane with “x” carbon atoms
NDIR	Nondispersive infrared
NERL	National Exposure Research Laboratory
NEX	Naval Exchange
ng	Nanogram
nm	Nanometer
OCMA-350	OCMA-350 Oil Content Analyzer
ORD	Office of Research and Development
ORO	Oil range organics
OSWER	Office of Solid Waste and Emergency Response
PC	Petroleum company
PCB	Polychlorinated biphenyl
PCE	Tetrachloroethene
PE	Performance evaluation
PHC	Petroleum hydrocarbon
PPE	Personal protective equipment
PRA	Phytoremediation Area
PRO	Petroleum range organics
QA	Quality assurance
QC	Quality control
R <sup>2</sup>	Square of the correlation coefficient
RPD	Relative percent difference
RSD	Relative standard deviation
SFT	Slop Fill Tank
SITE	Superfund Innovative Technology Evaluation
STL Tampa East	Severn Trent Laboratories in Tampa, Florida
SW-846	“Test Methods for Evaluating Solid Waste”
TPH	Total petroleum hydrocarbons
UST	Underground storage tank
VOA	Volatile organic analysis
VPH	Volatile petroleum hydrocarbon



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## Chapter 1 Introduction

The U.S. Environmental Protection Agency (EPA) Office of Research and Development (ORD) National Exposure Research Laboratory (NERL) conducted a demonstration of seven innovative field measurement devices for total petroleum hydrocarbons (TPH) in soil. The demonstration was conducted as part of the EPA Superfund Innovative Technology Evaluation (SITE) Monitoring and Measurement Technology (MMT) Program using TPH-contaminated soil from five areas located in three regions of the United States. The demonstration was conducted at Port Hueneme, California, during the week of June 12, 2000. The purpose of the demonstration was to obtain reliable performance and cost data on field measurement devices in order to provide (1) potential users with a better understanding of the devices' performance and operating costs under well-defined field conditions and (2) the developers with documented results that will assist them in promoting acceptance and use of their devices. The TPH results obtained using the seven field measurement devices were compared to the TPH results obtained from a reference laboratory chosen for the demonstration, which used a reference method modified for the demonstration.

This innovative technology verification report (ITVR) presents demonstration performance results and associated costs for the OCMA-350 Oil Content Analyzer (OCMA-350) developed by Horiba Instruments Incorporated (Horiba). Specifically, this report describes the SITE Program, the scope of the demonstration, and the components and definition of TPH (Chapter 1); the innovative field measurement device and the technology upon which it is based (Chapter 2); the three demonstration sites (Chapter 3); the demonstration approach (Chapter 4); the selection of the reference method and laboratory (Chapter 5); the assessment of reference method data quality (Chapter 6); the performance of the field measurement device (Chapter 7); the economic analysis for the field measurement device

and reference method (Chapter 8); the demonstration results in summary form (Chapter 9); and the references used to prepare the ITVR (Chapter 10). Supplemental information provided by Horiba is presented in the appendix.

### 1.1 Description of SITE Program

Performance verification of innovative environmental technologies is an integral part of the regulatory and research mission of the EPA. The SITE Program was established by the EPA Office of Solid Waste and Emergency Response (OSWER) and ORD under the Superfund Amendments and Reauthorization Act of 1986. The overall goal of the SITE Program is to conduct performance verification studies and to promote the acceptance of innovative technologies that may be used to achieve long-term protection of human health and the environment. The program is designed to meet three primary objectives: (1) identify and remove obstacles to the development and commercial use of innovative technologies, (2) demonstrate promising innovative technologies and gather reliable performance and cost information to support site characterization and cleanup activities, and (3) develop procedures and policies that encourage the use of innovative technologies at Superfund sites as well as at other waste sites or commercial facilities.

The intent of a SITE demonstration is to obtain representative, high-quality performance and cost data on one or more innovative technologies so that potential users can assess the suitability of a given technology for a specific application. The SITE Program includes the following elements:

- **MMT Program**—Evaluates innovative technologies that sample, detect, monitor, or measure hazardous

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and toxic substances. These technologies are expected to provide better, faster, or more cost-effective methods for producing real-time data during site characterization and remediation studies than do conventional technologies.

- **Remediation Technology Program**—Conducts demonstrations of innovative treatment technologies to provide reliable performance, cost, and applicability data for site cleanups.
- **Technology Transfer Program**—Provides and disseminates technical information in the form of updates, brochures, and other publications that promote the SITE Program and participating technologies. The Technology Transfer Program also offers technical assistance, training, and workshops to support the technologies. A significant number of these activities are performed by EPA's Technology Innovation Office.

The TPH field measurement device demonstration was conducted as part of the MMT Program, which provides developers of innovative hazardous waste sampling, detection, monitoring, and measurement devices with an opportunity to demonstrate the performance of their devices under actual field conditions. These devices may be used to sample, detect, monitor, or measure hazardous and toxic substances in water, soil gas, soil, and sediment. The technologies include chemical sensors for in situ (in place) measurements, soil and sediment samplers, soil gas samplers, groundwater samplers, field-portable analytical equipment, and other systems that support field sampling or data acquisition and analysis.

The MMT Program promotes acceptance of technologies that can be used to (1) accurately assess the degree of contamination at a site, (2) provide data to evaluate potential effects on human health and the environment, (3) apply data to assist in selecting the most appropriate cleanup action, and (4) monitor the effectiveness of a remediation process. The program places a high priority on innovative technologies that provide more cost-effective, faster, and safer methods for producing real-time or near-real-time data than do conventional, laboratory-based technologies. These innovative technologies are demonstrated under field conditions, and the results are compiled, evaluated, published, and disseminated by the ORD. The primary objectives of the MMT Program are as follows:

- Test and verify the performance of innovative field sampling and analytical technologies that enhance sampling, monitoring, and site characterization capabilities
- Identify performance attributes of innovative technologies to address field sampling, monitoring, and characterization problems in a more cost-effective and efficient manner
- Prepare protocols, guidelines, methods, and other technical publications that enhance acceptance of these technologies for routine use

The MMT Program is administered by the Environmental Sciences Division of the NERL in Las Vegas, Nevada. The NERL is the EPA center for investigation of technical and management approaches for identifying and quantifying risks to human health and the environment. The NERL mission components include (1) developing and evaluating methods and technologies for sampling, monitoring, and characterizing water, air, soil, and sediment; (2) supporting regulatory and policy decisions; and (3) providing the technical support needed to ensure effective implementation of environmental regulations and strategies. By demonstrating innovative field measurement devices for TPH in soil, the MMT Program is supporting the development and evaluation of methods and technologies for field measurement of TPH concentrations in a variety of soil types. Information regarding the selection of field measurement devices for TPH is available in American Petroleum Institute (API) publications (API 1996, 1998).

The MMT Program's technology verification process is designed to conduct demonstrations that will generate high-quality data so that potential users have reliable information regarding device performance and cost. Four steps are inherent in the process: (1) needs identification and technology selection, (2) demonstration planning and implementation, (3) report preparation, and (4) information distribution.

The first step of the verification process begins with identifying technology needs of the EPA and the regulated community. The EPA regional offices, the U.S. Department of Energy, the U.S. Department of Defense, industry, and state environmental regulatory agencies are asked to identify technology needs for sampling,

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monitoring, and measurement of environmental media. Once a need is identified, a search is conducted to identify suitable technologies that will address the need. The technology search and identification process consists of examining industry and trade publications, attending related conferences, exploring leads from technology developers and industry experts, and reviewing responses to *Commerce Business Daily* announcements. Selection of technologies for field testing includes evaluation of the candidate technologies based on several criteria. A suitable technology for field testing

- Is designed for use in the field
- Is applicable to a variety of environmentally contaminated sites
- Has potential for solving problems that current methods cannot satisfactorily address
- Has estimated costs that are lower than those of conventional methods
- Is likely to achieve better results than current methods in areas such as data quality and turnaround time
- Uses techniques that are easier or safer than current methods
- Is commercially available

Once candidate technologies are identified, their developers are asked to participate in a developer conference. This conference gives the developers an opportunity to describe their technologies' performance and to learn about the MMT Program.

The second step of the verification process is to plan and implement a demonstration that will generate high-quality data to assist potential users in selecting a technology. Demonstration planning activities include a predemonstration sampling and analysis investigation that assesses existing conditions at the proposed demonstration site or sites. The objectives of the predemonstration investigation are to (1) confirm available information on applicable physical, chemical, and biological characteristics of contaminated media at the sites to justify selection of site areas for the demonstration; (2) provide the technology developers with an opportunity to evaluate the areas, analyze representative samples, and identify logistical requirements; (3) assess the overall logistical

requirements for conducting the demonstration; and (4) provide the reference laboratory with an opportunity to identify any matrix-specific analytical problems associated with the contaminated media and to propose appropriate solutions. Information generated through the predemonstration investigation is used to develop the final demonstration design and sampling and analysis procedures.

Demonstration planning activities also include preparing a detailed demonstration plan that describes the procedures to be used to verify the performance and cost of each innovative technology. The demonstration plan incorporates information generated during the predemonstration investigation as well as input from technology developers, demonstration site representatives, and technical peer reviewers. The demonstration plan also incorporates the quality assurance (QA) and quality control (QC) elements needed to produce data of sufficient quality to document the performance and cost of each technology.

During the demonstration, each innovative technology is evaluated independently and, when possible and appropriate, is compared to a reference technology. The performance and cost of one innovative technology are not compared to those of another technology evaluated in the demonstration. Rather, demonstration data are used to evaluate the individual performance, cost, advantages, limitations, and field applicability of each technology.

As part of the third step of the verification process, the EPA publishes a verification statement and a detailed evaluation of each technology in an ITVR. To ensure its quality, the ITVR is published only after comments from the technology developer and external peer reviewers are satisfactorily addressed. In addition, all demonstration data used to evaluate each innovative technology are summarized in a data evaluation report (DER) that constitutes a complete record of the demonstration. The DER is not published as an EPA document, but an unpublished copy may be obtained from the EPA project manager.

The fourth step of the verification process is to distribute information regarding demonstration results. To benefit technology developers and potential technology users, the EPA distributes demonstration bulletins and ITVRs through direct mailings, at conferences, and on the Internet. The ITVRs and additional information on the

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SITE Program are available on the EPA ORD web site (<http://www.epa.gov/ORD/SITE>).

## 1.2 Scope of Demonstration

The purpose of the demonstration was to evaluate field measurement devices for TPH in soil in order to provide (1) potential users with a better understanding of the devices' performance and costs under well-defined field conditions and (2) the developers with documented results that will assist them in promoting acceptance and use of their devices.

Chapter 2 of this ITVR describes both the technology upon which the OCMA-350 is based and the field measurement device itself. Because TPH is a "method-defined parameter," the performance results for the device are compared to the results obtained using an off-site laboratory measurement method—that is, a reference method. Details on the selection of the reference method and laboratory are provided in Chapter 5.

The demonstration had both primary and secondary objectives. Primary objectives were critical to the technology verification and required the use of quantitative results to draw conclusions regarding each field measurement device's performance as well as to estimate the cost of operating the device. Secondary objectives pertained to information that was useful but did not necessarily require the use of quantitative results to draw conclusions regarding the performance of each device. Both the primary and secondary objectives are discussed in Chapter 4.

To meet the demonstration objectives, samples were collected from five individual areas at three sites. The first site is referred to as the Navy Base Ventura County (BVC) site; is located in Port Hueneme, California; and contained three sampling areas. The Navy BVC site lies in EPA Region 9. The second site is referred to as the Kelly Air Force Base (AFB) site; is located in San Antonio, Texas; and contained one sampling area. The Kelly AFB site lies in EPA Region 6. The third site is referred to as the petroleum company (PC) site, is located in north-central Indiana, and contained one sampling area. The PC site lies in EPA Region 5.

In preparation for the demonstration, a predemonstration sampling and analysis investigation was completed at the three sites in January 2000. The purpose of this

investigation was to assess whether the sites and sampling areas were appropriate for evaluating the seven field measurement devices based on the demonstration objectives. Demonstration field activities were conducted between June 5 and 18, 2000. The procedures used to verify the performance and costs of the field measurement devices are documented in a demonstration plan completed in June 2000 (EPA 2000). The plan also incorporates the QA/QC elements that were needed to generate data of sufficient quality to document field measurement device and reference laboratory performance and costs. The plan is available through the EPA ORD web site (<http://www.epa.gov/ORD/SITE>) or from the EPA project manager.

## 1.3 Components and Definition of TPH

To understand the term "TPH," it is necessary to understand the composition of petroleum and its products. This section briefly describes the composition of petroleum and its products and defines TPH from a measurement standpoint. The organic compounds containing only hydrogen and carbon that are present in petroleum and its derivatives are collectively referred to as petroleum hydrocarbons (PHC). Therefore, in this ITVR, the term "PHC" is used to identify sample constituents, and the term "TPH" is used to identify analyses performed and the associated results (for example, TPH concentrations).

### 1.3.1 Composition of Petroleum and Its Products

Petroleum is essentially a mixture of gaseous, liquid, and solid hydrocarbons that occur in sedimentary rock deposits. On the molecular level, petroleum is a complex mixture of hydrocarbons; organic compounds of sulfur, nitrogen, and oxygen; and compounds containing metallic constituents, particularly vanadium, nickel, iron, and copper. Based on the limited data available, the elemental composition of petroleum appears to vary over a relatively narrow range: 83 to 87 percent carbon, 10 to 14 percent hydrogen, 0.05 to 6 percent sulfur, 0.1 to 2 percent nitrogen, and 0.05 to 1.5 percent oxygen. Metals are present in petroleum at concentrations of up to 0.1 percent (Speight 1991).

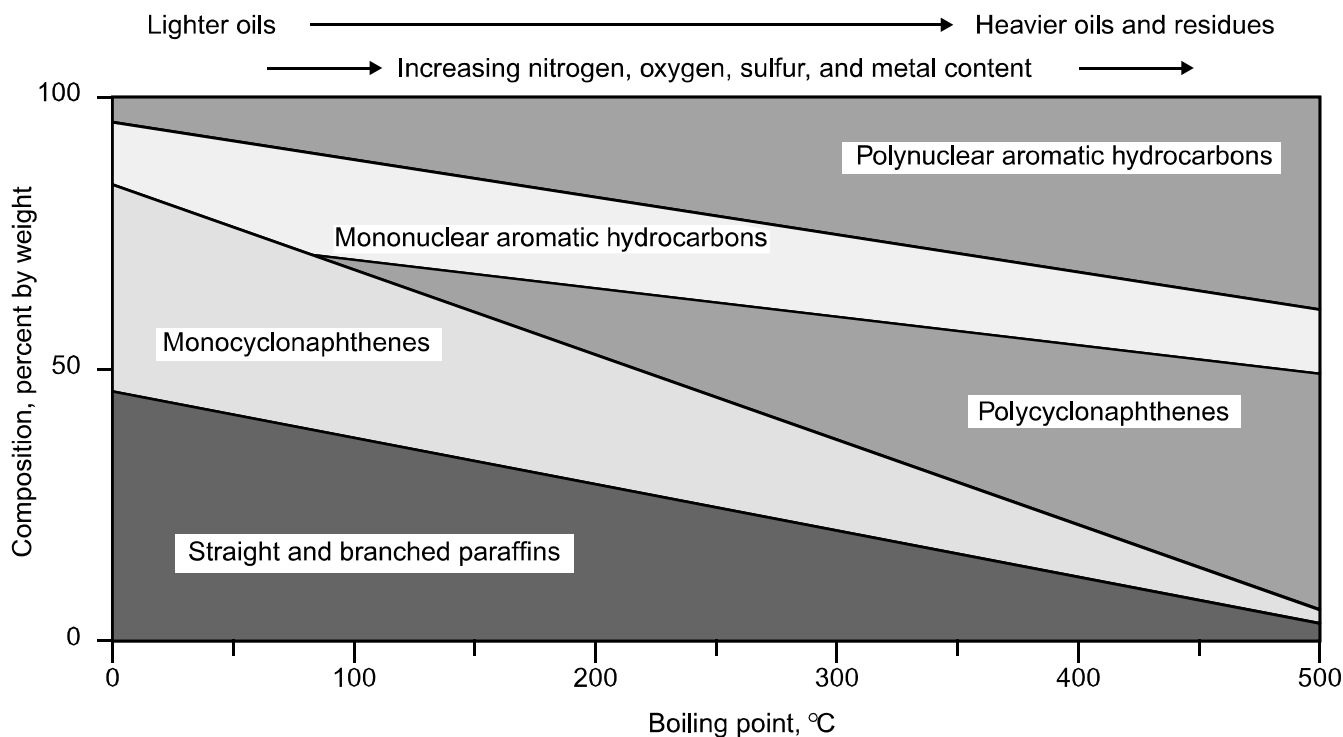
Petroleum in the crude state (crude oil) is a mineral resource, but when refined it provides liquid fuels, solvents, lubricants, and many other marketable products. The hydrocarbon components of crude oil include

paraffinic, naphthenic, and aromatic groups. Paraffins (alkanes) are saturated, aliphatic hydrocarbons with straight or branched chains but without any ring structure. Naphthenes are saturated, aliphatic hydrocarbons containing one or more rings, each of which may have one or more paraffinic side chains (alicyclic hydrocarbons). Aromatic hydrocarbons contain one or more aromatic nuclei, such as benzene, naphthalene, and phenanthrene ring systems, that may be linked with (substituted) naphthenic rings or paraffinic side chains. In crude oil, the relationship among the three primary groups of hydrocarbon components is a result of hydrogen gain or loss between any two groups. Another class of compounds that is present in petroleum products such as automobile gasoline but rarely in crude oil is known as olefins. Olefins (alkenes) are unsaturated, aliphatic hydrocarbons.

The distribution of paraffins, naphthenes, and aromatic hydrocarbons depends on the source of crude oil. For example, Pennsylvania crude oil contains high levels of paraffins (about 50 percent), whereas Borneo crude oil contains less than 1 percent paraffins. As shown in Figure 1-1, the proportion of straight or branched paraffins

decreases with increasing molecular weight or boiling point fraction for a given crude oil; however, this is not true for naphthenes or aromatic hydrocarbons. The proportion of monocyclonaphthenes decreases with increasing molecular weight or boiling point fraction, whereas the opposite is true for polycyclonaphthenes (for example, tetralin and decalin) and polynuclear aromatic hydrocarbons; the proportion of mononuclear aromatic hydrocarbons appears to be independent of molecular weight or boiling point fraction.

Various petroleum products consisting of carbon and hydrogen are formed when crude oil is subjected to distillation and other processes in a refinery. Processing of crude oil results in petroleum products with trace quantities of metals and organic compounds that contain nitrogen, sulfur, and oxygen. These products include liquefied petroleum gas, gasoline, naphthas, kerosene, fuel oils, lubricating oils, coke, waxes, and asphalt. Of these products, gasoline, naphthas, kerosene, fuel oils, and lubricating oils are liquids and may be present at petroleum-contaminated sites. Except for gasoline and some naphthas, these products are made primarily by collecting particular boiling point fractions of crude oil



Source: Speight 1991

Figure 1-1. Distribution of various petroleum hydrocarbon types throughout boiling point range of crude oil.

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from a distillation column. Because this classification of petroleum products is based on boiling point and not on chemical composition, the composition of these products, including the ratio of aliphatic to aromatic hydrocarbons, varies depending on the source of crude oil. In addition, specific information (such as boiling points and carbon ranges) for different petroleum products, varies slightly depending on the source of the information. Commonly encountered forms and blends of petroleum products are briefly described below. The descriptions are primarily based on information in books written by Speight (1991) and Gary and Handwerk (1993). Additional information is provided by Dryoff (1993).

### **1.3.1.1 Gasoline**

Gasoline is a major exception to the boiling point classification described above because “straight-run gasoline” (gasoline directly recovered from a distillation column) is only a small fraction of the blended gasoline that is commercially available as fuel. Commercially available gasolines are complex mixtures of hydrocarbons that boil below 180 °C or at most 225 °C and that contain hydrocarbons with 4 to 12 carbon atoms per molecule. Of the commercially available gasolines, aviation gasoline has a narrower boiling range (38 to 170 °C) than automobile gasoline (-1 to 200 °C). In addition, aviation gasoline may contain high levels of paraffins (50 to 60 percent), moderate levels of naphthenes (20 to 30 percent), a low level of aromatic hydrocarbons (10 percent), and no olefins, whereas automobile gasoline may contain up to 30 percent olefins and up to 40 percent aromatic hydrocarbons.

Gasoline composition can vary widely depending on the source of crude oil. In addition, gasoline composition varies from region to region because of consumer needs for gasoline with a high octane rating to prevent engine “knocking.” Moreover, EPA regulations regarding the vapor pressure of gasoline, the chemicals used to produce a high octane rating, and cleaner-burning fuels have affected gasoline composition. For example, when use of tetraethyl lead to produce gasoline with a high octane rating was banned by the EPA, oxygenated fuels came into existence. Production of these fuels included addition of methyl-tert-butyl ether (MTBE), ethanol, and other oxygenates. Use of oxygenated fuels also results in reduction of air pollutant emissions (for example, carbon monoxide and nitrogen oxides).

### **1.3.1.2 Naphthas**

“Naphtha” is a generic term applied to petroleum solvents. Under standardized distillation conditions, at least 10 percent of naphthas should distill below 175 °C, and at least 95 percent of naphthas should distill below 240 °C. Naphthas can be both aliphatic and aromatic and contain hydrocarbons with 6 to 14 carbon atoms per molecule. Depending on the intended use of a naphtha, it may be free of aromatic hydrocarbons (to make it odor-free) and sulfur (to make it less toxic and less corrosive). Many forms of naphthas are commercially available, including Varnish Makers’ and Painters’ naphthas (Types I and II), mineral spirits (Types I through IV), and aromatic naphthas (Types I and II). Stoddard solvent is an example of an aliphatic naphtha.

### **1.3.1.3 Kerosene**

Kerosene is a straight-run petroleum fraction that has a boiling point range of 205 to 260 °C. Kerosene typically contains hydrocarbons with 12 or more carbon atoms per molecule. Because of its use as an indoor fuel, kerosene must be free of aromatic and unsaturated hydrocarbons as well as sulfur compounds.

### **1.3.1.4 Jet Fuels**

Jet fuels, which are also known as aircraft turbine fuels, are manufactured by blending gasoline, naphtha, and kerosene in varying proportions. Therefore, jet fuels may contain a carbon range that covers gasoline through kerosene. Jet fuels are used in both military and commercial aircraft. Some examples of jet fuels include Type A, Type A-1, Type B, JP-4, JP-5, and JP-8. The aromatic hydrocarbon content of these fuels ranges from 20 to 25 percent. The military jet fuel JP-4 has a wide boiling point range (65 to 290 °C), whereas commercial jet fuels, including JP-5 and Types A and A-1, have a narrower boiling point range (175 to 290 °C) because of safety considerations. Increasing concerns over combat hazards associated with JP-4 jet fuel led to development of JP-8 jet fuel, which has a flash point of 38 °C and a boiling point range of 165 to 275 °C. JP-8 jet fuel contains hydrocarbons with 9 to 15 carbon atoms per molecule. Type B jet fuel has a boiling point range of 55 to 230 °C and a carbon range of 5 to 13 atoms per molecule. A new specification is currently being developed by the American Society for Testing and Materials (ASTM) for Type B jet fuel.

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### 1.3.1.5 Fuel Oils

Fuel oils are divided into two classes: distillates and residuals. No. 1 and 2 fuel oils are distillates and include kerosene, diesel, and home heating oil. No. 4, 5, and 6 fuel oils are residuals or black oils, and they all contain crude distillation tower bottoms (tar) to which cutter stocks (semirefined or refined distillates) have been added. No. 4 fuel oil contains the most cutter stock, and No. 6 fuel oil contains the least.

Commonly available fuel oils include No. 1, 2, 4, 5, and 6. The boiling points, viscosities, and densities of these fuel oils increase with increasing number designation. The boiling point ranges for No. 1, 2, and 4 fuel oils are about 180 to 320, 175 to 340, and 150 to 480 °C, respectively. No. 1 and 2 fuel oils contain hydrocarbons with 10 to 22 carbon atoms per molecule; the carbon range for No. 4 fuel oil is 22 to 40 atoms per molecule. No. 5 and 6 fuel oils have a boiling point range of 150 to 540 °C but differ in the amounts of residue they contain: No. 5 fuel oil contains a small amount of residue, whereas No. 6 fuel oil contains a large amount. No. 5 and 6 fuel oils contain hydrocarbons with 28 to 90 carbon atoms per molecule. Fuel oils typically contain about 60 percent aliphatic hydrocarbons and 40 percent aromatic hydrocarbons.

### 1.3.1.6 Diesel

Diesel is primarily used to operate motor vehicle and railroad diesel engines. Automobile diesel is available in two grades: No. 1 and 2. No. 1 diesel, which is sold in regions with cold climates, has a boiling point range of 180 to 320 °C and a cetane number above 50. The cetane number is similar to the octane number of gasoline; a higher number corresponds to less knocking. No. 2 diesel is very similar to No. 2 fuel oil. No. 2 diesel has a boiling point range of 175 to 340 °C and a minimum cetane number of 52. No. 1 diesel is used in high-speed engines such as truck and bus engines, whereas No. 2 diesel is used in other diesel engines. Railroad diesel is similar to No. 2 diesel but has a higher boiling point (up to 370 °C) and lower cetane number (40 to 45). The ratio of aliphatic to aromatic hydrocarbons in diesel is about 5. The carbon range for hydrocarbons present in diesel is 10 to 28 atoms per molecule.

### 1.3.1.7 Lubricating Oils

Lubricating oils can be distinguished from other crude oil fractions by their high boiling points (greater than 400 °C)

and viscosities. Materials suitable for production of lubricating oils are composed principally of hydrocarbons containing 25 to 35 or even 40 carbon atoms per molecule, whereas residual stocks may contain hydrocarbons with 50 to 60 or more (up to 80 or so) carbon atoms per molecule. Because it is difficult to isolate hydrocarbons from the lubricant fraction of petroleum, aliphatic to aromatic hydrocarbon ratios are not well documented for lubricating oils. However, these ratios are expected to be comparable to those of the source crude oil.

### 1.3.2 Measurement of TPH

As described in Section 1.3.1, the composition of petroleum and its products is complex and variable, which complicates TPH measurement. The measurement of TPH in soil is further complicated by weathering effects. When a petroleum product is released to soil, the product's composition immediately begins to change. The components with lower boiling points are volatilized, the more water-soluble components migrate to groundwater, and biodegradation can affect many other components. Within a short period, the contamination remaining in soil may have only some characteristics in common with the parent product.

This section provides a historical perspective on TPH measurement, reviews current options for TPH measurement in soil, and discusses the definition of TPH that was used for the demonstration.

#### 1.3.2.1 Historical Perspective

Most environmental measurements are focused on identifying and quantifying a particular trace element (such as lead) or organic compound (such as benzene). However, for some "method-defined" parameters, the particular substance being measured may yield different results depending on the measurement method used. Examples of such parameters include oil and grease and surfactants. Perhaps the most problematic of the method-defined parameters is TPH. TPH arose as a parameter for wastewater analyses in the 1960s because of petroleum industry concerns that the original "oil and grease" analytical method, which is gravimetric in nature, might inaccurately characterize petroleum industry wastewaters that contained naturally occurring vegetable oils and greases along with PHCs. These naturally occurring materials are typically long-chain fatty acids (for example, oleic acid, the major component of olive oil).



Originally, TPH was defined as any material extracted with a particular solvent that is not adsorbed by the silica gel used to remove fatty acids and that is not lost when the solvent is evaporated. Although this definition covers most of the components of petroleum products, it includes many other organic compounds as well, including chlorinated solvents, pesticides, and other synthetic organic chemicals. Furthermore, because of the evaporation step in the gravimetric analytical method, the definition excludes most of the petroleum-derived compounds in gasoline that are volatile in nature. For these reasons, an infrared analytical method was developed to measure TPH. In this method, a calibration standard consisting of three components is analyzed at a wavelength of 3.41 micrometers ( $\mu\text{m}$ ), which corresponds to an aliphatic  $\text{CH}_2$  hydrocarbon stretch. As shown in Table 1-1, the calibration standard is designed to mimic a petroleum product having a relative distribution of aliphatic and aromatic compounds as well as a certain percentage of aliphatic  $\text{CH}_2$  hydrocarbons. The infrared analytical method indicates that any compound that is extracted by the solvent, is not adsorbed by silica gel, and contains a  $\text{CH}_2$  bond is a PHC. Both the gravimetric and infrared analytical methods include an optional, silica gel fractionation step to remove polar, biogenic compounds such as fatty acids, but this cleanup step can also remove some petroleum degradation products that are polar in nature.

In the 1980s, because of the change in focus from wastewater analyses to characterization of hazardous waste sites that contained contaminated soil, many parties began to adapt the existing wastewater analytical methods for application to soil. Unfortunately, the term “TPH” was in common use, as many states had adopted this term (and the wastewater analytical methods) for cleanup activities at underground storage tank (UST) sites. Despite efforts by the API and others to establish new analyte names (for example, gasoline range organics [GRO] and diesel range organics [DRO]), “TPH” is still present in many state

regulations as a somewhat ill-defined term, and most state programs still have cleanup criteria for TPH.

### 1.3.2.2 Current Options for TPH Measurement in Soil

Three widely used technologies measure some form of TPH in soil to some degree. These technologies were used as starting points in deciding how to define TPH for the demonstration. The three technologies and the analytes measured are summarized in Table 1-2.

Of the three technologies, gravimetry and infrared are discussed in Section 1.3.2.1. The third technology, the gas chromatograph/flame ionization detector (GC/FID), came into use because of the documented shortcomings of the other two technologies. The GC/FID had long been used in the petroleum refining industry as a product QC tool to determine the boiling point distribution of pure petroleum products. In the 1980s, environmental laboratories began to apply this technology along with sample preparation methods developed for soil samples to measure PHCs at environmental levels (Zilis, McDevitt, and Parr 1988). GC/FID methods measure all organic compounds that are extracted by the solvent and that can be chromatographed. However, because of method limitations, the very volatile portion of gasoline compounds containing four or five carbon atoms per molecule is not addressed by GC/FID methods; therefore, 100 percent recovery cannot be achieved for pure gasoline. This omission is not considered significant because these low-boiling-point aliphatic compounds (1) are not expected to be present in environmental samples (because of volatilization) and (2) pose less environmental risk than the aromatic hydrocarbons in gasoline.

The primary limitation of GC/FID methods relates to the extraction solvent used. The solvent should not interfere with the analysis, but to achieve environmental levels of detection (in the low milligram per kilogram [mg/kg]

**Table 1-1. Summary of Calibration Information for Infrared Analytical Method**

Standard Constituent	Constituent Type	Portion of Constituent in Standard (percent by volume)	Number of Carbon Atoms				Portion of Aliphatic $\text{CH}_2$ in Standard Constituent (percent by weight)
			Aliphatic			Aromatic	
			$\text{CH}_3$	$\text{CH}_2$	CH	CH	
Hexadecane	Straight-chain aliphatic	37.5	2	14	0	0	91
Isooctane	Branched-chain aliphatic	37.5	5	1	1	0	14
Chlorobenzene	Aromatic	25	0	0	0	5	0
Average							35

**Table 1-2. Current Technologies for TPH Measurement**

Technology	What Is Measured	What Is Not Measured
Gravimetry	All analytes removed from the sample by the extraction solvent that are not volatilized	Volatiles; very polar organics
Infrared	All analytes removed from the sample by the extraction solvent that contain an aliphatic CH <sub>2</sub> stretch	Benzene, naphthalene, and other aromatic hydrocarbons with no aliphatic group attached; very polar organics
Gas chromatograph/flame ionization detector	All analytes removed from the sample by the extraction solvent that can be chromatographed and that respond to the detector	Very polar organics; compounds with high molecular weights or high boiling points

range) for soil, some concentration of the extract is needed because the sensitivity of the FID is in the nanogram (ng) range. This limitation has resulted in three basic approaches for GC/FID analyses for GRO, DRO, and PHCs.

For GRO analysis, a GC/FID method was developed as part of research sponsored by API and was the subject of an interlaboratory validation study (API 1994); the method was first published in 1990. In this method, GRO is defined as the sum of the organic compounds in the boiling point range of 60 to 170 °C, and the method uses a synthetic calibration standard as both a window-defining mix and a quantitation standard. The GRO method was specifically incorporated into EPA “Test Methods for Evaluating Solid Waste” (SW-846) Method 8015B in 1996 (EPA 1996). The GRO method uses the purge-and-trap technique for sample preparation, effectively limiting the TPH components to the volatile compounds only.

For DRO analysis, a GC/FID method was developed under the sponsorship of API as a companion to the GRO method and was interlaboratory-validated in 1994. In the DRO method, DRO is defined as the sum of the organic compounds in the boiling point range of 170 to 430 °C. As in the GRO method, a synthetic calibration standard is used for quantitation. The DRO method was also incorporated into SW-846 Method 8015B in 1996. The technology used in the DRO method can measure hydrocarbons with boiling points up to 540 °C. However, the hydrocarbons with boiling points in the range of 430 to 540 °C are specifically excluded from SW-846 Method 8015B so as not to include the higher-boiling-point petroleum products. The DRO method uses a solvent extraction and concentration step, effectively limiting the method to nonvolatile hydrocarbons.

For PHC analysis, a GC/FID method was developed by Shell Oil Company (now Equilon Enterprises). This

method was interlaboratory-validated along with the GRO and DRO methods in an API study in 1994. The PHC method originally defined PHC as the sum of the compounds in the boiling point range of about 70 to 400 °C, but it now defines PHC as the sum of the compounds in the boiling point range of 70 to 490 °C. The method provides options for instrument calibration, including use of synthetic standards, but it recommends use of products similar to the contaminants present at the site of concern. The PHC method has not been specifically incorporated into SW-846; however, the method has been used as the basis for the TPH methods in several states, including Massachusetts, Washington, and Texas. The PHC method uses solvent microextraction and thus has a higher detection limit than the GRO and DRO methods. The PHC method also begins peak integration after elution of the solvent peak for n-pentane. Thus, this method probably cannot measure some volatile compounds (for example, 2-methyl pentane and MTBE) that are measured using the GRO method.

### 1.3.2.3 Definition of TPH

It is not possible to establish a definition of TPH that would include crude oil and its refined products and exclude other organic compounds. Ideally, the TPH definition selected for the demonstration would have

- Included compounds that are PHCs, such as paraffins, naphthenes, and aromatic hydrocarbons
- Included, to the extent possible, the major liquid petroleum products (gasoline, naphthas, kerosene, jet fuels, fuel oils, diesel, and lubricating oils)
- Had little inherent bias based on the composition of an individual manufacturer’s product

- Had little inherent bias based on the relative concentrations of aliphatic and aromatic hydrocarbons present
- Included much of the volatile portion of gasoline, including all weathered gasoline
- Included MTBE
- Excluded crude oil residuals beyond the extended diesel range organic (EDRO) range
- Excluded nonpetroleum organic compounds (for example, chlorinated solvents, pesticides, polychlorinated biphenyls [PCB], and naturally occurring oils and greases)
- Allowed TPH measurement using a widely accepted method
- Reflected accepted TPH measurement practice in many states

Several states, including Massachusetts, Alaska, Louisiana, and North Carolina, have implemented or are planning to implement a TPH contamination cleanup approach based on the aliphatic and aromatic hydrocarbon fractions of TPH. The action levels for the aromatic hydrocarbon fraction are more stringent than those for the aliphatic hydrocarbon fraction. The approach used in the above-mentioned states involves performing a sample fractionation procedure and two analyses to determine the aliphatic and aromatic hydrocarbon concentrations in a sample. However, in most applications of this approach, only a few samples are subjected to the dual aliphatic and aromatic hydrocarbon analyses because of the costs associated with performing sample fractionation and two analyses.

For the demonstration, TPH was not defined based on the aliphatic and aromatic hydrocarbon fractions because

- Such a definition is used in only a few states.
- Variations exist among the sample fractionation and analysis procedures used in different states.

- The repeatability and versatility of sample fractionation and analysis procedures are not well documented.
- In some states, TPH-based action levels are still used.
- The associated analytical costs are high.

As stated in Section 1.3.2.2, analytical methods currently available for measurement of TPH each exclude some portion of TPH and are unable to measure TPH alone while excluding all other organic compounds, thus making TPH a method-defined parameter. After consideration of all the information presented above, the GRO and DRO analytical methods were selected for TPH measurement for the demonstration. However, because of the general interest in higher-boiling-point petroleum products, the integration range of the DRO method was extended to include compounds with boiling points up to 540 °C. Thus, for the demonstration, the TPH concentration was the sum of all organic compounds that have boiling points between 60 and 540 °C and that can be chromatographed, or the sum of the results obtained using the GRO and DRO methods. This approach accounts for most gasoline, including MTBE, and virtually all other petroleum products and excludes a portion (25 to 50 percent) of the heavy lubricating oils. Thus, TPH measurement for the demonstration included PHCs as well as some organic compounds that are not PHCs. More specifically, TPH measurement did not exclude nonpetroleum organic compounds such as chlorinated solvents, other synthetic organic chemicals such as pesticides and PCBs, and naturally occurring oils and greases. A silica gel fractionation step used to remove polar, biogenic compounds such as fatty acids in some GC/FID methods was not included in the sample preparation step because, according to the State of California, this step can also remove some petroleum degradation products that are also polar in nature (California Environmental Protection Agency 1999). The step-by-step approach used to select the reference method for the demonstration and the project-specific procedures implemented for soil sample preparation and analysis using the reference method are detailed in Chapter 5.

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## Chapter 2

### Description of Infrared Analysis and the OCMA-350

Measurement of TPH in soil by field measurement devices generally involves extraction of PHCs from soil using an appropriate solvent followed by measurement of the TPH concentration in the extract using an optical method. An extraction solvent is selected that will not interfere with the optical measurement of TPH in the extract. Some field measurement devices use light in the visible wavelength range, and others use light outside the visible wavelength range (for example, infrared radiation).

The optical measurements made by field measurement devices may involve absorbance, reflectance, or fluorescence. In general, the optical measurement for a soil extract is compared to a calibration curve in order to determine the TPH concentration. Calibration curves may be developed by (1) using a series of calibration standards selected based on the type of PHCs being measured at a site or (2) establishing a correlation between off-site laboratory measurements and field measurements for selected, site-specific soil samples.

Field measurement devices may be categorized as quantitative, semiquantitative, and qualitative. These categories are explained below.

- A **quantitative measurement device** measures TPH concentrations ranging from its reporting limit through its linear range. The measurement result is reported as a single, numerical value that has an established precision and accuracy.
- A **semiquantitative measurement device** measures TPH concentrations above its reporting limit. The measurement result may be reported as a concentration range with lower and upper limits.
- A **qualitative measurement device** indicates the presence or absence of PHCs above or below a

specified value (for example, the reporting limit or an action level).

The OCMA-350 is a field measurement device capable of providing quantitative TPH measurement results. Optical measurements made using the OCMA-350 are based on infrared analysis, which is described in Section 2.1. Section 2.2 describes the OCMA-350 itself, and Section 2.3 provides Horiba contact information. The technology and device descriptions presented below are not intended to provide complete operating procedures for measuring TPH concentrations in soil using the OCMA-350. Detailed operating procedures for the device, including soil extraction, TPH measurement, and TPH concentration calculation procedures, are available from Horiba. Supplemental information provided by Horiba is presented in the appendix.

#### 2.1 Description of Infrared Analysis

This section describes the technology, infrared analysis, upon which the OCMA-350 is based. This technology is suitable for measuring aromatic and aliphatic hydrocarbons independent of their carbon range. TPH measurement using infrared analysis involves extraction of PHCs in soil using an organic solvent. Light in the infrared range is used to irradiate the extract and measure its TPH concentration.

Infrared spectrophotometry generally covers the 1- to 15- $\mu\text{m}$  wavelength region. All organic molecules and some inorganic ions absorb light energy in this region. Absorbance of infrared energy results in changes in vibrational motion in a molecule. The molecular vibrations observed may be divided into two types, stretching and bending. Stretching is the rhythmic movement of the atoms back and forth along the bond axis, whereas bending involves a change in bond angle

between two atoms that are bonded to a third atom or the movement of a group of atoms with respect to the rest of the molecule. Based on the unique absorbance and vibrational motion associated with each compound, the type of compound in a sample can be identified using infrared analysis (Fritz and Schenk 1987).

The energy associated with shorter or near-infrared wavelengths (less than 4  $\mu\text{m}$ ) used for TPH measurement causes mostly stretching vibrations of bonds between hydrogen and heavier atoms. TPH measurement using infrared analysis involves absorbance measurement because the carbon-hydrogen bonds in the hydrocarbons absorb infrared light. During infrared analysis, absorbances associated with  $\text{CH}$ ,  $\text{CH}_2$ , and  $\text{CH}_3$  configurations are measured at a wavelength close to 3,400 nanometers (nm). Specifically, infrared devices that operate in the 3,380- to 3,500-nm wavelength range should be able to measure  $\text{CH}$  (3,380 nm),  $\text{CH}_2$  (3,420 nm), and  $\text{CH}_3$  (3,500 nm) configurations (Simard and others 1951).

Table 2-1 shows the absorbance values of a series of waste oils, refinery products, and pure compounds in samples collected from a wide variety of locations at a petroleum refinery. The absorbance variations shown in Table 2-1 are not great enough to seriously affect sample analytical results when TPH concentrations below 10 milligrams per liter (mg/L) are being measured unless high concentrations of the lower boiling point aromatic hydrocarbons are present. Based on this information, the most serious shortcoming of infrared analysis is likely its inability to detect the lower homologs of the aromatic hydrocarbon series. Because the aromatic C-H absorption is relatively weak, only aromatic hydrocarbons with appreciable paraffin or cycloparaffin side chains exhibit normal behavior during TPH measurement (Simard and others 1951).

During infrared analysis, a sample extract is placed in a glass or quartz cuvette that is then inserted into the spectrophotometer and covered with an opaque light shield. A beam of infrared light is then passed through the sample extract. Infrared sources are generally continuum sources, which emit radiation at intensities that vary smoothly over ranges of wavelengths. A typical example of an infrared source for near-infrared instruments used for TPH measurement is a tungsten lamp (Fritz and Schenk 1987; Ewing 1969).

**Table 2-1. Infrared Absorbance Values of  $\text{CH}$ ,  $\text{CH}_2$ , and  $\text{CH}_3$  Groups**

Sample	Absorbance of 16-Milligram per Liter Sample in Carbon Tetrachloride
<b>Waste oils</b>	
From kerosene treating area	0.424
From gasoline treating area	0.384
From pipe stills and gasoline desulfurization area	0.374
From solvent extraction area	0.415
From thermal cracking area	0.318
From catalytic cracking area	0.355
From wax refining area	0.399
From crude oil handling area	0.409
<b>Refinery products</b>	
Light lubricating oil	0.427
Heavy lubricating oil	0.491
Light Refugio crude oil	0.385
Furnace oil from catalytic cracking	0.339
No. 6 fuel oil	0.287
White oil (medicinal)	0.417
Kerosene	0.440
Gasoline base stock	0.387
<b>Pure compounds</b>	
Cetane	0.615
Isooctane	0.404
n-Heptane	0.613
p-Di-tert-butyl cyclohexane	0.396
Ethyl cyclohexane	0.543
Cyclohexane	0.703
1-Tetradecene	0.427
Decene	0.414
Diisobutylene	0.208
High molecular weight alkyl benzene	0.155
Cumene	0.109
Mixed xylenes	0.070
Benzene	0.000

Source: Simard and others 1951

Some of the infrared radiation emitted by the source is absorbed by compounds in the sample extract, and the rest of the radiation passes through the extract. Absorbance, which is defined as the logarithm of the ratio of the radiant power of the light source to that of the light that passes through the sample extract, is measured by a photoelectric detector in the spectrophotometer (Fritz and Schenk 1987). Absorbance can be calculated using Equation 2-1.

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$$A = \log (I_0/I) \quad (2-1)$$

where

- A = Absorbance
- $I_0$  = Intensity of light source
- I = Intensity of light that passes through the sample extract

Therefore, the intensity of the light that passes through the sample extract is inversely proportional to the concentration of target compounds in the extract, or the intensity of the light absorbed by the extract is directly proportional to the concentration of target compounds in the extract. The absorbance of a sample extract thus measured is directly proportional to the concentration of PHCs present in the extract in accordance with Beer-Lambert's law, which allows Equation 2-1 to be expressed as shown in Equation 2-2.

$$A = Obc \quad (2-2)$$

where

- A = Absorbance
- O = Molar absorptivity (centimeter [cm] per mole per L)
- b = Light path length (cm)
- c = Concentration of absorbing species (mole per L)

Thus, according to Beer-Lambert's law, the absorbance of hydrocarbons is directly proportional to the concentrations of the absorbing hydrocarbons and the path length of the infrared radiation that is not absorbed by the sample extract and passes through the extract. In Equation 2-2, the molar absorptivity is a proportionality constant, which is a characteristic of the absorbing hydrocarbons and changes as the wavelength of the light irradiating the sample extract changes. Therefore, Beer-Lambert's law applies only to monochromatic light (light energy of one wavelength).

After the absorbance of the sample extract is measured, the TPH concentration in the extract can be determined by comparing the absorbance reading to a calibration curve of absorbance values and corresponding hydrocarbon concentrations for a series of known standards selected based on the type of PHCs being measured at a site.

## 2.2 Description of OCMA-350

The OCMA-350 was developed by Horiba and has been commercially available since 1995. This section describes the device and summarizes its operating procedure.

### 2.2.1 Device Description

Infrared analysis using the OCMA-350 involves use of a single-beam, fixed-wavelength, nondispersive infrared (NDIR) spectrophotometer to determine the concentration of PHCs in a liquid sample extract. NDIR spectrophotometers offer several advantages over conventional, scanning infrared spectrophotometers that disperse infrared light using a diffraction grating component. Whereas scanning infrared spectrophotometers take about 1 to 3 minutes to scan a sample and have moderate sensitivity and stability, NDIR spectrophotometers can achieve a stable reading in about 5 seconds and have greater sensitivity and stability (Fritz and Schenk 1987).

In the OCMA-350, infrared radiation from a tungsten lamp is transmitted through a cylindrical, quartz cuvette containing a sample extract. The radiation that has passed through the extract enters a detector containing a filter that isolates analytical wavelengths in the 3,400- to 3,500-nm range. According to Horiba, the OCMA-350 can measure both aromatic and aliphatic hydrocarbons independent of their carbon range. The device's response to aliphatic hydrocarbons is greater than its response to aromatic hydrocarbons.

According to Horiba, several solvents can be used to complete extraction of soil samples for OCMA-350 analysis, including Horiba's proprietary S-316 extraction solvent, Freon 113, tetrachloroethene, and carbon tetrachloride. For the demonstration, Horiba used its proprietary S-316 extraction solvent to extract soil samples. Horiba recommends use of the S-316 extraction solvent because it has a higher boiling point (134 °C) and lower freezing point (-143 °C) than other extraction solvents. In addition, the S-316 extraction solvent is nonflammable, nontoxic, and relatively nonvolatile because of its low vapor pressure.

The OCMA-350 can be used to measure PHC concentrations in soil. Because hydrocarbons absorb infrared radiation, the OCMA-350 responds to their concentrations in sample extracts. Standards of known concentrations can be used to develop a calibration curve

of absorbance versus TPH concentration, that can in turn be used to calculate the TPH concentrations in actual samples. According to Horiba, the OCMA-350 can achieve a method detection limit (MDL) of 1 mg/kg for TPH and is linear up to 1,000 mg/kg in soil. Horiba also claims that the device can achieve repeatability of plus or minus ( $\pm$ ) 2 mg/kg from 0 to 99.9 mg/kg;  $\pm$ 4 mg/kg from 100 to 200 mg/kg; and  $\pm$ 10 mg/kg from 201 to 1,000 mg/kg. No information is currently available from Horiba regarding the accuracy of the device. An evaluation of the MDL, accuracy, and precision achieved by the OCMA-350 during the demonstration is presented in Chapter 7.

According to Horiba, the OCMA-350 has an operating temperature range of 0 to 40 °C and humidity range of 0 to 90 percent. Horiba does not specify a particular storage temperature for the device.

Table 2-2 lists components of the OCMA-350 and supplies that may or may not be required for measuring TPH in soil using the device. The supplies are categorized according to whether or not they are available from Horiba.

Supplies associated with TPH measurement using the OCMA-350 may also be categorized according to whether they are expendable or reusable. Expendable supplies include 10 milliliters (mL) of B-heavy oil that comes with the OCMA-350; S-316 extraction solvent; anhydrous sodium sulfate; 40-mL, volatile organic analysis (VOA) vials; 11-cm-diameter, No. 40 Whatman filter papers; and 10-mL, disposable, glass pipettes. Horiba generally recommends use of B-heavy oil as the default calibration standard when the hydrocarbon content of soil is unknown. According to Horiba, B-heavy oil may be replaced with diesel as the calibration standard based on the contamination at a site.

Reusable supplies include the infrared spectrophotometer and all its accessories except B-heavy oil, Model VC-50 ultrasonic mixer, Model SR-300 solvent reclaimer, Centronics printer cable, printer, balance, stainless-steel spatulas, filter forceps, glass funnels, glass beakers, pipette bulb, 10-microliter ( $\mu$ L) microsyringe, bottle-top dispenser, test tube rack, and funnel rack and stand. Of these reusable supplies, items required for TPH analysis using the OCMA-350 include the balance, stainless-steel spatulas, filter forceps, glass funnels, glass beakers, pipette bulb, test tube rack, and funnel rack and stand; Horiba considers the other items to be optional. During the demonstration, Horiba used the Model GE-50 ultrasonic

**Table 2-2. OCMA-350 Components and Supplies**

**Spectrophotometer and accessories**

- Infrared spectrophotometer
- Proprietary, 10-mm, quartz cuvette with Teflon® cap
- 25- $\mu$ L microsyringe
- 10-mL syringe
- 10 mL of B-heavy oil
- Three 40-mL, volatile organic analysis vials
- Three 11-centimeter-diameter, No. 40 Whatman filter papers
- Two 10-mL, disposable, glass pipettes
- Instruction manual and simplified operating instruction sheet

**Supplies available from Horiba**

- S-316 extraction solvent (1.5- or 7-kg bottle)
- Model VC-50 ultrasonic mixer<sup>a</sup>
- Model SR-300 solvent reclaimer
- Centronics printer cable

**Supplies not available from Horiba**

- Anhydrous sodium sulfate, 10-60 mesh
- Printer
- Balance
- Stainless-steel spatulas
- Filter forceps
- Glass funnels
- Glass beakers
- Pipette bulb
- 10- $\mu$ L microsyringe
- Bottle-top dispenser
- Test tube rack
- Funnel rack and stand

Notes:

$\mu$ L = Microliter                      mL = Milliliter  
 kg = Kilogram                        mm = Millimeter

<sup>a</sup> During the demonstration, Horiba used the Model GE-50 ultrasonic mixer, which is no longer available from the developer. According to Horiba, the Model GE-50 and VC-50 ultrasonic mixers are functionally the same.

mixer, which is no longer available from the developer. According to Horiba, the Model VC-50 ultrasonic mixer that is currently available is functionally the same as Model GE-50.

The OCMA-350 infrared spectrophotometer and its accessories come in an optional, hard-plastic carrying case and weigh 36 pounds. The carrying case is 22 inches long, 16 inches wide, and 15 inches high. The device can be operated using a 110- or 220-volt alternating current (AC) power source. It may also be operated using a direct current (DC) power source such as a 12-volt power outlet in an automobile along with a DC/AC power inverter. During the demonstration, Horiba operated the OCMA-350 using AC power from the demonstration field trailer.

The spectrophotometer presents results in units selected by the user during calibration, such as mg/kg in soil or

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absorbance values. During the demonstration, Horiba programmed the spectrophotometer to present results as mg/kg in soil. The spectrophotometer is also equipped with a parallel printer port and an RS232-C data port to allow transfer of data to a computer or other data logger. The spectrophotometer keeps a record of the time and date of each measurement and a record of each data set that it generates. Spectrophotometer printouts contain the time and date of each measurement along with the concentration or absorbance value, which facilitates recordkeeping.

According to Horiba, about 20 samples can be analyzed by one field technician using the OCMA-350 over an 8-hour period. The device is relatively easy to use. Normal training for using the device is limited to reading the instruction manual and simplified operating instruction sheet. Horiba offers a 1-day training course covering operation, maintenance, and service of the OCMA-350, but according to the developer, purchasers of the device rarely request this training. Horiba also provides technical support over the telephone during regular business hours at no additional cost.

According to Horiba, the OCMA-350 is innovative because it can reuse proprietary S-316 extraction solvent that has been recycled by the Model SR-300 solvent reclaimer. According to Horiba, the reuse of this extraction solvent can reduce solvent costs by up to 90 percent.

### **2.2.2 Operating Procedure**

The OCMA-350 is calibrated using known standards. Horiba generally recommends use of B-heavy oil, which

is provided with the OCMA-350, as the default calibration standard when the hydrocarbon content of soil is unknown. Based on the results of the predemonstration investigation, Horiba used diesel as the calibration standard for the demonstration. Horiba conducted a three-point calibration using S-316 extraction solvent as a blank and 100- and 200-mg/L diesel standards at the beginning and end of each day and after every batch of samples was analyzed. Concrete sand was also used as a sample blank for a calibration check once a day.

During the demonstration, Horiba dried soil by adding anhydrous sodium sulfate. Extraction of a given soil sample was typically performed by adding 20 mL of S-316 extraction solvent to 5.0 grams of the sample. The mixture was agitated using the Model GE-50 ultrasonic mixer. The sample extract was decanted into a beaker through a filter-lined funnel, and then the filtrate was poured into a quartz cuvette. The cuvette was placed in the spectrophotometer for TPH measurement. Horiba pressed the "Run" button and read the concentration on the digital display.

## **2.3 Developer Contact Information**

Additional information about the OCMA-350 can be obtained from the following source:

Horiba Instruments Incorporated  
Mr. Jim Vance  
17671 Armstrong Avenue  
Irvine, CA 92614  
Telephone: (800) 4HORIBA, extension 170  
Fax: (949) 250-0924  
E-mail: jim.vance@horiba.com  
Internet: www.horiba.com



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## Chapter 3

### Demonstration Site Descriptions

This chapter describes the three sites selected for conducting the demonstration. The first site is referred to as the Navy BVC site; it is located in Port Hueneme, California, and contains three sampling areas. The second site is referred to as the Kelly AFB site; it is located in San Antonio, Texas, and contains one sampling area. The third site is referred to as the PC site; it is located in north-central Indiana and contains one sampling area. After review of the information available on these and other candidate sites, the Navy BVC, Kelly AFB, and PC sites were selected based on the following criteria:

- **Site Diversity**—Collectively, the three sites contained sampling areas with the different soil types and the different levels and types of PHC contamination needed to evaluate the seven field measurement devices selected for the demonstration.
- **Access and Cooperation**—The site representatives were interested in supporting the demonstration by providing site access for collection of soil samples required for the demonstration. In addition, the field measurement devices were to be demonstrated at the Navy BVC site using soil samples from all three sites, and the Navy BVC site representatives were willing to provide the site support facilities required for the demonstration and to support a visitors' day during the demonstration. As a testing location for the Department of Defense National Environmental Technology Test Site program, the Navy BVC site is used to demonstrate technologies and systems for characterizing or remediating soil, sediment, and groundwater contaminated with fuel hydrocarbons or waste oil.

To ensure that the sampling areas were selected based on current site characteristics, a predemonstration

investigation was conducted. During this investigation, samples were collected from the five candidate areas and were analyzed for GRO and EDRO using SW-846 Method 8015B (modified) by the reference laboratory, Severn Trent Laboratories in Tampa, Florida (STL Tampa East). The site descriptions in Sections 3.1 through 3.3 are based on data collected during predemonstration investigation sampling activities, data collected during demonstration sampling activities, and information provided by the site representatives. Physical characterization of samples was performed in the field by a geologist during both predemonstration investigation and demonstration activities.

Some of the predemonstration investigation samples were also analyzed by the OCMA-350 developer, Horiba, at its facility. Horiba used reference laboratory and OCMA-350 results to gain a preliminary understanding of the demonstration samples and to prepare for the demonstration.

Table 3-1 summarizes key site characteristics, including the contamination type, sampling depth intervals, TPH concentration ranges, and soil type in each sampling area. The TPH concentration ranges and soil types presented in Table 3-1 and throughout this report are based on reference laboratory TPH results for demonstration samples and soil characterization completed during the demonstration, respectively. TPH concentration range and soil type information obtained during the demonstration was generally consistent with the information obtained during the predemonstration investigation except for the B-38 Area at Kelly AFB. Additional information on differences between demonstration and predemonstration investigation activities and results is presented in Section 3.2.

**Table 3-1. Summary of Site Characteristics**

Site	Sampling Area	Contamination Type <sup>a</sup>	Approximate Sampling Depth Interval (foot bgs)	TPH Concentration Range (mg/kg)	Type of Soil
Navy Base Ventura County	Fuel Farm Area	EDRO (weathered diesel with carbon range from n-C <sub>10</sub> through n-C <sub>40</sub> )	Upper layer <sup>b</sup>	44.1 to 93.7	Medium-grained sand
			Lower layer <sup>b</sup>	8,090 to 15,000	
	Naval Exchange Service Station Area	GRO and EDRO (fairly weathered gasoline with carbon range from n-C <sub>6</sub> through n-C <sub>14</sub> )	7 to 8	28.1 to 280	Medium-grained sand
			8 to 9	144 to 2,570	
			9 to 10	617 to 3,030	
			10 to 11	9.56 to 293	
	Phytoremediation Area	EDRO (heavy lubricating oil with carbon range from n-C <sub>14</sub> through n-C <sub>40+</sub> )	1.5 to 2.5	1,130 to 2,140	Silty sand
Kelly Air Force Base	B-38 Area	GRO and EDRO (fresh gasoline and diesel or weathered gasoline and trace amounts of lubricating oil with carbon range from n-C <sub>6</sub> through n-C <sub>40</sub> )	23 to 25	43.8 to 193	Sandy clay or silty sand and gravel in upper depth interval and clayey sand and gravel in deeper depth interval
			25 to 27	41.5 to 69.4	
Petroleum company	Slop Fill Tank Area	GRO and EDRO (combination of slightly weathered gasoline, kerosene, JP-5, and diesel with carbon range from n-C <sub>5</sub> through n-C <sub>32</sub> )	2 to 4	6.16 to 3,300	Silty clay with traces of sand and gravel in deeper depth intervals
			4 to 6	37.1 to 3,960	
			6 to 8	43.9 to 1,210	
			8 to 10	52.4 to 554	

Notes:

bgs = Below ground surface  
 mg/kg = Milligram per kilogram

- <sup>a</sup> The beginning or end point of the carbon range identified as "n-C<sub>x</sub>" represents an alkane marker consisting of "x" carbon atoms on a gas chromatogram.
- <sup>b</sup> Because of soil conditions encountered in the Fuel Farm Area, the sampling depth intervals could not be accurately determined. Sample collection was initiated approximately 10 feet bgs, and attempts were made to collect 4-foot-long soil cores. This approach resulted in varying degrees of core tube penetration up to 17 feet bgs. At each location in the area, the sample cores were divided into two samples based on visual observations. The upper layer of the soil core, which consisted of yellowish-brown, medium-grained sand, made up one sample, and the lower layer of the soil core, which consisted of grayish-black, medium-grained sand and smelled of hydrocarbons, made up the second sample.

### 3.1 Navy Base Ventura County Site

The Navy BVC site in Port Hueneme, California, covers about 1,600 acres along the south California coast. Three areas at the Navy BVC site were selected as sampling areas for the demonstration: (1) the Fuel Farm Area (FFA), (2) the Naval Exchange (NEX) Service Station Area, and (3) the Phytoremediation Area (PRA). These areas are briefly described below.

#### 3.1.1 Fuel Farm Area

The FFA is a tank farm in the southwest corner of the Navy BVC site. The area contains five tanks and was constructed to refuel ships and to supply heating fuel for

the Navy BVC site. Tank No. 5114 along the south edge of the FFA was used to store marine diesel. After Tank No. 5114 was deactivated in 1991, corroded pipelines leading into and out of the tank leaked and contaminated the surrounding soil with diesel.

The horizontal area of contamination in the FFA was estimated to be about 20 feet wide and 90 feet long. Demonstration samples were collected within several inches of the three predemonstration investigation sampling locations in the FFA using a Geoprobe<sup>®</sup>. Samples were collected at the three locations from east to west and about 5 feet apart. During the demonstration, soil in the area was found to generally consist of medium-grained sand, and the soil cores contained two distinct

layers. The upper layer consisted of yellowish-brown, medium-grained sand with no hydrocarbon odor and TPH concentrations ranging from 44.1 to 93.7 mg/kg; the upper layer's TPH concentration range during the predemonstration investigation was 38 to 470 mg/kg. The lower layer consisted of grayish-black, medium-grained sand with a strong hydrocarbon odor and TPH concentrations ranging from 8,090 to 15,000 mg/kg; the lower layer's TPH concentration range during the predemonstration investigation was 7,700 to 11,000 mg/kg.

Gas chromatograms from the predemonstration investigation and the demonstration showed that FFA soil samples contained (1) weathered diesel, (2) hydrocarbons in the n-C<sub>10</sub> through n-C<sub>28</sub> carbon range with the hydrocarbon hump maximizing at n-C<sub>17</sub>, and (3) hydrocarbons in the n-C<sub>12</sub> through n-C<sub>40</sub> carbon range with the hydrocarbon hump maximizing at n-C<sub>20</sub>.

### **3.1.2 Naval Exchange Service Station Area**

The NEX Service Station Area lies in the northeast portion of the Navy BVC site. About 11,000 gallons of regular and unleaded gasoline was released from UST lines in this area between September 1984 and March 1985. Although the primary soil contaminant in this area is gasoline, EDRO is also of concern because (1) another spill north of the area may have resulted in a commingled plume of gasoline and diesel and (2) a significant portion of weathered gasoline is associated with EDRO.

The horizontal area of contamination in the NEX Service Station Area was estimated to be about 450 feet wide and 750 feet long. During the demonstration, samples were collected at the three predemonstration investigation sampling locations in the NEX Service Station Area from south to north and about 60 feet apart using a Geoprobe®. Soil in the area was found to generally consist of (1) brownish-black, medium-grained sand in the uppermost depth interval and (2) grayish-black, medium-grained sand in the three deeper depth intervals. Traces of coarse sand were also present in the deepest depth interval. Soil samples collected from the area had a strong hydrocarbon odor. The water table in the area was encountered at about 9 feet below ground surface (bgs). During the demonstration, TPH concentrations ranged from 28.1 to 280 mg/kg in the 7- to 8-foot bgs depth interval; 144 to 3,030 mg/kg in the 8- to 9- and 9- to 10-foot bgs depth intervals; and 9.56 to 293 mg/kg in the 10-

to 11-foot bgs depth interval. During the predemonstration investigation, the TPH concentrations in the (1) top two depth intervals (7 to 8 and 8 to 9 feet bgs) ranged from 25 to 65 mg/kg and (2) bottom depth interval (10 to 11 feet bgs) ranged from 24 to 300 mg/kg.

Gas chromatograms from the predemonstration investigation and the demonstration showed that NEX Service Station Area soil samples contained (1) fairly weathered gasoline with a high aromatic hydrocarbon content and (2) hydrocarbons in the n-C<sub>6</sub> through n-C<sub>14</sub> carbon range. Benzene, toluene, ethylbenzene, and xylene (BTEX) analytical results for predemonstration investigation samples from the 9- to 10-foot bgs depth interval at the middle sampling location revealed a concentration of 347 mg/kg; BTEX made up 39 percent of the total GRO and 27 percent of the TPH at this location. During the predemonstration investigation, BTEX analyses were conducted at the request of a few developers to estimate the aromatic hydrocarbon content of the GRO; such analyses were not conducted for demonstration samples.

### **3.1.3 Phytoremediation Area**

The PRA lies north of the FFA and west of the NEX Service Station Area at the Navy BVC site. The PRA consists of soil from a fuel tank removal project conducted at the Naval Weapons Station in Seal Beach, California. The area is contained within concrete railings and is 60 feet wide, 100 feet long, and about 3 feet deep. It consists of 12 cells of equal size (20 by 25 feet) that have three different types of cover: (1) unvegetated cover, (2) a grass and legume mix, and (3) a native grass mix. There are four replicate cells of each cover type.

In the PRA, demonstration samples were collected from the 1.5- to 2.5-foot bgs depth interval within several inches of the six predemonstration investigation sampling locations using a split-core sampler. During the demonstration, soil at four adjacent sampling locations was found to generally consist of dark yellowish-brown, silty sand with some clay and no hydrocarbon odor. Soil at the two remaining adjacent sampling locations primarily consisted of dark yellowish-brown, clayey sand with no hydrocarbon odor, indicating the absence of volatile PHCs. The TPH concentrations in the demonstration samples ranged from 1,130 to 2,140 mg/kg; the TPH concentrations in the predemonstration investigation samples ranged from 1,500 to 2,700 mg/kg.

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Gas chromatograms from the predemonstration investigation and the demonstration showed that PRA soil samples contained (1) heavy lubricating oil and (2) hydrocarbons in the n-C<sub>14</sub> through n-C<sub>40+</sub> carbon range with the hydrocarbon hump maximizing at n-C<sub>32</sub>.

### 3.2 Kelly Air Force Base Site

The Kelly AFB site covers approximately 4,660 acres and is about 7 miles from the center of San Antonio, Texas. One area at Kelly AFB, the B-38 Area, was selected as a sampling area for the demonstration. The B-38 Area lies along the east boundary of Kelly AFB and is part of an active UST farm that serves the government vehicle refueling station at the base. In December 1992, subsurface soil contamination resulting from leaking diesel and gasoline USTs and associated piping was discovered in this area during UST removal and upgrading activities.

The B-38 Area was estimated to be about 150 square feet in size. Based on discussions with site representatives, predemonstration investigation samples were collected in the 13- to 17- and 29- to 30-foot bgs depth intervals at four locations in the area using a Geoprobe<sup>®</sup>. Based on historical information, the water table in the area fluctuates between 16 and 24 feet bgs. During the predemonstration investigation, soil in the area was found to generally consist of (1) clayey silt in the upper depth interval above the water table with a TPH concentration of 9 mg/kg and (2) sandy clay with significant gravel in the deeper depth interval below the water table with TPH concentrations ranging from 9 to 18 mg/kg. Gas chromatograms from the predemonstration investigation showed that B-38 Area soil samples contained (1) heavy lubricating oil and (2) hydrocarbons in the n-C<sub>24</sub> through n-C<sub>30</sub> carbon range.

Based on the low TPH concentrations and the type of contamination detected during the predemonstration investigation as well as discussions with site representatives who indicated that most of the contamination in the B-38 Area can be found at or near the water table, demonstration samples were collected near the water table. During the demonstration, the water table was 24 feet bgs. Therefore, the demonstration samples were collected in the 23- to 25- and 25- to 27-foot bgs depth intervals at three locations in the B-38 Area using a Geoprobe<sup>®</sup>. Air Force activities in the area during the demonstration prevented the sampling team from

accessing the fourth location sampled during the predemonstration investigation.

During the demonstration, soil in the area was found to generally consist of (1) sandy clay or silty sand and gravel in the upper depth interval with a TPH concentration between 43.8 and 193 mg/kg and (2) clayey sand and gravel in the deeper depth interval with TPH concentrations between 41.5 and 69.4 mg/kg. Soil samples collected in the area had little or no hydrocarbon odor. Gas chromatograms from the demonstration showed that B-38 Area soil samples contained either (1) fresh gasoline, diesel, and hydrocarbons in the n-C<sub>6</sub> through n-C<sub>25</sub> carbon range with the hydrocarbon hump maximizing at n-C<sub>17</sub>; (2) weathered gasoline with trace amounts of lubricating oil and hydrocarbons in the n-C<sub>6</sub> through n-C<sub>30</sub> carbon range with a hydrocarbon hump representing the lubricating oil between n-C<sub>20</sub> and n-C<sub>30</sub>; or (3) weathered gasoline with trace amounts of lubricating oil and hydrocarbons in the n-C<sub>6</sub> through n-C<sub>40</sub> carbon range with a hydrocarbon hump representing the lubricating oil maximizing at n-C<sub>31</sub>.

### 3.3 Petroleum Company Site

One area at the PC site in north-central Indiana, the Slop Fill Tank (SFT) Area, was selected as a sampling area for the demonstration. The SFT Area lies in the west-central portion of the PC site and is part of an active fuel tank farm. Although the primary soil contaminant in this area is gasoline, EDRO is also of concern because of a heating oil release that occurred north of the area.

The SFT Area was estimated to be 20 feet long and 20 feet wide. In this area, demonstration samples were collected from 2 to 10 feet bgs at 2-foot depth intervals within several inches of the five predemonstration investigation sampling locations using a Geoprobe<sup>®</sup>. Four of the sampling locations were spaced 15 feet apart to form the corners of a square, and the fifth sampling location was at the center of the square. During the demonstration, soil in the area was found to generally consist of brown to brownish-gray, silty clay with traces of sand and gravel in the deeper depth intervals. Demonstration soil samples collected in the area had little or no hydrocarbon odor. During the demonstration, soil in the three upper depth intervals had TPH concentrations ranging from 6.16 to 3,960 mg/kg, and soil in the deepest depth interval had TPH concentrations ranging from 52.4 to 554 mg/kg. During the predemonstration investigation, soils in the

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three upper depth intervals and the deepest depth interval had TPH concentrations ranging from 27 to 1,300 mg/kg and from 49 to 260 mg/kg, respectively.

Gas chromatograms from the predemonstration investigation and the demonstration showed that SFT Area soil samples contained (1) slightly weathered gasoline, kerosene, JP-5, and diesel and (2) hydrocarbons in the n-C<sub>5</sub> through n-C<sub>20</sub> carbon range. There was also evidence of an unidentified petroleum product containing hydrocarbons in the n-C<sub>24</sub> through n-C<sub>32</sub> carbon range.

BTEX analytical results for predemonstration investigation samples from the deepest depth interval revealed concentrations of 26, 197, and 67 mg/kg at the northwest, center, and southwest sampling locations, respectively. At the northwest location, BTEX made up 13 percent of the total GRO and 5 percent of the TPH. At the center location, BTEX made up 16 percent of the total GRO and 7 percent of the TPH. At the southwest location, BTEX made up 23 percent of the total GRO and 18 percent of the TPH. BTEX analyses were not conducted for demonstration samples.

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## Chapter 4 Demonstration Approach

This chapter presents the objectives (Section 4.1), design (Section 4.2), and sample preparation and management procedures (Section 4.3) for the demonstration.

### 4.1 Demonstration Objectives

The primary goal of the SITE MMT Program is to develop reliable performance and cost data on innovative, field-ready technologies. A SITE demonstration must provide detailed and reliable performance and cost data so that potential technology users have adequate information to make sound judgments regarding an innovative technology's applicability to a specific site and to compare the technology to conventional technologies.

The demonstration had both primary and secondary objectives. Primary objectives were critical to the technology evaluation and required the use of quantitative results to draw conclusions regarding a technology's performance. Secondary objectives pertained to information that was useful but did not necessarily require the use of quantitative results to draw conclusions regarding a technology's performance.

The primary objectives for the demonstration of the individual field measurement devices were as follows:

- P1. Determine the MDL
- P2. Evaluate the accuracy and precision of TPH measurement for a variety of contaminated soil samples
- P3. Evaluate the effect of interferences on TPH measurement
- P4. Evaluate the effect of soil moisture content on TPH measurement

- P5. Measure the time required for TPH measurement
- P6. Estimate costs associated with TPH measurement

The secondary objectives for the demonstration of the individual field measurement devices were as follows:

- S1. Document the skills and training required to properly operate the device
- S2. Document health and safety concerns associated with operating the device
- S3. Document the portability of the device
- S4. Evaluate the durability of the device based on its materials of construction and engineering design
- S5. Document the availability of the device and associated spare parts

The objectives for the demonstration were developed based on input from MMT Program stakeholders, general user expectations of field measurement devices, characteristics of the demonstration areas, the time available to complete the demonstration, and device capabilities that the developers intended to highlight.

### 4.2 Demonstration Design

A predemonstration sampling and analysis investigation was conducted to assess existing conditions and confirm available information on physical and chemical characteristics of soil in each demonstration area. Based on information from the predemonstration investigation as well as available historical data, a demonstration design was developed to address the demonstration objectives. Input regarding the demonstration design was obtained

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from the developers and demonstration site representatives. The demonstration design is summarized below.

The demonstration involved analysis of soil environmental samples, soil performance evaluation (PE) samples, and liquid PE samples. The environmental samples were collected from three contaminated sites, and the PE samples were obtained from a commercial provider, Environmental Resource Associates (ERA) in Arvada, Colorado. Collectively, the environmental and PE samples provided the different matrix types and the different levels and types of PHC contamination needed to perform a comprehensive demonstration.

The environmental samples were soil core samples collected from the demonstration areas at the Navy BVC, Kelly AFB, and PC sites described in Chapter 3. The soil core samples collected at the Kelly AFB and PC sites were shipped to the Navy BVC site 5 days prior to the start of the field analysis activities. Each soil core sample collected from a specific depth interval at a particular sampling location in a given area was homogenized and placed in individual sample containers. Soil samples were then provided to the developers and reference laboratory. In addition, the PE samples were obtained from ERA for distribution to the developers and reference laboratory. Field analysis of all environmental and PE samples was conducted near the PRA at the Navy BVC site.

The field measurement devices were evaluated based primarily on how they compared with the reference method selected for the demonstration. PE samples were used to verify that reference method performance was acceptable. However, for the comparison with the device results, the reference method results were not adjusted based on the recoveries observed during analysis of the PE samples.

The sample collection and homogenization procedures may have resulted in GRO losses of up to one order of magnitude in environmental samples. Despite any such losses, the homogenized samples were expected to contain sufficient levels of GRO to allow demonstration objectives to be achieved. Moreover, the environmental sample collection and homogenization procedures implemented during the demonstration ensured that the developers and reference laboratory received the same sample material for analysis, which was required to allow meaningful

comparisons of field measurement device and reference method results.

To facilitate effective use of available information on both the environmental and PE samples during the demonstration, the developers and reference laboratory were informed of (1) whether each sample was an environmental or PE sample, (2) the area where each environmental sample was collected, and (3) the contamination type and concentration range of each sample. This information was included in each sample identification number. Each sample was identified as having a low (less than 100 mg/kg), medium (100 to 1,000 mg/kg), or high (greater than 1,000 mg/kg) TPH concentration range. The concentration ranges were based primarily on predemonstration investigation results or the amount of weathered gasoline or diesel added during PE sample preparation. The concentration ranges were meant to be used only as a guide by the developers and reference laboratory. The gasoline used for PE sample preparation was 50 percent weathered; the weathering was achieved by bubbling nitrogen gas into a known volume of gasoline until the volume was reduced by 50 percent. Some PE samples also contained interferents specifically added to evaluate the effect of interferents on TPH measurement. The type of contamination and expected TPH concentration ranges were identified; however, the specific compounds used as interferents were not identified. All PE samples were prepared in triplicate as separate, blind samples.

During the demonstration, a Horiba field technician operated the OCMA-350, and EPA representatives made observations to evaluate the device. All the developers were given the opportunity to choose not to analyze samples collected in a particular area or a particular class of samples, depending on the intended uses of their devices. Horiba chose to analyze all the demonstration samples.

Details of the approach used to address the primary and secondary objectives for the demonstration are presented in Sections 4.2.1 and 4.2.2, respectively.

#### ***4.2.1 Approach for Addressing Primary Objectives***

This section presents the approach used to address each primary objective.

### Primary Objective P1: Method Detection Limit

To determine the MDL for each field measurement device, low-concentration-range soil PE samples containing weathered gasoline or diesel were to be analyzed. The low-range PE samples were prepared using Freon 113, which facilitated preparation of homogenous samples. The target concentrations of the PE samples were set to meet the following criteria: (1) at the minimum acceptable recoveries set by ERA, the samples contained measurable TPH concentrations, and (2) when feasible, the sample TPH concentrations were generally between 1 and 10 times the MDLs claimed by the developers and the reference laboratory, as recommended by 40 *Code of Federal Regulations* (CFR) Part 136, Appendix B, Revision 1.1.1. Horiba and the reference laboratory analyzed seven weathered gasoline and seven diesel PE samples to statistically determine the MDLs for GRO and EDRO soil samples. However, during the preparation of low-range weathered gasoline PE samples, significant volatilization of PHCs occurred because of the matrix used for preparing these samples. Because of the problems associated with preparation of low-range weathered gasoline PE samples, the results for these samples could not be used to determine the MDLs.

### Primary Objective P2: Accuracy and Precision

To estimate the accuracy and precision of each field measurement device, both environmental and PE samples

were analyzed. The evaluation of analytical accuracy was based on the assumption that a field measurement device may be used to (1) determine whether the TPH concentration in a given area exceeds an action level or (2) perform a preliminary characterization of soil in a given area. To evaluate whether the TPH concentration in a soil sample exceeded an action level, the developers and reference laboratory were asked to determine whether TPH concentrations in a given area or PE sample type exceeded the action levels listed in Table 4-1. The action levels chosen for environmental samples were based on the predemonstration investigation analytical results and state action levels. The action levels chosen for the PE samples were based in part on the ERA acceptance limits for PE samples; therefore, each PE sample was expected to have at least the TPH concentration indicated in Table 4-1. However, because of the problems associated with preparation of the low-concentration-range weathered gasoline PE samples, the results for these samples could not be used to address primary objective P2.

In addition, neat (liquid) samples of weathered gasoline and diesel were analyzed by the developers and reference laboratory to evaluate accuracy and precision. Because extraction of the neat samples was not necessary, the results for these samples provided accuracy and precision information strictly associated with the analyses and were not affected by extraction procedures.

**Table 4-1. Action Levels Used to Evaluate Analytical Accuracy**

Site	Area	Typical TPH Concentration Range <sup>a</sup>	Action Level (mg/kg)
Navy Base Ventura County	Fuel Farm Area	Low and high	100
	NEX Service Station Area	Low to high	50
	Phytoremediation Area	High	1,500
Kelly Air Force Base	B-38 Area	Low	100
Petroleum company	Slop Fill Tank Area	Medium	500
Performance evaluation samples (GRO analysis)		Medium	200
		High	2,000
Performance evaluation samples (EDRO analysis)		Low	15
		Medium	200
		High	2,000

Notes:

mg/kg = Milligram per kilogram

<sup>a</sup> The typical TPH concentration ranges shown cover all the depth intervals in each area. Table 4-2 shows the depth intervals that were sampled in each area and the typical TPH concentration range for each depth interval. The action level for each area was used as the basis for evaluating sample analytical results regardless of the typical TPH concentration ranges for the various depth intervals.



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Sample TPH results obtained using each field measurement device and the reference method were compared to the action levels presented in Table 4-1 in order to determine whether sample TPH concentrations were above the action levels. The results obtained using the device and reference method were compared to determine how many times the device's results agreed with those of the reference method for a particular area or sample type. In addition, the ratio of the TPH results of a given device to the TPH results of the reference method was calculated. The ratio was used to develop a frequency distribution in order to determine how many of the device and reference method results were within 30 percent, within 50 percent, and outside the 50 percent window.

To complete a preliminary characterization of soil in a given area using a field measurement device, the user may have to demonstrate to a regulatory agency that (1) no statistically significant difference exists between the results of the laboratory method selected for the project (the reference method) and the device results, indicating that the device may be used as a substitute for the laboratory method, or (2) a consistent correlation exists between the device and laboratory method results, indicating that the device results can be adjusted using the established correlation.

To evaluate whether a statistically significant difference existed between a given field measurement device and the reference method results, a two-tailed, paired Student's t-test was performed. To determine whether a consistent correlation existed between the TPH results of a given field measurement device and the reference method, a linear regression was performed to estimate the square of the correlation coefficient ( $R^2$ ), the slope, and the intercept of each regression equation. Separate regression equations were developed for each demonstration area and for the PE samples that did not contain interferents. The reliability of the regression equations was tested using the F-test; the regression equation probability derived from the F-test was used to evaluate whether the correlation between the TPH results of the device and the reference method occurred merely by chance.

To evaluate analytical precision, one set of blind field triplicate environmental samples was collected from each depth interval at one location in each demonstration area except the B-38 Area, where site conditions allowed collection of triplicates in the top depth interval only. Blind triplicate low-, medium-, and high-concentration-range PE samples were also used to evaluate analytical

precision because TPH concentrations in environmental samples collected during the demonstration sometimes differed from the analytical results for predemonstration investigation samples. The low- and medium-range PE samples were prepared using Freon 113 as a carrier, which facilitated preparation of homogenous samples.

Additional information regarding analytical precision was collected by having the developers and reference laboratory analyze extract duplicates. Extract duplicates were prepared by extracting a soil sample once and collecting two aliquots of the extract. For environmental samples, one sample from each depth interval was designated as an extract duplicate. Each sample designated as an extract duplicate was collected from a location where field triplicates were collected. To evaluate a given field measurement device's ability to precisely measure TPH, the relative standard deviation (RSD) of the device and reference method TPH results for triplicate samples was calculated. In addition, to evaluate the analytical precision of the device and reference method, the relative percent difference (RPD) was calculated using the TPH results for extract duplicates.

### **Primary Objective P3: Effect of Interferents**

To evaluate the effect of interferents on each field measurement device's ability to accurately measure TPH, high-concentration-range soil PE samples containing weathered gasoline or diesel with or without an interferent were analyzed. As explained in Chapter 1, the definition of TPH is quite variable. For the purposes of addressing primary objective P3, the term "interferent" is used in a broad sense and is applied to both PHC and non-PHC compounds. The six different interferents evaluated during the demonstration were MTBE; tetrachloroethene (PCE); Stoddard solvent; turpentine (an alpha and beta pinene mixture); 1,2,4-trichlorobenzene; and humic acid. The boiling points and vapor pressures of (1) MTBE and PCE are similar to those of GRO; (2) Stoddard solvent and turpentine are similar to those of GRO and EDRO; and (3) 1,2,4-trichlorobenzene and humic acid are similar to those of EDRO. The solubility, availability, and cost of the interferents were also considered during interferent selection. Specific reasons for the selection of the six interferents are presented below.

- MTBE is an oxygenated gasoline additive that is detected in the GRO analysis during TPH measurement using a GC.

- PCE is not a petroleum product but is detected in the GRO analysis during TPH measurement using a GC. PCE may also be viewed as a typical halogenated solvent that may be present in some environmental samples.
- Stoddard solvent is an aliphatic naphtha compound with a carbon range of n-C<sub>8</sub> through n-C<sub>14</sub> and is partly detected in both the GRO and EDRO analyses during TPH measurement using a GC.
- Turpentine is not a petroleum product but has a carbon range of n-C<sub>9</sub> through n-C<sub>15</sub> and is partly detected in both the GRO and EDRO analyses during TPH measurement using a GC. Turpentine may also be viewed as a substance that behaves similarly to a typical naturally occurring oil or grease during TPH measurement using a GC.
- The compound 1,2,4-trichlorobenzene is not a petroleum product but is detected in the EDRO analysis. This compound may also be viewed as a typical halogenated semivolatile organic compound that behaves similarly to a chlorinated pesticide or PCB during TPH measurement using a GC.
- Humic acid is a hydrocarbon mixture that is representative of naturally occurring organic carbon in soil and was suspected to be detected during EDRO analysis.

Based on the principles of operation of the field measurement devices, several of the interferents were suspected to be detected by the devices.

The PE samples containing MTBE and PCE were not prepared with diesel and the PE samples containing 1,2,4-trichlorobenzene and humic acid were not prepared with weathered gasoline because these interferents were not expected to impact the analyses and because practical difficulties such as solubility constraints were associated with preparation of such samples.

Appropriate control samples were also prepared and analyzed to address primary objective P3. These samples included processed garden soil, processed garden soil and weathered gasoline, processed garden soil and diesel, and processed garden soil and humic acid samples. Because of solubility constraints, control samples containing MTBE; PCE; Stoddard solvent; turpentine; or 1,2,4-trichlorobenzene could not be prepared. Instead, neat

(liquid) samples of these interferents were prepared and used as quasi-control samples to evaluate the effect of each interferent on the field measurement device and reference method results. Each PE sample was prepared in triplicate and submitted to the developers and reference laboratory as blind triplicate samples.

To evaluate the effects of interferents on a given field measurement device's ability to accurately measure TPH under primary objective P3, the means and standard deviations of the TPH results for triplicate PE samples were calculated. The mean for each group of samples was qualitatively evaluated to determine whether the data showed any trend—that is, whether an increase in the interferent concentration resulted in an increase or decrease in the measured TPH concentration. A one-way analysis of variance was performed to determine whether the group means were the same or different.

#### **Primary Objective P4: Effect of Soil Moisture Content**

To evaluate the effect of soil moisture content, high-concentration-range soil PE samples containing weathered gasoline or diesel were analyzed. PE samples containing weathered gasoline were prepared at two moisture levels: 9 percent moisture and 16 percent moisture. PE samples containing diesel were also prepared at two moisture levels: negligible moisture (less than 1 percent) and 9 percent moisture. All the moisture levels were selected based on the constraints associated with sample preparation. For example, 9 percent moisture represents the minimum moisture level for containerizing samples in EnCores and 16 percent moisture represents the saturation level of the soil used to prepare PE samples. Diesel samples with negligible moisture could be prepared because they did not require EnCores for containerization; based on vapor pressure data for diesel and weathered gasoline, 4-ounce jars were considered to be appropriate for containerizing diesel samples but not for containerizing weathered gasoline samples. Each PE sample was prepared in triplicate.

To measure the effect of soil moisture content on a given field measurement device's ability to accurately measure TPH under primary objective P4, the means and standard deviations of the TPH results for triplicate PE samples containing weathered gasoline and diesel at two moisture levels were calculated. A two-tailed, two-sample Student's t-test was performed to determine whether the device and reference method results were impacted by moisture—that is, to determine whether an increase in

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moisture resulted in an increase or decrease in the TPH concentrations measured.

#### **Primary Objective P5: Time Required for TPH Measurement**

The sample throughput (the number of TPH measurements per unit of time) was determined for each field measurement device by measuring the time required for each activity associated with TPH measurement, including device setup, sample extraction, sample analysis, and data package preparation. The EPA provided each developer with investigative samples stored in coolers. The developer unpacked the coolers and checked the chain-of-custody forms to verify that it had received the correct samples. Time measurement began when the developer began to set up its device. The total time required to complete analysis of all investigative samples was recorded. Analysis was considered to be complete and time measurement stopped when the developer provided the EPA with a summary table of results, a run log, and any supplementary information that the developer chose. The summary table listed all samples analyzed and their respective TPH concentrations.

For the reference laboratory, the total analytical time began to be measured when the laboratory received all the investigative samples, and time measurement continued until the EPA representatives received a complete data package from the laboratory.

#### **Primary Objective P6: Costs Associated with TPH Measurement**

To estimate the costs associated with TPH measurement for each field measurement device, the following five cost categories were identified: capital equipment, supplies, support equipment, labor, and investigation-derived waste (IDW) disposal. Chapter 8 of this ITVR discusses the costs estimated for the OCMA-350 based on these cost categories.

Table 4-2 summarizes the demonstration approach used to address the primary objectives and includes demonstration area characteristics, approximate sampling depth intervals, and the rationale for the analyses performed by the reference laboratory.

#### **4.2.2 Approach for Addressing Secondary Objectives**

Secondary objectives were addressed based on field observations made during the demonstration. Specifically, EPA representatives observed TPH measurement activities and documented them in a field logbook. Each developer was given the opportunity to review the field logbook at the end of each day of the demonstration. The approach used to address each secondary objective for each field measurement device is discussed below.

- The skills and training required for proper device operation (secondary objective S1) were evaluated by observing and noting the skills required to operate the device and prepare the data package during the demonstration and by discussing necessary user training with developer personnel.
- Health and safety concerns associated with device operation (secondary objective S2) were evaluated by observing and noting possible health and safety concerns during the demonstration, such as the types of hazardous substances handled by developer personnel during analysis, the number of times that hazardous substances were transferred from one container to another during the analytical procedure, and direct exposure of developer personnel to hazardous substances.
- The portability of the device (secondary objective S3) was evaluated by observing and noting the weight and size of the device and additional equipment required for TPH measurement as well as how easily the device was set up for use during the demonstration.
- The durability of the device (secondary objective S4) was evaluated by noting the materials of construction of the device and additional equipment required for TPH measurement. In addition, EPA representatives noted likely device failures or repairs that may be necessary during extended use of the device. Downtime required to make device repairs during the demonstration was also noted.
- The availability of the device and associated spare parts (secondary objective S5) was evaluated by discussing the availability of replacement devices with developer personnel and determining whether spare parts were available in retail stores or only from the

**Table 4-2. Demonstration Approach**

Site	Area	Approximate Sampling Interval (foot bgs)	Objective Addressed <sup>a</sup>	Soil Characteristics	Contamination Type	Typical TPH Concentration Range <sup>b</sup>	Rationale for Analyses by Reference Laboratory
Navy BVC	FFA	Upper layer <sup>c</sup>	P2	Medium-grained sand	Weathered diesel with carbon range from n-C <sub>10</sub> through n-C <sub>40</sub>	Low	Only EDRO because samples did not contain PHCs in gasoline range
		Lower layer <sup>c</sup>				High	
	NEX Service Station Area	7 to 8		Medium-grained sand	Fairly weathered gasoline with carbon range from n-C <sub>6</sub> through n-C <sub>14</sub>	Low to medium	GRO and EDRO because samples contained PHCs in both gasoline and diesel ranges
		8 to 9				Medium to high	
		9 to 10				High	
	PRA	10 to 11		Silty sand	Heavy lubricating oil with carbon range from n-C <sub>14</sub> through n-C <sub>40</sub>	Low	Only EDRO because samples did not contain PHCs in gasoline range
1.5 to 2.5		High					
Kelly AFB	B-38 Area	23 to 25	Sandy clay or silty sand and gravel in upper depth interval and clayey sand and gravel in deeper depth interval	Fresh gasoline and diesel or weathered gasoline and trace amounts of lubricating oil with carbon range from n-C <sub>6</sub> through n-C <sub>40</sub>	Low	GRO and EDRO because samples contained PHCs in both gasoline and diesel ranges	
		25 to 27					
PC	SFT Area	2 to 4	Silty clay with traces of sand in deeper depth intervals	Combination of slightly weathered gasoline, kerosene, JP-5, and diesel with carbon range from n-C <sub>5</sub> through n-C <sub>32</sub>	Medium		
		4 to 6					
		6 to 8					
Ottawa sand (PE sample)			Objective Addressed <sup>a</sup>	Soil Characteristics	Contamination Type	Typical TPH Concentration range <sup>b</sup>	Rationale for Analyses by Reference Laboratory
Processed garden soil (PE sample)			P2	Silty sand	Weathered gasoline	Medium and high	GRO and EDRO because weathered gasoline contains significant amounts of PHCs in both gasoline and diesel ranges

Table 4-2. Demonstration Approach (Continued)

Sample Matrix	Objective Addressed <sup>a</sup>	Soil Characteristics	Contamination Type	Typical TPH Concentration range <sup>b</sup>	Rationale for Analyses by Reference Laboratory
Not applicable (neat liquid PE sample)	P2 (Continued)	Not applicable	Weathered gasoline	High	GRO and EDRO because weathered gasoline contains significant amounts of PHCs in both gasoline and diesel ranges
			Diesel	High	Only EDRO because diesel does not contain PHCs in gasoline range
Processed garden soil (PE sample)	P3	Silty sand	Blank soil (control sample)	Trace	GRO and EDRO because processed garden soil may contain trace concentrations of PHCs in both gasoline and diesel ranges
			Weathered gasoline	High	GRO and EDRO because weathered gasoline contains significant amounts of PHCs in both gasoline and diesel ranges
			Weathered gasoline and MTBE (1,100 mg/kg), PCE (2,810 mg/kg), Stoddard solvent (2,900 mg/kg), or turpentine (2,730 mg/kg)		
			Weathered gasoline and MTBE (1,700 mg/kg), PCE (13,100 mg/kg), Stoddard solvent (15,400 mg/kg), or turpentine (12,900 mg/kg)		
			Diesel		
			Diesel and Stoddard solvent (3,650 mg/kg) or turpentine (3,850 mg/kg)		
			Diesel and Stoddard solvent (18,200 mg/kg) or turpentine (19,600 mg/kg)		
			Diesel and 1,2,4-trichlorobenzene (3,350 mg/kg) or humic acid (3,940 mg/kg)		
			Diesel and 1,2,4-trichlorobenzene (16,600 mg/kg) or humic acid (19,500 mg/kg)		
			Humic acid (3,940 mg/kg)		
				Trace	Only EDRO because diesel does not interfere with GRO analysis
					GRO and EDRO because (1) Stoddard solvent contains PHCs in both gasoline and diesel ranges and (2) turpentine interferes with both analyses
					Only EDRO because 1,2,4-trichlorobenzene and humic acid do not interfere with GRO analysis
					Only EDRO because humic acid does not interfere with GRO analysis
					The contribution of trace concentrations (less than 15 mg/kg) GRO found in processed garden soil during the predemonstration investigation was considered to be insignificant evaluation of the effect of humic acid interference, which occurs in the diesel range.

Table 4-2. Demonstration Approach (Continued)

Sample Matrix	Objective Addressed <sup>a</sup>	Soil Characteristics	Contamination Type	Typical TPH Concentration range <sup>b</sup>	Rationale for Analyses by Reference Laboratory
Not applicable (neat liquid PE sample)	P3 (Continued)	Not applicable	Weathered gasoline	High	GRO and EDRO because weathered gasoline contains significant amounts of PHCs in both gasoline and diesel ranges
			Diesel		Only EDRO because diesel does not contain PHCs in gasoline range
			MTBE		Only GRO because MTBE and PCE do not interfere with EDRO analysis
			PCE	Not applicable	
Processed garden soil (PE sample)	P4	Silty sand	Stoddard solvent	High	GRO and EDRO because Stoddard solvent contains PHCs in both gasoline and diesel ranges
			Turpentine	Not applicable	GRO and EDRO because turpentine interferes with both analyses
			1,2,4-Trichlorobenzene		Only EDRO because 1,2,4-trichlorobenzene does not interfere with GRO analysis
Processed garden soil (PE sample)	P4	Silty sand	Weathered gasoline (samples prepared at 9 and 16 percent moisture levels)	High	GRO and EDRO because weathered gasoline contains significant amounts of PHCs in both gasoline and diesel ranges
			Diesel (samples prepared at negligible [less than 1 percent] and 9 percent moisture levels)		Only EDRO because diesel does not contain PHCs in gasoline range

Notes:

AFB = Air Force Base  
 bgs = Below ground surface  
 BVC = Base Ventura County

FFA = Fuel Farm Area  
 mg/kg = Milligram per kilogram  
 MTBE = Methyl-tert-butyl ether

NEX = Naval Exchange  
 PC = Petroleum company  
 PCE = Tetrachloroethene

PE = Performance evaluation  
 PHC = Petroleum hydrocarbon  
 PRA = Phytoremediation Area  
 SFT = Slop Fill Tank

<sup>a</sup> Field observations of all sample analyses conducted during the demonstration were used to address primary objectives P5 and P6 and the secondary objectives.

<sup>b</sup> The typical TPH concentration range was based on reference laboratory results for the demonstration. The typical low, medium, and high ranges indicate TPH concentrations of less than 100 mg/kg; 100 to 1,000 mg/kg; and greater than 1,000 mg/kg, respectively.

<sup>c</sup> Because of soil conditions encountered in the FFA during the demonstration, the sampling depth intervals could not be accurately determined. Sample collection was initiated approximately 10 feet bgs, and attempts were made to collect 4-foot-long soil cores. For each sampling location in the area, the sample cores were divided into two samples based on visual observations. The upper layer of the soil core made up one sample, and the lower layer of the soil core made up the second sample.

<sup>d</sup> Because of problems that arose during preparation of PE samples with low concentrations of weathered gasoline, the results for these samples were not used to evaluate the field measurement devices.

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developer. In addition, the availability of spare parts required during the demonstration was noted.

Field observations of the analyses of all the samples described in Table 4-2 were used to address the secondary objectives for the demonstration.

### **4.3 Sample Preparation and Management**

This section presents sample preparation and management procedures used during the demonstration. Specifically, this section describes how samples were collected, containerized, labeled, stored, and shipped during the demonstration. Additional details about the sample preparation and management procedures are presented in the demonstration plan (EPA 2000).

#### **4.3.1 Sample Preparation**

The sample preparation procedures for both environmental and PE samples are described below.

##### **Environmental Samples**

For the demonstration, environmental samples were collected in the areas that were used for the predemonstration investigation: (1) the FFA, NEX Service Station Area, and PRA at the Navy BVC site; (2) the B-38 Area at the Kelly AFB site; and (3) the SFT Area at the PC site. Samples were collected in all areas except the PRA using a Geoprobe<sup>®</sup>; in the PRA, samples were collected using a Split Core Sampler.

The liners containing environmental samples were transported to the sample management trailer at the Navy BVC site, where the liners were cut open longitudinally. A geologist then profiled the samples based on soil characteristics to determine where the soil cores had to be sectioned. The soil characterization performed for each demonstration area is summarized in Chapter 3.

Each core sample section was then transferred to a stainless-steel bowl. The presence of any unrepresentative material such as sticks, roots, and stones was noted in a field logbook, and such material was removed to the extent possible using gloved hands. Any lump of clay in the sample that was greater than about 1/8 inch in diameter was crushed between gloved fingers before homogenization. Each soil sample was homogenized by stirring it for at least 2 minutes using a stainless-steel

spoon or gloved hands until the sample was visibly homogeneous. During or immediately following homogenization, any free water was poured from the stainless-steel bowl containing the soil sample into a container designated for IDW. During the demonstration, the field sampling team used only nitrile gloves to avoid the possibility of phthalate contamination from handling samples with plastic gloves. Such contamination had occurred during the predemonstration investigation.

After sample homogenization, the samples were placed in (1) EnCores of approximately 5-gram capacity for GRO analysis; (2) 4-ounce, glass jars provided by the reference laboratory for EDRO and percent moisture analyses; and (3) EnCores of approximately 25-gram capacity for TPH analysis. Using a quartering technique, each sample container was filled by alternately spooning soil from one quadrant of the mixing bowl and then from the opposite quadrant until the container was full. The 4-ounce, glass jars were filled after all the EnCores for a given sample had been filled. After a sample container was filled, it was immediately closed to minimize volatilization of contaminants. To minimize the time required for sample homogenization and filling of sample containers, these activities were simultaneously conducted by four personnel.

Because of the large number of containers being filled, some time elapsed between the filling of the first EnCore and the filling of the last. An attempt was made to eliminate any bias by alternating between filling EnCores for the developers and filling EnCores for the reference laboratory. Table 4-3 summarizes the demonstration sampling depth intervals, numbers of environmental and QA/QC samples collected, and numbers of environmental sample analyses associated with the demonstration of the OCMA-350.

##### **Performance Evaluation Samples**

All PE samples for the demonstration were prepared by ERA and shipped to the sample management trailer at the Navy BVC site. PE samples consisted of both soil samples and liquid samples. ERA prepared soil PE samples using two soil matrixes: Ottawa sand and processed garden soil (silty sand).

To prepare the soil PE samples, ERA spiked the required volume of soil based on the number of PE samples and the quantity of soil per PE sample requested. ERA then

**Table 4-3. Environmental Samples**

Site	Area	Depth Interval (foot bgs)	Number of Sampling Locations	Total Number of Samples, Including Field Triplicates, to Horiba and Reference Laboratory <sup>a</sup>	Number of MS/MSD <sup>b</sup> Pairs	Number of Extract Duplicates <sup>c</sup>	Number of TPH Analyses by Horiba	Number of Analyses by Reference Laboratory <sup>d</sup>	
								GRO	EDRO
Navy BVC	FFA	Upper layer	3	5	1	1	6	0	8
		Lower layer	3	5	1	1	5	0	8
	NEX Service Station Area	7 to 8	3	5	1	1	6	8	8
		8 to 9	3	5	1	1	5	8	8
		9 to 10	3	5	1	1	5	8	8
		10 to 11	3	5	1	1	6	8	8
	PRA	1.5 to 2.5	6 (4 vegetated and 2 unvegetated)	8	1	1	9	0	11
Kelly AFB	B-38 Area	23 to 25	3	5	1	1	6	8	8
		25 to 27	3	3	1	1	4	6	6
PC	SFT Area	2 to 4	5	7	1	1	8	10	10
		4 to 6	5	7	1	1	8	10	10
		6 to 8	5	7	1	1	8	10	10
		8 to 10	5	7	1	1	7	10	10
<b>Total</b>				<b>74</b>	<b>13</b>	<b>13</b>	<b>83</b>	<b>86</b>	<b>113</b>

Notes:

- |                            |  |                             |
|----------------------------|--|-----------------------------|
| AFB = Air Force Base       | FFA = Fuel Farm Area                             | PC = Petroleum company      |
| bgs = Below ground surface | MS/MSD = Matrix spike and matrix spike duplicate | PRA = Phytoremediation Area |
| BVC = Base Ventura County  | NEX = Naval Exchange                             | SFT = Slop Fill Tank        |

- <sup>a</sup> Field triplicates were collected at a frequency of one per depth interval in each sampling area except the B-38 Area. Because of conditions in the B-38 Area, triplicates were collected in the top depth interval only. Three separate, blind samples were prepared for each field triplicate.
- <sup>b</sup> MS/MSD samples were collected at a frequency of one per depth interval in each sampling area for analysis by the reference laboratory. MS/MSD samples were not analyzed by Horiba.
- <sup>c</sup> Because of site conditions, Horiba did not analyze extract duplicates for the lower layer in the FFA, the 8- to 9- and the 9- to 10-foot bgs depth intervals in the NEX Service Station Area, and the 8- to 10-foot bgs depth interval in the SFT Area. Therefore, Horiba analyzed only nine extract duplicates.
- <sup>d</sup> All environmental samples were also analyzed for moisture content by the reference laboratory.

homogenized the soil by manually mixing it. ERA used weathered gasoline or diesel as the spiking material, and spiking was done at three levels to depict the three TPH concentration ranges: low, medium, and high. A low-range sample was spiked to correspond to a TPH concentration of less than 100 mg/kg; a medium-range sample was spiked to correspond to a TPH concentration range of 100 to 1,000 mg/kg; and a high-range sample was spiked to correspond to a TPH concentration of more than 1,000 mg/kg. To spike each low- and medium-range soil sample, ERA used Freon 113 as a “carrier” to distribute the contaminant evenly throughout the sample. Soil PE samples were spiked with interferents at two different levels ranging from 50 to 500 percent of the TPH

concentration expected to be present. Whenever possible, the interferents were added at levels that best represented real-world conditions. ERA analyzed the samples containing weathered gasoline before shipping them to the Navy BVC site. The analytical results were used to confirm sample concentrations.

Liquid PE samples consisted of neat materials. Each liquid PE sample consisted of approximately 2 mL of liquid in a flame-sealed, glass ampule. During the demonstration, the developers and reference laboratory were given a table informing them of the amount of liquid sample to be used for analysis.



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ERA grouped like PE samples together in a resealable bag and placed all the PE samples in a cooler containing ice for overnight shipment to the Navy BVC site. When the PE samples arrived at the site, the samples were labeled with the appropriate sample identification numbers and placed in appropriate coolers for transfer to the developers on site or for shipment to the reference laboratory as summarized in Section 4.3.2. Table 4-4 summarizes the contaminant types and concentration ranges as well as the numbers of PE samples and analyses associated with the demonstration of the OCMA-350.

### **4.3.2 Sample Management**

Following sample containerization, each environmental sample was assigned a unique sample designation defining the sampling area, expected type of contamination, expected concentration range, sampling location, sample number, and QC identification, as appropriate. Each sample container was labeled with the unique sample designation, date, time, preservative, initials of personnel who had filled the container, and analysis to be performed. Each PE sample was also assigned a unique sample designation that identified it as a PE sample. Each PE

sample designation also identified the expected contaminant type and range, whether the sample was soil or liquid, and the sample number.

Sample custody began when samples were placed in iced coolers in the possession of the designated field sample custodian. Demonstration samples were divided into two groups to allow adequate time for the developers and reference laboratory to extract and analyze samples within the method-specified holding times presented in Table 4-5. The two groups of samples for reference laboratory analysis were placed in coolers containing ice and chain-of-custody forms and were shipped by overnight courier to the reference laboratory on the first and third days of the demonstration. The two groups of samples for developer analysis were placed in coolers containing ice and chain-of-custody forms and were hand-delivered to the developers at the Navy BVC site on the same days that the reference laboratory received its two groups of samples. During the demonstration, each developer was provided with a tent to provide shelter from direct sunlight during analysis of demonstration samples. In addition, at the end of each day, the developer placed any samples or sample extracts in its custody in coolers, and the coolers were stored in a refrigerated truck.

**Table 4-4. Performance Evaluation Samples**

Sample Type	Typical TPH Concentration Range <sup>a</sup>	Total Number of Samples to Horiba and Reference Laboratory	Number of MS/MSD <sup>b</sup> Pairs	Number of Analyses by Horiba	Number of Analyses by Reference Laboratory <sup>c</sup>		
					GRO	EDRO	
<b>Soil Samples (Ottawa Sand)</b>							
Weathered gasoline	Low	7	0	7	7	7	
Diesel		7	0	7	0	7	
<b>Soil Samples (Processed Garden Soil)</b>							
Weathered gasoline	Medium	3	0	3	3	3	
	High	3	1	3	5	5	
Diesel	Medium	3	0	3	0	3	
	High	3	1	3	0	5	
Blank soil (control sample)	Trace	3	1	3	5	5	
MTBE (1,100 mg/kg) and weathered gasoline	High	3	0	3	3	3	
MTBE (1,700 mg/kg) and weathered gasoline		3	0	3	3	3	
PCE (2,810 mg/kg) and weathered gasoline		3	0	3	3	3	
PCE (13,100 mg/kg) and weathered gasoline		3	0	3	3	3	
Stoddard solvent (2,900 mg/kg) and weathered gasoline		3	0	3	3	3	
Stoddard solvent (15,400 mg/kg) and weathered gasoline		3	0	3	3	3	
Turpentine (2,730 mg/kg) and weathered gasoline		3	0	3	3	3	
Turpentine (12,900 mg/kg) and weathered gasoline		3	0	3	3	3	
Stoddard solvent (3,650 mg/kg) and diesel		3	0	3	3	3	
Stoddard solvent (18,200 mg/kg) and diesel		3	0	3	3	3	
Turpentine (3,850 mg/kg) and diesel		3	0	3	3	3	
Turpentine (19,600 mg/kg) and diesel		3	0	3	3	3	
1,2,4-Trichlorobenzene (3,350 mg/kg) and diesel		3	0	3	0	3	
1,2,4-Trichlorobenzene (16,600 mg/kg) and diesel		3	0	3	0	3	
Humic acid (3,940 mg/kg) and diesel		3	0	3	0	3	
Humic acid (19,500 mg/kg) and diesel		3	0	3	0	3	
Humic acid (3,940 mg/kg)		Trace	3	0	3	0	3
Humic acid (19,500 mg/kg)			3	0	3	0	3
Weathered gasoline at 16 percent moisture		High	3	1	3	5	5
Diesel at negligible moisture (less than 1 percent)			3	1	3	0	5
<b>Liquid Samples (Neat Material)</b>							
Weathered gasoline	High	3	1	3	5	5	
Diesel		3	0	3	0	3	
MTBE		6	0	6	6	0	
PCE	Not applicable	6	0	6	6	0	



**Table 4-5. Sample Container, Preservation, and Holding Time Requirements**

Parameter <sup>a</sup>	Medium	Container	Preservation	Holding Time (days)	
				Extraction	Analysis
GRO	Soil	Two 5-gram EnCores	4 ± 2 °C	2 <sup>b</sup>	14
EDRO	Soil	Two 4-ounce, glass jars with Teflon™-lined lids	4 ± 2 °C	14 <sup>b</sup>	40
Percent moisture	Soil	Two 4-ounce, glass jars with Teflon™-lined lids	4 ± 2 °C	Not applicable	7
TPH	Soil	One 25-gram EnCore	4 ± 2 °C	Performed on site <sup>c</sup>	
GRO and EDRO	Liquid	One 2-milliliter ampule for each analysis	Not applicable	See note d	

Notes:

± = Plus or minus

<sup>a</sup> The reference laboratory measured percent moisture using part of the soil sample from the container designated for EDRO analysis.

<sup>b</sup> The extraction holding time started on the day that samples were shipped.

<sup>c</sup> If GRO analysis of a sample was to be completed by the reference laboratory, the developers completed on-site extraction of the corresponding sample within 2 days. Otherwise, all on-site extractions and analyses were completed within 7 days.

<sup>d</sup> The reference laboratory cracked open each ampule and immediately added the specified aliquot of the sample to methanol for GRO analysis and to methylene chloride for EDRO analysis. This procedure was performed in such a way that the final volumes of the extracts for GRO and EDRO analyses were 5.0 milliliters and 1.0 milliliter, respectively. Once the extracts were prepared, the GRO and EDRO analyses were performed within 14 and 40 days, respectively.

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## Chapter 5

### Confirmatory Process

The performance results for each field measurement device were compared to those for an off-site laboratory measurement method—that is, a reference method. This chapter describes the rationale for the selection of the reference method (Section 5.1) and reference laboratory (Section 5.2) and summarizes project-specific sample preparation and analysis procedures associated with the reference method (Section 5.3).

#### 5.1 Reference Method Selection

During the demonstration, environmental and PE samples were analyzed for TPH by the reference laboratory using SW-846 Method 8015B (modified). This section describes the analytical methods considered for the demonstration and provides a rationale for the reference method selected.

The reference method used was selected based on the following criteria:

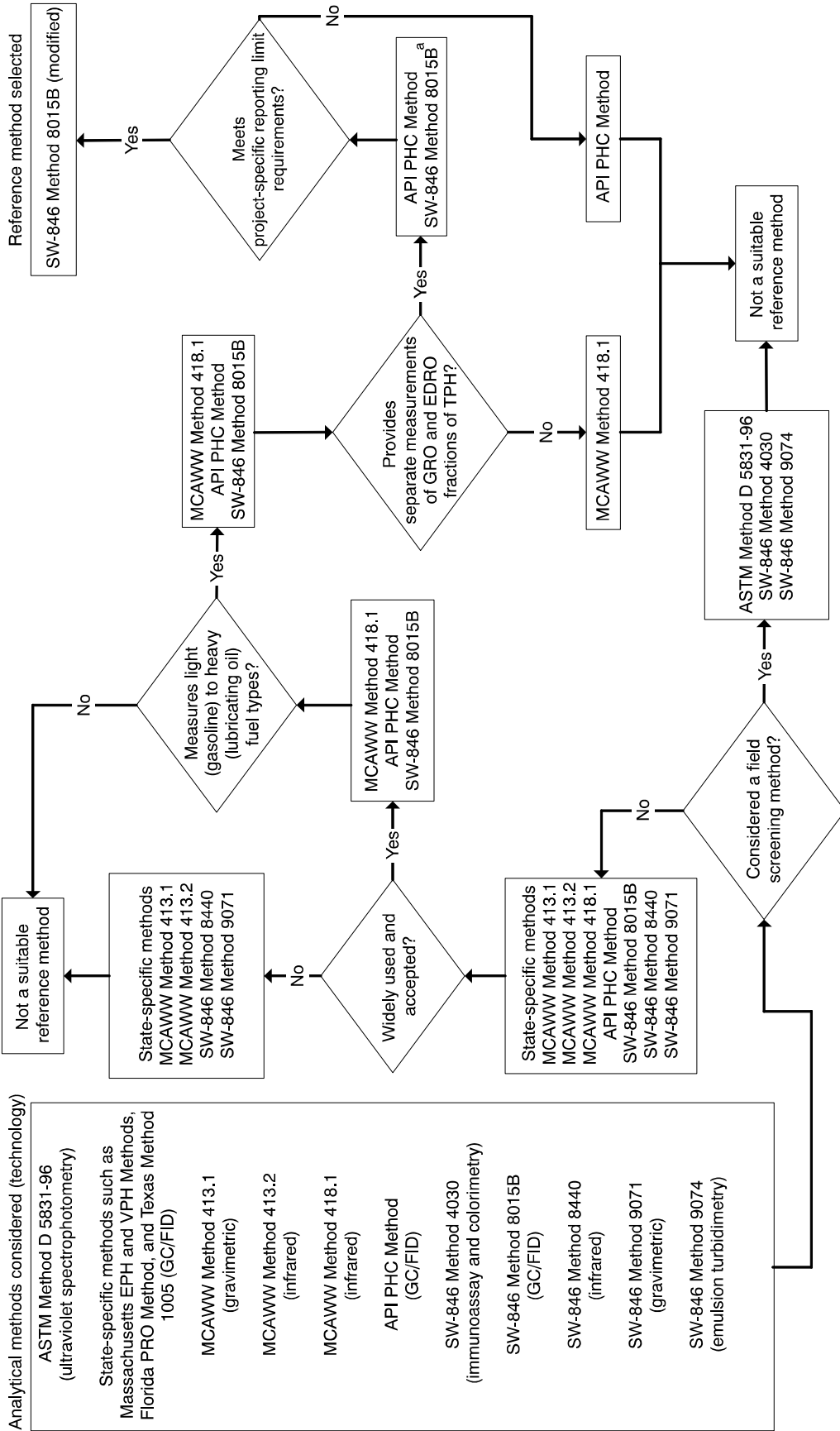
- It is not a field screening method.
- It is widely used and accepted.
- It measures light (gasoline) to heavy (lubricating oil) fuel types.
- It can provide separate measurements of GRO and EDRO fractions of TPH.
- It meets project-specific reporting limit requirements.

The analytical methods considered for the demonstration and the reference method selected based on the above-

listed criteria are illustrated in a flow diagram in Figure 5-1. The reference method selection process is discussed below.

Analytical methods considered for the demonstration were identified based on a review of SW-846, “Methods for Chemical Analysis of Water and Wastes” (MCAWW), ASTM, API, and state-specific methods. The analytical methods considered collectively represent six different measurement technologies. Of the methods reviewed, those identified as field screening methods, such as SW-846 Method 4030, were eliminated from further consideration in the reference method selection process.

A literature review was conducted to determine whether the remaining methods are widely used and accepted in the United States (Association for Environmental Health and Sciences [AEHS] 1999). As a result of this review, state-specific methods such as the Massachusetts Extractable Petroleum Hydrocarbon (EPH) and Volatile Petroleum Hydrocarbon (VPH) Methods (Massachusetts Department of Environmental Protection 2000), the Florida Petroleum Range Organic (PRO) Method (Florida Department of Environmental Protection 1996), and Texas Method 1005 (Texas Natural Resource Conservation Commission 2000) were eliminated from the selection process. Also eliminated were the gravimetric and infrared methods except for MCAWW Method 418.1 (EPA 1983). The use and acceptability of MCAWW Method 418.1 will likely decline because the extraction solvent used in this method is Freon 113, a chlorofluorocarbon (CFC), and use of CFCs will eventually be phased out under the Montreal Protocol. However, because several states still accept the use of MCAWW Method 418.1 for measuring TPH, the method was retained for further consideration in the selection process (AEHS 1999).



Notes:

API = American Petroleum Institute, ASTM = American Society for Testing and Materials, DRO = diesel range organics, EPH = extractable petroleum hydrocarbon, GC/FID = gas chromatograph/ flame ionization detector, MCAWW = "Methods for Chemical Analysis of Water and Wastes," PHC = petroleum hydrocarbon, PRO = petroleum range organics, SW-846 = "Test Methods for Evaluating Solid Waste," VPH = volatile petroleum hydrocarbon

<sup>a</sup> SW-846 Method 8015B provides separate GRO and DRO measurements and, when modified, can also provide EDRO measurements.

Figure 5-1. Reference method selection process.

Of the remaining methods, MCAWW Method 418.1, the API PHC Method, and SW-846 Method 8015B can all measure light (gasoline) to heavy (lubricating oil) fuel types. However, GRO and EDRO fractions cannot be measured separately using MCAWW Method 418.1. As a result, this method was eliminated from the selection process.

Both the API PHC Method and SW-846 Method 8015B can be used to separately measure the GRO and DRO fractions of TPH. These methods can also be modified to extend the DRO range to EDRO by using a calibration standard that includes even-numbered alkanes in the EDRO range.

Based on a review of state-specific action levels for TPH, a TPH reporting limit of 10 mg/kg was used for the demonstration. Because the TPH reporting limit for the API PHC Method (50 to 100 mg/kg) is greater than 10 mg/kg, this method was eliminated from the selection process (API 1994). SW-846 Method 8015B (modified) met the reporting limit requirements for the demonstration. For GRO, SW-846 Method 8015B (modified) has a reporting limit of 5 mg/kg, and for EDRO, this method has a reporting limit of 10 mg/kg. Therefore, SW-846 Method 8015B (modified) satisfied all the criteria established for selecting the reference method. As an added benefit, because this is a GC method, it also provides a fingerprint (chromatogram) of TPH components.

## 5.2 Reference Laboratory Selection

This section provides the rationale for the selection of the reference laboratory. STL Tampa East was selected as the reference laboratory because it (1) has been performing TPH analyses for many years, (2) has passed many external audits by successfully implementing a variety of TPH analytical methods, and (3) agreed to implement project-specific analytical requirements. In January 2000, a project-specific audit of the laboratory was conducted and determined that STL Tampa East satisfactorily implemented the reference method during the predemonstration investigation. In addition, STL Tampa East successfully analyzed double-blind PE samples and blind field triplicates for GRO and EDRO during the predemonstration investigation. Furthermore, in 1998 STL Tampa East was one of four recipients and in 1999 was one of six recipients of the Seal of Excellence Award issued by the American Council of Independent Laboratories. In each instance, this award was issued based on the results of PE sample analyses and client satisfaction surveys. Thus, the selection of the reference laboratory was based primarily on performance and not cost.

## 5.3 Summary of Reference Method

The laboratory sample preparation and analytical methods used for the demonstration are summarized in Table 5-1. The SW-846 methods listed in Table 5-1 for GRO and

**Table 5-1. Laboratory Sample Preparation and Analytical Methods**

Parameter	Method Reference (Step)	Method Title
GRO	Based on SW-846 Method 5035 (extraction)	Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples
	Based on SW-846 Method 5030B (purge-and-trap)	Purge-and-Trap for Aqueous Samples
	Based on SW-846 Method 8015B (analysis)	Nonhalogenated Volatile Organics by Gas Chromatography
EDRO	Based on SW-846 Method 3540C (extraction)	Soxhlet Extraction
	Based on SW-846 Method 8015B (analysis)	Nonhalogenated Volatile Organics by Gas Chromatography
Percent moisture	Based on MCAWW Method 160.3 <sup>a</sup>	Residue, Total (Gravimetric, Dried at 103-105 °C)

Notes:

MCAWW = "Methods for Chemical Analysis of Water and Wastes"  
 SW-846 = "Test Methods for Evaluating Solid Waste"

<sup>a</sup> MCAWW Method 160.3 was modified to include calculation and reporting of percent moisture in soil samples.

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EDRO analyses were tailored to meet the definition of TPH for the project (see Chapter 1). Project-specific procedures for soil sample preparation and analysis for GRO and EDRO are summarized in Tables 5-2 and 5-3, respectively. Project-specific procedures were applied (1) if a method used offered choices (for example, SW-846 Method 5035 for GRO extraction states that samples may be collected with or without use of a preservative solution), (2) if a method used did not provide specific details (for example, SW-846 Method 5035 for GRO extraction does not specify how unrepresentative material should be handled during sample preparation), or (3) if a modification to a method used was required in order to meet demonstration objectives (for example, SW-846 Method 8015B for EDRO analysis states that quantitation is performed by summing the areas of all chromatographic peaks eluting between the end of the 1,2,4-trimethyl

benzene or n-C<sub>10</sub> peak, whichever occurs later, and the n-octacosane peak; however, an additional quantitation was performed to sum the areas of all chromatographic peaks eluting from the end of the n-octacosane peak through the tetracontane peak in order to meet demonstration objectives).

Before analyzing a liquid PE sample, STL Tampa East added an aliquot of the liquid PE sample to the extraction solvent used for soil samples. A specified aliquot of the liquid PE sample was diluted in methanol for GRO analysis and in methylene chloride for EDRO analysis such that the final volume of the solution for GRO and EDRO analyses was 5.0 and 1.0 mL, respectively. The solution was then analyzed for GRO and EDRO using the same procedures as are used for soil sample extracts.



**Table 5-2. Summary of Project-Specific Procedures for GRO Analysis**

SW-846 Method Reference (Step)	Project-Specific Procedures
<b>5035 (Extraction)</b>	
Low-level (0.5 to 200 micrograms per kilogram) or high-level (greater than 200 micrograms per kilogram) samples may be prepared.	Because the project-specific reporting limit for GRO was 5 milligrams per kilogram, all samples analyzed for GRO were prepared using procedures for high-level samples.
Samples may be collected with or without use of a preservative solution.	Samples were collected without use of a preservative.
A variety of sample containers, including EnCores, may be used when high-level samples are collected without use of a preservative.	Samples were containerized in EnCores.
Samples collected in EnCores should be transferred to vials containing the extraction solvent as soon as possible or analyzed within 48 hours.	Samples were weighed and extracted within 2 calendar days of their shipment. The holding time for analysis was 14 days after extraction. A full set of quality control samples (method blanks, MS/MSDs, and LCS/LCSDs) was prepared within this time.
For samples not preserved in the field, a solubility test should be performed using methanol, polyethylene glycol, and hexadecane to determine an appropriate extraction solvent.	Because the reference laboratory obtained acceptable results for performance evaluation samples extracted with methanol during the predemonstration investigation, samples were extracted with methanol.
Removal of unrepresentative material from the sample is not discussed.	During sample homogenization, field sampling technicians attempted to remove unrepresentative material such as sticks, roots, and stones if present in the sample; the reference laboratory did not remove any remaining unrepresentative material.
Procedures for adding surrogates to the sample are inconsistently presented. Section 2.2.1 indicates that surrogates should be added to an aliquot of the extract solution. Section 7.3.3 indicates that soil should be added to a vial containing both the extraction solvent (methanol) and surrogate spiking solution.	The soil sample was ejected into a volatile organic analysis vial, an appropriate amount of surrogate solution was added to the sample, and then methanol was quickly added.
Nine mL of methanol should be added to a 5-gram (wet weight) soil sample.	Five mL of methanol was added to the entire soil sample contained in a 5-gram EnCore.
When practical, the sample should be dispersed to allow contact with the methanol by shaking or using other mechanical means for 2 min without opening the sample container. When shaking is not practical, the sample should be dispersed with a narrow, metal spatula, and the sample container should be immediately resealed.	The sample was dispersed using a stainless-steel spatula to allow contact with the methanol. The volatile organic analysis vial was then capped and shaken vigorously until the soil was dispersed in methanol, and the soil was allowed to settle.
<b>5030B (Purge-and-Trap)</b>	
<p>Screening of samples before the purge-and-trap procedure is recommended using one of the two following techniques:</p> <p>Use of an automated headspace sampler (see SW-846 Method 5021) connected to a GC equipped with a photoionization detector in series with an electrolytic conductivity detector</p> <p>Extraction of the samples with hexadecane (see SW-846 Method 3820) and analysis of the extracts using a GC equipped with a flame ionization detector or electron capture detector</p>	Samples were screened with an automated headspace sampler (see SW-846 Method 5021) connected to a GC equipped with a flame ionization detector.
SW-846 Method 5030B indicates that contamination by carryover can occur whenever high-level and low-level samples are analyzed in sequence. Where practical, analysis of samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. Because the trap and other parts of the system are subject to contamination, frequent bake-out and purging of the entire system may be required.	According to the reference laboratory, a sample extract concentration equivalent to 10,000 ng on-column is the minimum concentration of GRO that could result in carryover. Therefore, if a sample extract had a concentration that exceeded the minimum concentration for carryover, the next sample in the sequence was evaluated as follows: (1) if the sample was clean (had no chromatographic peaks), no carryover had occurred; (2) if the sample had detectable analyte concentrations (chromatographic peaks), it was reanalyzed under conditions in which carryover did not occur.

**Table 5-2. Summary of Project-Specific Procedures for GRO Analysis (Continued)**

SW-846 Method Reference (Step)	Project-Specific Procedures
<b>5030B (Purge-and-Trap) (Continued)</b>	
The sample purge device used must demonstrate adequate performance.	A Tekmar 2016 autosampler and a Tekmar LSC 2000 concentrator were used. Based on quality control sample results, the reference laboratory had demonstrated adequate performance using these devices.
<p>Purge-and-trap conditions for high-level samples are not clearly specified. According to SW-846, manufacturer recommendations for the purge-and-trap devices should be considered when the method is implemented. The following general purge-and-trap conditions are recommended for samples that are water-miscible (methanol extract):</p> <p>Purge gas: nitrogen or helium  Purge gas flow rate: 20 mL/min  Purge time: 15 ± 0.1 min  Purge temperature: 85 ± 2 °C  Desorb time: 1.5 min  Desorb temperature: 180 °C  Backflush inert gas flow rate: 20 to 60 mL/min  Bake time: not specified  Bake temperature: not specified  Multiport valve and transfer line temperatures: not specified</p>	<p>The purge-and-trap conditions that were used are listed below. These conditions were based on manufacturer recommendations for the purge device specified above and the VOCARB 3000 trap.</p> <p>Purge gas: helium  Purge gas flow rate: 35 mL/min  Purge time: 8 min with 2-min dry purge  Purge temperature: ambient temperature  Desorb time: 1 min  Desorb temperature: 250 °C  Backflush inert gas flow rate: 35 mL/min  Bake time: 7 min  Bake temperature: 270 °C  Multiport valve and transfer line temperatures: 115 and 120 °C</p>
<b>8015B (Analysis)</b>	
<b>GC Conditions</b>	
<p>The following GC conditions are recommended:</p> <p>Column: 30-meter x 0.53-millimeter-inside diameter, fused-silica capillary column chemically bonded with 5 percent methyl silicone, 1.5-micrometer field thickness</p> <p>Carrier gas: helium  Carrier gas flow rate: 5 to 7 mL/min  Makeup gas: helium  Makeup gas flow rate: 30 mL/min  Injector temperature: 200 °C  Detector temperature: 340 °C  Temperature program:  Initial temperature: 45 °C  Hold time: 1 min  Program rate: 45 to 100 °C at 5 °C/min  Program rate: 100 to 275 °C at 8 °C/min  Hold time: 5 min  Overall time: 38.9 min</p>	<p>The HP 5890 Series II was used as the GC. The following GC conditions were used based on manufacturer recommendations:</p> <p>Column: 30-meter x 0.53-millimeter-inside diameter, fused-silica capillary column chemically bonded with 5 percent methyl silicone, 1.5-micrometer field thickness</p> <p>Carrier gas: helium  Carrier gas flow rate: 15 mL/min  Makeup gas: helium  Makeup gas flow rate: 15 mL/min  Injector temperature: 200 °C  Detector temperature: 200 °C  Temperature program:  Initial temperature: 25 °C  Hold time: 3 min  Program rate: 25 to 120 °C at 25 °C/min  Hold time: 4 min  Program rate: 120 to 245 °C at 25 °C/min  Hold time: 5 min  Overall time: 20.4 min</p>
<b>Calibration</b>	
The chromatographic system may be calibrated using either internal or external standards.	The chromatographic system was calibrated using external standards with a concentration range equivalent to 100 to 10,000 ng on-column. The reference laboratory acceptance criterion for initial calibration was a relative standard deviation less than or equal to 20 percent of the average response factor or a correlation coefficient for the least-squares linear regression greater than or equal to 0.990.
Calibration should be performed using samples of the specific fuel type contaminating the site. When such samples are not available, recently purchased, commercially available fuel should be used.	Calibration was performed using a commercially available, 10-component GRO standard that contained 35 percent aliphatic hydrocarbons and 65 percent aromatic hydrocarbons.

**Table 5-2. Summary of Project-Specific Procedures for GRO Analysis (Continued)**

SW-846 Method Reference (Step)	Project-Specific Procedures
<b>8015B (Analysis) (Continued)</b>	
<b>Calibration (Continued)</b>	
Initial calibration verification is not required.	Initial calibration verification was performed using a second-source standard that contained a 10-component GRO standard made up of 35 percent aliphatic hydrocarbons and 65 percent aromatic hydrocarbons at a concentration equivalent to 2,000 ng on-column. The reference laboratory acceptance criterion for initial calibration verification was an instrument response within 25 percent of the response obtained during initial calibration.
CCV should be performed at the beginning of every 12-hour work shift and at the end of an analytical sequence. CCV throughout the 12-hour shift is also recommended; however, the frequency is not specified.	CCV was performed at the beginning of each analytical batch, after every tenth analysis, and at the end of the analytical batch. The reference laboratory acceptance criteria for CCV were instrument responses within 25 percent (for the closing CCV) and 15 percent (for all other CCVs) of the response obtained during initial calibration.
CCV should be performed using a fuel standard.	CCV was performed using a commercially available, 10-component GRO standard that contained 35 percent aliphatic hydrocarbons and 65 percent aromatic hydrocarbons.
According to SW-846 Method 8000, CCV should be performed at the same concentration as the midpoint concentration of the initial calibration curve; however, the concentration of each calibration point is not specified.	CCV was performed at a concentration equivalent to 2,000 ng on-column.
A method sensitivity check is not required.	A method sensitivity check was performed daily using a calibration standard with a concentration equivalent to 100 ng on-column. The reference laboratory acceptance criterion for the method sensitivity check was detection of the standard.
<b>Retention Time Windows</b>	
The retention time range (window) should be established using 2-methylpentane and 1,2,4-trimethylbenzene during initial calibration. Three measurements should be made over a 72-hour period; the results should be used to determine the average retention time. As a minimum requirement, the retention time should be verified using a midlevel calibration standard at the beginning of each 12-hour shift. Additional analysis of the standard throughout the 12-hour shift is strongly recommended.	The retention time range was established using the opening CCV specific to each analytical batch. The first eluter, 2-methylpentane, and the last eluter, 1,2,4-trimethylbenzene, of the GRO standard were used to establish each day's retention time range.
<b>Quantitation</b>	
Quantitation is performed by summing the areas of all chromatographic peaks eluting within the retention time range established using 2-methylpentane and 1,2,4-trimethylbenzene. Subtraction of the baseline rise for the method blank resulting from column bleed is generally not required.	Quantitation was performed by summing the areas of all chromatographic peaks from 2-methylpentane through 1,2,4-trimethylbenzene. This range includes n-C <sub>10</sub> . Baseline rise subtraction was not performed.
<b>Quality Control</b>	
Spiking compounds for MS/MSDs and LCSs are not specified.	The spiking compound mixture for MS/MSDs and LCSs was the 10-component GRO calibration standard.
According to SW-846 Method 8000, spiking levels for MS/MSDs are determined differently for compliance and noncompliance monitoring applications. For noncompliance applications, the laboratory may spike the sample (1) at the same concentration as the reference sample (LCS), (2) at 20 times the estimated quantitation limit for the matrix of interest, or (3) at a concentration near the middle of the calibration range.	MS/MSD spiking levels were targeted to be between 50 and 150 percent of the unspiked sample concentration. The reference laboratory used historical information to adjust spike amounts or to adjust sample amounts to a preset spike amount. The spiked samples and unspiked samples were prepared such that the sample mass and extract volume used for analysis were the same.

**Table 5-2. Summary of Project-Specific Procedures for GRO Analysis (Continued)**

SW-846 Method Reference (Step)	Project-Specific Procedures
<b>8015B (Analysis) (Continued)</b>	
<b>Quality Control (Continued)</b>	
According to SW-846 Method 8000, in-house laboratory acceptance criteria for MS/MSDs and LCSs should be established. As a general rule, the recoveries of most compounds spiked into a sample should fall within the range of 70 to 130 percent, and this range should be used as a guide in evaluating in-house performance.	The reference laboratory acceptance criteria for MS/MSDs and LCSs were a relative percent difference less than or equal to 25 with 33 to 115 percent recovery. The acceptance criteria were based on laboratory historical information. These acceptance criteria are similar to those of the methods cited in Figure 5-1.
The LCS should consist of an aliquot of a clean (control) matrix that is similar to the sample matrix.	The LCS/LCSD matrix was Ottawa sand.
No LCSD is required.	The spiking compound mixture for LCSDs was the 10-component GRO calibration standard.
The surrogate compound and spiking concentration are not specified. According to SW-846 Method 8000, in-house laboratory acceptance criteria for surrogate recoveries should be established.	The surrogate compound was 4-bromofluorobenzene. The reference laboratory acceptance criterion for surrogates was 39 to 163 percent recovery.
The method blank matrix is not specified.	The method blank matrix was Ottawa sand. The reference laboratory acceptance criterion for the method blank was less than or equal to the project-specific reporting limit.
The extract duplicate is not specified.	The extract duplicate was analyzed. The reference laboratory acceptance criterion for the extract duplicate was a relative percent difference less than or equal to 25.

Notes:

- |      |                                       |        |   |
|------|---------------------------------------|--------|---|
| ±    | = Plus or minus                       | min    | = Minute                                    |
| CCV  | = Continuing calibration verification | mL     | = Milliliter                                |
| GC   | = Gas chromatograph                   | MS     | = Matrix spike                              |
| LCS  | = Laboratory control sample           | MSD    | = Matrix spike duplicate                    |
| LCSD | = Laboratory control sample duplicate | ng     | = Nanogram                                  |
|      |                                       | SW-846 | = "Test Methods for Evaluating Solid Waste" |

**Table 5-3. Summary of Project-Specific Procedures for EDRO Analysis**

SW-846 Method Reference (Step)	Project-Specific Procedures
<b>3540C (Extraction)</b>	
Any free water present in the sample should be decanted and discarded. The sample should then be thoroughly mixed, and any unrepresentative material such as sticks, roots, and stones should be discarded.	During sample homogenization, field sampling technicians attempted to remove unrepresentative material such as sticks, roots, and stones. In addition, the field sampling technicians decanted any free water present in the sample. The reference laboratory did not decant water or remove any unrepresentative material from the sample. The reference laboratory mixed the sample with a stainless-steel tongue depressor.
Ten grams of soil sample should be blended with 10 grams of anhydrous sodium sulfate.	Thirty grams of sample was blended with at least 30 grams of anhydrous sodium sulfate. For medium- and high-level samples, 6 and 2 grams of soil were used for extraction, respectively, and proportionate amounts of anhydrous sodium sulfate were added. The amount of anhydrous sodium sulfate used was not measured gravimetrically but was sufficient to ensure that free moisture was effectively removed from the sample.
Extraction should be performed using 300 mL of extraction solvent.	Extraction was performed using 200 mL of extraction solvent.
Acetone and hexane (1:1 volume per volume) or methylene chloride and acetone (1:1 volume per volume) may be used as the extraction solvent.  Note: Methylene chloride and acetone are not constant-boiling solvents and thus are not suitable for the method. Methylene chloride was used as an extraction solvent for method validation.	Methylene chloride was used as the extraction solvent.
The micro Snyder column technique or nitrogen blowdown technique may be used to adjust (concentrate) the soil extract to the required final volume.	Kuderna Danish and nitrogen evaporation were used as the concentration techniques.
Procedures for addressing contamination carryover are not specified.	According to the reference laboratory, a sample extract concentration of 100,000 micrograms per mL is the minimum concentration of EDRO that could result in carryover. Therefore, if a sample extract had a concentration that exceeded the minimum concentration for carryover, the next sample in the sequence was evaluated as follows: (1) if the sample was clean (had no chromatographic peaks), no carryover occurred; (2) if the sample had detectable analyte concentrations (chromatographic peaks), it was reanalyzed under conditions in which carryover did not occur.
<b>8015B (Analysis)</b>	
<b>GC Conditions</b>	
<p>The following GC conditions are recommended:</p> <p>Column: 30-meter x 0.53-millimeter-inside diameter, fused-silica capillary column chemically bonded with 5 percent methyl silicone, 1.5-micrometer field thickness</p> <p>Carrier gas: helium Carrier gas flow rate: 5 to 7 mL/min Makeup gas: helium Makeup gas flow rate: 30 mL/min Injector temperature: 200 °C Detector temperature: 340 °C Temperature program: Initial temperature: 45 °C Hold time: 3 min Program rate: 45 to 275 °C at 12 °C/min Hold time: 12 min Overall time: 34.2 min</p>	<p>An HP 6890 GC was used with the following conditions:</p> <p>Column: 30-meter x 0.53-millimeter-inside diameter, fused-silica capillary column chemically bonded with 5 percent methyl silicone, 1.5-micrometer field thickness</p> <p>Carrier gas: hydrogen Carrier gas flow rate: 1.9 mL/min Makeup gas: hydrogen Makeup gas flow rate: 23 mL/min Injector temperature: 250 °C Detector temperature: 345 °C Temperature program: Initial temperature: 40 °C Hold time: 2 min Program rate: 40 to 345 °C at 30 °C/min Hold time: 5 min Overall time: 17.2 min</p>

**Table 5-3. Summary of Project-Specific Procedures for EDRO Analysis (Continued)**

SW-846 Method Reference (Step)	Project-Specific Procedures
<b>8015B (Analysis) (Continued)</b>	
<b>Calibration</b>	
The chromatographic system may be calibrated using either internal or external standards.	The chromatographic system was calibrated using external standards with a concentration range equivalent to 75 to 7,500 ng on-column. The reference laboratory acceptance criterion for initial calibration was a relative standard deviation less than or equal to 20 percent of the average response factor or a correlation coefficient for the least-squares linear regression greater than or equal to 0.990.
Calibration should be performed using samples of the specific fuel type contaminating the site. When such samples are not available, recently purchased, commercially available fuel should be used.	Calibration was performed using a commercially available standard that contained even-numbered alkanes from C <sub>10</sub> through C <sub>40</sub> .
ICV is not required.	ICV was performed using a second-source standard that contained even-numbered alkanes from C <sub>10</sub> through C <sub>40</sub> at a concentration equivalent to 3,750 ng on-column. The reference laboratory acceptance criterion for ICV was an instrument response within 25 percent of the response obtained during initial calibration.
CCV should be performed at the beginning of every 12-hour work shift and at the end of an analytical sequence. CCV throughout the 12-hour shift is also recommended; however, the frequency is not specified.	CCV was performed at the beginning of each analytical batch, after every tenth analysis, and at the end of the analytical batch. The reference laboratory acceptance criteria for CCV were instrument responses within 25 percent (for the closing CCV) and 15 percent (for all other CCVs) of the response obtained during initial calibration.
CCV should be performed using a fuel standard.	CCV was performed using a standard that contained only even-numbered alkanes from C <sub>10</sub> through C <sub>40</sub> .
According to SW-846 Method 8000, CCV should be performed at the same concentration as the midpoint concentration of the initial calibration curve; however, the concentration of each calibration point is not specified.	CCV was performed at a concentration equivalent to 3,750 ng on-column.
A method sensitivity check is not required.	A method sensitivity check was performed daily using a calibration standard with a concentration equivalent to 75 ng on-column. The reference laboratory acceptance criterion for the method sensitivity check was detection of the standard.
<b>Retention Time Windows</b>	
The retention time range (window) should be established using C <sub>10</sub> and C <sub>28</sub> alkanes during initial calibration. Three measurements should be made over a 72-hour period; the results should be used to determine the average retention time. As a minimum requirement, the retention time should be verified using a midlevel calibration standard at the beginning of each 12-hour shift. Additional analysis of the standard throughout the 12-hour shift is strongly recommended.	Two retention time ranges were established using the opening CCV for each analytical batch. The first range, which was labeled diesel range organics, was marked by the end of the 1,2,4-trimethylbenzene or n-C <sub>10</sub> peak, whichever occurred later, through the n-octacosane peak. The second range, which was labeled oil range organics, was marked by the end of the n-octacosane peak through the tetracontane peak.
<b>Quantitation</b>	
Quantitation is performed by summing the areas of all chromatographic peaks eluting between n-C <sub>10</sub> and n-octacosane.	Quantitation was performed by summing the areas of all chromatographic peaks from the end of the 1,2,4-trimethylbenzene or n-C <sub>10</sub> peak, whichever occurred later, through the n-octacosane peak. A separate quantitation was also performed to sum the areas of all chromatographic peaks from the end of the n-octacosane peak through the tetracontane peak. Separate average response factors for the carbon ranges were used for quantitation. The quantitation results were then summed to determine the total EDRO concentration.  All calibrations, ICVs, CCVs, and associated batch quality control measures were controlled for the entire EDRO range using a single quantitation performed over the entire EDRO range.

**Table 5-3. Summary of Project-Specific Procedures for EDRO Analysis (Continued)**

SW-846 Method Reference (Step)	Project-Specific Procedures
<b>8015B (Analysis) (Continued)</b>	
<b>Quantitation (Continued)</b>	
Subtraction of the baseline rise for the method blank resulting from column bleed is appropriate.	The reference laboratory identified occurrences of baseline rise in the data package. The baseline rise was evaluated during data validation and subtracted when appropriate based on analyst discretion.
Because phthalate esters contaminate many types of products commonly found in the laboratory, consistent quality control should be practiced.	Phthalate peaks were not noted during analysis.
<b>Quality Control</b>	
Spiking compounds for MS/MSDs and LCSs are not specified.	The spiking compound for MS/MSDs and LCSs was an EDRO standard that contained even-numbered alkanes from C <sub>10</sub> through C <sub>40</sub> .
According to SW-846 Method 8000, spiking levels for MS/MSDs are determined differently for compliance and noncompliance monitoring applications. For noncompliance applications, the laboratory may spike the sample (1) at the same concentration as the reference sample (LCS), (2) at 20 times the estimated quantitation limit for the matrix of interest, or (3) at a concentration near the middle of the calibration range.	MS/MSD spiking levels were targeted to be between 50 and 150 percent of the unspiked sample concentration. The reference laboratory used historical information to adjust spike amounts or to adjust sample amounts to a preset spike amount. The spiked samples and unspiked samples were prepared such that the sample mass and extract volume used for analysis were the same.
According to SW-846 Method 8000, in-house laboratory acceptance criteria for MS/MSDs and LCSs should be established. As a general rule, the recoveries of most compounds spiked into a sample should fall within the range of 70 to 130 percent, and this range should be used as a guide in evaluating in-house performance.	The reference laboratory acceptance criteria for MS/MSDs and LCSs were a relative percent difference less than or equal to 45 with 46 to 124 percent recovery. The acceptance criteria were based on laboratory historical information. These acceptance criteria are similar to those of the methods cited in Figure 5-1.
The LCS should consist of an aliquot of a clean (control) matrix that is similar to the sample matrix.	The LCS/LCSD matrix was Ottawa sand.
No LCSD is required.	The spiking compound for LCSDs was the EDRO standard that contained even-numbered alkanes from C <sub>10</sub> through C <sub>40</sub> .
The surrogate compound and spiking concentration are not specified. According to SW-846 Method 8000, in-house laboratory acceptance criteria for surrogate recoveries should be established.	The surrogate compound was o-terphenyl. The reference laboratory acceptance criterion for surrogates was 45 to 143 percent recovery.
The method blank matrix is not specified.	The method blank matrix was Ottawa sand. The reference laboratory acceptance criterion for the method blank was less than or equal to the project-specific reporting limit.
The extract duplicate is not specified.	The extract duplicate was analyzed. The reference laboratory acceptance criterion for the extract duplicate was a relative percent difference less than or equal to 45.

**Notes:**

- |  |  |
|--|--|
| CCV = Continuing calibration verification  | mL = Milliliter                                    |
| GC = Gas chromatograph                     | MS = Matrix spike                                  |
| ICV = Initial calibration verification     | MSD = Matrix spike duplicate                       |
| LCS = Laboratory control sample            | n-C <sub>x</sub> = Alkane with "x" carbon atoms    |
| LCSD = Laboratory control sample duplicate | ng = Nanogram                                      |
| min = Minute                               | SW-846 = "Test Methods for Evaluating Solid Waste" |

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## Chapter 6

### Assessment of Reference Method Data Quality

This chapter assesses reference method data quality based on QC check results and PE sample results. A summary of reference method data quality is included at the end of this chapter.

To ensure that the reference method results were of known and adequate quality, EPA representatives performed a predemonstration audit and an in-process audit of the reference laboratory. The predemonstration audit findings were used in developing the predemonstration design. The in-process audit was performed when the laboratory had analyzed a sufficient number of demonstration samples for both GRO and EDRO and had prepared its first data package. During the audit, EPA representatives (1) verified that the laboratory had properly implemented the EPA-approved demonstration plan and (2) performed a critical review of the first data package. All issues identified during the audit were fully addressed by the laboratory before it submitted the subsequent data packages to the EPA. The laboratory also addressed issues identified during the EPA final review of the data packages. Audit findings are summarized in the DER for the demonstration.

#### 6.1 Quality Control Check Results

This section summarizes QC check results for GRO and EDRO analyses performed using the reference method. The QC checks associated with soil sample analyses for GRO and EDRO included method blanks, surrogates, matrix spikes and matrix spike duplicates (MS/MSD), and laboratory control samples and laboratory control sample duplicates (LCS/LCSD). In addition, extract duplicates were analyzed for soil environmental samples. The QC checks associated with liquid PE sample analysis for GRO included method blanks, surrogates, MS/MSDs, and LCS/LCSDs. Because liquid PE sample analyses for

EDRO did not include a preparation step, surrogates, MS/MSDs, and LCS/LCSDs were not analyzed; however, an instrument blank was analyzed as a method blank equivalent. The results for the QC checks were compared to project-specific acceptance criteria. These criteria were based on the reference laboratory's historical QC limits and its experience in analyzing the predemonstration investigation samples using the reference method. The reference laboratory's QC limits were established as described in SW-846 and were within the general acceptance criteria recommended by SW-846 for organic analytical methods.

Laboratory duplicates were also analyzed to evaluate the precision associated with percent moisture analysis of soil samples. The acceptance criterion for the laboratory duplicate results was an RPD less than or equal to 20. All laboratory duplicate results met this criterion. The results for the laboratory duplicates are not separately discussed in this ITVR because soil sample TPH results were compared on a wet weight basis except for those used to address primary object P4 (effect of soil moisture content).

#### 6.1.1 GRO Analysis

This section summarizes the results for QC checks used by the reference laboratory during GRO analysis, including method blanks, surrogates, MS/MSDs, extract duplicates, and LCS/LCSDs. A summary of the QC check results is presented at the end of the section.

##### Method Blanks

Method blanks were analyzed to verify that steps in the analytical procedure did not introduce contaminants that affected analytical results. Ottawa sand and deionized water were used as method blanks for soil and liquid



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samples, respectively. These blanks underwent all the procedures required for sample preparation. The results for all method blanks met the acceptance criterion of being less than or equal to the required project-specific reporting limit (5 mg/kg). Based on method blank results, the GRO analysis results were considered to be valid.

### **Surrogates**

Each soil investigative and QC sample for GRO analysis was spiked with a surrogate, 4-bromofluorobenzene, before extraction to determine whether significant matrix effects existed within the sample and to estimate the efficiency of analyte recovery during sample preparation and analysis. A diluted, liquid PE sample was also spiked with the surrogate during sample preparation. The initial surrogate spiking levels for soil and liquid PE samples were 2 mg/kg and 40 µg/L, respectively. The acceptance criterion was 39 to 163 percent surrogate recovery. For samples analyzed at a dilution factor greater than four, the surrogate concentration was diluted to a level below the reference laboratory's reporting limit for the reference method; therefore, surrogate recoveries for these samples were not used to assess impacts on data quality.

A total of 101 surrogate measurements were made during analysis of environmental and associated QC samples. Fifty-six of these samples were analyzed at a dilution factor less than or equal to four. The surrogate recoveries for these 56 samples ranged from 43 to 345 percent with a mean recovery of 150 percent and a median recovery of 136 percent. Because the mean and median recoveries were greater than 100 percent, an overall positive bias was indicated.

The surrogate recoveries for 16 of the 56 samples did not meet the acceptance criterion. In each case, the surrogate was recovered at a concentration above the upper limit of the acceptance criterion. Examination of the gas chromatograms for the 16 samples revealed that some PHCs or naturally occurring interferences present in these environmental samples coeluted with the surrogate, resulting in higher surrogate recoveries. Such coelution is typical for hydrocarbon-containing samples analyzed using a GC/FID technique, which was the technique used in the reference method. The surrogate recoveries for QC samples such as method blanks and LCS/LCSDs met the acceptance criterion, indicating that the laboratory sample preparation and analysis procedures were in control. Because the coelution was observed only for

environmental samples and because the surrogate recoveries for QC samples met the acceptance criterion, the reference laboratory did not reanalyze the environmental samples with high surrogate recoveries. Calculations performed to evaluate whether the coelution resulted in underreporting of GRO concentrations indicated an insignificant impact of less than 3 percent. Based on the surrogate results for environmental and associated QC samples, the GRO analysis results for environmental samples were considered to be valid.

A total of 42 surrogate measurements were made during the analysis of soil PE and associated QC samples. Thirty-four of these samples were analyzed at a dilution factor less than or equal to four. The surrogate recoveries for these 34 samples ranged from 87 to 108 percent with a mean recovery of 96 percent and a median recovery of 95 percent. The surrogate recoveries for all 34 samples met the acceptance criterion. Based on the surrogate results for soil PE and associated QC samples, the GRO analysis results for soil PE samples were considered to be valid.

A total of 37 surrogate measurements were made during the analysis of liquid PE and associated QC samples. Six of these samples were analyzed at a dilution factor less than or equal to four. All six samples were QC samples (method blanks and LCS/LCSDs). The surrogate recoveries for these six samples ranged from 81 to 84 percent, indicating a small negative bias. However, the surrogate recoveries for all six samples met the acceptance criterion. Based on the surrogate results for liquid PE and associated QC samples, the GRO analysis results for liquid PE samples were considered to be valid.

### **Matrix Spikes and Matrix Spike Duplicates**

MS/MSD results were evaluated to determine the accuracy and precision of the analytical results with respect to the effects of the sample matrix. For GRO analysis, each soil sample designated as an MS or MSD was spiked with the GRO calibration standard at an initial spiking level of 20 mg/kg. MS/MSDs were also prepared for liquid PE samples. Each diluted, liquid PE sample designated as an MS or MSD was spiked with the GRO calibration standard at an initial spiking level of 40 µg/L. The acceptance criteria for MS/MSDs were 33 to 115 percent recovery and an RPD less than or equal to 25. When the MS/MSD percent recovery acceptance criterion was not met, instead of attributing the failure to meet the criterion to an

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inappropriate spiking level, the reference laboratory respiked the sample at a more appropriate and practical spiking level. Information on the selection of the spiking level and calculation of percent recoveries for MS/MSD samples is provided below.

According to Provost and Elder (1983), for percent recovery data to be reliable, spiking levels should be at least five times the unspiked sample concentration. For the demonstration, however, a large number of the unspiked sample concentrations were expected to range between 1,000 and 10,000 mg/kg, so use of such high spiking levels was not practical. Therefore, a target spiking level of 50 to 150 percent of the unspiked sample concentration was used for the demonstration. Provost and Elder (1983) also present an alternate approach for calculating percent recoveries for MS/MSD samples (100 times the ratio of the measured concentration in a spiked sample to the calculated concentration in the sample). However, for the demonstration, percent recoveries were calculated using the traditional approach (100 times the ratio of the amount recovered to the amount spiked) primarily because the alternate approach is not commonly used.

For environmental samples, a total of 10 MS/MSD pairs were analyzed. Four sample pairs collected in the NEX Service Station Area were designated as MS/MSDs. The sample matrix in this area primarily consisted of medium-grained sand. The percent recoveries for all but one of the MS/MSD samples ranged from 67 to 115 with RPDs ranging from 2 to 14. Only one MS sample with a 162 percent recovery did not meet the percent recovery acceptance criterion; however, the RPD acceptance criterion for the MS/MSD and the percent recovery and RPD acceptance criteria for the LCS/LCSD associated with the analytical batch for this sample were met. Based on the MS/MSD results, the GRO analysis results for the NEX Service Station Area samples were considered to be valid.

Two sample pairs collected in the B-38 Area were designated as MS/MSDs. The sample matrix in this area primarily consisted of sand and clay. The percent recoveries for the MS/MSD samples ranged from 60 to 94 with RPDs of 1 and 13. Therefore, the percent recoveries and RPDs for these samples met the acceptance criteria. Based on the MS/MSD results, the GRO analysis results for the B-38 Area samples were considered to be valid.

Four sample pairs collected in the SFT Area were designated as MS/MSDs. The sample matrix in this area primarily consisted of silty clay. The percent recoveries for the MS/MSD samples ranged from 0 to 127 with RPDs ranging from 4 to 21. Of the four sample pairs, two sample pairs met the percent recovery acceptance criterion, one sample pair exhibited percent recoveries less than the lower acceptance limit, and one sample pair exhibited percent recoveries greater than the upper acceptance limit. For the two sample pairs that did not meet the percent recovery acceptance criterion, the RPD acceptance criterion for the MS/MSDs and the percent recovery and RPD acceptance criteria for the LCS/LCSDs associated with the analytical batches for these samples were met. Because of the varied percent recoveries for the MS/MSD sample pairs, it was not possible to conclude whether the GRO analysis results for the SFT Area samples had a negative or positive bias. Although one-half of the MS/MSD results did not meet the percent recovery acceptance criterion, the out-of-control situations alone did not constitute adequate grounds for rejection of any of the GRO analysis results for the SFT Area samples. The out-of-control situations may have been associated with inadequate spiking levels (0.7 to 2.8 times the unspiked sample concentrations compared to the minimum recommended value of 5 times the concentrations).

Three soil PE sample pairs were designated as MS/MSDs. The sample matrix for these samples consisted of silty sand. The percent recoveries for these samples ranged from 88 to 103 with RPDs ranging from 4 to 6. The percent recoveries and RPDs for these samples met the acceptance criteria. Based on the MS/MSD results, the GRO analysis results for the soil PE samples were considered to be valid.

Two liquid PE sample pairs were designated as MS/MSDs. The percent recoveries for these samples ranged from 77 to 87 with RPDs of 1 and 5. The percent recoveries and RPDs for these samples met the acceptance criteria. Based on the MS/MSD results, the GRO analysis results for the liquid PE samples were considered to be valid.

### **Extract Duplicates**

For GRO analysis, after soil sample extraction, extract duplicates were analyzed to evaluate the precision associated with the reference laboratory's analytical procedure. The reference laboratory sampled duplicate

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aliquots of the GRO extracts for analysis. The acceptance criterion for extract duplicate precision was an RPD less than or equal to 25. Two or more environmental samples collected in each demonstration area whose samples were analyzed for GRO (the NEX Service Station, B-38, and SFT Areas) were designated as extract duplicates. A total of 10 samples designated as extract duplicates were analyzed for GRO. The RPDs for these samples ranged from 0.5 to 11. Therefore, the RPDs for all the extract duplicates met the acceptance criterion. Based on the extract duplicate results, the GRO analysis results were considered to be valid.

### **Laboratory Control Samples and Laboratory Control Sample Duplicates**

For GRO analysis, LCS/LCSD results were evaluated to determine the accuracy and precision associated with control samples prepared by the reference laboratory. To generate a soil LCS or LCSD, Ottawa sand was spiked with the GRO calibration standard at a spiking level of 20 mg/kg. To generate an LCS or LCSD for liquid PE sample analysis, deionized water was spiked with the GRO calibration standard at a spiking level of 40 µg/L. The acceptance criteria for LCS/LCSDs were 33 to 115 percent recovery and an RPD less than or equal to 25. The LCS/LCSD acceptance criteria were based on the reference laboratory's historical data.

Ten pairs of soil LCS/LCSD samples were prepared and analyzed. The percent recoveries for these samples ranged from 87 to 110 with RPDs ranging from 2 to 14. In addition, two pairs of liquid LCS/LCSD samples were prepared and analyzed. The percent recoveries for these samples ranged from 91 to 92 with RPDs equal to 0 and 1. Therefore, the percent recoveries and RPDs for the soil and liquid LCS/LCSD samples met the acceptance criteria, indicating that the GRO analysis procedure was in control. Based on the LCS/LCSD results, the GRO analysis results were considered to be valid.

### **Summary of Quality Control Check Results**

Table 6-1 summarizes the QC check results for GRO analysis. Based on the QC check results, the conclusions presented below were drawn regarding the accuracy and precision of GRO analysis results for the demonstration.

The project-specific percent recovery acceptance criteria were met for most environmental samples and all PE samples. As expected, the percent recovery ranges were broader for the environmental samples than for the PE samples. As indicated by the mean and median percent recoveries, the QC check results generally indicated a slight negative bias (up to 20 percent) in the GRO concentration measurements; the exceptions were the surrogate recoveries for environmental samples and the LCS/LCSD recoveries for soil PE samples. The observed bias did not exceed the generally acceptable bias ( $\pm 30$  percent) stated in SW-846 for organic analyses and is typical for most organic analytical methods for environmental samples. Because the percent recovery ranges were sometimes above and sometimes below 100, the observed bias did not appear to be systematic.

The project-specific RPD acceptance criterion was met for all samples. As expected, the RPD range and the mean and median RPDs for MS/MSDs associated with the soil environmental samples were greater than those for other QC checks and matrixes listed in Table 6-1. The low RPDs observed indicated good precision in the GRO concentration measurements made during the demonstration.

### **6.1.2 EDRO Analysis**

This section summarizes the results for QC checks used by the reference laboratory during EDRO analysis, including method and instrument blanks, surrogates, MS/MSDs, extract duplicates, and LCS/LCSDs. A summary of the QC check results is presented at the end of the section.

#### **Method and Instrument Blanks**

Method and instrument blanks were analyzed to verify that steps in the analytical procedures did not introduce contaminants that affected analytical results. Ottawa sand was used as a method blank for soil samples. The method blanks underwent all the procedures required for sample preparation. For liquid PE samples, the extraction solvent (methylene chloride) was used as an instrument blank. The results for all method and instrument blanks met the acceptance criterion of being less than or equal to the required project-specific reporting limit (10 mg/kg). Based on the method and instrument blank results, the EDRO analysis results were considered to be valid.

**Table 6-1. Summary of Quality Control Check Results for GRO Analysis**

QC Check <sup>a</sup>	Matrix Associated with QC Check	No. of Measurements Used to Evaluate Data Quality	Accuracy (Percent Recovery)				Precision (Relative Percent Difference)						
			Acceptance Criterion	Actual Range	No. of Measurements Meeting Acceptance Criterion	Mean	Median	Acceptance Criterion	Actual Range	No. of Measurements Meeting Acceptance Criterion	Mean	Median	
Surrogate	Soil environmental samples	56	39 to 163	43 to 345	40	150	136	Not applicable	#25	1 to 21	10 pairs	11	
	Soil PE samples	34		87 to 108	34	96	95						
	Liquid PE samples	6		81 to 84	6	83	84						
MS/MSD	Soil environmental samples	20 (10 pairs)	33 to 115	0 to 162	15	81	80	Not applicable	#25	1 to 21	10 pairs	11	
	Soil PE samples	6 (3 pairs)		88 to 103	6	94	92						
	Liquid PE samples	4 (2 pairs)		77 to 87	4	83	85						
Extract duplicate	Soil environmental samples	10 pairs								0.5 to 11	10 pairs	5	4
LCS/LCSD	Soil environmental and PE samples	10 pairs	33 to 115	87 to 110	20	100	100	Not applicable	#25	2 to 14	10 pairs	6	
	Liquid PE samples	2 pairs		91 to 92	4	92	92						

Notes:

- # = Less than or equal to
- LCS/LCSD = Laboratory control sample and laboratory control sample duplicate
- MS/MSD = Matrix spike and matrix spike duplicate
- PE = Performance evaluation
- QC = Quality control

<sup>a</sup> During the demonstration, 12 method blanks (10 for soil samples and 2 for liquid samples) were analyzed. The method blank results met the project-specific acceptance criteria.

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## Surrogates

Each soil investigative and QC sample for EDRO analysis was spiked with a surrogate, o-terphenyl, before extraction to determine whether significant matrix effects existed within the sample and to estimate the efficiency of analyte recovery during sample preparation and analysis. For a 30-gram sample, the spike concentration was 3.3 mg/kg. For samples with higher EDRO concentrations, for which smaller sample amounts were used during extraction, the spiking levels were proportionately higher. The acceptance criterion was 45 to 143 percent surrogate recovery. Liquid PE samples for EDRO analysis were not spiked with a surrogate because the analysis did not include a sample preparation step.

A total of 185 surrogate measurements were made during analysis of environmental and associated QC samples. Six of these samples did not meet the percent recovery acceptance criterion. Four of the six samples were environmental samples. When the reference laboratory reanalyzed the four samples, the surrogate recoveries for the samples met the acceptance criterion; therefore, the reference laboratory reported the EDRO concentrations measured during the reanalyses. The remaining two samples for which the surrogate recoveries did not meet the acceptance criterion were LCS/LCSD samples; these samples had low surrogate recoveries. According to the reference laboratory, these low recoveries were due to the extracts going dry during the extract concentration procedure. Because two samples were laboratory QC samples, the reference laboratory reanalyzed them as well as all the other samples in the QC lot; during the reanalyses, all surrogate recoveries met the acceptance criterion. The surrogate recoveries for all results reported ranged from 45 to 143 percent with mean and median recoveries of 77 percent, indicating an overall negative bias. The surrogate recoveries for all reported sample results met the acceptance criterion. Based on the surrogate results for environmental and associated QC samples, the EDRO analysis results were considered to be valid.

A total of 190 surrogate measurements were made during analysis of soil PE and associated QC samples. Five of these samples did not meet the percent recovery acceptance criterion. In each case, the surrogate was recovered at a concentration below the lower limit of the acceptance criterion. Three of the five samples were soil PE samples, and the remaining two samples were

LCS/LCSDs. The reference laboratory reanalyzed the three soil PE samples and the LCS/LCSD pair as well as all the other samples in the QC lot associated with the LCS/LCSDs; during the reanalyses, all surrogate recoveries met the acceptance criterion. The surrogate recoveries for all results reported ranged from 46 to 143 percent with mean and median recoveries of 76 percent, indicating an overall negative bias. The surrogate recoveries for all reported sample results met the acceptance criterion. Based on the surrogate results for soil PE and associated QC samples, the EDRO analysis results were considered to be valid.

## Matrix Spikes and Matrix Spike Duplicates

MS/MSD results were evaluated to determine the accuracy and precision of the analytical results with respect to the effects of the sample matrix. For EDRO analysis, each soil sample designated as an MS or MSD was spiked with the EDRO calibration standard at an initial spiking level of 50 mg/kg when a 30-gram sample was used during extraction. The initial spiking levels were proportionately higher when smaller sample amounts were used during extraction. The acceptance criteria for MS/MSDs were 46 to 124 percent recovery and an RPD less than or equal to 45. When the MS/MSD percent recovery acceptance criterion was not met, instead of attributing the failure to meet the criterion to an inappropriate spiking level, the reference laboratory respiked the samples at a target spiking level between 50 and 150 percent of the unspiked sample concentration. Additional information on spiking level selection for MS/MSDs is presented in Section 6.1.1. No MS/MSDs were prepared for liquid PE samples for EDRO analysis because the analysis did not include a sample preparation step.

For environmental samples, a total of 13 MS/MSD pairs were analyzed. Two sample pairs collected in the FFA were designated as MS/MSDs. The sample matrix in this area primarily consisted of medium-grained sand. The percent recoveries for the MS/MSD samples ranged from 0 to 183 with RPDs of 0 and 19. One of the two sample pairs exhibited percent recoveries less than the lower acceptance limit. In the second sample pair, one sample exhibited a percent recovery less than the lower acceptance limit, and one sample exhibited a percent recovery greater than the upper acceptance limit. For both sample pairs, the RPD acceptance criterion for the MS/MSDs and the percent recovery and RPD acceptance criteria for the LCS/LCSDs associated with the analytical

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batches for these samples were met. Because of the varied percent recoveries for the MS/MSD sample pairs, it was not possible to conclude whether the EDRO analysis results for the FFA samples had a negative or positive bias. Although the MS/MSD results did not meet the percent recovery acceptance criterion, the out-of-control situations alone did not constitute adequate grounds for rejection of any of the EDRO analysis results for the FFA samples. The out-of-control situations may have been associated with inadequate spiking levels (0.1 to 0.5 times the unspiked sample concentrations compared to the minimum recommended value of 5 times the concentrations).

Four sample pairs collected in the NEX Service Station Area were designated as MS/MSDs. The sample matrix in this area primarily consisted of medium-grained sand. The percent recoveries for the MS/MSD samples ranged from 81 to 109 with RPDs ranging from 4 to 20. The percent recoveries and RPDs for these samples met the acceptance criteria. Based on the MS/MSD results, the EDRO analysis results for the NEX Service Station Area samples were considered to be valid.

One sample pair collected in the PRA was designated as an MS/MSD. The sample matrix in this area primarily consisted of silty sand. The percent recoveries for the MS/MSD samples were 20 and 80 with an RPD equal to 19. One sample exhibited a percent recovery less than the lower acceptance limit, whereas the percent recovery for the other sample met the acceptance criterion. The RPD acceptance criterion for the MS/MSD and the percent recovery and RPD acceptance criteria for the LCS/LCSD associated with the analytical batch for this sample pair were met. Although the percent recoveries for the MS/MSD sample pair may indicate a negative bias, because the MS/MSD results for only one sample pair were available, it was not possible to conclude that the EDRO analysis results for the PRA samples had a negative bias. Although one of the percent recoveries for the MS/MSD did not meet the acceptance criterion, the out-of-control situation alone did not constitute adequate grounds for rejection of any of the EDRO analysis results for the PRA samples. The out-of-control situation may have been associated with inadequate spiking levels (0.4 times the unspiked sample concentration compared to the minimum recommended value of 5 times the concentration).

Two sample pairs collected in the B-38 Area were designated as MS/MSDs. The sample matrix in this area

primarily consisted of sand and clay. The percent recoveries for the MS/MSD samples ranged from 25 to 77 with RPDs of 6 and 11. Of the two sample pairs, one sample pair met the percent recovery acceptance criterion, and one sample pair exhibited percent recoveries less than the lower acceptance limit. For the sample pair that did not meet the percent recovery acceptance criterion, the RPD acceptance criterion for the MS/MSDs and the percent recovery and RPD acceptance criteria for the LCS/LCSDs associated with the analytical batch for the sample pair were met. Although the percent recoveries for one MS/MSD sample pair indicated a negative bias, because the percent recoveries for the other sample pair were acceptable, it was not possible to conclude that the EDRO analysis results for the B-38 Area samples had a negative bias. Although one-half of the MS/MSD results did not meet the percent recovery acceptance criterion, the out-of-control situations alone did not constitute adequate grounds for rejection of any of the EDRO analysis results for the B-38 Area samples. The out-of-control situations may have been associated with inadequate spiking levels (1.4 times the unspiked sample concentrations compared to the minimum recommended value of 5 times the concentrations).

Four sample pairs collected in the SFT Area were designated as MS/MSDs. The sample matrix in this area primarily consisted of silty clay. The percent recoveries for the MS/MSD samples ranged from 0 to 223 with RPDs ranging from 8 to 50. Of the four sample pairs, three sample pairs had one sample each that exhibited a percent recovery less than the lower acceptance limit and one sample pair had one sample that exhibited a percent recovery greater than the upper acceptance limit. The RPD acceptance criterion was met for all but one of the MS/MSDs. The percent recovery and RPD acceptance criteria for the LCS/LCSDs associated with the analytical batches for these samples were met. Because of the varied percent recoveries for the MS/MSD sample pairs, it was not possible to conclude whether the EDRO analysis results for the SFT Area samples had a negative or positive bias. Although one-half of the MS/MSD results did not meet the percent recovery acceptance criterion and one of the four sample pairs did not meet the RPD acceptance criterion, the out-of-control situations alone did not constitute adequate grounds for rejection of any of the EDRO analysis results for the SFT Area samples. The out-of-control situations may have been associated with inadequate spiking levels (0.4 to 0.7 times the unspiked

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sample concentrations compared to the minimum recommended value of 5 times the concentrations).

Five soil PE sample pairs were designated as MS/MSDs. The sample matrix for these samples primarily consisted of silty sand. The percent recoveries for these samples ranged from 0 to 146 with RPDs ranging from 3 to 17. Of the five sample pairs, three sample pairs met the percent recovery acceptance criterion, one sample pair exhibited percent recoveries less than the lower acceptance limit, and one sample pair exhibited percent recoveries greater than the upper acceptance limit. For the two sample pairs that did not meet the percent recovery acceptance criterion, the RPD acceptance criterion for the MS/MSDs and the percent recovery and RPD acceptance criteria for the LCS/LCSDs associated with the analytical batches for these samples were met. Because of the varied percent recoveries for the MS/MSD sample pairs, it was not possible to conclude whether the EDRO analysis results for the soil PE samples had a negative or positive bias. Although the percent recoveries for two of the five sample MS/MSD pairs did not meet the acceptance criterion, the out-of-control situations alone did not constitute adequate grounds for rejection of any of the EDRO analysis results for the soil PE samples.

### **Extract Duplicates**

For EDRO analysis, after soil sample extraction, extract duplicates were analyzed to evaluate the precision associated with the reference laboratory's analytical procedure. The reference laboratory sampled duplicate aliquots of the EDRO extracts for analysis. The acceptance criterion for extract duplicate precision was an RPD less than or equal to 45. One or more environmental samples collected in each demonstration area were designated as extract duplicates. A total of 13 samples designated as extract duplicates were analyzed for EDRO. The RPDs for these samples ranged from 0 to 11 except for one extract duplicate pair collected in the SFT Area that had an RPD equal to 34. The RPDs for all the extract duplicates met the acceptance criterion. Based on the extract duplicate results, all EDRO results were considered to be valid.

### **Laboratory Control Samples and Laboratory Control Sample Duplicates**

For EDRO analysis, LCS/LCSD results were evaluated to determine the accuracy and precision associated with

control samples prepared by the reference laboratory. To generate a soil LCS or LCSD, Ottawa sand was spiked with the EDRO calibration standard at a spiking level of 50 mg/kg. The acceptance criteria for LCS/LCSDs were 46 to 124 percent recovery and an RPD less than or equal to 45. The LCS/LCSD acceptance criteria were based on the reference laboratory's historical data. No LCS/LCSDs were prepared for liquid PE samples for EDRO analysis because the analysis did not include a sample preparation step.

Twenty-two pairs of LCS/LCSD samples were prepared and analyzed. The percent recoveries for these samples ranged from 47 to 88 with RPDs ranging from 0 to 29. Therefore, the percent recoveries and RPDs for these samples met the acceptance criteria, indicating that the EDRO analysis procedure was in control. Based on the LCS/LCSD results, the EDRO analysis results were considered to be valid.

### **Summary of Quality Control Check Results**

Table 6-2 summarizes the QC check results for EDRO analysis. Based on the QC check results, the conclusions presented below were drawn regarding the accuracy and precision of EDRO analysis results for the demonstration.

The project-specific percent recovery acceptance criteria were met for all surrogates and LCS/LCSDs. About one-half of the MS/MSDs did not meet the percent recovery acceptance criterion. As expected, the MS/MSD percent recovery range was broader for environmental samples than for PE samples. The mean and median percent recoveries for all the QC check samples indicated a negative bias (up to 33 percent) in the EDRO concentration measurements. Although the observed bias was slightly greater than the generally acceptable bias ( $\pm 30$  percent) stated in SW-846 for organic analyses, the observed recoveries were not atypical for most organic analytical methods for environmental samples. Because the percent recovery ranges were sometimes above and sometimes below 100, the observed bias did not appear to be systematic.

The project-specific RPD acceptance criterion was met for all samples except one environmental MS/MSD sample pair. As expected, the RPD range and the mean and median RPDs for MS/MSDs associated with the soil environmental samples were greater than those for other QC checks and matrixes listed in Table 6-2. The low

**Table 6-2. Summary of Quality Control Check Results for EDRO Analysis**

QC Check <sup>a</sup>	Matrix Associated with QC Check	No. of Measurements Used to Evaluate Data Quality	Accuracy (Percent Recovery)				Precision (Relative Percent Difference)						
			Acceptance Criterion	Actual Range	No. of Measurements Meeting Acceptance Criterion	Mean	Median	Acceptance Criterion	Actual Range	No. of Measurements Meeting Acceptance Criterion	Mean	Median	
Surrogate	Soil environmental samples	179	45 to 143	45 to 143	179	77	77	Not applicable					
	Soil PE samples	185	46 to 143	46 to 143	185	76	76						
MS/MSD	Soil environmental samples	26 (13 pairs)	46 to 124	0 to 223	14	67	79	#45	0 to 50	12 pairs	17	16	
	Soil PE samples	10 (5 pairs)		0 to 146	6	75	78						
Extract duplicate	Soil environmental samples	13 pairs	Not applicable										
LCS/LCSD	Soil environmental and PE samples	44 (22 pairs)	46 to 124	47 to 88	44	77	80		0 to 29	22 pairs	6	5	

Notes:

# = Less than or equal to

LCS/LCSD = Laboratory control sample and laboratory control sample duplicate

MS/MSD = Matrix spike and matrix spike duplicate

PE = Performance evaluation

QC = Quality control

<sup>a</sup> During the demonstration, 22 method blanks for soil samples and 2 instrument blanks for liquid samples were analyzed. The blank results met the project-specific acceptance criteria.



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RPDs observed indicated good precision in the EDRO concentration measurements made during the demonstration.

## 6.2 Selected Performance Evaluation Sample Results

Soil and liquid PE samples were analyzed during the demonstration to document the reference method's performance in analyzing samples prepared under controlled conditions. The PE sample results coupled with the QC check results were used to establish the reference method's performance in such a way that the overall assessment of the reference method would support interpretation of the OCMA-350's performance, which is discussed in Chapter 7. Soil PE samples were prepared by adding weathered gasoline or diesel to Ottawa sand or processed garden soil. For each sample, an amount of weathered gasoline or diesel was added to the sample matrix in order to prepare a PE sample with a low (less than 100 mg/kg), medium (100 to 1,000 mg/kg), or high (greater than 1,000 mg/kg) TPH concentration. Liquid PE samples consisted of neat materials. Triplicate samples of each type of PE sample were analyzed by the reference laboratory except for the low-concentration-range PE samples, for which seven replicate samples were analyzed.

As described in Section 4.2, some PE samples also contained interferents. Section 6.2 does not discuss the reference method results for PE samples containing interferents because the results address a specific demonstration objective. To facilitate comparisons, the reference method results that directly address demonstration objectives are discussed along with the OCMA-350 results in Chapter 7. Section 6.2 presents a comparison of the reference method's mean TPH results for selected PE samples to the certified values and performance acceptance limits provided by ERA, a commercial PE sample provider that prepared the PE samples for the demonstration. Although the reference laboratory reported sample results for GRO and EDRO analyses separately, because ERA provided certified values and performance acceptance limits, the reference method's mean TPH results (GRO plus EDRO analysis results) were used for comparison.

For soil samples containing weathered gasoline, the certified values used for comparison to the reference

method results were based on mean TPH results for triplicate samples analyzed by ERA using a GC/FID method. ERA extracted the PE samples on the day that PE samples were shipped to the Navy BVC site for distribution to the reference laboratory and developers. The reference laboratory completed methanol extraction of the demonstration samples within 2 days of receiving them. Between 5 and 7 days elapsed between the time that ERA and the time that the reference laboratory completed methanol extractions of the demonstration samples. The difference in extraction times is not believed to have had a significant effect on the reference method's TPH results because the samples for GRO analysis were containerized in EPA-approved EnCores and were stored at  $4 \pm 2$  °C to minimize volatilization. After methanol extraction of the PE samples, both ERA and the reference laboratory analyzed the sample extracts within the appropriate holding times for the extracts.

For soil samples containing diesel, the certified values were established by calculating the TPH concentrations based on the amounts of diesel spiked into known quantities of soil; these samples were not analyzed by ERA. Similarly, the densities of the neat materials were used as the certified values for the liquid PE samples.

The performance acceptance limits for soil PE samples were based on ERA's historical data on percent recoveries and RSDs from multiple laboratories that had analyzed similarly prepared ERA PE samples using a GC method. The performance acceptance limits were determined at the 95 percent confidence level using Equation 6-1.

$$\text{Performance Acceptance Limits} = \text{Certified Value} \times (\text{Average Percent Recovery} \pm 2(\text{Average RSD})) \quad (6-1)$$

According to SW-846, the 95 percent confidence limits should be treated as warning limits, whereas the 99 percent confidence limits should be treated as control limits. The 99 percent confidence limits are calculated by using three times the average RSD in Equation 6-1 instead of two times the average RSD.

When establishing the performance acceptance limits, ERA did not account for variables among the multiple laboratories, such as different extraction and analytical methods, calibration procedures, and chromatogram integration ranges (beginning and end points). For this reason, the performance acceptance limits should be used with caution.

Performance acceptance limits for liquid PE samples were not available because ERA did not have historical information on percent recoveries and RSDs for the neat materials used in the demonstration.

Table 6-3 presents the PE sample types, TPH concentration ranges, performance acceptance limits, certified values, reference method mean TPH concentrations, and ratios of reference method mean TPH concentrations to certified values.

In addition to the samples listed in Table 6-3, three blank soil PE samples (processed garden soil) were analyzed to determine whether the soil PE sample matrix contained a significant TPH concentration. Reference method GRO results for all triplicate samples were below the reporting limit of 0.54 mg/kg. Reference method EDRO results were calculated by adding the results for DRO and oil range organics (ORO) analyses. For one of the triplicate samples, both the DRO and ORO results were below the reporting limits of 4.61 and 5.10 mg/kg, respectively. For the remaining two triplicates, the DRO and ORO results were 1.5 times greater than the reporting limits. Based on the TPH concentrations in the medium- and high-

concentration-range soil PE samples listed in Table 6-3, the contribution of the processed garden soil to the TPH concentrations was insignificant and ranged between 0.5 and 5 percent.

The reference method's mean TPH results for the soil PE samples listed in Table 6-3 were within the performance acceptance limits except for the low-concentration-range diesel samples. For the low-range diesel samples, (1) the individual TPH concentrations for all seven replicates were less than the lower performance acceptance limit and (2) the upper 95 percent confidence limit for TPH results was also less than the lower performance acceptance limit. However, the reference method mean and individual TPH results for the low-range diesel samples were within the 99 percent confidence interval of 10.8 to 54.6 mg/kg, indicating that the reference method results met the control limits but not the warning limits. Collectively, these observations indicated a negative bias in TPH measurements for low-range diesel samples.

As noted above, Table 6-3 presents ratios of the reference method mean TPH concentrations to the certified values for PE samples. The ratios for weathered gasoline-

**Table 6-3. Comparison of Soil and Liquid Performance Evaluation Sample Results**

Sample Type <sup>a</sup>	TPH Concentration Range	Performance Acceptance Limits (mg/kg)	Certified Value	Reference Method Mean TPH Concentration	Reference Method Mean TPH Concentration/ Certified Value (percent)
<b>Soil Sample (Ottawa Sand)</b>					
Diesel	Low	18.1 to 47.4	37.3 mg/kg	14.7 mg/kg	39
<b>Soil Samples (Processed Garden Soil)</b>					
Weathered gasoline	Medium	196 to 781	550 mg/kg	344 mg/kg	62
	High	1,110 to 4,430	3,120 mg/kg	2,030 mg/kg	65
Weathered gasoline at 16 percent moisture	High	992 to 3,950	2,780 mg/kg	1,920 mg/kg	69
Diesel	Medium	220 to 577	454 mg/kg	281 mg/kg	62
	High	1,900 to 4,980	3,920 mg/kg	2,720 mg/kg	69
Diesel at less than 1 percent moisture	High	2,100 to 5,490	4,320 mg/kg	2,910 mg/kg	67
<b>Liquid Samples</b>					
Weathered gasoline	High	Not available	814,100 mg/L	648,000 mg/L	80
Diesel	High	Not available	851,900 mg/L	1,090,000 mg/L	128

Notes:

mg/kg = Milligram per kilogram  
 mg/L = Milligram per liter

<sup>a</sup> Soil samples were prepared at 9 percent moisture unless stated otherwise.

containing soil samples ranged from 62 to 69 percent and did not appear to depend on whether the samples were medium- or high-range samples. The ratio for neat, weathered gasoline (liquid sample) was 80 percent, which was 11 to 18 percentage points greater than the ratios for the soil samples. The difference in the ratios may be attributed to (1) potential loss of volatiles during soil sample transport and storage and during soil sample handling when extractions were performed and (2) lower analyte recovery during soil sample extraction. The less than 100 percent ratios observed indicated a negative bias in TPH measurement for soil and liquid samples containing weathered gasoline. The observed bias for the liquid samples did not exceed the generally acceptable bias ( $\pm 30$  percent) stated in SW-846 for most organic analyses. However, the bias for soil samples exceeded the acceptable bias by up to 8 percentage points.

The ratios for diesel-containing soil samples ranged from 39 to 69 percent and increased with increases in the TPH concentration range. The ratio for neat diesel (liquid sample) was 128 percent, which was substantially greater than the ratios for soil samples. Collectively, the negative bias observed for soil samples and the positive bias observed for liquid samples indicated a low analyte recovery during soil sample extraction because the soil and liquid samples were analyzed using the same calibration procedures but only the soil samples required extraction before analysis. The extraction procedure used during the demonstration is an EPA-approved method that is widely used by commercial laboratories in the United States. Details on the extraction procedure are presented in Table 5-3 of this ITVR.

The positive bias observed for liquid samples did not exceed the generally acceptable bias stated in SW-846. The negative bias observed for high-concentration-range soil samples exceeded the acceptable bias by an average of 2 percentage points. However, the negative bias observed for low- and medium-range samples exceeded the acceptable bias by 31 and 8 percentage points, respectively, indicating a negative bias.

Because the reference method results exhibited a negative bias for soil PE samples when compared to ERA-certified values, ERA's historical data on percent recoveries and RSDs from multiple laboratories were examined. Table 6-4 compares ERA's historical percent recoveries and RSDs to the reference method percent recoveries and RSDs obtained during the demonstration. Table 6-4 shows that ERA's historical recoveries also exhibited a negative bias for all sample types except weathered gasoline in water and that the reference method recoveries were less than ERA's historical recoveries for all sample types except diesel in water. The ratios of reference method mean recoveries to ERA historical mean recoveries for weathered gasoline-containing samples indicated that the reference method TPH results were 26 percent less than ERA's historical recoveries. The reference method recoveries for diesel-containing (1) soil samples were 32 percent less than the ERA historical recoveries and (2) water samples were 63 percent greater than the ERA historical recoveries. In all cases, the RSDs for the reference method were significantly lower than ERA's historical RSDs, indicating that the reference method achieved significantly greater precision. The greater precision observed for the reference method during the

**Table 6-4. Comparison of Environmental Resource Associates Historical Results to Reference Method Results**

Sample Type	ERA Historical Results		Reference Method Results		
	Mean Recovery (percent)	Mean Relative Standard Deviation (percent)	Mean Recovery <sup>a</sup> (percent)	Reference Method Mean Recovery/ERA Historical Mean Recovery (percent)	Mean Relative Standard Deviation <sup>a</sup> (percent)
Weathered gasoline in soil	88.7	26.5	65	74	8
Diesel in soil	87.7	19.6	59	68	7
Weathered gasoline in water	109	22.0	80	73	5
Diesel in water	78.5	22.8	128	163	6

Notes:

ERA = Environmental Resource Associates

<sup>a</sup> The reference method mean recovery and mean relative standard deviation were based on recoveries and relative standard deviations observed for all concentration ranges for a given type of performance evaluation sample.

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demonstration may be associated with the fact that the reference method was implemented by a single laboratory, whereas ERA's historical RSDs were based on results obtained from multiple laboratories that may have used different analytical protocols.

In summary, compared to ERA-certified values, the TPH results for all PE sample types except neat diesel exhibited a negative bias to a varying degree; the TPH results for neat diesel exhibited a positive bias of 28 percent. For weathered gasoline-containing soil samples, the bias was relatively independent of the TPH concentration range and exceeded the generally acceptable bias stated in SW-846 by up to 8 percentage points. For neat gasoline samples, the bias did not exceed the acceptable bias. For diesel-containing soil samples, the bias increased with decreases in the TPH concentration range, and the bias for low-, medium-, and high-range samples exceeded the acceptable bias by 31, 8, and 2 percentage points, respectively. For neat diesel samples, the observed positive bias did not exceed the acceptable bias. The low RSDs (5 to 8 percent) associated with the reference method indicated good precision in analyzing both soil and liquid samples. Collectively, these observations suggest that caution should be exercised during comparisons of OCMA-350 and reference method results for low- and medium-range soil samples containing diesel.

### 6.3 Data Quality

Based on the reference method's performance in analyzing the QC check samples and selected PE samples, the reference method results were considered to be of adequate quality for the following reasons: (1) the reference method was implemented with acceptable accuracy ( $\pm 30$  percent) for all samples except low- and medium-concentration-range soil samples containing diesel, which made up only 13 percent of the total number of samples analyzed during the demonstration, and (2) the reference method was implemented with good precision for all samples (the overall RPD range was 0 to 17). The reference method results generally exhibited a negative bias. However, the bias was considered to be significant primarily for low- and medium-range soil samples containing diesel because the bias exceeded the generally acceptable bias of  $\pm 30$  percent stated in SW-846 by 31 percentage points for low-range and 8 percentage points for medium-range samples. The reference method recoveries observed were typical of the recoveries obtained by most organic analytical methods for environmental samples.

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## Chapter 7

### Performance of the OCMA-350

To verify a wide range of performance attributes, the demonstration had both primary and secondary objectives. Primary objectives were critical to the technology evaluation and were intended to produce quantitative results regarding a technology's performance. Secondary objectives provided information that was useful but did not necessarily produce quantitative results regarding a technology's performance. This chapter discusses the performance of the OCMA-350 based on the primary objectives (excluding costs associated with TPH measurement) and secondary objectives. Costs associated with TPH measurement (primary objective P6) are presented in Chapter 8. The demonstration results for both the primary and secondary objectives are summarized in Chapter 9.

#### 7.1 Primary Objectives

This section discusses the performance results for the OCMA-350 based on primary objectives P1 through P5, which are listed below.

- P1. Determine the MDL
- P2. Evaluate the accuracy and precision of TPH measurement for a variety of contaminated soil samples
- P3. Evaluate the effect of interferents on TPH measurement
- P4. Evaluate the effect of soil moisture content on TPH measurement
- P5. Measure the time required for TPH measurement

To address primary objectives P1 through P5, samples were collected from five different sampling areas. In addition, soil and liquid PE samples were prepared and

distributed to Horiba and the reference laboratory. The numbers and types of environmental samples collected in each sampling area and the numbers and types of PE samples prepared are discussed in Chapter 4. Primary objectives P1 through P4 were addressed using statistical and nonstatistical approaches, as appropriate. The statistical tests performed to address these objectives are illustrated in the flow diagram in Figure 7-1. Before a parametric test was performed, the Wilk-Shapiro test was used to determine whether the OCMA-350 results and reference method results or, when appropriate, their differences were normally distributed at a significance level of 5 percent. If the results or their differences were not normally distributed, the Wilk-Shapiro test was performed on transformed results (for example, logarithm and square root transformations) to verify the normality assumption. If the normality assumption was not met, a nonparametric test was performed. Nonparametric tests are not as powerful as parametric tests because the nonparametric tests do not account for the magnitude of the difference between sample results. Despite this limitation, when the normality assumption was not met, performing a nonparametric test was considered to be a better alternative than performing no statistical comparison.

For the OCMA-350, when the TPH concentration in a given sample was reported as below the reporting limit, one-half the reporting limit was used as the TPH concentration for that sample, as is commonly done, so that necessary calculations could be performed without rejecting the data. The same approach was used for the reference method except that the appropriate reporting limits were used in calculating the TPH concentration depending on which TPH measurement components (GRO, DRO, and ORO) were reported at concentrations below the reporting limits. Caution was exercised to ensure that these necessary data manipulations did not alter the conclusions.

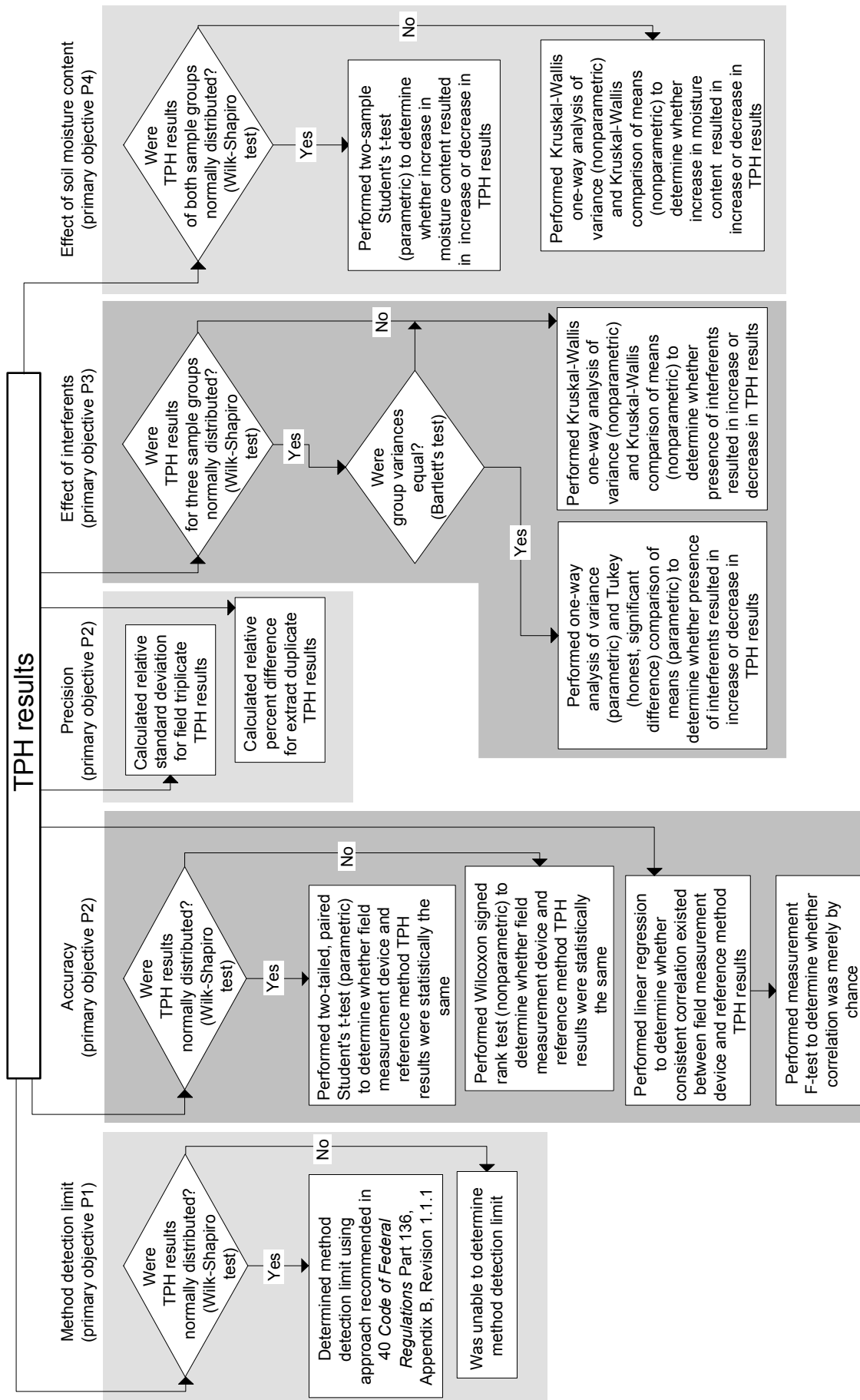


Figure 7-1. Summary of statistical analysis of TPH results.

The reference method GRO results were adjusted for solvent dilution associated with the soil sample moisture content because the method required use of methanol, a water-miscible solvent, for extraction of soil samples. In addition, based on discussions with Horiba and the reference laboratory, all TPH results for the OCMA-350 and the reference method were rounded to three significant figures.

### 7.1.1 Primary Objective P1: Method Detection Limit

To determine the MDLs for the OCMA-350 and reference method, both Horiba and the reference laboratory analyzed seven low-concentration-range soil PE samples containing weathered gasoline and seven low-concentration-range soil PE samples containing diesel. As discussed in Chapter 4, problems arose during preparation of the low-range weathered gasoline samples; therefore, the results for the soil PE samples containing weathered gasoline could not be used to determine MDLs.

Because the OCMA-350 and reference method results were both normally distributed, the MDLs for the soil PE samples containing diesel were calculated using Equation 7-1 (40 CFR Part 136, Appendix B, Revision 1.1.1). An MDL thus calculated is influenced by TPH concentrations because the standard deviation will likely decrease with a decrease in TPH concentrations. As a result, the MDL will be lower when low-concentration samples are used for MDL determination. Despite this limitation, Equation 7-1 is commonly used and provides a reasonable estimate of the MDL.

$$MDL = (S) t_{(n-1, 1-\alpha=0.99)} \quad (7-1)$$

where

S = Standard deviation of replicate TPH results

$t_{(n-1, 1-\alpha=0.99)}$  = Student's t-value appropriate for a 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom (3.143 for n = 7 replicates)

Because GRO compounds were not expected to be present in the soil PE samples containing diesel, the reference laboratory performed only EDRO analysis of these samples and reported the sums of the DRO and ORO concentrations as the TPH results. The OCMA-350 and reference method results for these samples are presented in Table 7-1.

**Table 7-1. TPH Results for Low-Concentration-Range Diesel Soil Performance Evaluation Samples**

OCMA-350 Result (mg/kg)	Reference Method Result (mg/kg)
28.8	16.4
21.0	16.4
30.6	13.2
24.2	16.0
33.4	14.2
23.2	14.1
32.2	12.8
MDL	15.2
	4.79

Notes:

MDL = Method detection limit  
mg/kg = Milligram per kilogram

Based on the TPH results for the low-concentration-range diesel soil PE samples, the MDLs were determined to be 15.2 and 4.79 mg/kg for the OCMA-350 and reference method, respectively. Because the ORO concentrations in all these samples were below the reference laboratory's estimated reporting limit (5.1 mg/kg), the MDL for the reference method was also calculated using only DRO results. The MDL for the reference method based on the DRO results was 4.79 mg/kg, which was the same as the MDL for the reference method based on the EDRO results, indicating that the ORO concentrations below the reporting limit did not impact the MDL for the reference method.

The MDL of 15.2 mg/kg for the OCMA-350 was greater than the MDL of 1 mg/kg claimed by Horiba. The MDL of 4.79 mg/kg for the reference method compared well with the MDL of 4.72 mg/kg published in SW-846 Method 8015C for diesel samples extracted using a pressurized fluid extraction method and analyzed for DRO.

### 7.1.2 Primary Objective P2: Accuracy and Precision

This section discusses the ability of the OCMA-350 to accurately and precisely measure TPH concentrations in a variety of contaminated soils. The OCMA-350 TPH results were compared to the reference method TPH results. Accuracy and precision are discussed in Sections 7.1.2.1 and 7.1.2.2, respectively.

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### 7.1.2.1 Accuracy

The accuracy of OCMA-350 measurement of TPH was assessed by determining

- Whether the conclusion reached using the OCMA-350 agreed with that reached using the reference method regarding whether the TPH concentration in a given sampling area or soil type exceeded a specified action level
- Whether the OCMA-350 results were biased high or low compared to the reference method results
- Whether the OCMA-350 results were different from the reference method results at a statistical significance level of 5 percent when a pairwise comparison was made
- Whether a significant correlation existed between the OCMA-350 and reference method results

During examination of these four factors, the data quality of the reference method and OCMA-350 TPH results was considered. For example, as discussed in Chapter 6, the reference method generally exhibited a low bias. However, the bias observed for all samples except low- and medium-concentration-range diesel soil samples did not exceed the generally acceptable bias of  $\pm 30$  percent stated in SW-846 for organic analyses. Therefore, caution was exercised during comparison of the OCMA-350 and reference method results, particularly those for low- and medium-range diesel soil samples. Caution was also exercised during interpretation of statistical test conclusions drawn based on a small number of samples. For example, only three samples were used for each type of PE sample except the low-range diesel samples; the small number of samples used increased the probability that the results being compared would be found to be statistically the same.

As discussed in Chapter 2, during the demonstration, the OCMA-350 was calibrated using diesel. The following sections discuss how the OCMA-350 results compared with the reference method results by addressing each of the four factors identified above.

#### Action Level Conclusions

Table 7-2 compares action level conclusions reached using the OCMA-350 and reference method results for

environmental and soil PE samples. Section 4.2 of this ITVR explains how the action levels were selected for the demonstration. Of the environmental samples, the percentage of samples for which the conclusions agreed ranged from 71 to 100. Of the PE samples, the percentage of samples for which the conclusions agreed ranged from 0 to 100. Overall, the conclusions were the same for 73 percent of the samples.

The least agreement observed for the environmental samples was for those from the SFT Area (71 percent). Regarding the PE samples, none of the OCMA-350 action level conclusions agreed with those of the reference method for the medium-concentration-range weathered gasoline and diesel samples and the high-concentration-range diesel samples with 9 percent moisture content. The 0 percent agreement observed for these samples cannot be explained.

When the action level conclusions did not agree, the TPH results were further interpreted to assess whether the OCMA-350 conclusion was conservative. The OCMA-350 conclusion was considered to be conservative when the OCMA-350 result was above the action level and the reference method result was below the action level. A regulatory agency would likely favor a field measurement device whose results are conservative; however, the party responsible for a site cleanup might not favor a device that is overly conservative because of the cost associated with unnecessary cleanup. For the OCMA-350, 29 of 107 action level conclusions did not agree with the reference method conclusions. Of the 29 OCMA-350 conclusions, 11 of the 13 conclusions for environmental samples and 12 of the 16 conclusions for PE samples were not conservative.

#### Measurement Bias

To determine the measurement bias, the ratios of the OCMA-350 TPH results to the reference method TPH results were calculated. The observed bias values were grouped to identify the number of OCMA-350 results within the following ranges of the reference method results: (1) greater than 0 to 30 percent, (2) greater than 30 to 50 percent, and (3) greater than 50 percent.

Figure 7-2 shows the distribution of measurement bias for the environmental samples. Of the five sampling areas, good agreement between the OCMA-350 and reference method results was observed for samples collected from the FFA and NEX Service Station Area; for these samples,



**Table 7-2. Action Level Conclusions**

Sampling Area or Sample Type		Action Level (mg/kg)	Total Number of Samples Analyzed	Percentage of Samples for Which OCMA-350 and Reference Method Conclusions Agreed	When Conclusions Did Not Agree, Were OCMA-350 Conclusions Conservative or Not Conservative? <sup>a</sup>
Fuel Farm Area		100	10	100	
Naval Exchange Service Station Area		50	20	95	Not conservative
Phytoremediation Area		1,500	8	75	Not conservative (one of two conclusions for each area)
B-38 Area		100	8	75	
Slop Fill Tank Area		500	28	71	Not conservative
PE sample	Blank soil (9 percent moisture content)	10	3 <sup>b</sup>	100	
PE sample	Blank soil and humic acid (9 percent moisture content)	200	6	100	
Soil PE sample containing weathered gasoline in	Medium-concentration range (9 percent moisture content)	200	3	0	Not conservative
	High-concentration range (9 percent moisture content)	2,000	3	33	
	High-concentration range (16 percent moisture content)	2,000	3	67	
Soil PE sample containing diesel in	Low-concentration range (9 percent moisture content)	15	7	43	Conservative
	Medium-concentration range (9 percent moisture content)	200	3	0	Not conservative
	High-concentration range (less than 1 percent moisture content)	2,000	3	100	
	High-concentration range (9 percent moisture content)	2,000	3	0	Not conservative
Total			108	73	

Notes:

mg/kg = Milligram per kilogram  
 PE = Performance evaluation

<sup>a</sup> A conclusion was considered to be conservative when the OCMA-350 result was above the action level and the reference method result was below the action level. A conservative conclusion may also be viewed as a false positive.

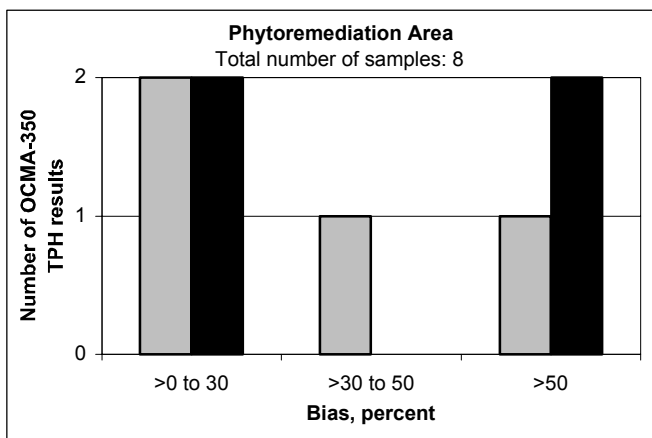
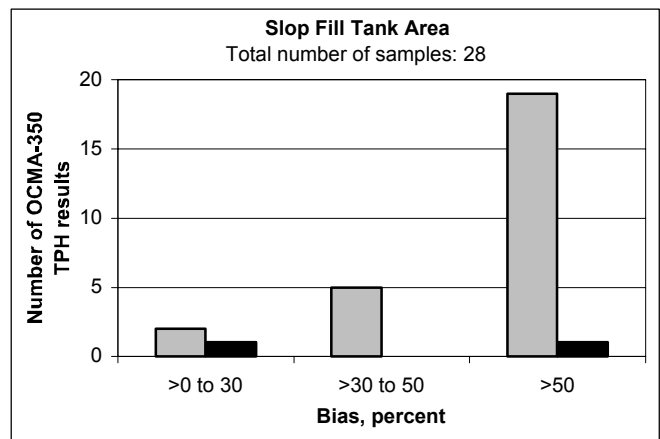
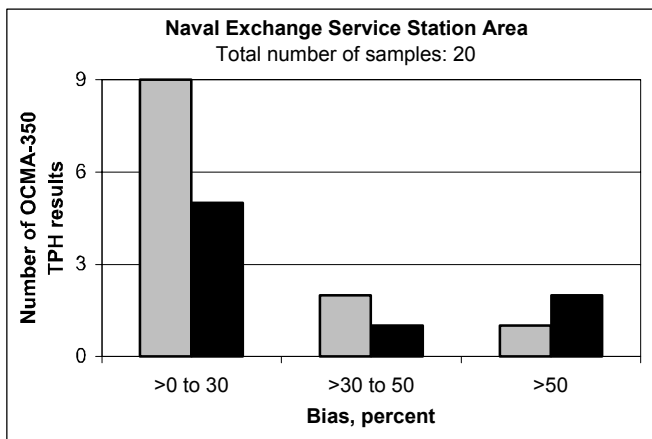
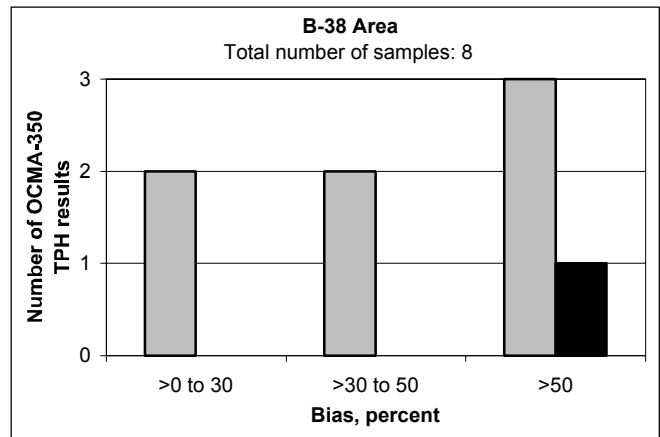
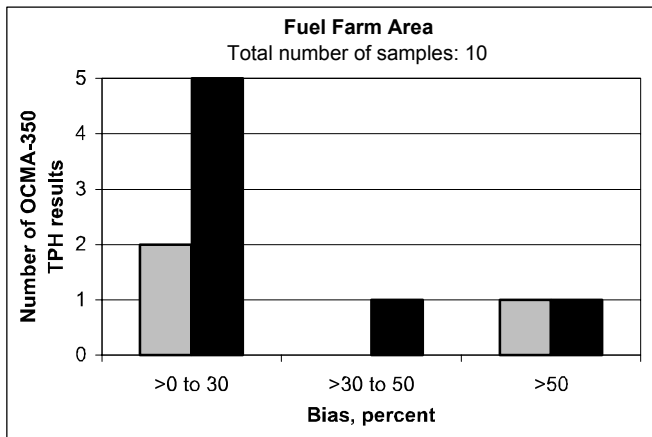
<sup>b</sup> Action level conclusions could be drawn for only two of three samples; the OCMA-350 TPH result for the remaining sample was reported as a “less than” value—specifically, less than 15.2 mg/kg, which was greater than the action level.

80 and 85 percent of the OCMA-350 results, respectively, were within 50 percent of the reference method results. Moderate agreement between the device and reference method results was observed for samples collected from the PRA and B-38 Area; for these samples, 62 and 50 percent of the OCMA-350 results, respectively, were within 50 percent of the reference method results. For samples collected from the SFT Area, 28 percent of the OCMA-350 results were within 50 percent of the reference method results.

Most of the OCMA-350 results were biased low except those for the PRA and FFA samples. Low and high biases were split equally for the samples collected from the PRA.

The results for 70 percent of the samples from the FFA were biased high, perhaps because of the significant negative bias associated with reference method results for diesel soil PE samples (see Chapter 6). The reason that most of the OCMA-350 results for the other sampling areas were biased low was unclear.

Figure 7-3 shows the distribution of measurement bias for selected soil PE samples. Of the five sets of samples containing PHCs and the one set of blank samples, moderate agreement between the OCMA-350 and reference method results was observed for the blank samples and the high-concentration-range weathered gasoline and diesel samples; for these samples, 67, 50, and



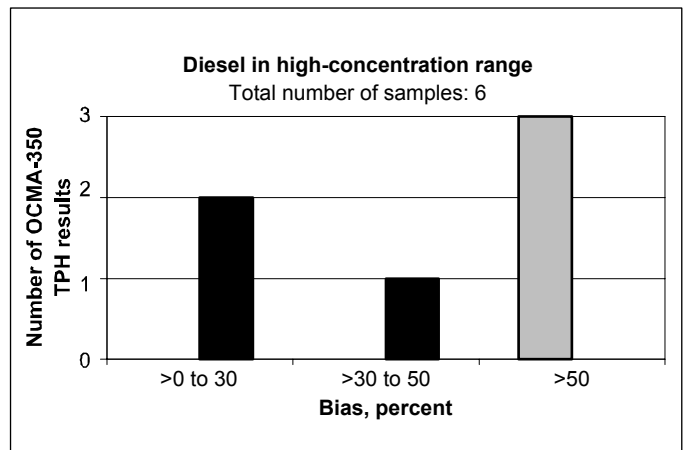
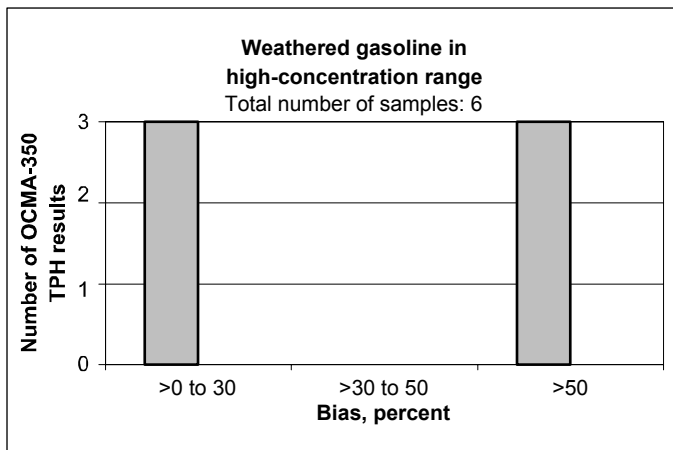
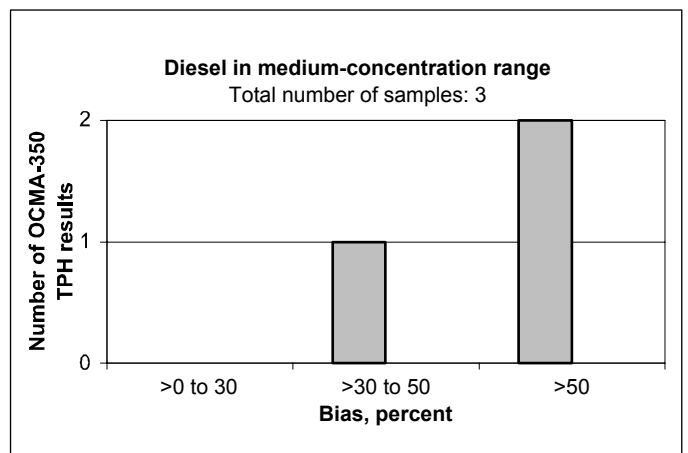
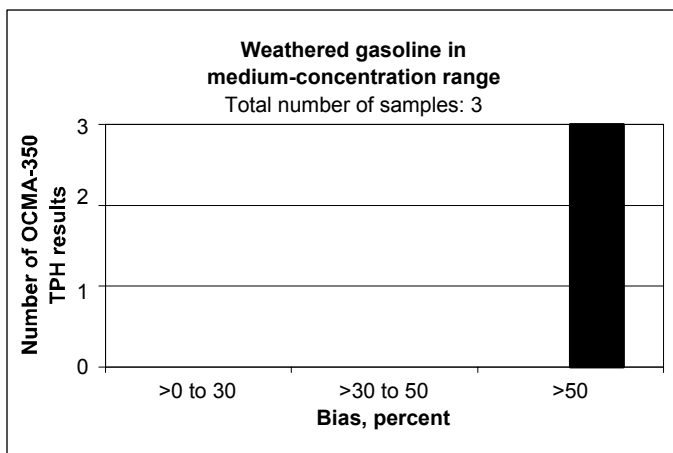
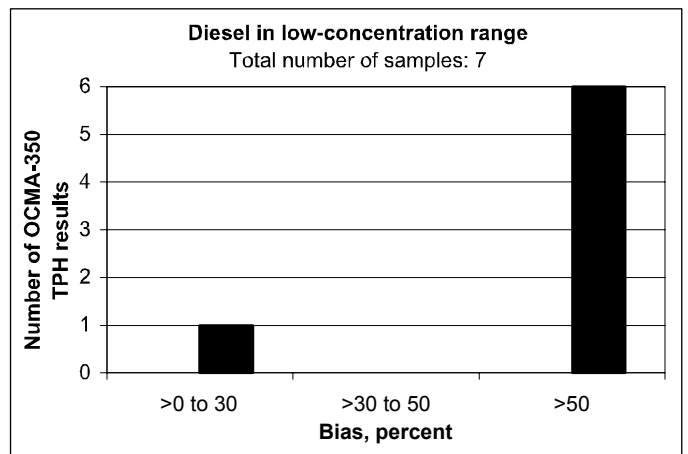
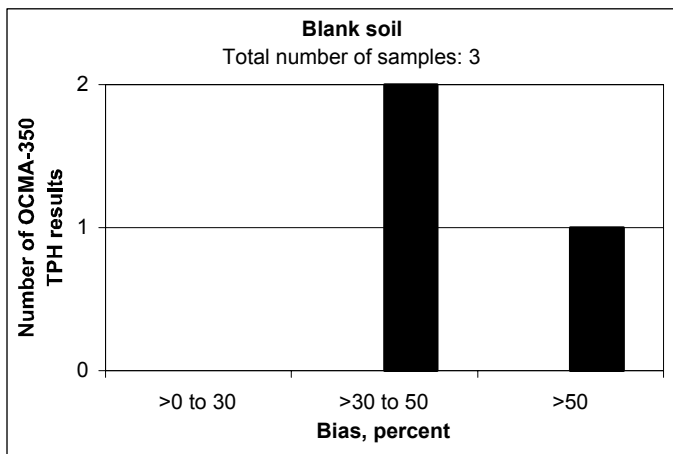
Notes:

> = Greater than

☐ OCMA-350 result biased low compared to reference method result

■ OCMA-350 result biased high compared to reference method result

Figure 7-2. Measurement bias for environmental samples.



Notes: > = Greater than;  OCMA-350 result biased low compared to reference method result;  OCMA-350 result biased high compared to reference method result

Figure 7-3. Measurement bias for soil performance evaluation samples.

50 percent of the OCMA-350 results, respectively, were within 50 percent of the reference method results. For medium-range diesel samples, 33 percent of the OCMA-350 results were within 50 percent of the reference method results. For the OCMA-350, only one of the seven low-range diesel sample results was within 30 percent of the reference method result, and the remaining six sample results exhibited a bias of greater than 50 percent. All three OCMA-350 results for medium-range weathered gasoline samples exhibited a bias of greater than 50 percent.

The OCMA-350 results were biased high for all PE samples except the high-concentration-range weathered gasoline samples, the medium-concentration-range diesel samples, and three high-concentration-range diesel samples. The high bias observed for the OCMA-350 results for low-range diesel samples might be explained by the significant negative bias associated with the reference method results for low-range diesel samples. However, the high bias of greater than 50 percent observed for the remaining OCMA-350 results cannot be explained based solely on the negative bias associated with the reference method (see Chapter 6).

### **Pairwise Comparison of TPH Results**

To evaluate whether a statistically significant difference existed between the OCMA-350 and reference method TPH results, a parametric test (a two-tailed, paired Student's t-test) or a nonparametric test (a Wilcoxon signed rank test) was selected based on the approach presented in Figure 7-1. Tables 7-3 and 7-4 present statistical comparisons of the OCMA-350 and reference method results for environmental and PE samples, respectively. The tables present the OCMA-350 and reference method results for each sampling area or PE sample type, the statistical test performed and the associated null hypothesis used to compare the results, whether the results were statistically the same or different, and the probability that the results were the same.

Table 7-3 shows that the OCMA-350 and reference method results were statistically the same at a significance level of 5 percent for all sampling areas except the SFT Area. Based on a simple comparison of the results, this conclusion appeared to be reasonable for all sampling areas. For example, for the SFT Area, the OCMA-350 results were biased low by up to one order of magnitude for 26 of 28 samples, which justified the statistical test conclusion.

Table 7-4 shows that the OCMA-350 and reference method results were statistically the same at a significance level of 5 percent for blank soil PE samples and neat weathered gasoline PE samples. The OCMA-350 and reference method results for all other PE sample types were statistically different. Based on a simple comparison of the results, these conclusions appeared to be reasonable, except for high-concentration-range weathered gasoline (16 percent moisture content) and high-concentration-range diesel (less than 1 percent moisture content). However, the statistical conclusions for high-range weathered gasoline (16 percent moisture content) and diesel (less than 1 percent moisture content) are justified considering that the OCMA-350 exhibited a consistent bias and that the differences between the OCMA-350 and reference method TPH results were considerably different than zero.

Of the OCMA-350 PE sample results that were statistically different from the reference method results, the OCMA-350 results for (1) all soil samples containing low-concentration-range diesel, and high-concentration-range diesel (less than 1 percent moisture content) were biased high by up to a factor of two; (2) all soil samples containing medium- and high-concentration-range diesel (9 percent moisture content) and medium- and high-concentration-range weathered gasoline were biased low by up to a factor of three; and (3) neat diesel samples were biased low by up to 35 percent. In addition, the OCMA-350 results for the liquid PE samples were biased low when compared to the sample densities. Specifically, the OCMA-350 results were biased low by 32 percent for neat weathered gasoline samples and by 13 percent for neat diesel samples.

### **Correlation of TPH Results**

To determine whether a significant correlation existed between the OCMA-350 and reference method TPH results, linear regression analysis was performed. A strong correlation between the OCMA-350 and reference method results would indicate that the device results could be adjusted using the established correlation and that field decisions could be made using the adjusted results in situations where the device results may not be the same as off-site laboratory results. Figures 7-4 and 7-5 show the linear regression plots for environmental and soil PE samples, respectively. Table 7-5 presents the regression model, square of the correlation coefficient ( $R^2$ ), and probability that the slope of the regression line is equal to

**Table 7-3. Statistical Comparison of OCMA-350 and Reference Method TPH Results for Environmental Samples**

Sampling Area	TPH Result (mg/kg)		Statistical Analysis Summary		
	OCMA-350	Reference Method	Statistical Test and Null Hypothesis	Were OCMA-350 and Reference Method Results Statistically the Same or Different?	Probability of Null Hypothesis Being True (percent)
Fuel Farm Area	87.6	68.2	<u>Statistical Test</u> Wilcoxon signed rank test (nonparametric)  <u>Null Hypothesis</u> The median of the differences between the paired observations (OCMA-350 and reference method results) is equal to zero.	Same	10.54
	14,600	15,000			
	69.1	90.2			
	17,200	12,000			
	94.4	44.1			
	15,300	13,900			
	1,570	1,330			
	8,990	8,090			
	44.4	93.7			
	14,400	12,300			
Naval Exchange Service Station Area	32.6	28.8	<u>Statistical Test</u> Two-tailed, paired Student's t-test (parametric)  <u>Null Hypothesis</u> The mean of the differences between the paired observations (OCMA-350 and reference method results) is equal to zero.	Same	72.75
	241	144			
	777	617			
	360	293			
	314	280			
	1,440	1,870			
	1,530	1,560			
	Less than 15.2	9.56			
	380	270			
	1,540	881			
	1,100	1,120			
	Less than 15.2	14.2			
	266	219			
	997	1,180			
	1,200	1,390			
	Less than 15.2	15.2			
	43.2	54.5			
	1,840	2,570			
2,390	3,030				
Less than 15.2	15.9				
Phytoremediation Area	2,050	2,140	<u>Statistical Test</u> Two-tailed, paired Student's t-test (parametric)  <u>Null Hypothesis</u> The mean of the differences between the paired observations (OCMA-350 and reference method results) is equal to zero.	Same	65.14
	3,070	1,790			
	2,840	1,390			
	786	1,420			
	798	1,130			
	1,590	1,530			
	771	1,580			
1,480	1,300				

**Table 7-3. Statistical Comparison of OCMA-350 and Reference Method TPH Results for Environmental Samples (Continued)**

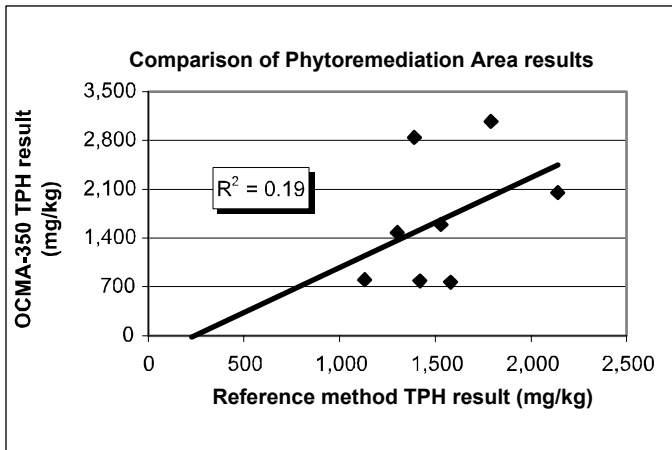
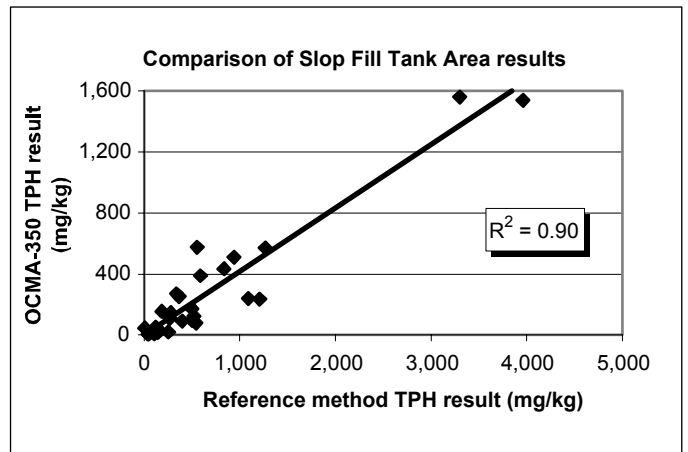
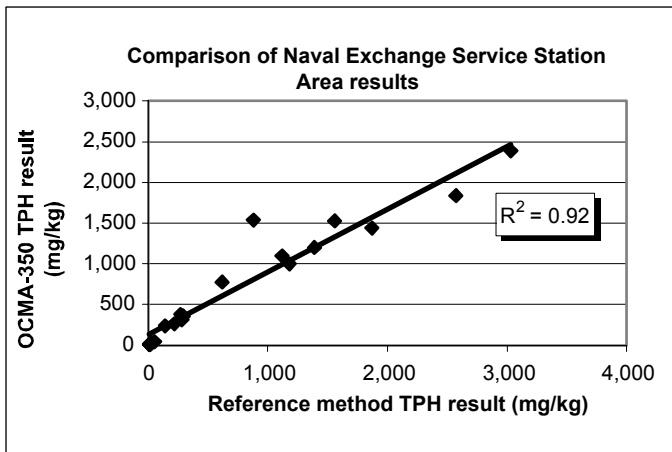
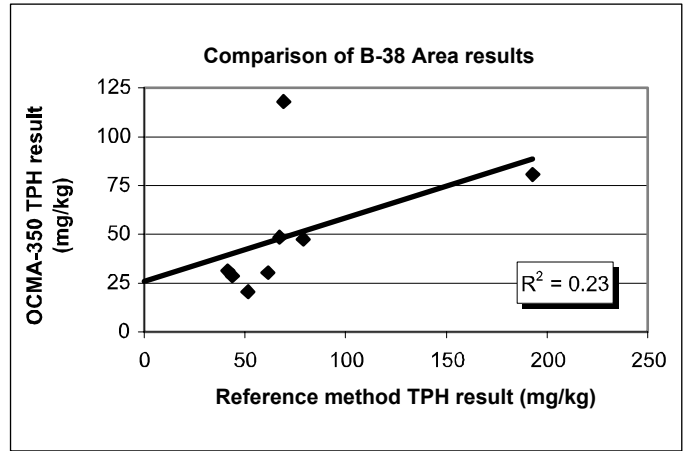
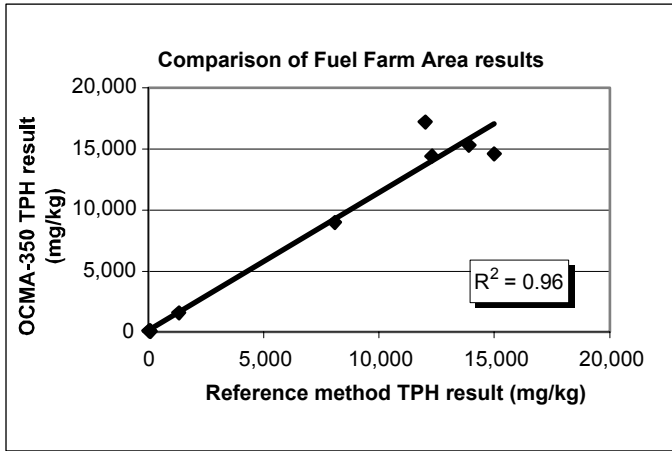
Sampling Area	TPH Result (mg/kg)		Statistical Analysis Summary		
	OCMA-350	Reference Method	Statistical Test and Null Hypothesis	Were OCMA-350 and Reference Method Results Statistically the Same or Different?	Probability of Null Hypothesis Being True (percent)
B-38 Area	47.5	79.0	<u>Statistical Test</u> Two-tailed, paired Student's t-test (parametric)  <u>Null Hypothesis</u> The mean of the differences between the paired observations (OCMA-350 and reference method results) is equal to zero.	Same	14.99
	31.4	41.5			
	30.4	61.4			
	48.6	67.3			
	80.6	193			
	118	69.4			
	28.8	43.8			
	20.6	51.6			
Slop Fill Tank Area	Less than 15.2	105	<u>Statistical Test</u> Two-tailed, paired Student's t-test (parametric)  <u>Null Hypothesis</u> The mean of the differences between the paired observations (OCMA-350 and reference method results) is equal to zero.	Different	0.00
	111	269			
	92.0	397			
	271	339			
	44.7	6.16			
	Less than 15.2	37.1			
	Less than 15.2	43.9			
	Less than 15.2	52.4			
	1,560	3,300			
	571	1,270			
	389	588			
	576	554			
	434	834			
	172	501			
	146	280			
	156	185			
	240	1,090			
	78.5	544			
	96.7	503			
	16.7	146			
	510	938			
	123	517			
	254	369			
	20.4	253			
35.1	151				
1,540	3,960				
235	1,210				
52.6	121				

Note:

mg/kg = Milligram per kilogram

**Table 7-4. Statistical Comparison of OCMA-350 and Reference Method TPH Results for Performance Evaluation Samples**

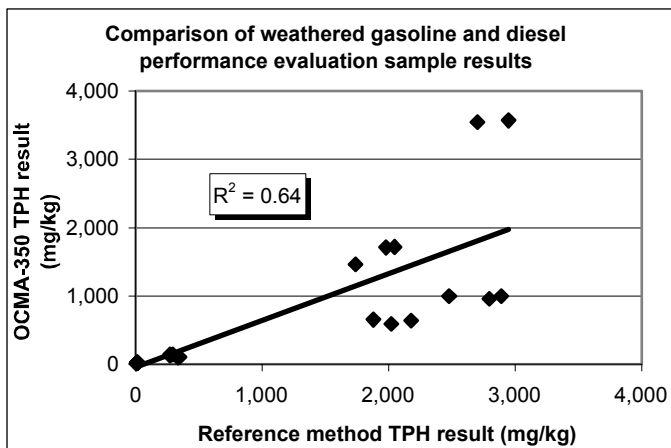
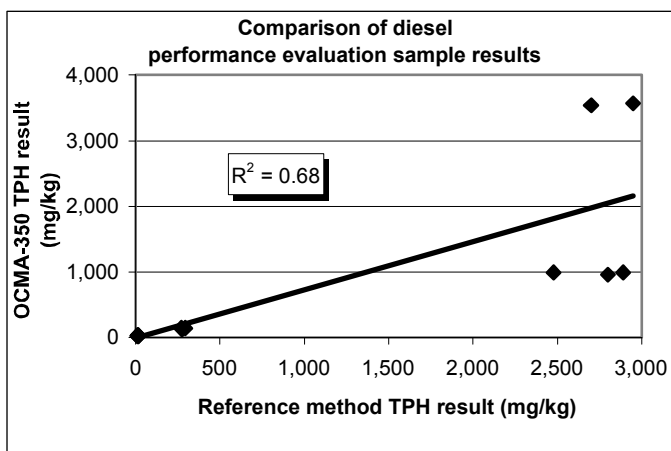
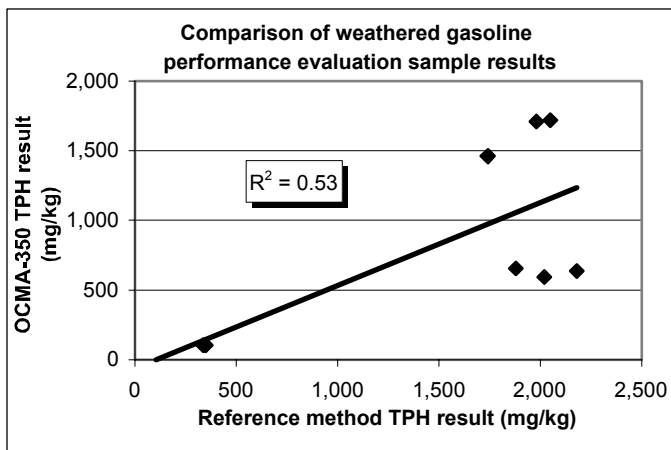
Sample Type		TPH Result		Statistical Analysis Summary		
		OCMA-350	Reference Method	Statistical Test and Null Hypothesis	Were OCMA-350 and Reference Method Results Statistically the Same or Different?	Probability of Null Hypothesis Being True (percent)
<b>Soil Samples (Processed Garden Soil) (TPH Results in Milligram per Kilogram)</b>						
Blank (9 percent moisture content)		Less than 15.2	5.12	<u>Statistical Test</u> Two-tailed, paired Student's t-test (parametric)	Same	7.83
		20.9	13.1			
		18.7	13.5			
Weathered gasoline	Medium-concentration range (9 percent moisture content)	107	350	<u>Null Hypothesis</u> The mean of the differences between the paired observations (OCMA-350 and reference method results) is equal to zero.	Different	0.02
		108	346			
		104	336			
	High-concentration range (9 percent moisture content)	657	1,880		Different	0.44
		595	2,020			
		638	2,180			
	High-concentration range (16 percent moisture content)	1,460	1,740		Different	0.40
		1,710	1,980			
		1,720	2,050			
Diesel	Low-concentration range (9 percent moisture content)	28.8	16.4		Different	0.12
		21.0	16.4			
		30.6	13.2			
		24.2	16			
		33.4	14.2			
		23.2	14.1			
	Medium-concentration range (9 percent moisture content)	124	276		Different	0.25
		143	273			
		144	295			
	High-concentration range (9 percent moisture content)	992	2,480		Different	0.53
		995	2,890			
		958	2,800			
	High-concentration range (less than 1 percent moisture content)	3,540	2,700		Different	4.16
		3,570	2,950			
		3,460	3,070			
<b>Liquid Samples (Neat Materials) (TPH Results in Milligram per Liter)</b>						
Weathered gasoline		541,000	656,000	<u>Statistical Test</u> Two-tailed, paired Student's t-test (parametric)	Same	5.99
		566,000	611,000			
		560,000	677,000			
Diesel		750,000	1,090,000	<u>Null Hypothesis</u> The mean of the differences between the paired observations (OCMA-350 and reference method results) is equal to zero.	Different	1.00
		737,000	1,020,000			
		758,000	1,160,000			



Notes:  
 mg/kg = Milligram per kilogram  
 $R^2$  = Square of the correlation coefficient

Figure 7-4. Linear regression plots for environmental samples.





Notes:

mg/kg = Milligram per kilogram

R<sup>2</sup> = Square of the correlation coefficient

**Figure 7-5. Linear regression plots for soil performance evaluation samples.**

zero (F-test probability) for each sampling area and soil PE sample type.

Table 7-5 shows that R<sup>2</sup> values for (1) environmental samples except PRA and B-38 Area samples ranged from 0.90 to 0.96 and (2) soil PE samples ranged from 0.53 to 0.68. The R<sup>2</sup> values for the PRA and B-38 Area samples were 0.19 and 0.23, respectively. The R<sup>2</sup> values for separate regression models for weathered gasoline and diesel soil PE samples were lower and higher, respectively, than the R<sup>2</sup> value for a combined regression model for these PE samples. For environmental samples, the probabilities of the slopes of the regression lines being equal to zero were 0.00 percent for the FFA, NEX Service Station Area, and SFT Area samples; 27.92 percent for the PRA samples; and 22.58 percent for the B-38 Area samples. These probabilities indicated that there was (1) a less than 5 percent probability for the FFA, NEX Service Station Area, and SFT Area samples and (2) a greater than 5 percent probability for the PRA and B-38 Area samples that the OCMA-350 and reference method results correlated only by chance. For soil PE samples, the probabilities of the slopes of the regression lines being equal to zero were 0.01 and 0.00 percent for the diesel samples and the combined weathered gasoline and diesel samples, respectively, and 62.68 percent for the weathered gasoline samples. These probabilities indicated that there was (1) a less than 5 percent probability for the diesel samples and the combined weathered gasoline and diesel samples and (2) a greater than 5 percent probability for the weathered gasoline samples that the OCMA-350 and reference method results correlated only by chance.

Based on the R<sup>2</sup> and probability values, the OCMA-350 and reference method results were considered to be (1) highly correlated for FFA, NEX Service Station Area, and SFT Area samples; (2) moderately correlated for diesel and combined weathered gasoline and diesel soil PE samples; and (3) weakly correlated for PRA and B-38 Area samples and for weathered gasoline soil PE samples.

### 7.1.2.2 Precision

Both environmental and PE samples were analyzed to evaluate the precision associated with TPH measurements using the OCMA-350 and reference method. The results of this evaluation are summarized below.

**Table 7-5. Summary of Linear Regression Analysis Results**

Sampling Area or Sample Type	Regression Model (y = OCMA-350 TPH result, x = reference method TPH result)	Square of Correlation Coefficient	Probability That Slope of Regression Line Was Equal to Zero (percent)
<b>Environmental Samples</b>			
Fuel Farm Area	y = 1.13x + 128.27	0.96	0.00
Naval Exchange Service Station Area	y = 0.77x + 123.21	0.92	0.00
Phytoremediation Area	y = 1.28x - 286.80	0.19	27.92
B-38 Area	y = 0.32x + 26.13	0.23	22.58
Slop Fill Tank Area	y = 0.41x + 2.22	0.90	0.00
<b>Soil Performance Evaluation Samples</b>			
Weathered gasoline	y = 0.59x - 61.65	0.53	62.68
Diesel	y = 0.82x - 33.84	0.68	0.01
Weathered gasoline and diesel	y = 0.77x - 93.46	0.64	0.00

### Environmental Samples

Blind field triplicates were analyzed to evaluate the overall precision of the sampling, extraction, and analysis steps associated with TPH measurement. Each set of field triplicates was collected from a well-homogenized sample. Also, extract duplicates were analyzed to evaluate analytical precision only. Each set of extract duplicates was collected by extracting a given soil sample and collecting two aliquots of the extract. Additional information on field triplicate and extract duplicate preparation is included in Chapter 4.

Tables 7-6 and 7-7 present the OCMA-350 and reference method results for field triplicates and extract duplicates, respectively. Precision was estimated using RSDs for field triplicates and RPDs for extract duplicates.

Table 7-6 presents the TPH results and RSDs for 12 sets of field triplicates analyzed using the OCMA-350 and reference method. For the OCMA-350, the RSD calculated for one set of field triplicates from the SFT Area (field triplicate set 12) was not considered in evaluating the device’s precision because the TPH result for one of the three samples (156 mg/kg) was one order of magnitude higher than the results for the other two samples and was thus considered to be an analytical outlier. The RSDs for the remaining 11 triplicate sets ranged from 0 to 49 percent with a median of 20 percent. For the reference method, the RSDs ranged from 4 to 39 percent with a median of 18 percent. Comparison of the OCMA-350 and reference method median RSDs showed that the OCMA-350 exhibited less overall precision than the reference method. The OCMA-350 and

reference method RSDs did not exhibit consistent trends based on soil type, PHC contamination type, or TPH concentration.

Table 7-7 presents the TPH results and RPDs for 13 sets of extract duplicates analyzed using the OCMA-350 and reference method. For the OCMA-350, the RPDs ranged from 0 to 3 with a median of 1. The RPDs for the reference method ranged from 0 to 11 with a median of 4. Comparison of the median RPDs for the OCMA-350 and reference method indicated that the OCMA-350 achieved a higher level of precision than the reference method. The OCMA-350 and reference method RPDs did not exhibit consistent trends based on PHC contamination type or TPH concentration. As expected, the median RPDs for extract duplicates were less than the median RSDs for field triplicates for both the OCMA-350 and reference method. These findings indicated that greater precision was achieved when only the analysis step could have contributed to TPH measurement error than when all three steps (sampling, extraction, and analysis) could have contributed to such error.

### Performance Evaluation Samples

Table 7-8 presents the OCMA-350 and reference method TPH results and RSDs for eight sets of replicates for soil PE samples and two sets of triplicates for liquid PE samples.

For the OCMA-350, the RSD calculated for the blank soil samples was not considered in evaluating the device’s precision because one of the three blank soil sample results was below the MDL (15.2 mg/kg) and the

**Table 7-6. Summary of OCMA-350 and Reference Method Precision for Field Triplicates of Environmental Samples**

Sampling Area	Field Triplicate Set	OCMA-350		Reference Method	
		TPH Result (milligram per kilogram)	Relative Standard Deviation (percent)	TPH Result (milligram per kilogram)	Relative Standard Deviation (percent)
Fuel Farm Area	1	87.6	16	68.2	34
		69.1		90.2	
		94.4		44.1	
	2	14,600	9	15,000	11
		17,200		12,000	
		15,300		13,900	
Naval Exchange Service Station Area	3	314	18	280	13
		380		270	
		267		219	
	4	1,440	22	1,870	39
		1,540		881	
		997		1,180	
	5	1,530	18	1,560	16
		1,100		1,120	
		1,200		1,390	
	6	Less than 15.2	0	9.56	23
		Less than 15.2		14.2	
		Less than 15.2		15.2	
Phytoremediation Area	7	2,050	20	2,140	21
		3,070		1,790	
		2,840		1,390	
B-38 Area	8	47.5	24	79	13
		30.4		61.4	
		48.6		67.3	
Slop Fill Tank Area	9	434	35	834	14
		240		1,090	
		510		938	
	10	172	38	501	4
		78.5		544	
		123		517	
	11	146	49	280	29
		96.7		503	
		254		369	
	12	156	123	185	28
		16.7		146	
		20.4		253	

**Table 7-7. Summary of OCMA-350 and Reference Method Precision for Extract Duplicates**

Sampling Area	Extract Duplicate Set	OCMA-350		Reference Method	
		TPH Result (milligram per kilogram)	Relative Percent Difference	TPH Result (milligram per kilogram)	Relative Percent Difference
Fuel Farm Area	1	94.6	0	44.1	0
		94.2		44.1	
	2	15,300	Not calculated <sup>a</sup>	13,700	2
		Not analyzed <sup>a</sup>		14,000	
Naval Exchange Service Station Area	3	266	0	226	6
		267		213	
	4	997	Not calculated <sup>a</sup>	1,190	2
		Not analyzed <sup>a</sup>		1,170	
	5	1,200	Not calculated <sup>a</sup>	1,420	4
		Not analyzed <sup>a</sup>		1,360	
	6	Less than 15.2	0	15.5	4
		Less than 15.2		14.9	
Phytoremediation Area	7	3,090	1	1,710	8
		3,060		1,860	
B-38 Area	8	48.2	3	79.6	2
		46.8		78.4	
	9	32.5	2 percent <sup>b</sup>	41.4	0
		28.6		41.5	
33.2					
Slop Fill Tank Area	10	439	2	829	1
		429		838	
	11	174	2	528	11
		170		473	
	12	147	1	271	6
		145		289	
	13	156	Not calculated <sup>a</sup>	189	4
		Not analyzed <sup>a</sup>		181	

Notes:

- <sup>a</sup> The extract was disposed of before an extract duplicate sample was analyzed; therefore, a relative percent difference could not be calculated.
- <sup>b</sup> Two extract duplicates of the sample extract were analyzed. Therefore, the relative standard deviation is reported instead of the relative percent difference.

**Table 7-8. Comparison of OCMA-350 and Reference Method Precision for Replicate Performance Evaluation Samples**

Sample Type		Replicate Set	OCMA-350		Reference Method		
			TPH Result	Relative Standard Deviation (percent)	TPH Result	Relative Standard Deviation (percent)	
<b>Soil Samples (Processed Garden Soil) (TPH Results in Milligram per Kilogram)</b>							
Blank (9 percent moisture content)		1	Less than 15.2	45	5.12	45	
			20.9		13.1		
			18.7		13.5		
Weathered gasoline	Medium-range TPH concentration (9 percent moisture content)	2	107	2	350	2	
			108		346		
			104		336		
	High-range TPH concentration (9 percent moisture content)	3	657	5	1,880	7	
			595		2,020		
			638		2,180		
	High-range TPH concentration (16 percent moisture content)	4	1,460	9	1,740	8	
			1,710		1,980		
			1,720		2,050		
	Diesel	Low-range TPH concentration (9 percent moisture content)	5	28.8	17	16.4	10
				21		16.4	
				30.6		13.2	
24.2				16.0			
33.4				14.2			
23.2				14.1			
32.2				12.8			
Medium-range TPH concentration (9 percent moisture content)				6		124	
		143	273				
		144	295				
High-range TPH concentration (9 percent moisture content)		7	992	2	2,480	8	
			995		2,890		
			958		2,800		
High-range TPH concentration (less than 1 percent moisture content)		8	3,540	2	2,700	6	
			3,570		2,950		
			3,460		3,070		
<b>Liquid Samples (Neat Materials) (TPH Results in Milligram per Liter)</b>							
Weathered gasoline			9	541,000	2	656,000	5
				566,000		611,000	
				560,000		677,000	
Diesel			10	750,000	1	1,090,000	6
				737,000		1,020,000	
				758,000		1,160,000	

remaining two results were above the MDL. The RSDs for the remaining seven replicate sets ranged from 2 to 17 percent with a median of 5 percent. The RSDs for the two triplicate sets of liquid samples were 1 and 2 percent with a median of 1.5 percent.

For the reference method, the RSD calculated for the blank soil samples was not considered in evaluating the method's precision because one of the three blank soil sample results (5.12 mg/kg) was estimated by adding one-half the reporting limits for the GRO, DRO, and ORO components of TPH measurement. The RSDs for the remaining seven replicate sets ranged from 2 to 10 percent with a median of 7 percent. The RSDs for the two triplicate sets of liquid samples were 5 and 6 percent with a median of 5.5 percent. Comparison of the OCMA-350 and reference method median RSDs showed that the OCMA-350 exhibited better precision than the reference method for both soil and liquid PE samples. Finally, for the reference method, the median RSD for the soil PE samples (7 percent) was less than that for the environmental samples (18 percent), indicating that greater precision was achieved for the samples prepared under more controlled conditions (the PE samples). Similarly, for the OCMA-350, the median RSD for the soil PE samples (5 percent) was less than that for the environmental samples (20 percent).

### **7.1.3 Primary Objective P3: Effect of Interferents**

The effect of interferents on TPH measurement using the OCMA-350 and reference method was evaluated through analysis of high-concentration-range soil PE samples that contained weathered gasoline or diesel with or without an interferent. The six interferents used were MTBE; PCE; Stoddard solvent; turpentine; 1,2,4-trichlorobenzene; and humic acid. In addition, neat (liquid) samples of each interferent except humic acid were used as quasi-control samples to evaluate the effect of each interferent on the TPH results obtained using the OCMA-350 and the reference method. Liquid interferent samples were submitted for analysis as blind triplicate samples. Horiba and the reference laboratory were provided with flame-sealed ampules of each interferent and were given specific instructions to prepare dilutions of the liquid interferents for analysis. Two dilutions of each interferent were prepared; therefore, there were six OCMA-350 and reference method TPH results for each interferent. Blank soil was mixed with humic acid at two levels to prepare quasi-control samples for this interferent. Additional details regarding the interferents are provided in

Chapter 4. The results for the quasi-control interferent samples are discussed first below, followed by the effects of the interferents on the TPH results for soil samples.

#### **7.1.3.1 Interferent Sample Results**

Table 7-9 presents the OCMA-350 and reference method TPH results, mean TPH results, and mean responses for triplicate sets of liquid PE samples and soil PE samples containing humic acid. Each mean response was calculated by dividing the mean TPH result for a triplicate set by the interferent concentration and multiplying by 100. For liquid PE samples, the interferent concentration was estimated using its density and purity.

The mean responses for the OCMA-350 ranged from 0 to 94 percent for the liquid interferent samples; the mean response for humic acid was 0 percent. The TPH results for a given triplicate set and between the triplicate sets showed good agreement except for Stoddard solvent. The mean responses for MTBE (72.5 percent) and Stoddard solvent (86 percent) indicated that these compounds can be measured as TPH using the OCMA-350. The mean response for turpentine (85 percent) indicated that turpentine would result in false positives during TPH measurement. The mean response of 0 percent for PCE; 1,2,4-trichlorobenzene; and humic acid indicated that these compounds would not result in either false positives or false negatives during TPH measurement.

The mean responses for the reference method ranged from 17 to 92 percent for the liquid interferent samples; the mean response for humic acid was 0 percent. The TPH results for a given triplicate set and between the triplicate sets showed good agreement. The mean responses for MTBE (39 percent) and Stoddard solvent (85 percent) indicated that these compounds can be measured as TPH using the reference method. The mean responses for PCE (17.5 percent); turpentine (52 percent); and 1,2,4-trichlorobenzene (50 percent) indicated that these interferents will likely result in false positives during TPH measurement. The mean response of 0 percent for humic acid indicated that humic acid would not result in either false positives or false negatives during TPH measurement.

#### **7.1.3.2 Effects of Interferents on TPH Results for Soil Samples**

The effects of interferents on TPH measurement for soil samples containing weathered gasoline or diesel were

**Table 7-9. Comparison of OCMA-350 and Reference Method Results for Interferent Samples**

Interferent and Concentration <sup>a</sup>	OCMA-350			Reference Method		
	TPH Result	Mean TPH Result	Mean Response <sup>b</sup> (percent)	TPH Result	Mean TPH Result	Mean Response <sup>b</sup> (percent)
<b>Liquid Interferent Samples (TPH Results in Milligram per Liter)</b>						
Methyl-tert-butyl ether (740,000 milligrams per liter)	544,000	530,000	72	309,000	284,000	38
	526,000			272,000		
	520,000			270,000		
	547,000	540,000	73	303,000	299,000	40
	510,000			313,000		
	562,000			282,000		
Tetrachloroethene (1,621,000 milligrams per liter)	Less than 6,080	3,040	0	269,000	272,000	17
	Less than 6,080			270,000		
	Less than 6,080			277,000		
	Less than 1,220	610	0	290,000	295,000	18
	Less than 1,220			288,000		
	Less than 1,220			307,000		
Stoddard solvent (771,500 milligrams per liter)	511,000	730,000	94	561,000	598,000	78
	824,000			628,000		
	847,000			606,000		
	463,000	600,000	78	703,000	708,000	92
	762,000			Not reported		
	576,000			713,000		
Turpentine (845,600 milligrams per liter)	722,000	718,000	85	504,000	468,000	55
	711,000			459,000		
	720,000			442,000		
	685,000	712,000	85	523,000	408,000	48
	746,000			353,000		
	721,000			349,000		
1,2,4-Trichlorobenzene (1,439,000 milligrams per liter)	Less than 6,080	3,040	0	711,000	688,000	48
	Less than 6,080			620,000		
	Less than 6,080			732,000		
	1,690	1,690	0	754,000	754,000	52
	1,600			756,000		
	1,780			752,000		
<b>Interferent Samples (Processed Garden Soil) (TPH Results in Milligram per Kilogram)</b>						
Humic acid at 3,940 milligrams per kilogram	Less than 15.2	7.6	0	8.99	9.00	0
	Less than 15.2			8.96		
	Less than 15.2			8.12		
Humic acid at 19,500 milligrams per kilogram	Less than 15.2	7.6	0	69.3	76.0	0
	Less than 15.2			79.1		
	Less than 15.2			78.5		

Notes:

<sup>a</sup> A given liquid interferent concentration was estimated using its density and purity.

<sup>b</sup> The mean response was calculated by dividing the mean TPH result for a triplicate set by the interferent concentration and multiplying by 100.

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examined through analysis of PE samples containing (1) weathered gasoline or diesel (control) and (2) weathered gasoline or diesel plus a given interferent at two levels. Information on the selection of interferents is provided in Chapter 4.

Triplicate sets of control samples and samples containing interferents were prepared for analysis using the OCMA-350 and reference method. A parametric or nonparametric test was selected for statistical evaluation of the results using the approach presented in Figure 7-1.

TPH results for samples with and without interferents, statistical tests performed, and statistical test conclusions for both the OCMA-350 and reference method are presented in Table 7-10. The null hypothesis for the statistical tests was that mean TPH results for samples with and without interferents were equal. The statistical results for each interferent are discussed below.

#### **Effect of Methyl-Tert-Butyl Ether**

The effect of MTBE was evaluated for soil PE samples containing weathered gasoline. Based on the liquid PE sample (neat material) analytical results, MTBE was expected to bias both the OCMA-350 and reference method results high.

For the OCMA-350, at the interferent levels used, MTBE was expected to bias the TPH results high by 127 percent (low level) and 196 percent (high level). The expected bias would be lower (37 and 58 percent, respectively) if MTBE in soil samples was assumed to be extracted as efficiently as weathered gasoline in soil samples. Table 7-10 shows that MTBE biased the OCMA-350 TPH results high at both low and high interferent levels, which confirmed the conclusions drawn from the results of the neat MTBE analysis. Although the statistical tests confirmed the observed bias, they indicated that the observed bias was statistically the same at both low and high MTBE levels.

For the reference method, at the interferent levels used, MTBE was expected to bias the TPH results high by 21 percent (low level) and 33 percent (high level). The expected bias would be lower (17 and 27 percent, respectively) if MTBE in soil samples was assumed to be extracted as efficiently as weathered gasoline in soil samples. However, no effect on TPH measurement was observed for soil PE samples analyzed during the demonstration. A significant amount of MTBE, a highly

volatile compound, may have been lost during PE sample preparation, transport, storage, and handling, thus lowering the MTBE concentrations to levels that would not have increased the TPH results beyond the reference method's precision (7 percent).

#### **Effect of Tetrachloroethene**

The effect of PCE was evaluated for soil PE samples containing weathered gasoline. Based on the liquid PE sample (neat material) analytical results, PCE was expected to have no effect on the TPH results for the OCMA-350; however, it was expected to bias the reference method results high.

For the OCMA-350, PCE appeared to have biased the TPH results high. However, the bias decreased with an increase in the PCE level. Specifically, the bias was 144 percent at the low level and 90 percent at the high level. For this reason, no conclusion was drawn regarding the effect of PCE on TPH measurement using the OCMA-350.

For the reference method, at the interferent levels used, PCE was expected to bias the TPH results high by 24 percent (low level) and 113 percent (high level). The expected bias would be lower (20 and 92 percent, respectively) if PCE in soil samples was assumed to be extracted as efficiently as weathered gasoline in soil samples. The statistical tests showed that the probability of the three means being equal was less than 5 percent. However, the tests also showed that at the high level, PCE biased the TPH results high, which appeared to be reasonable based on the conclusions drawn from the analytical results for neat PCE. As to the reason for PCE at the low level having no effect on the TPH results, volatilization during PE sample preparation, transport, storage, and handling may have lowered the PCE concentrations to levels that would not have increased the TPH results beyond the reference method's precision (7 percent).

#### **Effect of Stoddard Solvent**

The effect of Stoddard solvent was evaluated for weathered gasoline and diesel soil PE samples. Based on the liquid PE sample (neat material) analytical results, Stoddard solvent was expected to bias both the OCMA-350 and reference method results high.

For the OCMA-350, at the interferent levels used, Stoddard solvent was expected to bias the TPH results



Table 7-10. Comparison of OCMA-350 and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents

Sample Matrix and Interferent*	OCMA-350					Reference Method					
	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	
<b>Soil Samples Without Interferents</b>											
Weathered gasoline	657	630		Not applicable		1,880	2,030		Not applicable		
	595					2,020					
	638					2,180					
Diesel	992	982		Not applicable		2,480	2,720		Not applicable		
	995					2,890					
	958					2,800					
<b>Soil Samples With Interferents</b>											
Weathered gasoline	MTBE (1,100 mg/kg)	1,150	1,210	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Mean without interferent was different from means with interferent at low and high levels	0.29	1,900	1,950	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Same	11.21
		882					1,750				
		1,610					2,210				
PCE (2,810 mg/kg)	MTBE (1,700 mg/kg)	1,580	1,540	Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis pairwise comparison of means (nonparametric)	Mean without interferent was same as mean with interferent at high level; mean with interferent at low level was same as mean with interferent at high level	2.73	2,150	2,340			0.00
		1,370					2,320				
		1,680					2,560				
PCE (13,100 mg/kg)	PCE (13,100 mg/kg)	1,590	1,200				2,540	2,380			
		1,530					2,160				
		1,510					2,450				
		1,290	934				4,740	4,450			
	1,390	4,570									

**Table 7-10. Comparison of OCMA-350 and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents (Continued)**

Sample Matrix and Interferent*	OCMA-350					Reference Method				
	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)
<b>Soil Samples With Interferents (Continued)</b>										
Weathered gasoline (Continued)	1,930	1,910	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00	4,350	4,410	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00
	2,030					4,760				
	1,770					4,110				
Stoddard solvent (15,400 mg/kg)	13,000	15,400	Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis pairwise comparison of means (nonparametric)	Mean without interferent was same as mean with interferent at low level; mean with interferent at low level was same as mean with interferent at high level	2.73	10,300	11,900	Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis pairwise comparison of means (nonparametric)	All three means (with and without interferents) were significantly different from one another	0.00
	17,700					14,300				
	15,400					11,000				
Diesel	2,650	2,630	Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis pairwise comparison of means (nonparametric)	Mean without interferent was same as mean with interferent at low level; mean with interferent at low level was same as mean with interferent at high level	0.00	4,390	4,520	Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis pairwise comparison of means (nonparametric)	All three means (with and without interferents) were significantly different from one another	0.00
	3,400					4,640				
	1,840					4,520				
Weathered gasoline	13,400	14,700	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00	8,770	7,880	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00
	13,800					6,580				
	16,900					8,280				
Turpentine (2,730 mg/kg)	1,870	1,820	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00	4,410	4,240	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00
	1,650					3,870				
	1,930					4,440				
Turpentine (12,900 mg/kg)	12,500	12,700	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00	12,800	12,900	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00
	12,200					11,200				
	13,300					14,600				

Table 7-10. Comparison of OCMA-350 and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents (Continued)

Sample Matrix and Interferent*	OCMA-350				Reference Method																								
	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)																			
Diesel	<b>Soil Samples With Interferents (Continued)</b>																												
	Turpentine (3,850 mg/kg)	2,380	2,690	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00	5,860	5,760	Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis pairwise comparison of means (nonparametric)	Mean without interferent was same as mean with interferent at low level; mean with interferent at low level was same as mean with interferent at high level	2.65																		
		2,710																											
		2,980																											
	Turpentine (19,600 mg/kg)	13,500	12,800				One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another				0.00	15,000	13,900	Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis pairwise comparison of means (nonparametric)	Mean with interferent at high level was different from means without interferent and with interferent at low level	0.01												
		13,100																											
		11,900																											
	1,2,4-Trichlorobenzene (3,350 mg/kg)	981	1,100										One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Mean with interferent at high level was different from means without interferent and with interferent at low level				0.00	3,220	3,510	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Mean with interferent at high level was different from means without interferent and with interferent at low level	0.01						
		1,220																											
		1,100																											
	1,2,4-Trichlorobenzene (16,600 mg/kg)	1,980	1,870																One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Mean with interferent at high level was different from means without interferent and with interferent at low level				0.00	7,940	7,060	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Mean with interferent at high level was different from means without interferent and with interferent at low level	0.01
		1,810																											
1,820																													

Table 7-10. Comparison of OCMA-350 and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents (Continued)

Sample Matrix and Interferent <sup>a</sup>	OCMA-350				Reference Method						
	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	
Diesel (Continued)	612	529	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00	2,150	2,200	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Mean without interferent was same as mean with interferent at high level; mean with interferent at low level was same as mean with interferent at high level	3.87	
	504					2,080					
	470					2,360					
	Humic acid (19,500 mg/kg)	318				325	2,660				2,450
		292					2,420				
		364					2,270				

**Soil Samples With Interferents (Continued)**

Notes:

mg/kg = Milligram per kilogram  
 MTBE = Methyl-tert-butyl ether  
 PCE = Tetrachloroethene

<sup>a</sup> All samples were prepared at a 9 percent moisture level.

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high by 396 percent (low level) and 2,100 percent (high level) for weathered gasoline soil PE samples and by 320 percent (low level) and 1,600 percent (high level) for diesel soil PE samples. The expected bias would be lower (116 and 618 percent, respectively, for weathered gasoline soil PE samples and 92 and 458 percent, respectively, for diesel soil PE samples) if Stoddard solvent in soil samples was assumed to be extracted as efficiently as weathered gasoline and diesel in soil samples. The statistical tests showed that the mean TPH results with and without the interferent were different for weathered gasoline soil PE samples, which confirmed the conclusions drawn from the analytical results for neat Stoddard solvent. However, for diesel soil PE samples, (1) the mean TPH result without the interferent and the mean TPH result with the interferent at the low level were equal and (2) the mean TPH results with the interferent at the low and high levels were equal, indicating that Stoddard solvent at the low level did not affect the TPH results for the diesel soil PE samples but that Stoddard solvent at the high level did affect the TPH results. The conclusion reached for the interferent at the low level was unexpected and did not seem reasonable based on a simple comparison of means that differed by a factor of three. The anomaly might have been associated with the nonparametric test used to evaluate the effect of Stoddard solvent on TPH results for diesel soil PE samples, as nonparametric tests do not account for the magnitude of the difference between TPH results.

For the reference method, at the interferent levels used, Stoddard solvent was expected to bias the TPH results high by 121 percent (low level) and 645 percent (high level) for weathered gasoline soil PE samples and by 114 percent (low level) and 569 percent (high level) for diesel soil PE samples. The expected bias would be lower (99 and 524 percent, respectively, for weathered gasoline soil PE samples and 61 and 289 percent, respectively, for diesel soil PE samples) if Stoddard solvent in soil samples was assumed to be extracted as efficiently as weathered gasoline and diesel in soil samples. The statistical tests showed that the mean TPH results with and without the interferent were different for both weathered gasoline and diesel soil PE samples, which confirmed the conclusions drawn from the analytical results for neat Stoddard solvent.

### **Effect of Turpentine**

The effect of turpentine was evaluated for weathered gasoline and diesel soil PE samples. Based on the liquid

PE sample (neat material) analytical results, turpentine was expected to bias both the OCMA-350 and reference method results high.

For the OCMA-350, at the interferent levels used, turpentine was expected to bias the TPH results high by 368 percent (low level) and 1,740 percent (high level) for weathered gasoline soil PE samples and by 333 percent (low level) and 1,700 percent (high level) for diesel soil PE samples. The expected bias would be lower (108 and 512 percent, respectively, for weathered gasoline soil PE samples and 96 and 488 percent, respectively, for diesel soil PE samples) if turpentine in soil samples was assumed to be extracted as efficiently as weathered gasoline and diesel in soil samples. The statistical tests showed that the mean TPH results with and without the interferent were different for both weathered gasoline and diesel soil PE samples, which confirmed the conclusions drawn from the analytical results for neat turpentine.

For the reference method, at the interferent levels used, turpentine was expected to bias the TPH results high by 69 percent (low level) and 327 percent (high level) for weathered gasoline soil PE samples and by 72 percent (low level) and 371 percent (high level) for diesel soil PE samples. The expected bias would be lower (56 and 266 percent, respectively, for weathered gasoline soil PE samples and 39 and 200 percent, respectively, for diesel soil PE samples) if turpentine in soil samples was assumed to be extracted as efficiently as weathered gasoline and diesel in soil samples. The statistical tests showed that the mean TPH results with and without the interferent were different for weathered gasoline soil PE samples, which confirmed the conclusions drawn from the analytical results for neat turpentine. However, for diesel soil PE samples, (1) the mean TPH result without the interferent and the mean TPH result with the interferent at the low level were equal and (2) the mean TPH results with the interferent at the low and high levels were equal, indicating that turpentine at the low level did not affect the TPH results for the diesel soil PE samples but that turpentine at the high level did affect the TPH results. The conclusion reached for the interferent at the low level was unexpected and did not seem reasonable based on a simple comparison of means that differed by a factor of three. The anomaly might have been associated with the nonparametric test used to evaluate the effect of turpentine on TPH results for diesel soil PE samples, as nonparametric tests do not account for the magnitude of the difference between TPH results.

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### **Effect of 1,2,4-Trichlorobenzene**

The effect of 1,2,4-trichlorobenzene was evaluated for diesel soil PE samples. Based on the liquid PE sample (neat material) analytical results, 1,2,4-trichlorobenzene was expected to have no effect on the TPH results for the OCMA-350; however, it was expected to bias the reference method results high.

For the OCMA-350, 1,2,4-trichlorobenzene appears to have biased the TPH results high; the bias was statistically significant only at the high interferent level. The observed bias contradicted the conclusions drawn from the results of the neat 1,2,4-trichlorobenzene analysis, which cannot be explained.

For the reference method, at the interferent levels used, 1,2,4-trichlorobenzene was expected to bias the TPH results high by 62 percent (low level) and 305 percent (high level). The expected bias would be lower (33 and 164 percent, respectively) if 1,2,4-trichlorobenzene in soil samples was assumed to be extracted as efficiently as diesel in soil samples. The statistical tests showed that the probability of three means being equal was less than 5 percent. However, the tests also showed that when the interferent was present at the high level, TPH results were biased high. The effect observed at the high level confirmed the conclusions drawn from the analytical results for neat 1,2,4-trichlorobenzene. The statistical tests indicated that the mean TPH result with the interferent at the low level was not different from the mean TPH result without the interferent, indicating that the low level of 1,2,4-trichlorobenzene did not affect TPH measurement. However, a simple comparison of the mean TPH results revealed that the low level of 1,2,4-trichlorobenzene increased the TPH result to nearly the result based on the expected bias of 33 percent. Specifically, the mean TPH result with the interferent at the low level was 3,510 mg/kg rather than the expected value of 3,620 mg/kg. The conclusions drawn from the statistical tests were justified when the variabilities associated with the mean TPH results were taken into account.

### **Effect of Humic Acid**

The effect of humic acid was evaluated for diesel soil PE samples. Based on the analytical results for soil PE samples containing humic acid, this interferent was expected to have no effect on the TPH results for the OCMA-350 and reference method.

For the OCMA-350, humic acid biased the TPH results low; the bias was statistically significant at both the low and high interferent levels. This observation appeared to contradict the conclusions drawn from the analytical results for soil PE samples containing humic acid (quasi-control samples); however, the apparent contradiction was attributable to the fact that the quasi-control sample analyses could predict only a positive bias (a negative bias is equivalent to a negative concentration).

For the reference method, humic acid appeared to have biased the TPH results low. However, the bias decreased with an increase in the humic acid level. Specifically, the negative bias was 19 percent at the low level and 10 percent at the high level. For this reason, no conclusion was drawn regarding the effect of humic acid on TPH measurement using the reference method.

#### ***7.1.4 Primary Objective P4: Effect of Soil Moisture Content***

To measure the effect of soil moisture content on the ability of the OCMA-350 and reference method to accurately measure TPH, high-concentration-range soil PE samples containing weathered gasoline or diesel at two moisture levels were analyzed. The OCMA-350 and reference method results were converted from a wet weight basis to a dry weight basis in order to evaluate the effect of moisture content on the sample TPH results. The OCMA-350 and reference method dry weight TPH results for weathered gasoline samples and the reference method dry weight TPH results for diesel samples were normally distributed; therefore, a two-tailed, two-sample Student's t-test was performed to determine whether the device and reference method results were impacted by soil moisture content—that is, to determine whether an increase in soil moisture content resulted in an increase or decrease in the TPH concentrations measured. Because the OCMA-350 dry weight TPH results for diesel samples were not normally distributed, a Kruskal-Wallis one-way analysis of variance (a nonparametric test) was performed. The null hypothesis for the t-test and the analysis of variance was that the two means were equal or that the difference between the means was equal to zero. Table 7-11 shows the sample moisture levels, TPH results, mean TPH results for sets of triplicate samples, whether the mean TPH results at different moisture levels were the same, and the probability of the null hypothesis being true.

**Table 7-11. Comparison of Results for Soil Performance Evaluation Samples at Different Moisture Levels**

Sample Type and Moisture Level	OCMA-350				Reference Method			
	TPH Result on Dry Weight Basis (milligram per kilogram)	Mean TPH Result (milligram per kilogram)	Were Mean TPH Results at Different Moisture Levels the Same or Different? <sup>a,b</sup>	Probability of Null Hypothesis Being True <sup>c</sup> (percent)	TPH Result on Dry Weight Basis (milligram per kilogram)	Mean TPH Result (milligram per kilogram)	Were Mean TPH Results at Different Moisture Levels the Same or Different? <sup>a</sup>	Probability of Null Hypothesis Being True <sup>c</sup> (percent)
Weathered gasoline at 9 percent moisture level	724	694	Different	3.64	2,070	2,230	Same	66.52
	655				2,220			
	703				2,400			
Weathered gasoline at 16 percent moisture level	1,740	1,950			2,070	2,300		
	2,060				2,390			
	2,050				2,440			
Diesel at less than 1 percent moisture level	3,570	3,550	Different	4.63	2,740	3,000	Same	71.95
	3,600				3,180			
	3,490				3,070			
Diesel at 9 percent moisture level	1,100	1,080			2,720	2,930		
	1,100				2,970			
	1,050				3,100			

**Notes:**

- <sup>a</sup> A two-tailed, two-sample Student's t-test (parametric) was used to evaluate the effect of soil moisture content on OCMA-350 and reference method TPH results for weathered gasoline samples and on reference method TPH results for diesel samples.
- <sup>b</sup> A Kruskal-Wallis one-way analysis of variance (nonparametric) was used to evaluate the effect of moisture content on OCMA-350 TPH results for diesel samples.
- <sup>c</sup> The null hypothesis was that the two means were equal or that the difference between the two means was equal to zero.

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Table 7-11 shows that OCMA-350 results for weathered gasoline and diesel soil samples at different moisture levels were statistically different at a significance level of 5 percent; therefore, the OCMA-350 results were impacted by soil moisture content. Based on a simple comparison of the results, this conclusion appeared to be reasonable. Specifically, on average at the higher moisture level, the mean TPH result (1) for weathered gasoline soil samples was higher by a factor of three and (2) for diesel soil samples was lower by a factor of three. The opposite effect of soil moisture content on TPH results for weathered gasoline and diesel soil samples could not be explained.

Table 7-11 also shows that reference method results for weathered gasoline soil samples and diesel soil samples at different moisture levels were statistically the same at a significance level of 5 percent; therefore, the reference method results were not impacted by soil moisture content. Based on a simple comparison of the results, this conclusion appeared to be reasonable.

### **7.1.5 Primary Objective P5: Time Required for TPH Measurement**

During the demonstration, the time required for TPH measurement activities, including OCMA-350 setup, sample extraction, sample analysis, OCMA-350 disassembly, and data package preparation, was measured. During the demonstration, one field technician performed the TPH measurement activities using the OCMA-350. Time measurement began at the start of each demonstration day when the technician began to set up the OCMA-350 and ended when he disassembled the OCMA-350. Time not measured included (1) the time spent by the technician verifying that he had received all the demonstration samples indicated on chain-of-custody forms and (2) the times when he took breaks. In addition to the total time required for TPH measurement, the time required to extract and analyze the first and last analytical batches of soil samples was measured. The number and type of samples in a batch were selected by Horiba.

The time required to complete TPH measurement activities using the OCMA-350 is shown in Table 7-12. The time required for each activity was rounded to the nearest 5 minutes.

Overall, Horiba required 46 hours, 15 minutes, for TPH measurement of 74 soil environmental samples, 89 soil PE samples, 36 liquid PE samples, and 9 extract duplicates.

Information regarding the time required for each measurement activity during the entire 6-day demonstration and for extraction and analysis of the first and last batches of soil samples is provided below.

The setup time for the OCMA-350 was measured at the beginning of each day during the 6-day demonstration period. Setup activities included OCMA-350 setup; analysis of QC check standards; and organization of extraction, dilution, analysis, and decontamination supplies. OCMA-350 setup required a total of 1 hour, 45 minutes, during the 6-day demonstration, or an average of 17.5 minutes per day. The setup times on the days when the first and last soil sample batches were analyzed were 25 and 10 minutes, respectively, or an average of 17.5 minutes per day. The total setup time for the entire demonstration and the setup time on the days when the first and last soil sample batches were analyzed suggested that the field technician gradually became more familiar with the OCMA-350 setup procedure as the demonstration progressed.

Extraction of all 163 soil samples required 25 hours, 45 minutes, resulting in an average extraction time of 9 minutes per sample. However, the field technician also completed other activities associated with sample extraction during the demonstration, such as decontaminating metal spatulas and glass beakers. Thus, the average sample extraction time of 9 minutes included the time required to complete these activities.

The time required for extraction of the first and last batches of soil samples was also recorded. In general, Horiba designated 24 samples for each analytical batch. The number of samples was based on the capacity of the test tube rack used during extraction. However, fewer than 24 samples comprised an analytical batch in some cases; for example, the last batch of soil samples consisted of only 17 samples. The first batch of soil samples (which consisted of 24 samples) required 2 hours, 50 minutes, for extraction, or an average of 7 minutes per sample. The last batch of soil samples (which consisted of 17 samples) required 1 hour, 30 minutes, for extraction, or an average of 5 minutes per sample. The decrease in the average extraction time between the first and last batches of soil samples suggested that the field technician became more familiar with the OCMA-350 extraction procedure as the demonstration progressed. The difference between the 9-minute average extraction time for all the soil samples and the average extraction time for the first and last batches of soil samples (6 minutes) may be attributable to



**Table 7-12. Time Required to Complete TPH Measurement Activities Using the OCMA-350**

Measurement Activity	Time Required <sup>a</sup>		
	First Soil Sample Batch <sup>b</sup>	Last Soil Sample Batch <sup>b</sup>	6-Day Demonstration Period
OCMA-350 setup <sup>c</sup>	25 minutes	10 minutes	1 hour, 45 minutes
Sample extraction	2 hours, 50 minutes	1 hour, 30 minutes	25 hours, 45 minutes
Sample analysis	2 hours	1 hour, 10 minutes	16 hours, 45 minutes
OCMA-350 disassembly <sup>c</sup>	20 minutes	10 minutes	1 hour, 30 minutes
Data package preparation	Not measured	Not measured	30 minutes
<b>Total</b>	<b>5 hours, 35 minutes</b>	<b>3 hours</b>	<b>46 hours, 15 minutes</b>

Notes:

- <sup>a</sup> The time required for each activity was rounded to the nearest 5 minutes.
- <sup>b</sup> The first sample batch required 29 TPH analyses (24 sample extract analyses, 3 extract duplicate analyses, and 2 reanalyses). The last sample batch required 22 TPH analyses (17 sample extract analyses and 5 reanalyses).
- <sup>c</sup> The OCMA-350 setup and disassembly times were measured at the beginning and end of each day, respectively. The times reported for the first soil sample batch were the times recorded on the first day and the times reported for the last soil sample batch were the times recorded on the fifth day of the 6-day demonstration period.

the additional extraction activities mentioned above that were conducted by the field technician.

A total of 16 hours, 45 minutes, was required to obtain and report 208 TPH results using the OCMA-350, resulting in an average analysis time of 5 minutes per sample. In addition to performing the 208 analyses required to report 208 TPH results, the field technician performed extract dilutions and reanalyses for the high-concentration-range samples. The average analysis time does not include the time taken to perform these additional activities.

The time required to analyze the first and last batches of soil samples was also recorded. A total of 2 hours was required to analyze the first batch of samples, which required 29 TPH analyses (24 sample extract analyses, 3 extract duplicate analyses, and 2 reanalyses); therefore, an average of 4 minutes was required to complete one analysis. A total of 1 hour, 10 minutes, was required to analyze the last batch of soil samples, which required 22 TPH analyses (17 sample extract analyses and 5 reanalyses); therefore, an average of 3 minutes was required to complete one analysis. The decrease in the average analysis time between the first and last batches of soil samples suggested that the field technician became more familiar with the OCMA-350 analysis procedure as the demonstration progressed. The difference between the 5-minute average sample analysis time for the entire demonstration and the average sample analysis time for the first and last batches (3.5 minutes) may be attributable to the additional analysis activities mentioned above that were conducted by the field technician.

The disassembly time was measured at the end of each day of the 6-day demonstration. Disassembly included packing up the OCMA-350 and associated supplies required for TPH measurement. OCMA-350 disassembly required 10 to 20 minutes each day, totaling 1 hour, 30 minutes, for the 6-day demonstration. Thus, the average disassembly time was 15 minutes per day. The disassembly times on the days when the first and last soil sample batches were analyzed were 20 and 10 minutes, respectively, or an average of 15 minutes per day. The total disassembly time for the entire demonstration and the setup times on the days when the first and last soil sample batches were analyzed suggested that the field technician gradually became more familiar with the OCMA-350 disassembly procedure as the demonstration progressed.

Preparation of the OCMA-350 data package required 30 minutes in the field. Preparation of the data package submitted to the EPA at the end of the demonstration involved compiling printouts of TPH results and photocopying Horiba’s log sheets, which included sample identification numbers, the mass of soil and volume of solvent used, and TPH results. Additional information was provided in cases when dilutions had been necessary. Although the data package preparation time was 30 minutes in the field, during the weeks following the demonstration, Horiba spent additional time revising the data package to address EPA comments. The revisions primarily consisted of identifying in the data package TPH results below the reporting limit based on the revised MDL. The amount of additional time that Horiba spent

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finalizing the data package could not be quantified and was not included as part of the time for TPH measurement.

For the reference method, time measurement began when the reference laboratory received all the investigative samples and continued until the EPA received the first draft data package from the laboratory. The reference laboratory took 30 days to deliver the first draft data package to the EPA. Additional time taken by the reference laboratory to address EPA comments on all the draft laboratory data packages was not included as part of the time required for TPH measurement.

## **7.2 Secondary Objectives**

This section discusses the performance results for the OCMA-350 in terms of the secondary objectives stated in Section 4.1. The secondary objectives were addressed based on (1) observations of the performance of the OCMA-350 during the demonstration and (2) information provided by Horiba.

### **7.2.1 Skill and Training Requirements for Proper Device Operation**

Based on observations made during the demonstration, the OCMA-350 is easy to operate, requiring one field technician with basic wet chemistry skills acquired on the job or in a university. Because the amount of sample drying agent (sodium sulfate) used and the sample extraction time may need to be adjusted based on soil type and moisture content, basic knowledge of soil types is also recommended so that the technician can differentiate among sand, silt, and clay soil types and modify the sample drying and extraction steps accordingly. During the demonstration, Horiba chose to conduct sample analyses using one technician.

According to Horiba, normal training for using the OCMA-350 is limited to reading the instruction manual and simplified operating instruction sheet that are included with the device. The sample analysis procedure for the OCMA-350 can be learned in the field with a few practice attempts. In addition, during regular business hours, Horiba provides technical support over the telephone at no additional cost. Horiba also offers a 1-day training course at its facility or at a user-specified site for \$960; for this cost, Horiba provides one OCMA-350 for training purposes and one instructor to train up to 10 people. If the training is conducted at a user-specified site, the user would have to pay an additional cost to cover the

instructor's travel and per diem for 1 day. Horiba does not provide a training video for the OCMA-350.

With the OCMA-350, minimal effort is required to calculate a TPH concentration because the mass of soil and volume of solvent used during sample extraction can be programmed into the device, and the concentration can be read from the digital display in units of mg/kg TPH on a wet weight basis. For a diluted sample extract, the user must multiply the digital display reading by an appropriate dilution factor. During the demonstration, Horiba connected the OCMA-350 to a printer that printed a hard copy of the TPH concentrations. After the demonstration, Horiba made minimal revisions to the TPH results reported in the field. Specifically, of the 208 TPH results reported in the field at the end of the demonstration, fewer than 5 percent were corrected based on EPA review of the data package. The corrections primarily involved use of inappropriate reporting limits.

During the demonstration, Horiba used supplies and took steps that significantly increased the time and effort associated with sample preparation and analysis activities. For example, to calculate TPH concentrations, Horiba used the built-in function of the OCMA-350 that specified the standard mass of soil and volume of solvent used during sample extraction. As a result, Horiba had to measure exactly 5.0 grams of each soil sample and carefully place the measured amount in a narrow-mouthed, 40-mL vial without losing any mass; this step took a significant amount of the field technician's time (an average of 5 minutes per sample). Taking full advantage of the device features that allow use of varying amounts of soil and solvent during sample extraction as well as using vials with wider mouths would have made the extraction process less time-consuming. In addition, Horiba used a gravity filtration setup that required significant time, space, and supplies—such as glass funnels, a funnel rack, Whatman No. 40 filter paper, and glass beakers—and that may have resulted in loss of some volatiles. Use of disposable filter syringes may have resulted in savings of time, space, and supplies. Horiba also used its Model SR-300 solvent reclaimer to recycle spent solvent. Although the solvent reclaimer was easy to set up and use, it took a significant amount of time to generate solvent. In summary, some of the TPH measurement steps described above reduced the quantity of waste generated during the demonstration but made the TPH measurement procedures less simple and more time-consuming.

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### **7.2.2 Health and Safety Concerns Associated with Device Operation**

The chemical hazards associated with operating the OCMA-350 are considered to be insignificant. The two chemicals required for use of the OCMA-350 are anhydrous sodium sulfate drying agent and Horiba's proprietary S-316 extraction solvent, both of which are nontoxic.

During the demonstration, the Horiba field technician operated the OCMA-350 in modified Level D personal protective equipment (PPE) to prevent eye and skin contact with chemicals. The PPE included safety glasses, work boots, work clothes with long sleeves and long pants, and occasionally disposable gloves when soil samples were wet. Sample analyses were performed outdoors in a well-ventilated area; therefore, exposure to volatile chemicals through inhalation was not a concern.

During the demonstration, Horiba used the Model GE-50 ultrasonic mixer, which is no longer available from the developer. According to Horiba, the ultrasonic mixer that is currently available (Model VC-50) is functionally the same as Model GE-50. A potential physical hazard observed during the demonstration involved use of the ultrasonic mixer, which emitted a very high-frequency sound; Horiba's field technician wore ear plugs while using the mixer to prevent ear damage.

In general, a user of the OCMA-350 should employ good laboratory practices during sample analysis to minimize exposure to potential chemical and physical hazards. Example guidelines for good laboratory practices are described in ASTM's "Standard Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water" (ASTM 1998).

### **7.2.3 Portability of the Device**

The OCMA-350 infrared spectrophotometer and its accessories come in an optional, hard-plastic carrying case and weigh 36 pounds. The carrying case is 22 inches long, 16 inches wide, and 15 inches high. The OCMA-350 is operated using a 110- or 220-volt AC power source or a DC power source such as a 12-volt power outlet in an automobile along with a DC/AC power inverter. Because the OCMA-350 comes in an optional carrying case, and because an AC power source is not required to operate the device, it is easily transported between sampling areas in the field.

Other supplies that Horiba used during the demonstration come in several boxes but not in carrying cases that would facilitate transport of the supplies between sampling areas. As a result, significant effort would be required for the user to move these supplies between sampling areas in the field. For example, the Model SR-300 solvent reclaimer and 7-kg bottle of S-316 extraction solvent each come in a cardboard box and weigh 15 and 18 pounds, respectively. Glassware and other laboratory supplies—such as 40-mL vials, a test tube rack, funnels, a funnel rack, and beakers—also come in separate boxes. In addition, the Model GE-50 ultrasonic mixer (6 pounds) and the Epson LQ-500 dot-matrix printer (10 pounds) come in separate boxes and require an AC power source for operation; however, because a typical user does not require these two items for TPH measurement using the OCMA-350, they are considered to be optional. In summary, the portability of the OCMA-350 and other required supplies depends on the number of samples to be analyzed, site characteristics (for example, the availability of AC power), and the needs of the user (for example, a printer is needed only if a printout of the TPH results is required).

To operate the OCMA-350, a sample preparation and analysis area is required. The area must be large enough to accommodate the infrared spectrophotometer and its accessories, the Model SR-300 solvent reclaimer, and glassware and other laboratory supplies. The size of the area depends on the number of samples to be analyzed and is thus project-specific. During the demonstration, Horiba performed sample preparation and analysis under one 8-by-8-foot tent that housed two 8-foot-long, folding tables; two folding chairs; one 20-gallon laboratory pack for flammable waste; and one 55-gallon drum for general refuse. Horiba used the AC power source available at the demonstration site to operate the OCMA-350, ultrasonic mixer, and printer.

### **7.2.4 Durability of the Device**

Horiba used several reusable items during the demonstration. Of the reusable items that Horiba provides, the infrared spectrophotometer and Model GE-50 ultrasonic mixer contain mechanical or electronic parts that could potentially malfunction during sample analysis. Based on observations made during the demonstration, these reusable items are durable; neither of them malfunctioned or was damaged. These items are manufactured by Horiba and are distributed by Horiba and authorized distributors of Horiba products. The infrared

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spectrophotometer is housed in an optional, hard-plastic carrying case to prevent damage during transport, and the Model GE-50 ultrasonic mixer comes in a padded, cardboard box.

The Mettler-Toledo digital balance (Model BD202) and the Epson LQ-500 dot-matrix printer are reusable supplies that were used during the demonstration but that Horiba does not provide. These supplies also proved to be durable and did not malfunction or become damaged.

Based on observations made during the demonstration, the operation of the OCMA-350 was unaffected by the varying temperature and humidity conditions encountered between 8:00 a.m. and 5:00 p.m. on any given day. During the daytime, the temperature ranged from about 17 to 24 °C, and the relative humidity ranged from 53 to 88 percent. During sample analysis, wind speeds up to 20 miles per hour did not affect the operation of the reusable items.

### **7.2.5 Availability of the Device and Spare Parts**

During the demonstration, none of the reusable items provided by Horiba—specifically, the infrared spectrophotometer, Model SR-300 solvent reclaimer, Model GE-50 ultrasonic mixer, and Centronics printer cable—required repair or replacement. Except for the Centronics printer cable, replacement parts for these items would not have been available in stores. The Centronics

printer cable can be replaced with other brands of cable that are compatible with the OCMA-350 and are available in computer hardware stores. According to Horiba, replacement parts for the other items can be obtained from Horiba or an authorized distributor of Horiba products within 2 days, depending on the shipping procedures and site location. Except for an extra 3.15-ampere fuse for the infrared spectrophotometer, spare parts for reusable items are not provided with the OCMA-350. Horiba recommends that the infrared spectrophotometer, Model SR-300 solvent reclaimer, and Model GE-50 ultrasonic mixer be returned to Horiba or an authorized distributor of Horiba products for service if they malfunction. Because Horiba provides a 1-year warranty for these items, they will be repaired at no additional cost during the warranty period. According to Horiba, repairs are generally completed in 1 week or less, depending on the repairs needed.

All reusable items not provided by Horiba can be obtained from a scientific equipment or computer hardware supplier, as appropriate.

Of the expendable items used during the demonstration, the S-316 extraction solvent can be obtained from Horiba or an authorized distributor of Horiba products. Expendable items not provided by Horiba can be obtained from a scientific equipment supplier.

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## Chapter 8

### Economic Analysis

As discussed throughout this ITVR, the OCMA-350 was demonstrated by using it to analyze soil environmental samples, soil PE samples, and liquid PE samples. The environmental samples were collected from three contaminated sites, and the PE samples were obtained from a commercial provider, ERA. Collectively, the environmental and PE samples provided the different matrix types and the different levels and types of PHC contamination needed to perform a comprehensive economic analysis for the OCMA-350.

During the demonstration, the OCMA-350 and the off-site laboratory reference method were each used to perform more than 200 TPH analyses. The purpose of the economic analysis was to estimate the total cost of TPH measurement for the OCMA-350 and then compare this cost to that for the reference method. The cost per analysis was not estimated for the OCMA-350 because the cost per analysis would increase as the number of samples analyzed decreased. This increase would be primarily the result of the distribution of the initial capital equipment cost across a smaller number of samples. Thus, this increase in the cost per analysis cannot be fairly compared to the reference laboratory's fixed cost per analysis.

This chapter provides information on the issues and assumptions involved in the economic analysis (Section 8.1), discusses the costs associated with using the OCMA-350 (Section 8.2), discusses the costs associated with using the reference method (Section 8.3), and presents a comparison of the economic analysis results for the OCMA-350 and the reference method (Section 8.4).

#### 8.1 Issues and Assumptions

Several factors affect TPH measurement costs. Wherever possible in this chapter, these factors are identified in such a way that decision-makers can independently complete a project-specific economic analysis. The following five

cost categories were included in the economic analysis for the demonstration: capital equipment, supplies, support equipment, labor, and IDW disposal. The issues and assumptions associated with these categories and the costs not included in the analysis are briefly discussed below. Because the reference method costs were based on a fixed cost per analysis, the issues and assumptions discussed below apply only to the OCMA-350 unless otherwise stated.

##### 8.1.1 Capital Equipment Cost

The capital equipment cost was the cost associated with the purchase of the OCMA-350 used during the demonstration. This cost was obtained from a standard price list provided by Horiba. Because the device must be purchased, no salvage value was included in the capital equipment cost.

##### 8.1.2 Cost of Supplies

The cost of supplies was estimated based on the supplies required to analyze all demonstration samples using the OCMA-350 that were not included in the capital equipment cost category. The supplies that Horiba used during the demonstration fall into two general categories: expendable and reusable. Examples of expendable supplies include anhydrous sodium sulfate and solvent as well as disposable gloves and pipettes; however, Horiba promotes solvent recovery and reuse by providing an optional accessory, the Model SR-300 solvent reclaimer. Examples of reusable supplies include beakers and a digital balance. During the demonstration, the types and quantities of all supplies used by Horiba were noted each day.

For supplies provided by Horiba during the demonstration, Horiba's costs were used to estimate the cost of supplies. The costs for supplies not provided by Horiba were

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estimated based on price quotes from independent sources. Because a user cannot typically return unused supplies, no salvage value for supplies that were not used during the demonstration was included in the cost of supplies.

### **8.1.3 Support Equipment Cost**

During the demonstration, the OCMA-350, the Model GE-50 ultrasonic mixer, and the Epson LQ-500 dot-matrix printer were operated using an AC power source. The costs associated with providing the power supply and the electrical energy consumed were not included in the economic analysis; the demonstration site provided AC power at no cost. Of the three items mentioned above, the OCMA-350 can also be operated using a DC power source such as an automobile cigarette lighter. A typical user does not require the other two items for TPH measurement using the OCMA-350, so these items are considered to be optional.

Because of the large number of samples analyzed during the demonstration, the EPA provided support equipment, including a tent, tables, and chairs, for the field technician's comfort during sample extraction and analysis. For the economic analysis, the support equipment costs were estimated based on price quotes from independent sources.

### **8.1.4 Labor Cost**

The labor cost was estimated based on the time required for OCMA-350 setup, sample preparation, sample analysis, and summary data package preparation. The data package included, at a minimum, a result summary table, a run log, and any supplementary information submitted by Horiba. The measurement of the time required for Horiba to complete all analyses and submit the data package to the EPA was rounded to the nearest half-hour. For the economic analysis, it was assumed that a field technician who had worked for a fraction of a day would be paid for an entire 8-hour day. Based on this assumption, a daily rate for a field technician was used in the analysis.

During the demonstration, EPA representatives evaluated the skill level required for the field technician to complete analyses and calculate TPH concentrations. Based on the field observations, a field technician with basic wet chemistry skills acquired on the job or in a university and a few hours of device-specific training was considered to be qualified to operate the OCMA-350. For the economic analysis, an hourly rate of \$16.63 was used for a field

technician (R.S. Means Company [Means] 2000), and a multiplication factor of 2.5 was applied to labor costs in order to account for overhead costs. Based on this hourly rate and multiplication factor, a daily rate of \$332.60 was used for the economic analysis.

### **8.1.5 Investigation-Derived Waste Disposal Cost**

During the demonstration, Horiba was provided with two 20-gallon laboratory packs for collecting hazardous wastes generated (one for flammable wastes and one for corrosive wastes) and was charged for each laboratory pack used. Unused samples and sample extracts, used EnCores, and unused chemicals that could not be returned to Horiba or an independent vendor were disposed of in a laboratory pack. Items such as used PPE and disposable glassware were disposed of with municipal garbage in accordance with demonstration site waste disposal guidelines. Horiba was required to provide any containers necessary to containerize individual wastes prior to their placement in a laboratory pack. The cost for these containers was not included in the IDW disposal cost estimate.

### **8.1.6 Costs Not Included**

Items whose costs were not included in the economic analysis are identified below along with a rationale for the exclusion of each.

**Oversight of Sample Analysis Activities.** A typical user of the OCMA-350 would not be required to pay for customer oversight of sample analysis. EPA representatives audited all activities associated with sample analysis during the demonstration, but costs for EPA oversight were not included in the economic analysis because these activities were project-specific. For the same reason, costs for EPA oversight of the reference laboratory were also not included in the analysis.

**Travel and Per Diem for Field Technicians.** Field technicians may be available locally. Because the availability of field technicians is primarily a function of the location of the project site, travel and per diem costs for field technicians were not included in the economic analysis.

**Sample Collection and Management.** Costs for sample collection and management activities, including sample homogenization and labeling, were not included in the economic analysis because these activities were project-

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specific and were not device- or reference method-dependent.

**Shipping.** Costs for shipping (1) the OCMA-350 and necessary supplies to the demonstration site and (2) sample coolers to the reference laboratory were not included in the economic analysis because such costs vary depending on the shipping distance and the service used (for example, a courier or overnight shipping versus economy shipping).

**Items Costing Less Than \$10.** The cost of inexpensive items such as ice used for sample preservation in the field was not included in the economic analysis because the estimated cost was less than \$10.

## 8.2 OCMA-350 Costs

This section presents information on the individual costs of capital equipment, supplies, support equipment, labor, and IDW disposal for the OCMA-350 as well as a summary of these costs. Additionally, Table 8-1 summarizes the OCMA-350 costs.

### 8.2.1 Capital Equipment Cost

The capital equipment cost was the cost associated with the purchase of the OCMA-350. Horiba does not rent the OCMA-350. As discussed in Chapter 2, the OCMA-350 consists of the infrared spectrophotometer and its accessories, including (1) a proprietary, 10-mm, quartz cuvette with a Teflon<sup>®</sup> cap; (2) a 25- $\mu$ L microsyringe; (3) a 10-mL syringe; (4) 10 mL of B-heavy oil for calibration; (5) three 40-mL, VOA vials; (6) three 11-cm-diameter, No. 40 Whatman filter papers; and (7) two 10-mL, disposable, glass pipettes. The OCMA-350 also contains an instruction manual and a simplified operating instruction sheet. The OCMA-350 can be purchased from Horiba for \$6,500.

### 8.2.2 Cost of Supplies

The supplies that Horiba used during the demonstration fall into two general categories: expendable and reusable. Table 8-1 lists all the expendable and reusable supplies that Horiba used during the demonstration. Of the expendable supplies, Horiba's proprietary S-316 extraction solvent was used for extracting PHCs from soil and for cleaning glassware, anhydrous sodium sulfate was used for drying wet soil samples, and the VOA vials were used for soil sample extraction; the use of the other expendable supplies is self-explanatory. Of the reusable supplies, the

Model GE-50 ultrasonic mixer was used to disperse soil samples in the extraction solvent, and the Model SR-300 solvent reclaimer was used to recycle spent solvent; the use of the other reusable supplies is self-explanatory.

Cost information for all the supplies used during the demonstration is presented in Table 8-1. The total cost of the supplies used by Horiba during the demonstration was \$6,715 (the cost of each item was rounded to the nearest \$1). Of these supplies, the S-316 extraction solvent, Model GE-50 ultrasonic mixer, Model SR-300 solvent reclaimer, and Centronics printer cable are available from Horiba. The other supplies have to be purchased from a retail vendor of laboratory supplies. The Centronics printer cable can be replaced with other brands that are compatible with the OCMA-350 and are available in computer hardware stores.

During the demonstration, Horiba also used the following supplies that cost less than \$10 each: (1) a 280-count box of Kimwipes<sup>®</sup> (\$3.60) for wiping the quartz cuvette and (2) a 50-pound bag of concrete sand (\$1.89) used as blank material for QC checks (only about 50 grams of sand was used during the demonstration).

Other supplies that can be purchased from Horiba if additional quantities are needed include the proprietary, 10-mm, quartz cuvette (\$535) with the Teflon<sup>®</sup> cap (\$60); the 25- $\mu$ L microsyringe (\$210); 10-mL syringe (\$34); 10 mL of B-heavy oil for calibration (\$11); a 3.15-ampere fuse (\$3); a power supply cable (\$17); and the instruction manual (\$25). Horiba provides an electronic copy of the simplified operating instruction sheet at no cost to the user. During the demonstration, Horiba did not require additional quantities of these supplies; therefore, the costs of these items are not listed in Table 8-1.

### 8.2.3 Support Equipment Cost

Horiba was provided with one 8- by 8-foot tent for protection from inclement weather during the demonstration as well as two tables and two chairs for use during sample preparation and analysis activities. The purchase cost for the tent (\$159) and the rental cost for two tables and two chairs for 1 week (\$39) totaled \$198.

### 8.2.4 Labor Cost

One field technician was required for 6 days during the demonstration to complete all sample analyses and prepare the summary data package. Based on a labor rate of

**Table 8-1. OCMA-350 Cost Summary**

Item	Quantity	Unit Cost (\$)	Itemized Cost <sup>a</sup> (\$)
Capital equipment			
Purchase of infrared spectrophotometer and its accessories	1 unit	6,500	6,500
Supplies			
Expendable			
S-316 extraction solvent (7-kilogram bottle)	1 unit	1,040	1,040
Anhydrous sodium sulfate, 10-60 mesh (500-gram bottle)	2 units	19.75	40
40-mL, VOA vials (72 per box)	3 units	62.50	188
11-cm-diameter, No. 40 Whatman filter papers (100 per box)	2 units	26	52
10-mL, disposable, glass pipettes (12 per case)	1 unit	75.60	76
Disposable, latex gloves (100 per box)	1 unit	20.50	21
Reusable			
Model GE-50 ultrasonic mixer	1 unit	2,080	2,080
Model SR-300 solvent reclaimer	1 unit	1,650	1,650
Epson LQ-500 dot-matrix printer	1 unit	275	275
Centronics printer cable	1 unit	40	40
Mettler-Toledo digital balance (Model BD202)	1 unit	715	715
Stainless-steel spatulas (three per pack)	1 unit	20.30	20
Filter forceps	1 unit	20	20
Glass funnel	4 units	17.67	71
50-mL, glass beakers (12 per pack)	1 unit	38.80	39
Pipette bulb	1 unit	19.50	20
10-microliter microsyringe	1 unit	19.80	20
VWR Model 511 bottle-top dispenser	1 unit	234.90	235
Test tube rack (24 holes)	1 unit	22.50	23
Funnel rack and stand (holds four small funnels)	1 unit	90	90
Support equipment			
Tent	1 unit	159	159
Tables and chairs (two each)	1 set for 1 week	39	39
Labor			
Field technician	6 person-days	332.60	1,996
Investigation-derived waste disposal	1 20-gallon container	345	345
<b>Total Cost<sup>b</sup></b>			<b>15,750</b>

## Notes:

cm = Centimeter  
mL = Milliliter  
VOA = Volatile organic analysis

<sup>a</sup> Itemized costs were rounded to the nearest \$1.

<sup>b</sup> The total dollar amount was rounded to the nearest \$10.



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\$332.60 per day, the total labor cost for the OCMA-350 was \$1,996 (rounded to the nearest \$1).

### **8.2.5 Investigation-Derived Waste Disposal Cost**

Horiba used one laboratory pack to collect flammable hazardous waste, including unused soil and liquid samples that contained PHCs and used EnCores and ampules, generated during the demonstration. Horiba collected all the proprietary S-316 extraction solvent, including unused solvent; reclaimed solvent; and to-be-reclaimed, used solvent, in different bottles. At the end of the demonstration, Horiba took all the solvent to its laboratory for reuse. As a result, the IDW disposal cost included only the purchase cost of the laboratory pack (\$38) and the cost associated with hazardous waste disposal in a landfill (\$307) (Means 2000). The total IDW disposal cost was \$345.

### **8.2.6 Summary of OCMA-350 Costs**

The total cost for performing more than 200 TPH analyses using the OCMA-350 and for preparing a summary data package was \$15,750 (rounded to the nearest \$10). The TPH analyses were performed for 74 soil environmental samples, 89 soil PE samples, and 36 liquid PE samples. In addition to these 199 samples, 9 extract duplicates were analyzed for specified soil environmental samples. When Horiba performed multiple extractions, dilutions, or reanalyses for a sample, these were not included in the number of samples analyzed. During the demonstration, the multiple extractions, dilutions, and reanalyses collectively required only about 6 percent more supplies than would otherwise have been needed. The total cost included \$6,500 for capital equipment; \$6,715 for supplies; \$198 for support equipment; \$1,996 for labor; and \$345 for IDW disposal. Of these five costs, the two largest were the capital cost (41 percent of the total cost) and the cost of supplies (43 percent of the total cost).

A significant portion of the cost of supplies was associated with the Model GE-50 ultrasonic mixer (31 percent) and Model SR-300 solvent reclaimer (25 percent). Although these two items were useful during the demonstration, they are considered to be optional, and their purchase is justified only when a large number of samples will be analyzed. When a small number of samples will be analyzed, the ultrasonic mixer can be replaced with a cheaper means of agitation to disperse samples in solvent. Purchase of the solvent reclaimer should be considered only after evaluation of the disposal cost for spent solvent,

purchase cost for virgin solvent, and potential environmental concerns associated with hazardous waste disposal.

### **8.3 Reference Method Costs**

This section presents the costs associated with the reference method used to analyze the demonstration samples for TPH. Depending on the nature of a given sample, the reference laboratory analyzed the sample for GRO, EDRO, or both and calculated the TPH concentration by adding the GRO and EDRO concentrations, as appropriate. The reference method costs were calculated using unit cost information from the reference laboratory invoices. To allow an accurate comparison of the OCMA-350 and reference method costs, the reference method costs were estimated for the same number of samples as was analyzed by Horiba. For example, although the reference laboratory analyzed MS/MSD samples for TPH and all soil samples for percent moisture, the associated sample analytical costs were not included in the reference method costs because Horiba did not analyze MS/MSD samples for TPH or soil samples for percent moisture during the demonstration.

Table 8-2 summarizes the reference method costs, which totaled \$42,050. This cost covered preparation of demonstration samples and their analysis for TPH. In addition, at no additional cost, the reference laboratory provided (1) analytical results for internal QC check samples such as method blanks and LCS/LCSDs and (2) an electronic data deliverable and two paper copies of full, EPA Contract Laboratory Program-style data packages within 30 calendar days of the receipt of the last demonstration sample by the reference laboratory.

### **8.4 Comparison of Economic Analysis Results**

The total costs for the OCMA-350 (\$15,750) and the reference method (\$42,050) are listed in Tables 8-1 and 8-2, respectively. The total TPH measurement cost for the OCMA-350 was 62 percent less than that for the reference method. Although the OCMA-350 analytical results did not have the same level of detail (for example, carbon ranges) as the reference method analytical results or comparable QA/QC data, the OCMA-350 provided TPH analytical results on site at significant cost savings. In addition, use of the OCMA-350 in the field will likely produce additional cost savings because the results will be available within a few hours of sample collection; therefore, critical decisions regarding sampling and

**Table 8-2. Reference Method Cost Summary**

Item	Number of Samples Analyzed	Cost per Analysis (\$)	Itemized Cost <sup>a</sup> (\$)
Soil environmental samples			
GRO	56	111	6,216
Extract duplicates	7	55.50	388
EDRO	74	142	10,508
Extract duplicates	9	71	639
Soil performance evaluation samples			
GRO	55	111	6,105
EDRO	89	142	12,638
Liquid performance evaluation samples			
GRO	27	111	2,997
EDRO	24	106.50	2,556
<b>Total Cost<sup>b</sup></b>			<b>42,050</b>

Notes:

<sup>a</sup> Itemized costs were rounded to the nearest \$1.

<sup>b</sup> The total dollar amount was rounded to the nearest \$10.

analysis can be made in the field, resulting in a more complete data set. However, these savings cannot be

accurately estimated and thus were not included in the economic analysis.

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## Chapter 9

### Summary of Demonstration Results

As discussed throughout this ITVR, the OCMA-350 was demonstrated by using it to analyze 74 soil environmental samples, 89 soil PE samples, and 36 liquid PE samples. In addition to these 199 samples, 9 extract duplicates prepared using the environmental samples were analyzed. The environmental samples were collected from five individual areas at three contaminated sites, and the PE samples were obtained from a commercial provider, ERA. Collectively, the environmental and PE samples provided the different matrix types and the different levels and types of PHC contamination needed to perform a comprehensive evaluation of the OCMA-350.

The OCMA-350 performance and cost data were compared to those for an off-site laboratory reference method, SW-846 8015B (modified). As discussed in Chapter 6, the reference method results were considered to be of adequate quality for the following reasons: (1) the reference method was implemented with acceptable accuracy ( $\pm 30$  percent) for all the samples except low- and medium-concentration-range soil samples containing diesel, which made up only 13 percent of the total number of samples analyzed during the demonstration, and (2) the reference method was implemented with good precision for all samples. The reference method results generally exhibited a negative bias. However, the bias was considered to be significant primarily for low- and medium-range soil samples containing diesel. The reference method recoveries observed during the demonstration were typical of the recoveries obtained by most organic analytical methods for environmental samples.

This chapter compares the performance and cost results for the OCMA-350 with those for the reference method, as appropriate. The performance and cost results are discussed in detail in Chapters 7 and 8, respectively. Tables 9-1 and 9-2 summarize the results for the primary and secondary objectives, respectively. As shown in these tables, during the demonstration, the OCMA-350 exhibited the following desirable characteristics of a field TPH measurement device: (1) good precision, (2) sensitivity to interferents that are PHCs (MTBE and Stoddard solvent), and (3) high sample throughput. In addition, the OCMA-350 exhibited moderate measurement costs.

In general, the OCMA-350 TPH results for the PE samples did not compare well with the reference method results. In addition, turpentine biased the OCMA-350 TPH results high, whereas humic acid biased the results low. These findings indicated that the accuracy of TPH measurement using the device will likely be impacted by naturally occurring oil and grease and organic matter present in soil samples. PCE and 1,2,4-trichlorobenzene did not impact the OCMA-350 results in a consistent manner when the effect of these interferents was tested using neat materials and spiked soil samples. Finally, the device results were significantly impacted by soil moisture content: a 7 percentage point increase in soil moisture content resulted in (1) a three-fold increase in TPH results for weathered gasoline soil PE samples and (2) a three-fold decrease in TPH results for diesel soil PE samples. Collectively, the demonstration findings indicated that the OCMA-350 may be considered for TPH screening purposes; however, the user should exercise caution when considering the device for a field TPH measurement application requiring definitive results.

**Table 9-1. Summary of OCMA-350 Results for the Primary Objectives**

Primary Objective	Evaluation Basis <sup>a</sup>	Performance Results	
		OCMA-350	Reference Method
P1 Determine the method detection limit	Method detection limit based on TPH analysis of seven low-concentration-range diesel soil PE samples	15.2 mg/kg	4.79 mg/kg
P2 Evaluate the accuracy and precision of TPH measurement	<p>Comparison of project-specific action level conclusions of the OCMA-350 with those of the reference method for 74 soil environmental and 34 soil PE samples</p> <p>Comparison of OCMA-350 TPH results with those of the reference method for 74 soil environmental and 28 soil PE samples</p> <p>Pairwise comparison of OCMA-350 and reference method TPH results for (1) soil environmental samples collected from five areas; (2) soil PE samples, including blank, weathered gasoline, and diesel soil samples; and (3) liquid PE samples consisting of neat weathered gasoline and diesel</p> <p>Correlation (as determined by linear regression analysis) between OCMA-350 and reference method TPH results for (1) soil environmental samples collected from five areas and (2) soil PE samples, including weathered gasoline and diesel soil samples</p>	<p>Of the 108 OCMA-350 results, 1 result was inconclusive. Of the 107 remaining OCMA-350 conclusions, 78 (73 percent) agreed with those of the reference method; 6 OCMA-350 conclusions were false positives, and 23 were false negatives.</p> <p>36 of 102 OCMA-350 results (35 percent) were within 30 percent of the reference method results; 16 OCMA-350 results were biased high, and 20 were biased low.</p> <p>16 of 102 OCMA-350 results (16 percent) were within 30 to 50 percent of the reference method results; 5 OCMA-350 results were biased high, and 11 were biased low.</p> <p>50 of 102 OCMA-350 results (49 percent) were not within 50 percent of the reference method results; 17 OCMA-350 results were biased high, and 33 were biased low.</p> <p>For soil environmental samples, the OCMA-350 results were statistically (1) the same as the reference method results for four of the five sampling areas and (2) different from the reference method results for one sampling area.</p> <p>For soil PE samples, the OCMA-350 results were statistically (1) the same as the reference method results for blank samples and (2) different from the reference method results for medium- and high-concentration-range weathered gasoline samples and low-, medium-, and high-concentration-range diesel samples.</p> <p>For liquid PE samples, the OCMA-350 results were statistically (1) the same as the reference method results for weathered gasoline samples and (2) different from the reference method results for diesel samples.</p> <p>The OCMA-350 results correlated highly with the reference method results for three of the five sampling areas (<math>R^2</math> values were greater than or equal to 0.90, and F-test probability values were less than 5 percent).</p> <p>The OCMA-350 results correlated moderately with the reference method results for diesel soil PE samples (the <math>R^2</math> value was 0.68, and the F-test probability value was less than 5 percent).</p> <p>The OCMA-350 results correlated weakly with the reference method results for two sampling areas and for weathered gasoline soil PE samples (<math>R^2</math> values ranged from 0.19 to 0.53, and F-test probability values ranged from 22.58 to 62.68 percent).</p>	

Table 9-1. Summary of OCMA-350 Results for the Primary Objectives (Continued)

Primary Objective	Evaluation Basis <sup>a</sup>	Performance Results	
		OCMA-350	Reference Method
P2 Evaluate the accuracy and precision of TPH measurement (continued)	Overall precision (RSD) for soil environmental, soil PE, and liquid PE sample replicates	Soil environmental samples (11 triplicates) RSD range: 0 to 49 percent Median RSD: 20 percent	Soil environmental samples (12 triplicates) RSD range: 4 to 39 percent Median RSD: 18 percent
	Analytical precision (RPD) for extract duplicates for soil environmental samples (9 for the OCMA-350 and 13 for the reference method)	Soil PE samples (7 replicates) RSD range: 2 to 17 percent Median RSD: 5 percent	Soil PE samples (7 replicates) RSD range: 2 to 10 percent Median RSD: 7 percent
P3 Evaluate the effect of interferences on TPH measurement	Mean responses for neat materials, including MTBE; PCE; Stoddard solvent; turpentine; and 1,2,4-trichlorobenzene, and for soil spiked with humic acid (two triplicate sets each)	Liquid PE samples (2 triplicates) RSDs: 1 and 2 percent Median RSD: 1.5 percent	Liquid PE samples (2 triplicates) RSDs: 5 and 6 percent Median RSD: 5.5 percent
	Comparison of TPH results (one-way analysis of variance) for weathered gasoline and diesel soil PE samples without and with interferences at two levels	RPD range: 0 to 3 Median RPD: 1	RPD range: 0 to 11 Median RPD: 4
P4 Evaluate the effect of soil moisture content on TPH measurement	Interferents for neat materials, including MTBE; PCE; Stoddard solvent, and for soil spiked with humic acid (two triplicate sets each)	MTBE: 72.5 percent PCE: 0 percent Stoddard solvent: 86 percent Turpentine: 85 percent 1,2,4-Trichlorobenzene: 0 percent Humic acid: 0 percent	MTBE: 39 percent PCE: 17.5 percent Stoddard solvent: 85 percent Turpentine: 52 percent 1,2,4-Trichlorobenzene: 50 percent Humic acid: 0 percent
	Interferents for weathered gasoline soil PE samples: MTBE, PCE, Stoddard solvent, and turpentine	MTBE, a petroleum hydrocarbon, caused statistically significant interference at both levels.	MTBE, a petroleum hydrocarbon, did not cause statistically significant interference at either of the two levels.
P4 Evaluate the effect of soil moisture content on TPH measurement	Interferents for diesel soil PE samples: Stoddard solvent; turpentine; 1,2,4-trichlorobenzene; and humic acid	PCE results were inconclusive.	PCE caused statistically significant interference only at the high level.
	Comparison of TPH results (two-sample Student's t-test) for weathered gasoline and diesel soil PE samples at two moisture levels: 9 and 16 percent for weathered gasoline samples and less than 1 and 9 percent for diesel samples	Stoddard solvent, a petroleum hydrocarbon, caused statistically significant interference (1) at both levels for weathered gasoline samples and (2) only at the high level for diesel samples.	Stoddard solvent, a petroleum hydrocarbon, caused statistically significant interference at both levels for weathered gasoline and diesel samples.
P4 Evaluate the effect of soil moisture content on TPH measurement	Comparison of TPH results (two-sample Student's t-test) for weathered gasoline and diesel soil PE samples at two moisture levels: 9 and 16 percent for weathered gasoline samples and less than 1 and 9 percent for diesel samples	Turpentine caused statistically significant interference at both levels for weathered gasoline and diesel samples.	Turpentine caused statistically significant interference (1) at both levels for weathered gasoline samples and (2) only at the high level for diesel samples.
		1,2,4-Trichlorobenzene caused statistically significant interference only at the high level.	1,2,4-Trichlorobenzene caused statistically significant interference only at the high level.
P4 Evaluate the effect of soil moisture content on TPH measurement	Comparison of TPH results (two-sample Student's t-test) for weathered gasoline and diesel soil PE samples at two moisture levels: 9 and 16 percent for weathered gasoline samples and less than 1 and 9 percent for diesel samples	Humic acid caused statistically significant interference at both levels.	Humic acid results were inconclusive.
		Soil moisture content had a statistically significant impact on both weathered gasoline sample and diesel sample results.	Soil moisture content did not have a statistically significant impact.

**Table 9-1. Summary of OCMA-350 Results for the Primary Objectives (Continued)**

Primary Objective	Evaluation Basis <sup>a</sup>	Performance Results	
		OCMA-350	Reference Method
P5 Measure the time required for TPH measurement (sample throughput)	Total time from sample receipt through preparation of the draft data package	46 hours, 15 minutes, for TPH measurement of 74 soil environmental samples, 89 soil PE samples, 36 liquid PE samples, and 9 extract duplicates	30 days for TPH measurement of 74 soil environmental samples, 89 soil PE samples, 36 liquid PE samples, and 13 extract duplicates
P6 Estimate TPH measurement costs	Total cost (costs of capital equipment, supplies, support equipment, labor, and IDW disposal) for TPH measurement of 74 soil environmental samples, 89 soil PE samples, 36 liquid PE samples, and 9 extract duplicates	\$15,750 (including the capital equipment purchase cost of \$6,500 for the OCMA-350)	\$42,050

Notes:

IDW = Investigation-derived waste  
 mg/kg = Milligram per kilogram  
 MTBE = Methyl-tert-butyl ether  
 PCE = Tetrachloroethene  
 PE = Performance evaluation  
 R<sup>2</sup> = Square of the correlation coefficient  
 RPD = Relative percent difference  
 RSD = Relative standard deviation

<sup>a</sup> All statistical comparisons were made at a significance level of 5 percent.

**Table 9-2. Summary of OCMA-350 Results for the Secondary Objectives**

Secondary Objective	Performance Results
<p>S1 Skill and training requirements for proper device operation</p>	<p>The device can be operated by one person with basic wet chemistry skills.</p> <p>The device's instruction manual and simplified operating instruction sheet are considered to be adequate training materials for proper device operation. The sample analysis procedure for the device can be learned in the field with a few practice attempts.</p> <p>The device's digital display provides a sample's TPH concentration in milligrams per kilogram TPH on a wet weight basis; minimal effort is required to calculate a TPH concentration. At the end of the demonstration, Horiba reported 208 TPH results. Of these, fewer than 5 percent required corrections, which primarily involved use of inappropriate reporting limits.</p> <p>Some of the device's items, including the narrow-mouth vials used for weighing and extracting soil samples and the gravity filtration setup, made the TPH measurement procedure less simple and more time-consuming.</p>
<p>S2 Health and safety concerns associated with device operation</p>	<p>No significant health and safety concerns were noted; when the device is used in a well-ventilated area, basic eye and skin protection (safety glasses, disposable gloves, work boots, and work clothes with long sleeves and long pants) should be adequate for safe device operation.</p>
<p>S3 Portability of the device</p>	<p>The device can be easily moved between sampling areas in the field, if necessary.</p> <p>The device can be operated using a 110-volt alternating current power source or a direct current power source such as a 12-volt power outlet in an automobile.</p>
<p>S4 Durability of the device</p>	<p>The primary component of the device, the infrared analyzer, is provided in an optional, hard-plastic carrying case to prevent damage to the analyzer. During the demonstration, none of the device's reusable items malfunctioned or was damaged. The moderate temperatures (17 to 24 °C) and high relative humidities (53 to 88 percent) encountered during the demonstration did not affect device operation.</p>
<p>S5 Availability of device and spare parts</p>	<p>During a 1-year warranty period, Horiba will repair any malfunctioning items of the device at no cost.</p> <p>Horiba does not supply some items necessary for TPH measurement using the device, including a test tube rack, a funnel rack and stand, a digital balance, and miscellaneous glassware and laboratory supplies; the availability of replacement or spare parts not supplied by Horiba depends on their manufacturer or distributor.</p>

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## Chapter 10

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## **Appendix**

### **Supplemental Information Provided by the Developer**

This appendix contains supplemental information provided by Horiba. Specifically, updates and improvements to the OCMA-350 resulting from the SITE demonstration are summarized below.

#### **Sampling Technique**

During the SITE demonstration, the weight of each sample was measured and adjusted to  $5.0 \pm 0.04$  grams to take advantage of the preset value in the OCMA-350. Significant time was used to adjust the sample weight to exactly 5 grams. It was noted that much time could be saved by quickly weighing the sample to obtain a nominal value of 5 grams (say  $\pm 0.5$  gram) but measuring its weight to the nearest 0.1 gram. It is a simple matter to reset the sample weight in the microprocessor of the OCMA-350.

The balance used during the SITE demonstration measured sample weight to within  $\pm 0.01$  gram. The precision of the balance measurement and the balance's sensitivity to gusty winds encountered during the demonstration suggest that the OCMA-350 instruction manual is correct in recommending use of a balance with a resolution of  $\pm 0.1$  gram.

During the SITE demonstration, a given soil sample was extracted using Horiba's proprietary S-316 extraction solvent. The extract was then filtered through a Whatman No. 40 filter by gravity. It has been noted that use of a syringe filter could reduce the filtering time by more than 50 percent.

#### **Efficient Use of Resources**

The Horiba Model SR-300 Solvent Reclaimer was used during the SITE demonstration and reduced the cost of solvent used by reclaiming spent solvent. However, during the demonstration, only a small portion of the spent solvent was regenerated because of time constraints. Greater efficiency and cost-effectiveness would be achieved by collecting larger volumes of spent solvent and regenerating larger batches of spent solvent using the Model SR-300 solvent reclaimer.

#### **Consistency in Sample Preparation**

The GE-50 ultrasonic disruptor was used to facilitate extraction of PHCs in soil. The sonication time varied from 30 seconds to 1 minute. After reviewing the extraction process, Horiba believes that 1 minute should have been a fixed value for the sonication time for all samples to be consistent.

#### **Safety Issue**

While using the GE-50 ultrasonic disruptor during the SITE demonstration, Horiba made no provision for donning ear protection. Horiba now believes that ear protection is necessary during use of the GE-50 ultrasonic disruptor.

This appendix was written solely by Horiba. The statements presented in this appendix represent the developer's point of view and summarize the claims made by the developer regarding the OCMA-350. Publication of this material does not represent the EPA's approval or endorsement of the statements made in this appendix; performance assessment and economic analysis results for the OCMA-350 are discussed in the body of this ITVR.

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### **Efficient Use of Time**

During the SITE demonstration, the sample concentration was initially measured by allowing the microprocessor of the OCMA-350 to achieve a stable reading even if it was off the scale. The reasoning was that the OCMA

350's printer port allowed Horiba to get an estimated value for subsequent dilution purposes. However, it was learned that the time used to get the printout for the off-scale reading would have been better spent by simply estimating a dilution factor and not waiting for the printout.

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