⊕EPA

Innovative Technology Verification Report

Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil

Strategic Diagnostics Inc. EnSys Petro Test System

Innovative Technology Verification Report

Strategic Diagnostics Inc. EnSys Petro Test System

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ETV

Notice

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

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ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM
VERIFICATION STATEMENT

TECHNOLOGY TYPE:	**FIELD MEASUREMENT DEVICE**
APPLICATION:	**MEASUREMENT OF TOTAL PETROLEUM HYDROCARBONS**
TECHNOLOGY NAME:	**EnSys PETRO TEST SYSTEM**
COMPANY:	**STRATEGIC DIAGNOSTICS INC.**
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VERIFICATION PROGRAM DESCRIPTION

The U.S. Environmental Protection Agency (EPA) created the Superfund Innovative Tec hnology Evaluation (SITE) and Environmental Technology Verification (ETV) Programs to facilitate deployment of innovative technologies through performance verification and information dissemination. The goa l 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 EnSys Petro Test System developed by Strategic Diagnostics Inc. (SDI).

PROGRAM OPERATION

Under the SITE and ETV Programs, with the full participa tion of the technology developers, the EPA evaluates and documents the performance of innovative technologies by developi ng 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 tec hnologies, selected Tetra Tech EM Inc. as the verification organization to assist in field testing seven field measuremen t 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 EnSys Petro Test System and six other field measurement devices for TPH in soil. This verification statement focuses on the EnSys Petro Test System; a similar statement has been prepared for each of the other six devices. The performance and co st of the EnSys Petro Test System 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 demons tration 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 interferents, and (4) evaluating the effect of moisture content on TPH measurement for each device. Additional primary objectives were to m easure 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 EnSys Petro Test System was demonstrated by using it to analyze 66 soil environmental samples, 89 soil performance evaluation (PE) samples, and 36 liquid PE samples. In add ition to these 191 samples, 12 extract duplicates prepared using the environmental samples were analyzed. The environmenta l samples were collected in four areas contaminated with gasoline, diesel, or other petroleum products, and the PE sa mples were obtained from a commercial provider. SDI chose not to analyze soil samples collected in a fifth area because accord ing to SDI, the EnSys Petro Test System was not designed to measure the heavy lubricating oil present in the area.

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Collectively, the environmental and PE samples provided the di fferent matrix types and the different levels and types of petroleum hydrocarbon contamination needed to perform a comp rehensive evaluation of the EnSys Petro Test System. 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 Pe troleum Hydrocarbons in Soil—Strategic Diagnostics Inc., EnSys Petro Test System" (EPA/600/R-01/084).

TECHNOLOGY DESCRIPTION

The EnSys Petro Test System manufactured by SDI is based on a combination of immunoassay (specifically, enzyme-linked immunosorbent assay) and colorimetry. The EnSys Petro Test System includes the SDI Sample Extraction Kit, the EnSys Petro 12T Soil Test Kit, and the EnSys/EnviroGard ® Common Accessory Kit. With this device, methanol is used for extraction of petroleum hydrocarbons from soil samples. Each sa mple extract is mixed with an enzyme conjugate solution. The reaction mixture is then transferred to an antibody-coated test tube. The hydrocarbons in the sample extract and those in the enzyme conjugate competitively bind to specific antibody sites on the test tube. The test tube is rinsed with a dilute detergent solution to remove any enzyme conjugate and hydro carbons not bound to the antibodies. A color developer solution and hydrogen peroxide are added to the test tube in order to give yellow color to the enzymes that remain attached to the test tube. The color intensity is inversely proportional to the c oncentration of hydrocarbons in the extract. To accomplish color measurement, the absorbance of the antibody-coated tube c ontaining the sample extract and an antibody-coated tube containing a reference standard (m-xylene) is compared using a differential photometer. A positive reading on the photometer indicates that the total concentration of petroleum hydrocarbons in the sample extract is less than that in the reference standard. Similarly, a negative reading on the photometer i ndicates that the total concentration of petroleum hydrocarbons in the sample extract is greater th an that in the reference standard.

During the demonstration, extraction of petroleum hydrocarbons in a given soil sample was completed by adding 20 milliliters of methanol to 10 grams of the sample. SDI performed each an alysis at three detection levels by diluting the sample extract twice during sample and standard preparation. The refere nce standard concentrations for gasoline (10 milligrams per kilogram [mg/kg]) and diesel (15 mg/kg) were multiplied by th e dilution factors used. Thus, the concentration ranges used to estimate sample TPH concentrations were (1) less than (<)10; greater than (>)10 to <100; >100 to <1,000; and >1,000 mg/kg for samples containing gasoline range organics a nd (2) <15; >15 to <100; >100 to <1,000; and >1,000 mg/kg for samples containing extended diesel range organics.

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-s pecific 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 obs erved 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 comp aring it to reference methods because the reference methods themselves may have limitations. Key demonstration fi ndings are summarized below for the primary objectives.

Method Detection Limit : Based on the TPH results for seven low-concentr ation-range diesel soil PE samples, the method detection limit for the reference method was determined to be 6.32 mg/kg. Because the EnSys Petro Test System is a semiquantitative device, a method detection limit could not be determined for the device; however, the device's TPH concentration ranges for six of seven samp les overlapped the reference method results.

Accuracy and Precision : The EnSys Petro Test System results for 16 of 66 soil environmental samples were inconclusive. Of the remaining 50 results, the device's TPH concentrati on ranges overlapped the reference method results for only 8 samples (16 percent); 36 EnSys Petro Test System results were biased high, and 6 results were biased low. The EnSys Petro Test System results for 12 of 28 soil PE samples were inconclusive. Of the remaining 16 results, the device's TPH concentration ranges overlapped the reference method results for only 5 samples (31 percent); 9 EnSys Petro Test System results were biased high, and 2 results were biased low. The EnSys Petro Test System results for all 6 liquid PE samples were inconclusive.

The EnSys Petro Test System results for 3 of 66 soil environmen tal samples used to draw conclusions regarding whether the TPH concentrations in a given sampling area or sample type exceeded a specified action level were inconclusive. Of the remaining 63 results, the device's conclusions agreed with those of the reference method for 41 samples (65 percent); 21 EnSys Petro Test System conclusions were false positives, and 1 was a false negative. The EnSys Petro Test System results for 14 of 34 soil PE samples were inconclusive. Of the remaining 20 results, the device's conclusions agreed with those of the reference method for 15 samples (75 percent); 3 En Sys Petro Test System conclusions were false positives, and 2 were false negatives.

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Both the EnSys Petro Test System and reference method exhibited good precision. Specifically, for 17 of 19 soil sample replicate sets and 2 of 2 liquid sample replicate sets, the En Sys Petro Test System TPH concentration ranges were the same for each replicate set. For 12 of 12 extract duplicate sets, the device's TPH concentration ranges were the same for each extract duplicate set. For the reference method, the median relative standard deviation ranged from 5.5 to 16 percent for 18 soil and 2 liquid sample replicate sets, and the median re lative percent difference was 3 for 12 extract duplicate sets.

Effect of Interferents: The EnSys Petro Test System showed a mean response of at least 24 percent for neat tetrachloroethene (PCE); Stoddard solvent; turpentine; and 1,2,4-trichlorobenzen e. The device showed no response for neat methyl-tert-butyl ether (MTBE) or soil spiked with humic acid. 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 St oddard solvent were included in the definition of TPH.

Effect of Moisture Content: The EnSys Petro Test System TPH results were in conclusive with regard to the effect of soil moisture content. The reference method TPH results were unaffected when the soil moisture content was increased from (1) 9 to 16 percent for weathered gasoline soil PE samples and (2) less than 1 to 9 percent for diesel soil PE samples.

Measurement Time: From the time of sample receipt, SDI required 39 hours, 35 minutes, to prepare a draft data package containing TPH results for 191 samples and 12 extract duplicates compared to 30 days for the reference method, which was used to analyze 199 samples and 13 extract duplicates.

Measurement Costs: For the EnSys Petro Test System, the TPH measurement cost for 191 samples and 12 extract duplicates was estimated to be $10,210 (including the daily rental cost of the EnSys/EnviroGard ® Common Accessory Kit, whose purchase price is $1,999) compared to $41,290 for the reference method.

Key demonstration findings are summarized below for the secondary objectives.

Skill and Training Requirements: The EnSys Petro Test System can be opera ted 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.

Portability: The EnSys Petro Test System is battery-operated and requires no alternating current power source. The device can be easily moved between sampling areas in the field, if necessary.

Durability and Availability of the Device: All items in the EnSys Petro Test System are available from SDI. During a 1-year warranty period, SDI will supply replacement parts for the de vice by overnight courier service at no cost. During the demonstration, none of the device's reus able items malfunctioned or was damaged.

In summary, during the demonstration, the EnSys Petro Test System exhibited the following desirable characteristics of a field TPH measurement device: (1) good precision and (2) high sa mple throughput. In addition, the EnSys Petro Test System exhibited moderate measurement costs. However, a signifi cant number of the EnSys Petro Test System TPH results were determined to be inconclusive because the detection levels used by SDI were not appropriate to address the demonstration objectives. Overall, the device's results did not compare well with those of the reference method; in general, the device exhibited a high positive bias. Collectively, the demonstration findings indicated that the user should exercise caution when considering the device for a site-specific field TPH measurement application.

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 t echnology performance under specific, predetermined criteria and appropriate quality assurance procedures. The EPA make s 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 knowle dge base needed to manage ecological resources wisely, understand how pollutants affect public hea lth, 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 identifyi ng 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 ai r, soil, and water; (2) support regulatory and policy decisions; and (3) provide the scientific s upport needed to ensure effective implementation of environmental regulations and strategies.

The EPA's Superfund Innovative Technology Evalua tion (SITE) Program evaluates technologies designed for characterization and remediati on of contaminated Superfund and Resource Conservation and Recovery Act sites. The SITE Pr ogram 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 t echnologies 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 fe deral government or the private sector. Through the SITE Program, developers are given the opportun ity to conduct a rigorous demonstration of their technologies under actual field conditions. By comp leting 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 Sc iences Division of NERL in Las Vegas, Nevada.

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Abstract

The EnSys Petro Test System developed by Strate gic Diagnostics Inc. (SDI) 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 performan ce and cost data for the EnSys Petro Test System and six other field measurement devices for total pe troleum hydrocarbons (TPH) in soil. In addition to assessing ease of device operation, the key objectiv es 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 thr oughput, and (5) TPH measurement costs for each device. The demonstration involved analysis of both performance evaluation samples and environmental samples collected in four areas contam inated with gasoline, diesel, 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 met hod, "Test Methods for Evaluating Solid Waste" (SW-846) Method 8015B (modified). During the de monstration, SDI required 39 hours, 35 minutes, for TPH measurement of 191 samples and 12 extract duplicates. The TPH measurement costs for these samples were estimated to be $10,210 for the EnSys Petro Test System compared to $41,290 for the reference method. The method detection limit for the reference method was determined to be 6.32 milligrams per kilogram; a method detection limit could not be determined for the EnSys Petro Test System because it is a semiquantitative device. During the demonstration, the device exhibited good precision and lack of sensitivity to soil spiked with humic acid. The device showed a mean response of at least 24 percent for interferents that are not petroleum hydrocarbons (neat materials, including tetrachloroethene; turpentine; and 1,2,4-trichlorobenzene). A significant number of the EnSys Petro Test System TPH results we re determined to be inconclusive because the detection levels used by SDI were not appropriate to address the demonstration objectives. Overall, the device's results did not compare well with those of the reference method; in general, the device exhibited a high positive bias. Collectively, the dem onstration findings indicated that the user should exercise caution when considering the device for a site-specific field TPH measurement application.

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Abbreviations, Acronyms, and Symbols

<	Less than
>	Greater than
≤	Less than or equal to
±	Plus or minus
μg	Microgram
μm	Micrometer
12T Soil Test Kit	EnSys Petro 12T Soil Test Kit
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	*Code of Federal Regulations*
Common Accessory Kit	EnSys/EnviroGard® Common Accessory Kit
DER	Data evaluation report
DRO	Diesel range organics
EDRO	Extended diesel range organics
ELISA	Enzyme-linked immunosorbent assay
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
ICV	Initial calibration verification
IDW	Investigation-derived waste
Ig	Immunoglobulin
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
Means	R.S. Means Company

Abbreviations, Acronyms, and Symbols (Continued)

mg	Milligram
min	Minute
mL	Milliliter
MMT	Monitoring and Measurement Technology
MS	Matrix spike
MSD	Matrix spike duplicate
MTBE	Methyl-tert-butyl ether
$n\text{-}C_x$	Alkane with "x" carbon atoms
NERL	National Exposure Research Laboratory
NEX	Naval Exchange
ng	Nanogram
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 hydrocarbons
PPE	Personal protective equipment
PRA	Phytoremediation Area
PRO	Petroleum range organics
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
RSD	Relative standard deviation
Sample Extraction Kit	SDI Sample Extraction Kit
SDI	Strategic Diagnostics Inc.
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
VPH	Volatile petroleum hydrocarbons

Acknowledgments

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 EnSys Petro Test System developed by Strategic Diagnostics Inc. (SDI). 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 SDI 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 and toxic substances. These technologies are expected to provide better, faster, or more cost-effective

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

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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 EnSys Petro Test System 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 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,
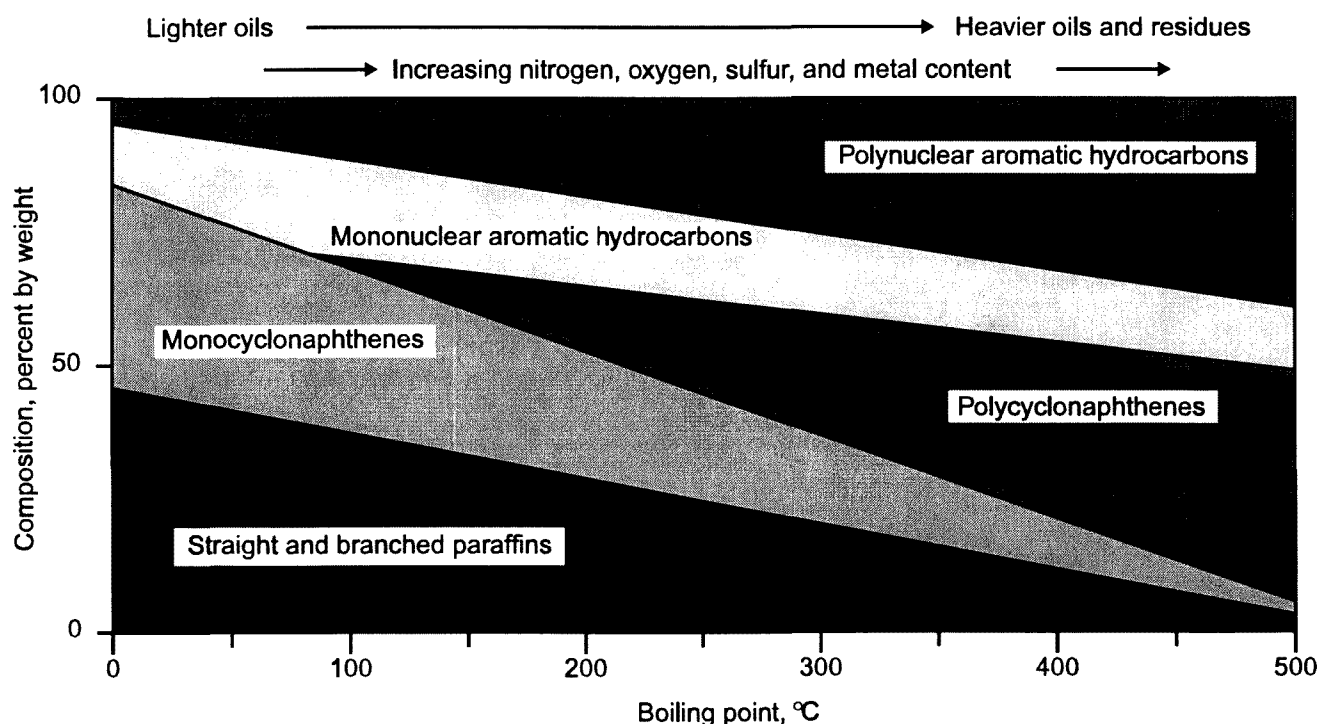
Source: Speight 1991

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

5

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.

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 (μm), which corresponds to an aliphatic 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 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 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.

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 CH_2 in Standard Constituent (percent by weight)
			Aliphatic			Aromatic	
			CH_3	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_2 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

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] 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.

Chapter 2
Description of Immunoassay and Colorimetry and the EnSys Petro Test System

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, ultraviolet light).

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 EnSys Petro Test System is a field measurement device capable of providing semiquantitative TPH measurement results. Measurements made by the EnSys Petro Test System are based on immunoassay and colorimetry using light in the visible wavelength range. Immunoassay and colorimetry are described in Section 2.1. The EnSys Petro Test System does not require generation of a calibration curve because it provides semiquantitative results. A concentration range is reported by evaluating whether the TPH concentration in a given sample is greater or less than the concentration in one or more reference standards; SDI does not report an absolute sample concentration through interpolation of reference standard concentrations.

Section 2.1 describes the technology upon which the EnSys Petro Test System is based, Section 2.2 describes the EnSys Petro Test System itself, and Section 2.3 provides SDI 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 EnSys Petro Test System. Detailed operating procedures for the device, including soil extraction, TPH measurement, and TPH concentration range calculation procedures, are available from SDI. Supplemental information provided by SDI is presented in the appendix.

2.1 Description of Immunoassay and Colorimetry

Measurement of TPH in soil using the EnSys Petro Test System is based on a combination of immunoassay and colorimetry. According to SDI, this combination of technologies is suitable for measuring a large portion of

the aromatic hydrocarbons and a few aliphatic hydrocarbons in the C_6 through C_{22} carbon range. Immunoassay and colorimetry are described below.

2.1.1 Immunoassay

Immunoassay is a technique for measuring a target compound's concentration using biologically engineered antibodies. Antibodies are a class of proteins known as immunoglobulins that are produced by the immune system of animals in response to a foreign substance (an antigen). The antibodies produced can bind with the antigen that stimulated their production. Specifically, antibodies are produced in response to localized, reactive sites called antigenic determinants on the surface of the antigen. Antigenic determinants consist of amino acid sequences (Rittenburg 1990). Because an antigen may possess more than one type of antigenic determinant, more than one type of antibody may be produced by the immune system. In general, the antibodies produced are structured in such a way that they selectively bind to the antigenic determinants on the antigen that stimulated their production, resulting in formation of an antibody-antigen complex.

Five major classes of antibodies (immunoglobulin [Ig] A, IgD, IgE, IgG, and IgM) are produced by the immune system. IgG is the most common type of antibody used in immunoassay (Rittenburg 1990). IgG is a Y-shaped molecule consisting of two identical heavy polypeptide chains and two identical light polypeptide chains bound together by disulfide bonds. Both the heavy and light chains have variable and constant regions. The variable regions at the ends of the two arms of the Y-shaped antibody form areas called antigen-binding sites; therefore, two antigen-binding sites are present on each antibody. The general structure of the IgG antibody is shown in Figure 2-1.

The dimensions and contours of antigen-binding sites are determined by the sequence of amino acids in the variable regions of the antibody. On a single antibody molecule, the two binding sites have identical variable regions. As a result, the two binding sites have identical specificity for a particular antigenic determinant (Rittenburg 1990). However, the binding sites of antibodies produced in response to different antigenic determinants are not the same.

The binding affinity between an antibody and antigen is determined by (1) the sequence of amino acids in the

variable regions of the antibody, (2) the structure and location of the antigenic determinant on the antigen, and (3) the attractive forces that stabilize the antibody-antigen complex. The attractive forces include a combination of hydrogen bonds, hydrophobic bonds, coulombic interaction, and van der Waals forces (Rittenburg 1990). The closer the antigenic determinant is to the antigen-binding site on the antibody, the higher the binding affinity.

Immunoassays employ either polyclonal or monoclonal antibodies. Because an antigen generally contains more than one type of antigenic determinant, more than one type of antibody may be produced in the immune response. Therefore, the antibodies produced are not identical and are called polyclonal antibodies. Because polyclonal antibodies are not identical, they will, as a group, exhibit varied specificities and binding affinities for antigenic determinants. Monoclonal antibodies are produced by isolating those antibodies produced in response to one type of antigenic determinant. As a result, monoclonal antibodies are structurally identical and exhibit the same specificities and binding affinities for the antigenic determinant that stimulated their production.

Although an antibody has a particular specificity and binding affinity for the antigenic determinant that produced the antibody, cross-reactivity with other compounds may occur. For example, cross-reactivity may occur when the antigenic determinant that stimulated the antibody's production is present in other compounds (SDI 2000). Cross-reactivity may also occur with other compounds that possess structurally similar antigenic determinants (Rittenburg 1990).

Immunoassay effectiveness is primarily a function of (1) the specificities and binding affinities of the polyclonal or monoclonal antibodies used and (2) whether one compound or a group of compounds is being measured. For example, cross-reactivity will result in false positives when only one compound is being measured. However, cross-reactivity is desirable when a group of compounds, such as PHCs, is being measured. Whether polyclonal or monoclonal antibodies are better suited for measuring PHCs depends on the individual antibodies used; for example, highly cross-reactive, monoclonal antibodies can be as effective as less cross-reactive, polyclonal antibodies.
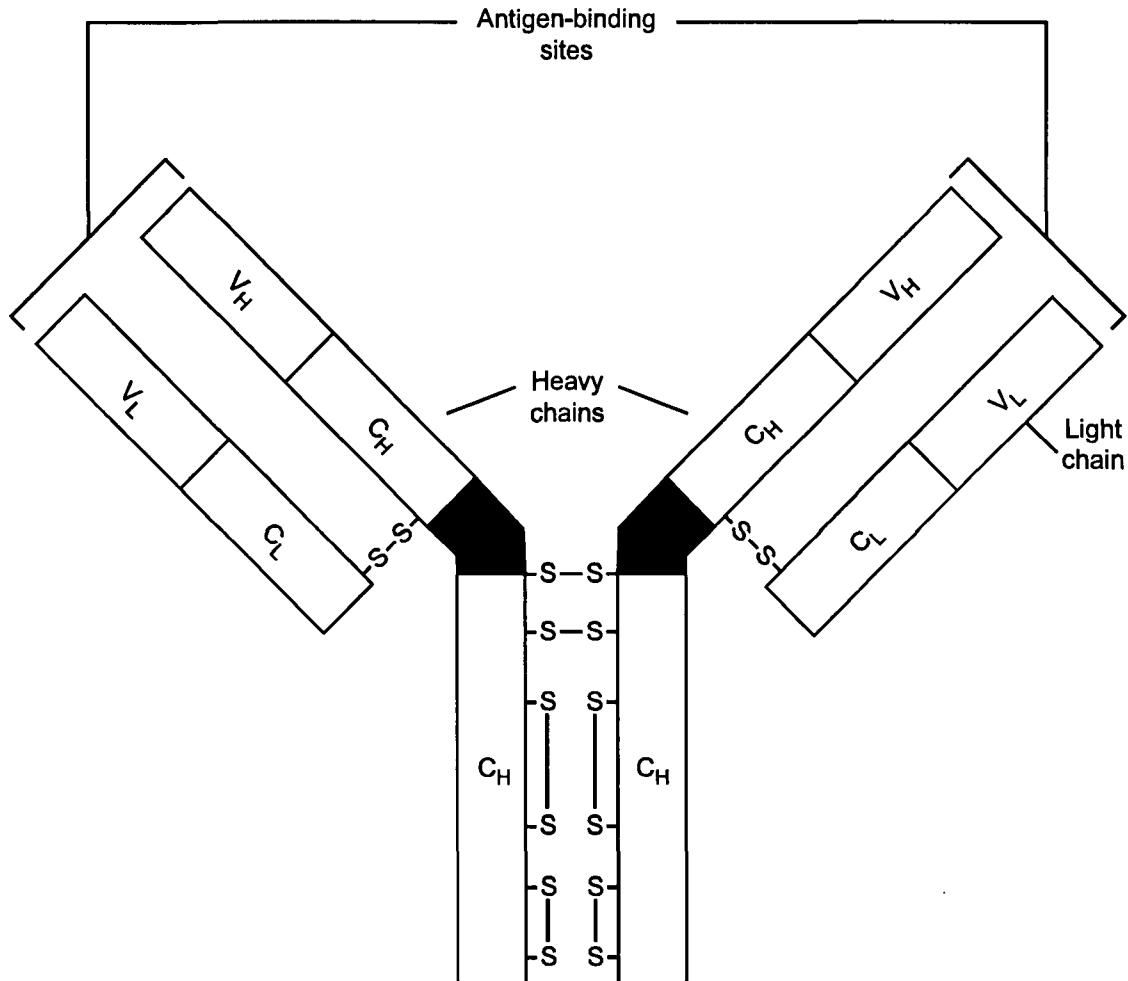
Notes:
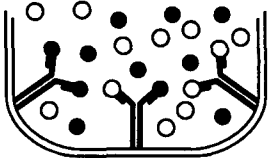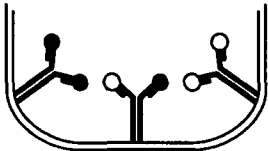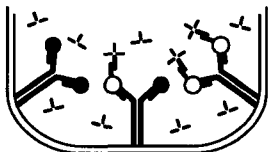
-S-S- = Disulfide bond
C   = Constant region
H   = Heavy polypeptide chain
L   = Light polypeptide chain
V   = Variable region

Figure 2-1. Immunoglobulin G antibody structure and locations of antigen-binding sites.

The EnSys Petro Test System is based on a type of immunoassay called enzyme-linked immunosorbent assay (ELISA). ELISA uses either polyclonal or monoclonal antibodies adsorbed to the inside wall of a test tube in order to facilitate separation of target compounds from nontarget compounds during a washing step. In ELISA, an enzyme conjugate solution is used to produce color whose intensity is inversely proportional to the total concentration of PHCs in a sample extract. ELISA involves the following three steps: (1) enzyme conjugate and sample extract addition, (2) washing, and (3) color development. These steps are described below and are illustrated in Figure 2-2. The intensity of the color produced during color development is measured using standard colorimetric principles as described in Section 2.1.2.

Enzyme Conjugate and Sample Extract Addition . As a first step, an enzyme conjugate solution is added to the soil sample extract. An enzyme conjugate is an enzyme

Step	Schematic	Description
Enzyme conjugate and sample extract addition		A reaction mixture containing the sample extract and enzyme conjugate solution is added to an antibody-coated test tube. The sample extract target compound and enzyme conjugate compete for antigen-binding sites.
Washing		The unbound sample extract target compound and enzyme conjugate are removed from the test tube.
Color development		A substrate and chromogen are added to the test tube.
		The substrate and chromogen react with the enzyme in the enzyme conjugate to produce color. The lower the color intensity, the higher the sample extract target compound concentration.

Notes:

Y = Antibody
● = Sample extract target compound
O = Enzyme conjugate
↗ = Substrate
⌐ = Chromogen

Figure 2-2. Enzyme-linked immunosorbent assay.

bound to a target compound. The antigen used to initiate antibody production is also used as the target compound portion of the enzyme conjugate. The enzyme portion of the enzyme conjugate plays its role in ELISA during the color development step; the enzyme typically used in ELISA is horseradish peroxidase. The reaction mixture containing the sample extract and enzyme conjugate solution is added to an antibody-coated test tube. Because both the sample extract target compound and the enzyme conjugate can bind with the antibodies, the sample extract target compound and the enzyme conjugate compete for the antigen-binding sites on the antibodies. The sample extract target compound and the enzyme conjugate bind to the antibodies in direct proportion to their relative concentrations in the reaction mixture. For example, the greater the ratio of the sample extract target compound concentration to the enzyme conjugate concentration, the greater the proportion of antigen-binding sites that are occupied by the sample extract target compound.

Washing. The sample extract target compound and the enzyme conjugate that are bound to the antibodies are separated from the unbound sample extract target compound and enzyme conjugate by emptying the reaction mixture from the test tube and washing the test tube with potable water or a dilute detergent solution.

Color Development. A substrate, such as hydrogen peroxide, and a chromogen, such as tetramethylbenzidine or orthophenylenediamine, are then added to the test tube in order to produce color when they react with the enzyme in the enzyme conjugate. For example, the enzyme horseradish peroxidase reacts with the hydrogen peroxide to release a proton, which in turn reduces the chromogen

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to form the colored product. After a specified period of time, color development in the test tube is terminated using a stopping solution such as hydrochloric acid. The amount of color formed is directly proportional to the amount of enzyme conjugate bound to the antibodies. Because the sample extract target compound competes with the enzyme conjugate for antigen-binding sites, ELISA results in formation of color in the test tube whose intensity is inversely proportional to the concentration of the sample extract target compound; for example, less color indicates a higher concentration of the sample extract target compound.

2.1.2 Colorimetry

After completion of color development, the concentration of PHCs in the sample extract is determined using colorimetry. Colorimetry is a technique by which the intensity of color is assessed using visual or spectrophotometric means. Use of a spectrophotometer is preferred over visual assessment of color charts because the spectrophotometer provides a more accurate and precise measurement and does not rely on a person's skill in interpreting color charts. A reflectance spectrophotometer measures the intensity of light reflected from solid particles in a reaction mixture, and an absorbance spectrophotometer measures the intensity of light that passes through the liquid portion of a reaction mixture. The EnSys Petro Test System uses an absorbance spectrophotometer because the colored reaction product is present in the liquid phase.

When a spectrophotometer is used in the visible wavelength range, the reaction mixture is placed in a glass or quartz cuvette that is then inserted into the spectrophotometer. A beam of visible light is then passed through the reaction mixture. The wavelength of the light entering the reaction mixture is initially selected by performing a series of absorbance measurements over a range of wavelengths; the selected wavelength generally provides maximum absorbance and allows target compound measurement over a wide concentration range.

Some of the light is absorbed by the chemicals in the reaction mixture, and the rest of the light passes through. 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 reaction mixture, is measured by a photoelectric detector in the spectrophotometer (Fritz and Schenk 1987). Absorbance can be calculated using Equation 2-1.

$$A = \log (I_0/I) \qquad (2\text{-}1)$$

where
A = Absorbance

I_0 = Intensity of light source

I = Intensity of light that passes through the reaction mixture

Therefore, the intensity of the light that passes through the reaction mixture is inversely proportional to the concentration of the colored product in the reaction mixture, or the intensity of the light absorbed by the reaction mixture is directly proportional to the concentration of the colored product in the reaction mixture.

According to Beer-Lambert's law, Equation 2-1 may be expressed as shown in Equation 2-2.

$$A = \epsilon\, b\, c \qquad (2\text{-}2)$$

where
A = Absorbance

ϵ = Molar absorptivity (centimeter per mole per liter [L])

b = Light path length (centimeter)

c = Concentration of absorbing species (mole per L)

Thus, according to Beer-Lambert's law, the absorbance of a chemical species is directly proportional to the concentration of the absorbing chemical species (colored reaction product) and the path length of the light that is not absorbed by the reaction mixture and passes through the mixture. In Equation 2-2, the molar absorptivity is a proportionality constant, which is a characteristic of the absorbing species and changes as the wavelength of the light irradiating the reaction mixture changes. Therefore, Beer-Lambert's law applies only to monochromatic light (light energy of one wavelength).

For the EnSys Petro Test System, the absorbance of the colored reaction mixture is assessed using a differential photometer. The differential photometer is a double-beam instrument in which two equivalent beams of light are produced within the visible range of the electromagnetic spectrum. One beam passes through the colored reaction mixture developed using the sample extract, while the other beam passes through a colored reaction mixture developed using a reference standard. The photometer

measures the difference in absorbance between the two colored reaction mixtures. Because color intensity is inversely proportional to the concentration of the sample extract target compound, a positive reading on the photometer indicates that the total concentration of PHCs in the sample extract is less than that in the reference standard. Similarly, a negative reading on the photometer indicates that the total concentration of PHCs in the sample extract is greater than that in the reference standard.

2.2 Description of EnSys Petro Test System

The EnSys Petro Test System is manufactured by SDI and has been commercially available since 1992. The device conforms to SW-846 Method 4030 for screening PHCs using immunoassay detection (EPA 1996). This section describes the device and summarizes its operating procedure.

2.2.1 Device Description

The EnSys Petro Test System consists of three kits: the (1) SDI Sample Extraction Kit (Sample Extraction Kit), (2) EnSys Petro 12T Soil Test Kit (12T Soil Test Kit), and (3) EnSys/EnviroGard® Common Accessory Kit (Common Accessory Kit). The EnSys Petro Test System includes antibody-coated test tubes containing monoclonal antibodies, which are produced using m-xylene as the antigen. The enzyme conjugate used to produce color is composed of m-xylene as the target compound and horseradish peroxidase as the enzyme. The washing step is performed with a dilute detergent solution. Color development is achieved using hydrogen peroxide as the substrate and tetramethylbenzidine as the chromogen. The stop solution added to terminate color development is 0.5 percent sulfuric acid. A differential photometer that emits light in the visible range of the electromagnetic spectrum at a 450-nanometer wavelength is used to measure the absorbance of the sample extract and of a reference standard containing 3 mg/L m-xylene during color measurement. The total concentration of PHCs in the sample extract is then determined by comparing the absorbance readings associated with the sample extract and reference standard.

According to SDI, the EnSys Petro Test System can be used to measure the following petroleum products in soil: gasoline, diesel, Jet A fuel, JP-4, kerosene, No. 2 fuel oil, No. 6 fuel oil, and mineral spirits. The monoclonal

antibodies used in the device are specific to a subset of petroleum product components, including a large portion of the aromatic hydrocarbons and a few aliphatic hydrocarbons in the C_6 through C_{22} carbon range.

The method detection limits (MDL) of the EnSys Petro Test System claimed by SDI for a variety of aromatic and aliphatic hydrocarbons are presented in Table 2-1. Except for benzene, which has an MDL of 400 mg/kg, the aromatic hydrocarbons listed in Table 2-1 have MDLs that are less than or equal to ($\leq$) 40 mg/kg, indicating a high degree of selectivity. A few aliphatic hydrocarbons, such as 2-methylpentane and isooctane, also have low MDLs. Table 2-1 also presents the MDLs for various petroleum products. These MDLs generally range from 10 mg/kg (gasoline) to 40 mg/kg (mineral spirits). The MDLs for machine oil, brake fluid, unused motor oil, grease, and mineral oil are all >1,000 mg/kg, indicating that the EnSys Petro Test System is not as sensitive to these formulated petroleum products.

According to SDI, the operating temperature range for the 12T Soil Test Kit is 16 to 38 °C and the test kit should be stored at $\leq$27 °C when not in use. SDI does not have an operating humidity restriction for the test kit. The shelf life of the test kit is typically 1 year after its date of manufacture; lot-specific expiration date information is provided on the test kit packaging. The chromogen and substrate solutions should not be exposed to direct sunlight during test kit operation or storage.

The components of the EnSys Petro Test System are listed in Table 2-2. The Sample Extraction Kit contains enough supplies to perform 12 soil sample extractions. The 12T Soil Test Kit contains enough supplies to process up to 12 samples (for example, 10 soil sample extracts and duplicate calibration standards). The Common Accessory Kit contains multi-use items that do not require frequent replacement. All Common Accessory Kit items are housed in a hard-plastic carrying case to prevent damage to the items during kit transport. The Sample Extraction Kit and 12T Soil Test Kit items are shipped in cardboard boxes.

The differential photometer (Artel DP™ Differential Photometer) included in the Common Accessory Kit is designed to provide an immediate, direct comparison of the absorbance of two liquid samples (for example, a soil sample extract and a reference standard) by means of a digital display; the display indicates the difference in

Table 2-1. EnSys Petro Test System Method Detection Limits

Compound or Substance	Method Detection Limit (milligram per kilogram)[a]
Petroleum fuel product	
Gasoline	10
Diesel	15
Jet A fuel	15
JP-4	15
Kerosene	15
No. 2 fuel oil	15
No. 6 fuel oil	25
Formulated petroleum product	
Mineral spirits	40[b]
Machine oil	>1,000[b]
Brake fluid	>1,000[b]
Unused motor oil	>1,000[b]
Grease	>1,000[b]
Mineral oil	>1,000[b]
Aromatic hydrocarbon	
Benzene	400
Toluene	40
Ethylbenzene	7
o-Xylene	8.5
m-Xylene	8
p-Xylene	4.5
Styrene	7
1,2-Dichlorobenzene	2.5
Hexachlorobenzene	10
Naphthalene	0.8
Acenaphthalene	0.5
Biphenyl	10
Creosote	1.5
Aliphatic hydrocarbon	
2-Methylpentane	35
Hexanes (mixed)	65
Heptane	130
Isooctane	8.5[b]
Undecane	>1,000[b]
Trichloroethylene	>1,000[b]
Methyl-tert-butyl ether	>1,000

Notes:

> = Greater than

[a] Minimum soil concentration necessary to obtain a positive result more than 95 percent of the time

[b] Highest concentration tested; positive result not obtained at this concentration

Source: SDI 1999

Table 2-2. EnSys Petro Test System Components

SDI Sample Extraction Kit
- 12 extraction jars with screw caps (each jar contains 3 stainless-steel mixing balls)
- 12 filter units (tops and bottoms)
- 12 ampule crackers
- 12 dilution ampules for each dilution level
- 12 wooden spatulas
- 12 plastic weigh canoes
- 12 disposable transfer pipettes
- 12 ampules containing 100 percent methanol solvent
- User guide

EnSys Petro 12T Soil Test Kit
- 48 monoclonal antibody-coated tubes
- 48 conjugate tubes
- 1 80-milliliter bottle of phosphate buffer solution
- 1 15-milliliter bottle of chromogen (tetramethylbenzidine)
- 1 15-milliliter bottle of substrate (hydrogen peroxide)
- 1 15-milliliter bottle of stop solution (0.5 percent sulfuric acid)
- 3 1-milliliter vials of Petro standard (3 milligrams per liter m-xylene)
- 24 Microman® positive displacement pipettor tips
- 3 5-milliliter Combitips® for the repeater pipettor
- 1 12.5-milliliter Combitip® for the repeater pipettor
- 12 plastic ampule crackers
- 3 amber vials (for storage of remnant solution from cracked ampules)
- 3 disposable transfer pipettes
- 2 480-milliliter bottles of dilute detergent solution (Tween-20)
- User guide

EnSys/EnviroGard® Common Accessory Kit
- 1 battery-powered Artel DP™ Differential Photometer, including 4 rechargeable nickel-cadmium batteries and 1 battery recharger
- 1 battery-powered ACCULAB® digital balance, including 1 100-gram calibration weight and 1 9-volt battery
- 1 battery-powered digital timer, including 1 G-13 cell button battery
- 1 Gilson M-25 Microman® positive displacement pipettor
- 1 Eppendorf™ repeater pipettor
- 3 5-milliliter Combitips® for the repeater pipettor
- 5 12.5-milliliter Combitips® for the repeater pipettor
- 1 50-milliliter Combitip® for the repeater pipettor
- 1 wash bottle
- 1 foam workstation
- 2 foam 30-position test tube racks
- User guides for differential photometer, balance, timer, and pipettors
- Carrying case

absorbance between the two samples. The photometer is 3.4 inches long, 5.3 inches wide, and 2.6 inches high and weighs 0.8 pound. The power supply for the photometer consists of four rechargeable nickel-cadmium batteries; the photometer cannot be operated using an alternating current power source. The batteries require 8 to 10 hours to achieve a full recharge after discharge and last for about 500 readings between recharges. According to SDI, the operating temperature range for the photometer is

10 to 40 °C and the photometer should be stored at a temperature between -20 and 66 °C when not in use. SDI does not have an operating humidity restriction for the photometer.

According to SDI, 12 samples (including soil sample extracts and reference standards) can be analyzed as one batch by one person using the EnSys Petro Test System in approximately 45 minutes. The device is easy to operate

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and is designed to be used by those with basic wet chemistry skills. In addition to the user guide or guides that accompany each kit of the device, SDI provides technical support over the telephone at no additional cost. SDI also offers a 1-day, on-site training program.

According to SDI, the EnSys Petro Test System is innovative because the device uses biologically engineered antibodies to measure PHCs in soil. SDI also claims that the device measures most aromatic hydrocarbons and some aliphatic hydrocarbons in the C_6 through C_{22} carbon range.

2.2.2 Operating Procedure

During the demonstration, measuring TPH in soil using the EnSys Petro Test System involved the following five steps: (1) extraction, (2) sample and standard preparation, (3) washing, (4) color development, and (5) color measurement and estimation of TPH concentration. Extraction of a given soil sample was completed by adding 20 milliliters (mL) of methanol to 10 grams of the sample. During sample and standard preparation, the sample extract and a reference standard were transferred to conjugate tubes containing phosphate buffer solution. The mixtures were then transferred from the conjugate tubes to antibody-coated tubes. Washing was accomplished by first discarding the contents of the antibody-coated tubes and then washing each tube with dilute detergent solution. Color development included addition of chromogen and substrate to each antibody-coated tube; the addition of substrate turned the reaction mixture blue. Stop solution was then added to stop color development; the addition of stop solution turned the reaction mixture yellow. To accomplish color measurement, the absorbance of the antibody-coated tubes containing the sample extract and of the antibody-coated tube containing the reference standard was compared using the differential photometer. Because color intensity is inversely proportional to the concentration of the sample extract target compound, a positive reading on the photometer indicated that the total

concentration of PHCs in the sample extract was less than that in the reference standard. Similarly, a negative reading on the photometer indicated that the total concentration of PHCs in the sample extract was greater than that in the reference standard.

During the demonstration, SDI performed each analysis at three detection levels by diluting the sample extract twice during the sample and standard preparation step. The reference standard concentrations for gasoline (10 mg/kg) and diesel (15 mg/kg) were multiplied by the dilution factors used. Thus, the concentration ranges used to estimate sample TPH concentrations were (1) <10; >10 to <100; >100 to <1,000; and >1,000 mg/kg for GRO-containing samples and (2) <15; >15 to <100; >100 to <1,000; and >1,000 mg/kg for EDRO-containing samples.

During the demonstration, a QC check was performed for the EnSys Petro Test System during the fifth step (color measurement and estimation of TPH concentration) of the operating procedure. Two reference standard tubes (duplicates) were switched in the photometer until the photometer reading was negative or zero. Device performance was considered to be acceptable if the difference in the absorbance values between the standards was <-0.30.

2.3   Developer Contact Information

Additional information about the EnSys Petro Test System can be obtained from the following source:

Strategic Diagnostics Inc.
Mr. Joseph Dautlick
111 Pencader Drive
Newark, DE 19702
Telephone: (800) 544-8881, extension 222
Fax: (302) 456-6770
E-mail: jdautlick@sdix.com
Internet: www.sdix.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 EnSys Petro Test System developer, SDI, at its facility. SDI used reference laboratory and EnSys Petro Test System 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[a]	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_{10} through n-C_{40})	Upper layer[b]	44.1 to 93.7	Medium-grained sand
			Lower layer[b]	8,090 to 15,000	
	Naval Exchange Service Station Area	GRO and EDRO (fairly weathered gasoline with carbon range from n-C_6 through n-C_{14})	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_{14} through n-C_{40+})	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_6 through n-C_{40})	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_5 through n-C_{32})	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

[a] The beginning or end point of the carbon range identified as "n-C_x" represents an alkane marker consisting of "x" carbon atoms on a gas chromatogram.

[b] 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®. 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_{10} through n-C_{28} carbon range with the hydrocarbon hump maximizing at n-C_{17}, and (3) hydrocarbons in the n-C_{12} through n-C_{40} carbon range with the hydrocarbon hump maximizing at n-C_{20}.

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_6 through n-C_{14} 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

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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.

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_{14} through n-C_{40+} carbon range with the hydrocarbon hump maximizing at n-C_{32}.

SDI chose not to demonstrate the EnSys Petro Test System using soil samples collected in the PRA because according to SDI, its device was not designed to measure heavy lubricating oil, the primary contaminant in the area.

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®.   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_{24} through n-C_{30} 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®. 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_6 through n-C_{25} carbon range with the hydrocarbon hump maximizing at n-C_{17}; (2) weathered gasoline with trace amounts of lubricating oil and hydrocarbons in the n-C_6 through n-C_{30} carbon range with a hydrocarbon hump representing the lubricating oil between n-C_{20} and n-C_{30}; or (3) weathered gasoline with trace amounts of lubricating oil and hydrocarbons in the n-C_6 through n-C_{40} carbon range with a hydrocarbon hump representing the lubricating oil maximizing at n-C_{31}.

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®.   Four of the

sampling locations were spaced about 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 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_5 through n-C_{20} carbon range. There was also evidence of an unidentified petroleum product containing hydrocarbons in the n-C_{24} through n-C_{32} 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.

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 interferents 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 (<100 mg/kg), medium (100 to 1,000 mg/kg), or high (>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, SDI field technicians operated the EnSys Petro Test System, 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. SDI chose not to analyze soil samples collected in the PRA because according to SDI, the EnSys Petro Test System was not designed to measure the heavy lubricating oil present in the PRA.

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 methanol, 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. SDI 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 th e 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. Moreover, because the EnSys Petro Test System is a semiquantitative device that does not report absolute TPH concentrations, the device's MDL was not to be determined using a statistical approach;

rather, the device MDL claimed by SDI was to be verified using a nonstatistical approach. Specifically, the device's MDL was to be verified by evaluating whether the TPH concentration ranges reported by the device overlapped the TPH results obtained using the reference method.

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

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

Site		Typical TPH Concentration Range[a]	Action Level (mg/kg)
Navy Base Ventura County	Fuel Farm Area	Low and high	100
	Naval Exchange Service Station Area	Low to high	50
	Phytoremediation Area[b]	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

[a] 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.

[b] SDI chose not to analyze soil samples collected in the Phytoremediation Area because according to SDI, the EnSys Petro Test System was not designed to measure the heavy lubricating oil present in the Phytoremediation Area.

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.

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, for each quantitative measurement device, the ratio of the TPH results of the 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. However, the statistical comparison and correlation activities conducted for the demonstration were limited to the evaluations of quantitative field measurement devices.

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 methanol 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 quantitative 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. For the EnSys Petro Test System, a semiquantitative device, analytical precision was assessed in a qualitative manner. Specifically, to evaluate the overall precision, the device's TPH concentration ranges for the triplicate samples were compared to determine whether they were the same or different. Similarly, to evaluate the analytical precision, the TPH concentration ranges for the extract duplicates were compared to determine whether they were the same or different.

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 $n-C_8$ through $n-C_{14}$ 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 $n-C_9$ through $n-C_{15}$ 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. For the EnSys Petro Test System, a semiquantitative device, the effects of interferents on TPH measurement were assessed in a qualitative manner. Specifically, the device's TPH concentration ranges for the control samples and the samples containing interferents were qualitatively evaluated to determine whether the data showed any trend.

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 (<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 moisture resulted in an increase or decrease in the TPH concentrations measured. For the EnSys Petro Test System, a semiquantitative device, the effect of moisture was assessed by qualitatively evaluating the device's TPH concentration ranges at two different moisture levels.

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 EnSys Petro Test System 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 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

Table 4-2. Demonstration Approach

Site	Area	Approximate Sampling Depth Interval (foot bgs)	Objective Addressed[a]	Soil Characteristics	Contamination Type	Typical TPH Concentration Range[b]	Rationale for Analyses by Reference Laboratory
Navy BVC	FFA	Upper layer[c]	P2	Medium-grained sand	Weathered diesel with carbon range from n-C_{10} through n-C_{40}	Low	Only EDRO because samples did not contain PHCs in gasoline range
		Lower layer[c]				High	
	NEX Service Station Area	7 to 8		Medium-grained sand	Fairly weathered gasoline with carbon range from n-C_6 through n-C_{14}	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	
		10 to 11				Low	
	PRA[d]	1.5 to 2.5		Silty sand	Heavy lubricating oil with carbon range from n-C_{14} through n-C_{40}	High	Only EDRO because samples did not contain PHCs in gasoline range
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_6 through n-C_{40}	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_5 through n-C_{32}	Medium	
		4 to 6					
		6 to 8					
		8 to 10					

Sample Matrix			Objective Addressed[a]	Soil Characteristics	Contamination Type	Typical TPH Concentration range[b]	Rationale for Analyses by Reference Laboratory
Ottawa sand (PE sample)			P1, P2	Fine-grained sand	Weathered gasoline	Low	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
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
					Diesel		Only EDRO because diesel does not contain PHCs in gasoline range

Table 4-2. Demonstration Approach (Continued)

Sample Matrix	Objective Addressed[a]	Soil Characteristics	Contamination Type	Typical TPH Concentration range[b]	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		Only EDRO because diesel does not contain PHCs in gasoline range
			Diesel and Stoddard solvent (3,650 mg/kg) or turpentine (3,850 mg/kg)		GRO and EDRO because (1) Stoddard solvent contains PHCs in both gasoline and diesel ranges and (2) turpentine interferes with both analyses
			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)		Only EDRO because 1,2,4-trichloro-benzene and humic acid do not interfere with GRO analysis
			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 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. |
| | | | Humic acid (19,500 mg/kg) | | |

Table 4-2. Demonstration Approach (Continued)

Sample Matrix	Objective Addressed[a]	Soil Characteristics	Contamination Type	Typical TPH Concentration range[b]	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	
			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	FFA	=	Fuel Farm Area	NEX	=	Naval Exchange	PE = Performance evaluation SFT = Slop Fill Tank
bgs	=	Below ground surface	mg/kg	=	Milligram per kilogram	PC	=	Petroleum company	PHC = Petroleum hydrocarbon
BVC	=	Base Ventura County	MTBE	=	Methyl-tert-butyl ether	PCE	=	Tetrachloroethene	PRA = Phytoremediation Area

[a]   Field observations of all sample analyses conducted during the demonstration were used to address primary objectives P5 and P6 and the secondary objectives.

[b]   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.

[c]   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 core 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.

[d]   SDI chose not to analyze soil samples collected in the PRA because according to SDI, the EnSys Petro Test System was not designed to measure the heavy lubricating oil present in the PRA.

[e]   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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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 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. For the EnSys Petro Test System, the sampling areas were (1) FFA and NEX Service Station Area at the Navy BVC site, (2) B-38 Area at the Kelly AFB site, and (3) SFT Area at the PC site. Samples were collected in all areas using a Geoprobe®.

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

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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 EnSys Petro Test System.

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

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 <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 methanol 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

Table 4-3. Environmental Samples

Site	Area	Depth Interval (foot bgs)	Number of Sampling Locations	Total Number of Samples, Including Field Triplicates, to SDI and Reference Laboratory[a]	Number of MS/MSD[b] Pairs	Number of Extract Duplicates	Number of TPH Analyses by SDI	Number of Analyses by Reference Laboratory[c]	
								GRO	EDRO
Navy BVC	FFA	Upper layer	3	5	1	1	6	0	8
		Lower layer	3	5	1	1	6	0	8
	NEX Service Station Area	7 to 8	3	5	1	1	6	8	8
		8 to 9	3	5	1	1	6	8	8
		9 to 10	3	5	1	1	6	8	8
		10 to 11	3	5	1	1	6	8	8
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	8	10	10
Total				66	12	12	78	86	102

Notes:

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

[a] 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.

[b] 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 SDI.

[c] All environmental samples were also analyzed for moisture content by the reference laboratory.

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.

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 EnSys Petro Test System.

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[a]	Total Number of Samples to SDI and Reference Laboratory	Number of MS/MSD[b] Pairs	Number of Analyses by SDI	Number of Analyses by Reference Laboratory[c]	
					GRO	EDRO
Soil Samples (Ottawa Sand)						
Weathered gasoline	Low	7	0	7	7	7
Diesel		7	0	7	0	7
Soil Samples (Processed Garden Soil)						
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
Liquid Samples (Neat Material)						
Weathered gasoline	High	3	1	3	5	5
Diesel		3	0	3	0	3
MTBE		6	0	6	6	0

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Table 4-4. Performance Evaluation Samples (Continued)

Sample Type	Typical TPH Concentration Range[a]	Total Number of Samples to SDI and Reference Laboratory	Number of MS/MSD[b] Pairs	Number of Analyses by SDI	Number of Analyses by Reference Laboratory[c]	
					GRO	EDRO
Liquid Samples (Neat Material) (Continued)						
PCE	Not applicable	6	0	6	6	0
Stoddard solvent	High	6	0	6	6	6
Turpentine	Not applicable	6	0	6	6	6
1,2,4-Trichlorobenzene		6	0	6	0	6
Total		**125**	**6**	**125**	**90**	**125**

Notes:

mg/kg	=	Milligram per kilogram	MTBE	=	Methyl-tert-butyl ether
MS/MSD	=	Matrix spike and matrix spike duplicate	PCE	=	Tetrachloroethene

[a]   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. The typical TPH concentration range for the liquid sample concentrations was based on the definition of TPH used for the demonstration and knowledge of the sample (neat material).

[b]   MS/MSD samples were analyzed only by the reference laboratory.

[c]   All soil performance evaluation samples were also analyzed for moisture content by the reference laboratory.

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

Parameter[a]	Medium	Container	Preservation	Holding Time (days) Extraction	Analysis
GRO	Soil	Two 5-gram EnCores	4 ± 2 °C	2[b]	14
EDRO	Soil	Two 4-ounce, glass jars with Teflon™-lined lids	4 ± 2 °C	14[b]	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[c]	
GRO and EDRO	Liquid	One 2-milliliter ampule for each analysis	Not applicable	See note d	

Notes:

±   = Plus or minus

[a]   The reference laboratory measured percent moisture using part of the soil sample from the container designated for EDRO analysis.

[b]   The extraction holding time started on the day that samples were shipped.

[c]   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.

[d]   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.

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).

Figure 5-1. Reference method selection process.

Analytical methods considered (technology)

ASTM Method D 5831-96 (ultraviolet spectrophotometry)

State-specific methods such as Massachusetts EPH and VPH Methods, Florida PRO Method, and Texas Method 1005 (GC/FID)

MCAWW Method 413.1 (gravimetric)

MCAWW Method 413.2 (infrared)

MCAWW Method 418.1 (infrared)

API PHC Method (GC/FID)

SW-846 Method 4030 (immunoassay and colorimetry)

SW-846 Method 8015B (GC/FID)

SW-846 Method 8440 (infrared)

SW-846 Method 9071 (gravimetric)

SW-846 Method 9074 (emulsion turbidimetry)

Reference method selected

SW-846 Method 8015B (modified)

Not a suitable reference method

State-specific methods
MCAWW Method 413.1
MCAWW Method 413.2
SW-846 Method 8440
SW-846 Method 9071

Measures light (gasoline) to heavy (lubricating oil) fuel types? — Yes →
MCAWW Method 418.1
API PHC Method
SW-846 Method 8015B

Widely used and accepted? — Yes →
MCAWW Method 418.1
API PHC Method
SW-846 Method 8015B

Provides separate measurements of GRO and EDRO fractions of TPH? — Yes →
API PHC Method
SW-846 Method 8015B[a]

Meets project-specific reporting limit requirements? — Yes → SW-846 Method 8015B (modified) / No

MCAWW Method 418.1

API PHC Method

State-specific methods
MCAWW Method 413.1
MCAWW Method 413.2
MCAWW Method 418.1
API PHC Method
SW-846 Method 8015B
SW-846 Method 8440
SW-846 Method 9071

Considered a field screening method? — Yes →
ASTM Method D 5831-96
SW-846 Method 4030
SW-846 Method 9074
→ Not a suitable reference method

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

[a] 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 >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 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-trimethylbenzene or n-C_{10} 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 5-1. 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[a]	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"

[a]   MCAWW Method 160.3 was modified to include calculation and reporting of percent moisture in soil samples.

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

SW-846 Method Reference (Step)	Project-Specific Procedures
5035 (Extraction)	
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.
5030B (Purge-and-Trap)	
Screening of samples before the purge-and-trap procedure is recommended using one of the two following techniques: 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 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	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.

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

SW-846 Method Reference (Step)	Project-Specific Procedures
5030B (Purge-and-Trap) (Continued)	
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.
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):	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.
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	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
8015B (Analysis)	
GC Conditions	

The following GC conditions are recommended:
 	
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
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
	The HP 5890 Series II was used as the GC. The following GC conditions were used based on manufacturer recommendations:
	
	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
	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

Calibration	
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
8015B (Analysis) (Continued)	
Calibration (Continued)	
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.
Retention Time Windows	
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.
Quantitation	
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 $n\text{-}C_{10}$. Baseline rise subtraction was not performed.
Quality Control	
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
8015B (Analysis) (Continued)	
Quality Control (Continued)	
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"

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

SW-846 Method Reference (Step)	Project-Specific Procedures
3540C (Extraction)	
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.
8015B (Analysis)	
GC Conditions	

The following GC conditions are recommended:
 	
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
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
	An HP 6890 GC was used with the following conditions:
	
	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
	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

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

SW-846 Method Reference (Step)	Project-Specific Procedures
8015B (Analysis) (Continued)	
Calibration	
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_{10} through C_{40}.
ICV is not required.	ICV was performed using a second-source standard that contained even-numbered alkanes from C_{10} through C_{40} 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_{10} through C_{40}.
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.
Retention Time Windows	
The retention time range (window) should be established using C_{10} and C_{28} 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_{10} 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.
Quantitation	
Quantitation is performed by summing the areas of all chromatographic peaks eluting between n-C_{10} 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_{10} 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
8015B (Analysis) (Continued)	
Quantitation (Continued)	
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.
Quality Control	
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_{10} through C_{40}.
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_{10} through C_{40}.
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$_x$	=	Alkane with "x" carbon atoms
LCSD	= Laboratory control sample duplicate		ng	=	Nanogram
min	= Minute		SW-846	=	"Test Methods for Evaluating Solid Waste"

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 ≤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 objective 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

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 micrograms per liter (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 >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 interferents 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 $\leq$25. 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 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 aliquots of the GRO extracts for analysis. The acceptance criterion for extract duplicate precision was an RPD ≤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 ≤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 (plus or minus [±] 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[a]	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				
	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	≤25	1 to 21	10 pairs	11	12
	Soil PE samples	6 (3 pairs)		88 to 103	6	94	92		4 to 6	3 pairs	5	5
	Liquid PE samples	4 (2 pairs)		77 to 87	4	83	85		1 to 5	2 pairs	3	3
Extract duplicate	Soil environmental samples	10 pairs	Not applicable						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		2 to 14	10 pairs	6	6
	Liquid PE samples	2 pairs		91 to 92	4	92	92		0 to 1	2 pairs	0.5	0.5

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

[a]   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.

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 ≤ 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

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

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 ≤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 ≤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 (± 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 RPDs observed indicated good precision in the EDRO

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

QC Check[a]	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	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		3 to 17	5 pairs	7	4
Extract duplicate	Soil environmental samples	13 pairs	Not applicable						0 to 34	13 pairs	6	2
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

[a] 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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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 EnSys Petro Test System'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 (>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 EnSys Petro Test System 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 ± 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.

Performance Acceptance Limits = Certified Value x (Average Percent Recovery $\pm$ 2(Average RSD)) (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.

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

Sample Type[a]	TPH Concentration Range	Performance Acceptance Limits (mg/kg)	Certified Value	Reference Method Mean TPH Concentration	Reference Method Mean TPH Concentration/ Certified Value (percent)
Soil Sample (Ottawa Sand)					
Diesel	Low	18.1 to 47.4	37.3 mg/kg	15.4 mg/kg	41
Soil Samples (Processed Garden Soil)					
Weathered gasoline	Medium	389 to 1,548	1,090 mg/kg	705 mg/kg	65
	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	252 mg/kg	56
	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
Liquid Samples					
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

[a]   Soil samples were prepared at 9 percent moisture unless stated otherwise.

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-containing soil samples ranged from 65 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 15 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 (± 30 percent) stated in SW-846 for most organic analyses. However, the bias for soil samples exceeded the acceptable bias by up to 5 percentage points.

The ratios for diesel-containing soil samples ranged from 41 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 29 and 14 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 34 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 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 5 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 29, 14, and 2 percentage points, respectively. For neat diesel samples, the observed positive bias did not exceed the acceptable bias. The low RSDs (5 to 9 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 EnSys Petro Test System and reference method results for low- and medium-range soil samples containing diesel.

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

| | ERA Historical Results | | Reference Method Results | | |
Sample Type	Mean Recovery (percent)	Mean Relative Standard Deviation (percent)	Mean Recovery[a] (percent)	Reference Method Mean Recovery/ERA Historical Mean Recovery (percent)	Mean Relative Standard Deviation[a] (percent)
Weathered gasoline in soil	88.7	26.5	66	75	7
Diesel in soil	87.7	19.6	58	66	9
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

[a] 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.

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 (± 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 ± 30 percent stated in SW-846 by 29 percentage points for low-range and 14 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.

Chapter 7
Performance of the EnSys Petro Test System

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 EnSys Petro Test System 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 EnSys Petro Test System 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 four different sampling areas. In addition, soil and liquid PE samples were prepared and

distributed to SDI 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. Because the EnSys Petro Test System is a semiquantitative device, the TPH concentration in a sample cannot be reported as an absolute value; therefore, statistical approaches could not be used to address the primary objectives for the EnSys Petro Test System. The statistical tests performed to address primary objectives for the reference method 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 reference method results were normally distributed at a significance level of 5 percent. If the results 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 reference method, when the analyte concentration in a given sample was reported as below the reporting limit, one-half the reporting limit was used as the analyte concentration for that sample, as is commonly done, so that necessary calculations could be performed without rejecting the data. 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

TPH results

Method detection limit (primary objective P1)

Were TPH results normally distributed? (Wilk-Shapiro test)

Yes → Determined method detection limit using approach recommended in 40 *Code of Federal Regulations* Part 136, Appendix B, Revision 1.1.1

No → Was unable to determine method detection limit

Precision (primary objective P2)

Calculated relative standard deviation for field triplicate TPH results

Calculated relative percent difference for extract duplicate TPH results

Effect of interferents (primary objective P3)

Were TPH results for three sample groups normally distributed? (Wilk-Shapiro test)

Yes → Were group variances equal? (Bartlett's test)

No → Performed Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis comparison of means (nonparametric) to determine whether presence of interferents resulted in increase or decrease in TPH results

Yes → Performed one-way analysis of variance (parametric) and Tukey (honest, significant difference) comparison of means (parametric) to determine whether presence of interferents resulted in increase or decrease in TPH results

Effect of soil moisture content (primary objective P4)

Were TPH results for both sample groups normally distributed? (Wilk-Shapiro test)

Yes → Performed two-sample Student's t-test (parametric) to determine whether increase in moisture content resulted in increase or decrease in TPH results

No → Performed Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis comparison of means (nonparametric) to determine whether increase in moisture content resulted in increase or decrease in TPH results
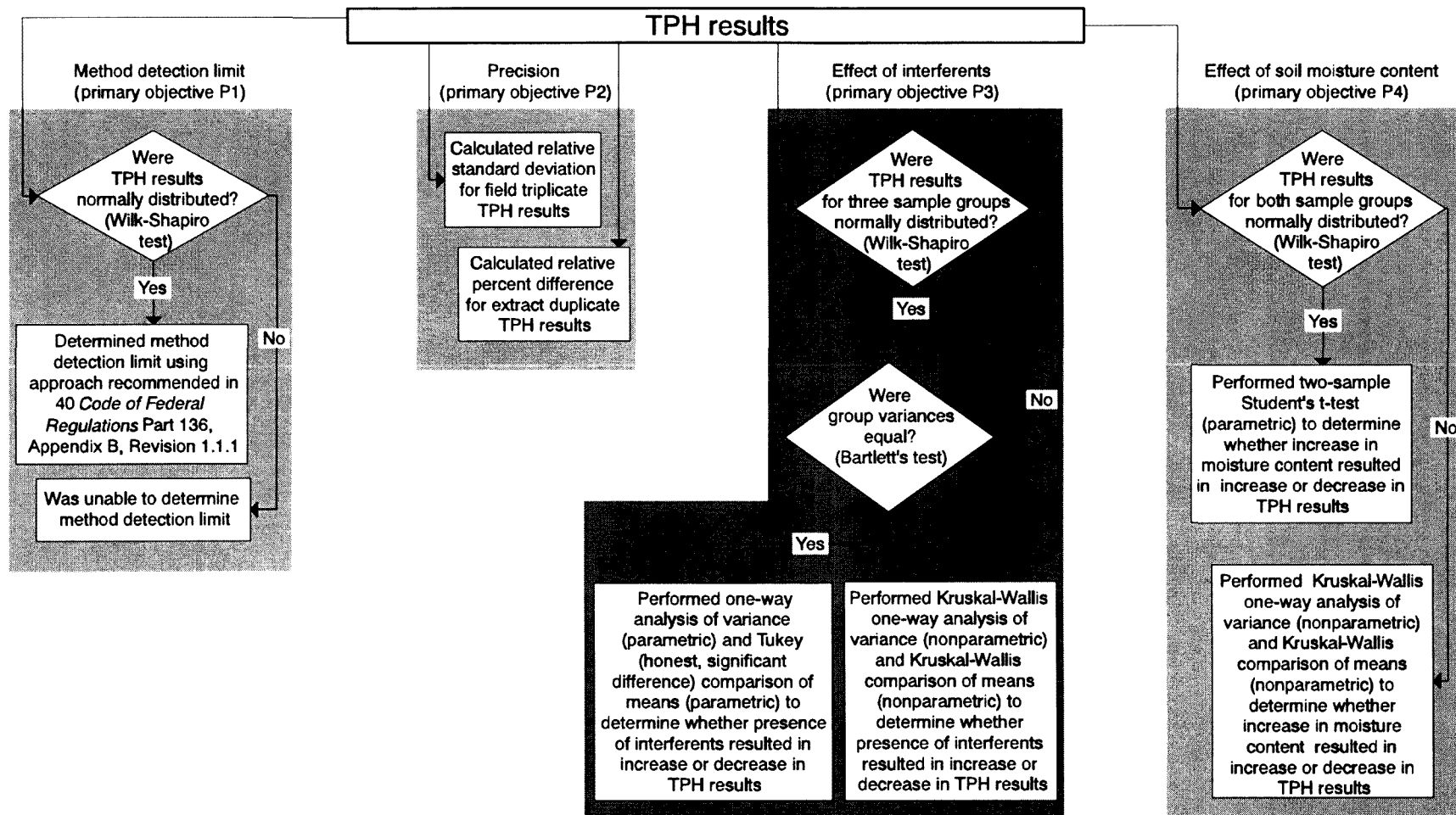
Figure 7-1. Summary of statistical analysis of TPH results.

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limits. Caution was exercised to ensure that these necessary data manipulations did not alter the conclusions.

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 the reference laboratory, all TPH results for the reference method were rounded to three significant figures. No data manipulations were required to evaluate EnSys Petro Test System performance. The developer's perspective regarding this ITVR's evaluation of EnSys Petro Test System TPH results reported as >1,000 mg/kg is provided in the appendix.

7.1.1 Primary Objective P1: Method Detection Limit

To address primary objective P1, both SDI and the reference laboratory analyzed seven low-concentration-range weathered gasoline soil PE samples and seven low-concentration-range diesel soil PE samples. 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 EnSys Petro Test System is a semiquantitative device, the TPH concentration in a sample cannot be reported as an absolute value. Therefore, the device results for the low-range soil PE diesel samples could not be used to statistically determine the MDL. Instead, the EnSys Petro Test System MDL was verified by evaluating whether the TPH concentration ranges measured using the device overlapped the TPH concentrations measured using the reference method.

Because the reference method results were 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.

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

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 EnSys Petro Test System 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

EnSys Petro Test System Result (mg/kg)	Reference Method Result (mg/kg)	Did the EnSys Petro Test System Result Overlap the Reference Method Result?
>15 to <100	12.0	No
>15 to <100	16.5	Yes
>15 to <100	13.7	No
>15 to <100	16.4	Yes
>100 to <1,000	17.4	No
>15 to <100	17.2	Yes
>15 to <100	14.8	No
MDL Not calculated	6.32	

Notes:

>	=	Greater than	MDL	=	Method detection limit
<	=	Less than	mg/kg	=	Milligram per kilogram

Based on the TPH results for the low-concentration-range diesel soil PE samples, the MDL was determined to be 6.32 mg/kg for the reference method. 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 6.29 mg/kg, whereas the MDL for the reference method based on the EDRO results was 6.32 mg/kg, indicating that

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the ORO concentrations below the reporting limit did not impact the MDL for the reference method. The MDL of 6.32 mg/kg for the reference method compares 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.

Table 7-1 shows that the TPH results for the reference method were near the detection limit for diesel (15 mg/kg) claimed by SDI for the EnSys Petro Test System. Specifically, three reference method results were below and four were above 15 mg/kg; all seven results were within 20 percent of the detection limit. Because the reference method exhibited a significant negative bias (59 percent) for the low-concentration-range diesel soil PE samples (see Table 6-3), all the reference method results for these samples could be considered to be in the concentration range of >15 to <100 mg/kg, the reported concentration range for six of the seven EnSys Petro Test System results. Thus, the device's TPH results for six of the samples could be considered to compare well with the reference method TPH results; the device result of >100 to <1,000 mg/kg for one sample cannot be explained. In summary, the device was considered to have accurately measured the TPH concentrations in six of seven low-range diesel soil PE samples.

7.1.2 Primary Objective P2: Accuracy and Precision

This section discusses the ability of the EnSys Petro Test System to accurately and precisely measure TPH concentrations in a variety of contaminated soils. The EnSys Petro Test System 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.

7.1.2.1 Accuracy

The accuracy of EnSys Petro Test System measurement of TPH was assessed by determining

- Whether the EnSys Petro Test System TPH concentration ranges overlapped the reference method results

- Whether the conclusion reached using the EnSys Petro Test System 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

During examination of these two factors, the data quality of the reference method and EnSys Petro Test System 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 ±30 percent stated in SW-846 for organic analyses. Therefore, caution was exercised during comparison of the EnSys Petro Test System and reference method results, particularly those for low- and medium-range diesel soil samples.

The following sections discuss how the EnSys Petro Test System results compared with the reference method results by addressing each of the two factors identified above.

Pairwise Comparison of TPH Results

To evaluate whether the EnSys Petro Test System and reference method TPH results were the same or different, the device's TPH concentration ranges were compared to the reference method TPH results. Tables 7-2 and 7-3 present comparisons of the device and reference method TPH results for environmental and PE samples, respectively. The tables present the TPH results for each sampling area or PE sample type.

Table 7-2 shows that the EnSys Petro Test System TPH concentration ranges overlapped the reference method results for only 8 of 50 (16 percent) environmental samples. No conclusions could be drawn for 16 samples for which the reference method TPH results were greater than the highest detection level used by SDI (1,000 mg/kg). The best agreement between the EnSys Petro Test System and reference method results was observed for B-38 Area samples (25 percent), followed by samples from the SFT Area (21 percent), NEX Service Station Area (8 percent), and FFA (0 percent). Lack of agreement between an EnSys Petro Test System concentration range and a reference method result did not appear to be a function of the type of contamination (gasoline or diesel), sample TPH concentration range (low, medium, or high), or type of soil (sand, silt, or clay).

Table 7-2. Comparison of EnSys Petro Test System and Reference Method TPH Results for Environmental Samples

| Sampling Area | TPH Result (mg/kg) | | Analysis Summary | |
	EnSys Petro Test System	Reference Method	Did the EnSys Petro Test System TPH Concentration Range Overlap the Reference Method TPH Result?[a]	EnSys Petro Test System Bias (minimum percent bias)
Fuel Farm Area	<15	68.2	No	Low (78)
	>1,000	15,000	Inconclusive	
	<15	90.2	No	Low (83)
	>1,000	12,000	Inconclusive	
	<15	44.1	No	Low (66)
	>1,000	13,900	Inconclusive	
	>15 to <100	1,330	No	Low (92)
	>1,000	8,090	Inconclusive	
	<15	93.7	No	Low (84)
	>1,000	12,300	Inconclusive	
Naval Exchange Service Station Area	>100 to <1,000	28.8	No	High (250)
	>1,000	144	No	High (590)
	>1,000	617	No	High (62)
	>100 to <1,000	293	Yes	
	>1,000	280	No	High (260)
	>1,000	1,870	Inconclusive	
	>1,000	1,560	Inconclusive	
	>1,000	9.56	No	High (10,000)
	>1,000	270	No	High (270)
	>1,000	881	No	High (14)
	>1,000	1,120	Inconclusive	
	>1,000	14.2	No	High (6,900)
	>1,000	219	No	High (360)
	>1,000	1,180	Inconclusive	
	>1,000	1,390	Inconclusive	
	>1,000	15.2	No	High (6,500)
	>1,000	54.5	No	High (1,700)
	>1,000	2,570	Inconclusive	
	>1,000	3,030	Inconclusive	
	>100 to <1,000	15.9	No	High (530)
B-38 Area	>100 to <1,000	79.0	No	High (27)
	>15 to <100	41.5	Yes	
	>100 to <1,000	61.4	No	High (63)
	>100 to <1,000	67.3	No	High (49)
	>100 to <1,000	193	Yes	
	>100 to <1,000	69.4	No	High (44)
	>100 to <1,000	43.8	No	High (130)
	>100 to <1,000	51.6	No	High (94)
Slop Fill Tank Area	>100 to <1,000	105	Yes	
	>1,000	269	No	High (270)
	>1,000	397	No	High (150)
	>1,000	339	No	High (200)
	<15	6.16	Yes	
	>1,000	37.1	No	High (2,600)
	>15 to <100	43.9	Yes	

Table 7-2. Comparison of EnSys Petro Test System and Reference Method TPH Results for Environmental Samples (Continued)

| Sampling Area | TPH Result (mg/kg) | | Analysis Summary | |
	EnSys Petro Test System	Reference Method	Did the EnSys Petro Test System TPH Concentration Range Overlap the Reference Method TPH Result?[a]	EnSys Petro Test System Bias (minimum percent bias)
Slop Fill Tank Area (continued)	>15 to <100	52.4	Yes	
	>1,000	3,300	Inconclusive	
	>1,000	1,270	Inconclusive	
	>1,000	588	No	High (70)
	>1,000	554	No	High (81)
	>1,000	834	No	High (20)
	>1,000	501	No	High (100)
	>1,000	280	No	High (260)
	>1,000	185	No	High (440)
	>1,000	1,090	Inconclusive	
	>1,000	544	No	High (84)
	>1,000	503	No	High (99)
	>1,000	146	No	High (580)
	>1,000	938	No	High (7)
	>1,000	517	No	High (93)
	>1,000	369	No	High (170)
	>1,000	253	No	High (300)
	>1,000	151	No	High (560)
	>1,000	3,960	Inconclusive	
	>100 to <1,000	1,210	No	Low (17)
	>100 to <1,000	121	Yes	

Notes:

> = Greater than
< = Less than
mg/kg = Milligram per kilogram

[a]   No conclusion could be drawn for 16 samples for which the reference method TPH results were greater than the highest detection level used by SDI during the demonstration (1,000 mg/kg). In these cases, SDI's results did not have the upper limits that defined concentration ranges.

Table 7-3. Comparison of EnSys Petro Test System and Reference Method TPH Results for Performance Evaluation Samples

Sample Type		TPH Result		Analysis Summary	
		EnSys Petro Test System	Reference Method	Did the EnSys Petro Test System TPH Concentration Range Overlap the Reference Method TPH Result?[a]	EnSys Petro Test System Bias (minimum percent bias)
Soil Samples (Processed Garden Soil) (TPH Results in Milligram per Kilogram)					
Blank (9 percent moisture content)		<10	5.12	Yes	
		<10	13.1	No	Low (24)
		<10	13.5	No	Low (26)
Weathered gasoline	Medium-concentration range (9 percent moisture content)	>1,000	702	No	High (42)
		>1,000	743	No	High (35)
		>1,000	671	No	High (49)
	High-concentration range (9 percent moisture content)	>1,000	1,880	Inconclusive	
		>1,000	2,020	Inconclusive	
		>1,000	2,180	Inconclusive	
	High-concentration range (16 percent moisture content)	>1,000	1,740	Inconclusive	
		>1,000	1,980	Inconclusive	
		>1,000	2,050	Inconclusive	
Diesel	Low-concentration range (9 percent moisture content)	>15 to <100	12.0	No	High (25)
		>15 to <100	16.5	Yes	
		>15 to <100	13.7	No	High (9)
		>15 to <100	16.4	Yes	
		>100 to <1,000	17.4	No	High (470)
		>15 to <100	17.2	Yes	
		>15 to <100	14.8	No	High (1)
	Medium-concentration range (9 percent moisture content)	>1,000	226	No	High (340)
		>1,000	265	No	High (280)
		>100 to <1,000	267	Yes	
	High-concentration range (9 percent moisture content)	>1,000	2,480	Inconclusive	
		>1,000	2,890	Inconclusive	
		>1,000	2,800	Inconclusive	
	High-concentration range (less than 1 percent moisture content)	>1,000	2,700	Inconclusive	
		>1,000	2,950	Inconclusive	
		>1,000	3,070	Inconclusive	
Liquid Samples (Neat Materials) (TPH Results in Milligram per Liter)					
Weathered gasoline		>200,500	656,000	Inconclusive	
		>200,500	611,000	Inconclusive	
		>200,500	677,000	Inconclusive	
Diesel		>200,500	1,090,000	Inconclusive	
		>200,500	1,020,000	Inconclusive	
		>200,500	1,160,000	Inconclusive	

Notes:

> = Greater than
< = Less than

[a] No conclusions could be drawn for 18 soil and liquid samples for which the reference method TPH results were greater than the highest detection levels used by SDI during the demonstration (1,000 milligrams per kilogram for soil samples and 200,500 milligrams per liter for liquid samples). In these cases, SDI's results did not have the upper limits that defined concentration ranges.

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When the EnSys Petro Test System concentration range and reference method result did not agree, the device result was biased high relative to the reference method result except for all the FFA samples and one SFT Area sample. As shown in Table 7-2, the minimum bias ranged from 14 to 10,000 percent for NEX Service Station Area samples; 27 to 130 percent for the B-38 Area samples; and 7 to 2,600 percent for the SFT Area samples. The minimum median bias was 440, 56, and 150 percent for the NEX Service Station, B-38, and SFT Area samples, respectively. As a result, the high bias observed for the EnSys Petro Test System results for environmental samples cannot be explained based solely on the negative bias associated with reference method TPH measurements for GRO-containing samples (up to 20 percent) and EDRO-containing samples (up to 33 percent) discussed in Chapter 6. The EnSys Petro Test System results for the FFA samples were biased low relative to the reference method results; the minimum bias ranged from 66 to 92 percent with a median of 83 percent. The low bias observed for FFA samples is inconsistent with the negative bias associated with reference method TPH measurements for EDRO-containing samples and cannot be explained.

Table 7-3 shows that the EnSys Petro Test System TPH concentration ranges overlapped the reference method results for only 5 of 16 (31 percent) soil PE samples. No conclusions could be drawn for 12 soil PE samples for which the reference method TPH results were greater than the highest detection level used by SDI for soil samples (1,000 mg/kg). Similarly, no conclusions could be drawn for the six liquid PE samples because the reference method TPH results were greater than the highest detection level used by SDI for liquid samples (200,500 mg/L). When the EnSys Petro Test System and reference method results did not agree, the device results were biased (1) low for blank soil samples and (2) high for medium-concentration-range weathered gasoline soil samples and low- and medium-range diesel soil samples.

The minimum low biases for blank soil samples were 24 and 26 percent with a median of 25 percent. The bias observed for the blank samples may be explained by SDI's selection of gasoline as the fuel product equivalent (see Chapter 2). Had SDI used diesel as the fuel product equivalent, the device results for these blank samples would have been reported as <15 mg/kg, which would have agreed with the reference method results.

The minimum high bias for the medium-concentration-range weathered gasoline soil samples ranged from 35 to

49 percent with a median of 42 percent. A significant portion of the bias may be explained by the negative bias associated with the reference method results for medium-range weathered gasoline soil samples (35 percent) discussed in Section 6.2. The minimum high bias for the low-range diesel soil samples ranged from 1 to 470 percent with a median of 17 percent. The bias may be explained by the significant negative bias associated with the reference method results for the low-range diesel soil samples (59 percent) discussed in Section 6.2. The minimum high biases for medium-range diesel soil samples were 280 and 340 percent with a median of 310 percent, which cannot be explained.

Action Level Conclusions

Table 7-4 compares action level conclusions reached using the EnSys Petro Test System 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. No conclusions could be drawn for 17 of 100 samples. Of the samples for which conclusions could be drawn, the percentage of samples for which the conclusions agreed ranged from 25 to 90 for environmental samples and from 33 to 100 for PE samples. Overall, the conclusions were the same for 67 percent of the samples. The lack of agreement observed for B-38 Area soil samples (25 percent) and for the blank soil PE samples (33 percent) was not surprising because the sample TPH concentrations were mostly near (within 30 percent) the action levels and because the EnSys Petro Test System detection levels were the same as the action levels for the two sets of samples, making it difficult to accurately assess whether a sample concentration was above or below the action level.

When the action level conclusions did not agree, the TPH results were further interpreted to assess whether the EnSys Petro Test System conclusion was conservative. The EnSys Petro Test System conclusion was considered to be conservative when the device's 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.

EnSys Petro Test System conclusions that did not agree with reference method conclusions were conservative for NEX Service Station, B-38, and SFT Area samples and for

Table 7-4. Action Level Conclusions

Sampling Area or Sample Type		Action Level (mg/kg)	Total Number of Samples Analyzed	Total Number of Samples for Which Action Level Conclusions Could Be Drawn[a]	Percentage of Samples for Which EnSys Petro Test System and Reference Method Conclusions Agreed	When Conclusions Did Not Agree, Were EnSys Petro Test System Conclusions Conservative or Not Conservative?[b]
Fuel Farm Area		100	10	10	90	Not conservative
Naval Exchange Service Station Area		50	20	20	75	Conservative
B-38 Area		100	8	8	25	Conservative
Slop Fill Tank Area		500	28	25	60	Conservative
PE sample	Blank soil (9 percent moisture content)	10	3	3	33	Not conservative
PE sample	Blank soil and humic acid (9 percent moisture content)	200	6	5	100	
Soil PE sample containing weathered gasoline in	Medium-concentration range (9 percent moisture content)	200	3	3	100	
	High-concentration range (9 percent moisture content)	2,000	3	0		
	High-concentration range (16 percent moisture content)	2,000	3	0		
Soil PE sample containing diesel in	Low-concentration range (9 percent moisture content)	15	7	7	57	Conservative
	Medium-concentration range (9 percent moisture content)	200	3	2	100	
	High-concentration range (less than 1 percent moisture content)	2,000	3	0		
	High-concentration range (9 percent moisture content)	2,000	3	0		
Total			100	83	67	

Notes:

mg/kg = Milligram per kilogram
PE = Performance evaluation

[a] Based on the detection levels selected by SDI during the demonstration (10, 100, and 1,000 mg/kg for weathered gasoline-containing soil samples and 15, 100, and 1,000 mg/kg for diesel-containing soil samples), no conclusions could be drawn for 17 samples.

[b] A conclusion was considered to be conservative when the EnSys Petro Test System 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.

low-concentration-range soil PE samples containing diesel. One conclusion for an FFA sample and two conclusions for blank soil PE samples were not conservative. The conclusion for the FFA sample appears to be an outlier because the reference method result for the sample was 13 times the action level. The conclusions for the blank soil PE samples may be attributed to difficulty in accurately measuring TPH at trace levels. In summary, the EnSys Petro Test System action level conclusions were considered to be conservative because 24 of 27 conclusions (89 percent) were conservative.

7.1.2.2   Precision

Both environmental and PE samples were analyzed to evaluate the precision associated with TPH measurements using the EnSys Petro Test System and reference method. The results of this evaluation are summarized below.

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 7-5 and 7-6 present the EnSys Petro Test System and reference method results for 11 sets of field triplicates and 12 sets of extract duplicates, respectively. EnSys Petro Test System precision was evaluated by assessing the comparability of the TPH concentration ranges reported for field triplicates and extract duplicates. Reference method precision was estimated using RSDs for field triplicates and RPDs for extract duplicates.

As shown in Table 7-5, the TPH concentration ranges reported by the EnSys Petro Test System were the same for each field triplicate set. Of the 11 field triplicate sets, two (18 percent) had a finite TPH concentration range of <15 mg/kg (field triplicate set 1) or >100 to <1,000 mg/kg (field triplicate set 7). However, the TPH results for the remaining field triplicate sets (82 percent) were reported as >1,000 mg/kg; the infinite concentration range associated with these TPH results may have contributed to the outcome that the results for a given set of field triplicates were the same. Table 7-5 also shows that the RSDs for the reference method ranged from 4 to 39 percent with a median of 16 percent. In summary, the field triplicate results for both the EnSys Petro Test System and the reference method exhibited good overall precision.

As shown in Table 7-6, the TPH concentration ranges reported by the EnSys Petro Test System were the same for each extract duplicate set. Three of the 12 extract duplicate sets (25 percent) had a finite TPH concentration range of <15 mg/kg (extract duplicate set 1), >15 to <100 mg/kg (extract duplicate set 8), or >100 to <1,000 mg/kg (extract duplicate set 7). However, the TPH results for the remaining extract duplicate sets (75 percent) were reported as >1,000 mg/kg; the infinite concentration range associated with the TPH result (>1,000 mg/kg) may have contributed to the outcome that the results for a given set of extract duplicates were the same.

Table 7-6 also shows that the RPDs for the reference method ranged from 0 to 11 with a median of 3. As expected, the median RPD for extract duplicates was less

than the median RSD for field triplicates for the reference method. This finding 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.

Because the EnSys Petro Test System TPH results for the field triplicates exhibited the highest precision that can be achieved by a semiquantitative device, no conclusions could be drawn regarding whether greater precision was achieved when only the analysis step could have contributed to TPH measurement error.

Performance Evaluation Samples

Table 7-7 presents the EnSys Petro Test System and reference method TPH results for eight sets of replicates for soil PE samples and two sets of replicate liquid PE samples.

For the EnSys Petro Test System, the TPH concentration ranges were the same for 8 of the 10 sets of replicates. In the remaining two sets of replicates for which the TPH concentration ranges were not the same, only one of seven (replicate set 5) and one of three (replicate set 6) TPH results were different. Three of the 10 replicate sets (30 percent) had a finite TPH concentration range of <10 mg/kg (replicate set 1), >15 to <100 mg/kg (replicate set 5), or >100 to <1,000 mg/kg (one sample each in replicate sets 5 and 6). However, the TPH results for the remaining replicate sets (70 percent) were reported as >1,000 mg/kg or >200,500 mg/L; the infinite concentration ranges associated with the TPH results (>1,000 mg/kg and >200,500 mg/L) may have contributed to the outcome that the results for a given set of replicates were the same.

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 5 to 13 percent with a median of 8 percent. The RSDs for the two triplicate sets of liquid samples were 5 and 6 percent with a median of 5.5 percent. In summary, the EnSys Petro Test System and reference method results for PE samples exhibited good overall precision.

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Table 7-5. Summary of EnSys Petro Test System and Reference Method Precision for Field Triplicates of Environmental Samples

| Sampling Area | Field Triplicate Set | EnSys Petro Test System | | Reference Method | |
		TPH Result (milligram per kilogram)	Were TPH Concentration Ranges for a Given Field Triplicate the Same or Different?	TPH Result (milligram per kilogram)	Relative Standard Deviation (percent)
Fuel Farm Area	1	<15	Same	68.2	34
		<15		90.2	
		<15		44.1	
	2	>1,000	Same	15,000	11
		>1,000		12,000	
		>1,000		13,900	
Naval Exchange Service Station Area	3	>1,000	Same	280	13
		>1,000		270	
		>1,000		219	
	4	>1,000	Same	1,870	39
		>1,000		881	
		>1,000		1,180	
	5	>1,000	Same	1,560	16
		>1,000		1,120	
		>1,000		1,390	
	6	>1,000	Same	9.56	23
		>1,000		14.2	
		>1,000		15.2	
B-38 Area	7	>100 to <1,000	Same	79	13
		>100 to <1,000		61.4	
		>100 to <1,000		67.3	
Slop Fill Tank Area	8	>1,000	Same	834	14
		>1,000		1,090	
		>1,000		938	
	9	>1,000	Same	501	4
		>1,000		544	
		>1,000		517	
	10	>1,000	Same	280	29
		>1,000		503	
		>1,000		369	
	11	>1,000	Same	185	28
		>1,000		146	
		>1,000		253	

Notes:

> = Greater than
< = Less than

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Table 7-6. Summary of EnSys Petro Test System and Reference Method Precision for Extract Duplicates

| Sampling Area | Extract Duplicate Set | EnSys Petro Test System | | Reference Method | |
		TPH Result (milligram per kilogram)	Were TPH Concentration Ranges for a Given Extract Duplicate Set the Same or Different?	TPH Result (milligram per kilogram)	Relative Percent Difference
Fuel Farm Area	1	<15	Same	44.1	0
		<15		44.1	
	2	>1,000	Same	13,700	2
		>1,000		14,000	
Naval Exchange Service Station Area	3	>1,000	Same	226	6
		>1,000		213	
	4	>1,000	Same	1,190	2
		>1,000		1,170	
	5	>1,000	Same	1,420	4
		>1,000		1,360	
	6	>1,000	Same	15.5	4
		>1,000		14.9	
B-38 Area	7	>100 to <1,000	Same	79.6	2
		>100 to <1,000		78.4	
	8	>15 to <100	Same	41.4	0
		>15 to <100		41.5	
Slop Fill Tank Area	9	>1,000	Same	829	1
		>1,000		838	
	10	>1,000	Same	528	11
		>1,000		473	
	11	>1,000	Same	271	6
		>1,000		289	
	12	>1,000	Same	189	4
		>1,000		181	

Notes:

> = Greater than
< = Less than

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Table 7-7. Comparison of EnSys Petro Test System and Reference Method Precision for Replicate Performance Evaluation Samples

Sample Type		Replicate Set	EnSys Petro Test System		Reference Method	
			TPH Result	Were TPH Concentration Ranges for a Given Replicate Set the Same or Different?	TPH Result	Relative Standard Deviation (percent)
Soil Samples (Processed Garden Soil) (TPH Results in Milligram per Kilogram)						
Blank (9 percent moisture content)		1	<10	Same	5.12	45
			<10		13.1	
			<10		13.5	
Weathered gasoline	Medium-range TPH concentration (9 percent moisture content)	2	>1,000	Same	702	5
			>1,000		743	
			>1,000		671	
	High-range TPH concentration (9 percent moisture content)	3	>1,000	Same	1,880	7
			>1,000		2,020	
			>1,000		2,180	
	High-range TPH concentration (16 percent moisture content)	4	>1,000	Same	1,740	8
			>1,000		1,980	
			>1,000		2,050	
Diesel	Low-range TPH concentration (9 percent moisture content)	5	>15 to <100	Same for six of seven	12.0	13
			>15 to <100		16.5	
			>15 to <100		13.7	
			>15 to <100		16.4	
			>100 to <1,000		17.4	
			>15 to <100		17.2	
			>15 to <100		14.8	
	Medium-range TPH concentration (9 percent moisture content)	6	>1,000	Same for two of three	226	9
			>1,000		265	
			>100 to <1,000		267	
	High-range TPH concentration (9 percent moisture content)	7	>1,000	Same	2,480	8
			>1,000		2,890	
			>1,000		2,800	
	High-range TPH concentration (<1 percent moisture content)	8	>1,000	Same	2,700	6
			>1,000		2,950	
			>1,000		3,070	
Liquid Samples (Neat Materials) (TPH Results in Milligram per Liter)						
Weathered gasoline		9	>200,500	Same	656,000	5
			>200,500		611,000	
			>200,500		677,000	
Diesel		10	>200,500	Same	1,090,000	6
			>200,500		1,020,000	
			>200,500		1,160,000	

Notes:

> = Greater than
< = Less than

Finally, for the reference method, the median RSD for the soil PE samples (8 percent) was less than that for the environmental samples (16 percent), indicating that greater precision was achieved for the samples prepared under more controlled conditions (the PE samples). A similar comparison could not be made for the EnSys Petro Test System becaues the device's results were semiquantitative.

7.1.3 Primary Objective P3: Effect of Interferents

The effect of interferents on TPH measurement using the EnSys Petro Test System 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 EnSys Petro Test System and the reference method. Liquid interferent samples were submitted for analysis as blind triplicate samples. SDI 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 EnSys Petro Test System 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 7-8 presents the EnSys Petro Test System 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 EnSys Petro Test System ranged from 0 to >28 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. Because SDI performed TPH measurements for each liquid interferent at two different dilutions, a conclusion regarding the effect of each interferent on TPH results was drawn using (1) the higher mean TPH result between triplicate sets when the TPH results were reported as "greater than" values and (2) the lower mean TPH result between triplicate sets when the TPH results were reported as "less than" values. Therefore, the mean response for MTBE (0 percent) indicated that this compound cannot be measured as TPH using the EnSys Petro Test System. However, the mean responses for Stoddard solvent (>26 percent) indicated that this compound can be measured as TPH using the device. The mean responses for PCE (>25 percent); turpentine (>24 percent); and 1,2,4-trichlorobenzene (>28 percent) indicated that these interferents will likely result in false positives during TPH measurement. Also, 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.

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 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 EnSys Petro Test System and reference method. Because the

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Table 7-8. Comparison of EnSys Petro Test System and Reference Method Results for Interferent Samples

Interferent and Concentration[a]	EnSys Petro Test System			Reference Method		
	TPH Result	Mean TPH Result	Mean Response[b] (percent)	TPH Result	Mean TPH Result	Mean Response[b] (percent)
Liquid Interferent Samples (TPH Results in Milligram per Liter)						
Methyl-tert-butyl ether (740,000 milligrams per liter)	<2,005	<2,005	0	309,000	284,000	38
	<2,005			272,000		
	<2,005			270,000		
	>10,050 to <100,500	<1,005[c]	0	303,000	299,000	40
	<1,005			313,000		
	<1,005			282,000		
Tetrachloroethene (1,621,000 milligrams per liter)	>400,500	>400,500	>25	269,000	272,000	17
	>400,500			270,000		
	>400,500			277,000		
	>80,500	>80,500	>5	290,000	295,000	18
	>80,500			288,000		
	>80,500			307,000		
Stoddard solvent (771,500 milligrams per liter)	>200,500	>200,500	>26	561,000	598,000	78
	>200,500			628,000		
	>200,500			606,000		
	>40,500	>40,500	>5	703,000	708,000	92
	>40,500			Not reported		
	>40,500			713,000		
Turpentine (845,600 milligrams per liter)	>200,500	>200,500	>24	504,000	468,000	55
	>200,500			459,000		
	>200,500			442,000		
	>40,500	>40,500	>5	523,000	408,000	48
	>40,500			353,000		
	>40,500			349,000		
1,2,4-Trichlorobenzene (1,439,000 milligrams per liter)	>400,500	>400,500	>28	711,000	688,000	48
	>400,500			620,000		
	>400,500			732,000		
	>80,500	>80,500	>6	754,000	754,000	52
	>80,500			756,000		
	>80,500			752,000		
Interferent Samples (Processed Garden Soil) (TPH Results in Milligram per Kilogram)						
Humic acid at 3,940 milligrams per kilogram	<15	<15[d]	0	8.99	9.00	0
	<15			8.96		
	>100 to <1,000			8.12		
Humic acid at 19,500 milligrams per kilogram	>15 to <1,000	<15[d]	0	69.3	76.0	0
	<15			79.1		
	<15			78.5		

Notes:

> = Greater than   < = Less than

[a] A given liquid interferent concentration was estimated using its density and purity.

[b] The mean response was calculated by dividing the mean TPH result for a triplicate set by the interferent concentration and multiplying by 100.

[c] Because the EnSys Petro Test System TPH results for five of six samples containing methyl-tert-butyl ether were below the lowest detection level used by SDI, the device result of >10,050 to <100,500 milligrams per liter (an analytical outlier) was not considered.

[d] Because the EnSys Petro Test System TPH results for four of six samples containing humic acid were below the lowest detection level used by SDI, the device results of >100 to <1,000 and >15 to <1,000 milligrams per kilogram (analytical outliers) were not considered.

EnSys Petro Test System is a semiquantitative device, the TPH concentration of a sample cannot be reported as an absolute value, and a statistical approach could not be used to evaluate the effect of interferents on TPH measurement. For the reference method, a parametric or nonparametric test was selected for statistical evaluation of the analytical 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 the reference method are presented in Table 7-9. The null hypothesis for the statistical tests was that mean TPH results for samples with and without interferents were equal. The effects of the interferents are discussed below for both the EnSys Petro Test System and the reference method.

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 have no effect on the TPH results for the EnSys Petro Test System; however, it was expected to bias the reference method results high.

Table 7-9 shows that no conclusions could be drawn regarding the effect of MTBE on EnSys Petro Test System TPH results for soil PE samples; the TPH concentrations in soil PE samples containing weathered gasoline with and without MTBE exceeded the highest detection level used by SDI during the demonstration (1,000 mg/kg).

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 bias the EnSys Petro Test System and reference method TPH results high.

Table 7-9 shows that no conclusions could be drawn regarding the effect of PCE on EnSys Petro Test System TPH results for soil PE samples; the TPH concentrations in soil PE samples containing weathered gasoline with and without PCE exceeded the highest detection level used by SDI during the demonstration (1,000 mg/kg).

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 < 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 the EnSys Petro Test System and reference method results high.

Table 7-9 shows that no conclusions could be drawn regarding the effect of Stoddard solvent on EnSys Petro Test System TPH results for soil PE samples; the TPH concentrations in soil PE samples containing weathered gasoline and diesel with and without Stoddard solvent exceeded the highest detection level used by SDI during the demonstration (1,000 mg/kg).

Table 7-9. Comparison of EnSys Petro Test System and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents

Sample Matrix and Interferent[a]		EnSys Petro Test System[b]			Reference Method				
		TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	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)
Soil Samples Without Interferents									
Weathered gasoline		>1,000	>1,000		1,880	2,030			
		>1,000		Not applicable	2,020			Not applicable	
		>1,000			2,180				
Diesel		>1,000	>1,000		2,480	2,720			
		>1,000		Not applicable	2,890			Not applicable	
		>1,000			2,800				
Soil Samples With Interferents									
Weathered gasoline	MTBE (1,100 mg/kg)	>1,000	>1,000		1,900	1,950	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Same	11.21
		>1,000		Inconclusive	1,750				
		>1,000			2,210				
	MTBE (1,700 mg/kg)	>1,000	>1,000		2,150	2,340			
		>1,000		Inconclusive	2,320				
		>1,000			2,560				
	PCE (2,810 mg/kg)	>1,000	>1,000		2,540	2,380		Mean with interferent at high level was different from means without interferent and with interferent at low level	0.00
		>1,000		Inconclusive	2,160				
		>1,000			2,450				
	PCE (13,100 mg/kg)	>1,000	>1,000		4,740	4,450			
		>1,000		Inconclusive	4,570				
		>1,000			4,040				
	Stoddard solvent (2,900 mg/kg)	>1,000	>1,000		4,350	4,410		All three means (with and without interferents) were significantly different from one another	0.00
		>1,000		Inconclusive	4,760				
		>1,000			4,110				
	Stoddard solvent (15,400 mg/kg)	>1,000	>1,000		10,300	11,900			
		>1,000		Inconclusive	14,300				
		>1,000			11,000				

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Table 7-9. Comparison of EnSys Petro Test System and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents (Continued)

Sample Matrix and Interferent[a]		EnSys Petro Test System[b]			Reference Method				
		TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	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)
Soil Samples With Interferents (Continued)									
Diesel	Stoddard solvent (3,650 mg/kg)	>1,000	>1,000		4,390	4,520	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
		>1,000		Inconclusive	4,640				
		>1,000			4,520				
	Stoddard solvent (18,200 mg/kg)	>1,000	>1,000		8,770	7,880			
		>1,000		Inconclusive	6,580				
		>1,000			8,280				
Weathered gasoline	Turpentine (2,730 mg/kg)	>1,000	>1,000		4,410	4,240		All three means (with and without interferents) were significantly different from one another	0.00
		>1,000		Inconclusive	3,870				
		>1,000			4,440				
	Turpentine (12,900 mg/kg)	>1,000	>1,000		12,800	12,900			
		>1,000		Inconclusive	11,200				
		>1,000			14,600				
Diesel	Turpentine (3,850 mg/kg)	>1,000	>1,000		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
		>1,000		Inconclusive	5,810				
		>1,000			5,610				
	Turpentine (19,600 mg/kg)	>1,000	>1,000		15,000	13,900			
		>1,000		Inconclusive	13,300				
		>1,000			13,300				
	1,2,4-Trichloro-benzene (3,350 mg/kg)	>1,000	>1,000		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
		>1,000		Inconclusive	3,750				
		>1,000			3,550				
	1,2,4-Trichloro-benzene (16,600 mg/kg)	>1,000	>1,000		7,940	7,060			
		>1,000		Inconclusive	6,560				
		>1,000			6,690				

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Table 7-9. Comparison of EnSys Petro Test System and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents (Continued)

Sample Matrix and Interferent[a]		EnSys Petro Test System[b]			Reference Method				
		TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	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)
Soil Samples With Interferents (Continued)									
Diesel (Continued)	Humic acid (3,940 mg/kg)	>1,000	>1,000	Inconclusive	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
		>1,000			2,080				
		>1,000			2,360				
	Humic acid (19,500 mg/kg)	>1,000	>1,000	Inconclusive	2,660	2,450			
		>1,000			2,420				
		>1,000			2,270				

Notes:

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

[a] All samples were prepared at a 9 percent moisture level.

[b] Because the EnSys Petro Test System is a semiquantitative device, a statistical approach could not be used to draw conclusions regarding the effect of a given interferent on TPH measurement. In addition, based on the detection levels selected by SDI during the demonstration, the TPH results for samples with and without interferents were reported as >1,000 mg/kg. Therefore, no conclusions could be drawn regarding the effect of a given interferent on TPH measurement.

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 the EnSys Petro Test System and reference method results high.

Table 7-9 shows that no conclusions could be drawn regarding the effect of turpentine on EnSys Petro Test System TPH results for soil PE samples; the TPH concentrations in soil PE samples containing weathered gasoline and diesel with and without turpentine exceeded the highest detection level used by SDI during the demonstration (1,000 mg/kg).

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.

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 bias the EnSys Petro Test System and reference method results high.

Table 7-9 shows that no conclusions could be drawn regarding the effect of 1,2,4-trichlorobenzene on EnSys Petro Test System TPH results for soil PE samples; the TPH concentrations in soil PE samples containing diesel with and without 1,2,4-trichlorobenzene exceeded the highest detection level used by SDI during the demonstration (1,000 mg/kg).

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 <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 EnSys Petro Test System and reference method.

Table 7-9 shows that no conclusions could be drawn regarding the effect of humic acid on EnSys Petro Test System TPH results for soil PE samples; the TPH concentrations in soil PE samples containing diesel with and without humic acid exceeded the highest detection level used by SDI during the demonstration (1,000 mg/kg).

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 EnSys Petro Test System 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 EnSys Petro Test System 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. Because the EnSys Petro Test System is a semiquantitative device, the TPH concentration in a sample cannot be reported as an absolute value, and a statistical approach could not be used to evaluate the effect of soil moisture content on TPH measurement. Therefore, a qualitative evaluation was performed to determine whether the device's TPH results were impacted by soil moisture content—that is, to determine whether an increase in soil moisture resulted in an increase or decrease in the TPH concentrations measured. The reference method dry weight TPH results were normally distributed; therefore, a two-tailed, two-

sample Student's t-test was performed to determine whether the reference method results were impacted by soil moisture content. The null hypothesis for the t-test was that the two means were equal or that the difference between the means was equal to zero. Table 7-10 shows the sample moisture levels, TPH results, mean TPH results for sets of triplicate samples, whether the mean TPH results at different soil moisture levels were the same, and the probability of the null hypothesis being true.

Table 7-10 shows that no conclusions could be drawn regarding the effect of soil moisture content on EnSys Petro Test System TPH results for soil PE samples; the TPH concentrations in soil PE samples containing weathered gasoline and diesel exceeded the highest detection level used by SDI during the demonstration, which was 1,000 mg/kg on a wet weight basis. The apparent differences in mean TPH concentrations resulted from conversion of the concentrations to a dry weight basis.

Table 7-10 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 EnSys Petro Test System setup, sample extraction, sample analysis and data package preparation, and device disassembly, was measured. During the demonstration, either two or three field technicians performed the TPH measurement activities using the EnSys Petro Test System. Time measurement began at the start of each demonstration day when the technicians began to set up the device and ended when they disassembled the device. Time not measured included (1) the time spent by the technicians verifying that they had received all the demonstration samples indicated on chain-of-custody forms, (2) the times when the technicians took breaks, and (3) the time that the technicians spent away from the demonstration site preparing and analyzing calibration standards. In addition to the total time required for TPH measurement, the time required to perform sample extraction and the time required to perform sample analysis and prepare the data

Table 7-10. Comparison of Results for Soil Performance Evaluation Samples at Different Moisture Levels

Sample Type and Moisture Level	EnSys Petro Test System			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?[a]	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?[b]	Probability of Null Hypothesis Being True[c] (percent)
Weathered gasoline at 9 percent moisture level	>1,100	>1,100	Inconclusive	2,070	2,230	Same	66.52
	>1,100			2,220			
	>1,100			2,400			
Weathered gasoline at 16 percent moisture level	>1,200	>1,200		2,070	2,300		
	>1,200			2,390			
	>1,200			2,440			
Diesel at less than 1 percent moisture level	>1,000	>1,000	Inconclusive	2,740	3,000	Same	71.95
	>1,000			3,180			
	>1,000			3,070			
Diesel at 9 percent moisture level	>1,100	>1,100		2,720	2,930		
	>1,100			2,970			
	>1,100			3,100			

Notes:

> = Greater than

[a] Because the EnSys Petro Test System is a semiquantitative device, a statistical approach could not be used to draw conclusions regarding the effect of soil moisture content on TPH measurement. In addition, based on the detection levels selected by SDI during the demonstration, the TPH results for samples with different moisture levels were reported as >1,000 milligrams per kilogram on a wet weight basis. The small differences in the mean TPH concentrations resulted from conversion of the concentrations to a dry weight basis. Therefore, no conclusions could be drawn regarding the effect of moisture content on TPH measurement.

[b] A two-tailed, two-sample Student's t-test (parametric) was used to evaluate the effect of soil moisture content on TPH results.

[c] The null hypothesis for the t-test was that the two means were equal or that the difference between the two means was equal to zero.

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package for the first analytical batch of soil samples during each day of the demonstration were measured. The number and type of samples in a batch were selected by SDI.

The time required to complete TPH measurement activities using the EnSys Petro Test System is shown in Table 7-11. When a given activity was performed by two or three field technicians simultaneously, the time measurement for the activity was the total time spent by the technicians. The time required for each activity was rounded to the nearest 5 minutes.

Overall, SDI required 39 hours, 35 minutes, for TPH measurement of 66 soil environmental samples, 89 soil PE samples, 36 liquid PE samples, and 12 extract duplicates. In addition, SDI performed m-xylene reference standard duplicate QC checks at a rate of one per analytical batch (five samples). Information regarding the time required for each measurement activity during the 2-day demonstration and for extraction and analysis of the first analytical batch of soil samples during each day of the demonstration is provided below.

EnSys Petro Test System setup required 15 minutes each day, totaling 30 minutes for the entire demonstration. This activity included device setup; performing calibration checks for the differential photometer and digital balance; and organization of extraction, analysis, and waste

disposal supplies. The setup time was not separately measured for the first sample batch on the first day of the demonstration; instead, the setup time recorded for the first sample batch on the second day of the demonstration was used as an estimate.

The sample extraction time and the sample analysis and data package preparation time were not separately measured for each analytical batch during the demonstration because these activities were performed concurrently by two or more SDI technicians. A total of 38 hours, 45 minutes, was required to perform 155 soil sample extractions and 210 TPH analyses using the EnSys Petro Test System. The 210 analyses included analyses of 155 soil samples, 36 liquid samples, and 12 extract duplicates as well as reanalyses of 7 samples. During most of the demonstration, two SDI technicians performed measurement activities. On the first day of the demonstration, a third SDI technician assisted with sample extractions for 2 hours, 25 minutes, and with sample analyses for 1 hour, 30 minutes.

The time required for extraction of the first analytical batch of soil samples during each day of the demonstration was recorded. SDI designated five samples for each analytical batch. The number of samples was based on the capacity of the foam workstation provided in the Common Accessory Kit. A total of 20 minutes was required to extract the first batch of soil samples on the first day of

Table 7-11. Time Required to Complete TPH Measurement Activities Using the EnSys Petro Test System

| Measurement Activity | Time Required[a] | | |
	First Sample Batch, First Day	First Sample Batch, Second Day	2-Day Demonstration Period
EnSys Petro Test System setup	15 minutes[b]	15 minutes	30 minutes
Sample extraction	20 minutes	15 minutes	38 hours, 45 minutes[c]
Sample analysis and data package preparation[d]	35 minutes	25 minutes	
EnSys Petro Test System disassembly	10 minutes[e]	10 minutes[e]	20 minutes
Total	**1 hour, 20 minutes**	**1 hour, 5 minutes**	**39 hours, 35 minutes**

Notes:

[a] The time required for each activity was rounded to the nearest 5 minutes.

[b] The device setup time was not separately measured for the first sample batch on the first day of the demonstration; instead, the setup time recorded for the first sample batch on the second day of the demonstration was used as an estimate.

[c] The sample extraction time and the sample analysis and data package preparation time were not separately measured for each analytical batch during the demonstration because two or three SDI technicians concurrently performed these activities.

[d] The data package preparation time was not separately measured during the demonstration because the raw TPH results recorded on the field data form constituted the data package submitted by SDI; no additional calculations were required in the field.

[e] The device disassembly time was not separately measured during the demonstration. The disassembly time reported was estimated based on field observations. Specifically, this estimate was based on the device setup time, excluding the time required for (1) differential photometer and digital balance calibration checks and (2) organization of extraction, analysis, and waste disposal supplies.

first day of the demonstration; therefore, an average of 4 minutes was required for extraction of a sample. A total of 15 minutes was required to extract the first batch of samples on the second day of the demonstration; therefore, an average of 3 minutes was required for extraction of a sample. The decrease in the average extraction time for the first batch of soil samples on the second day of the demonstration suggested that the field technicians became more familiar with the EnSys Petro Test System extraction procedures as the demonstration progressed.

The time required to analyze samples and prepare the data package for the first analytical batch of soil samples during each day of the demonstration was also recorded. On the first day of the demonstration, a total of 35 minutes was required to analyze the first batch of samples and record the TPH result in the data package, or an average of 7 minutes per sample. On the second day of the demonstration, a total of 25 minutes was required to analyze the first batch of samples and record the TPH result in the data package, or an average of 5 minutes per sample. The decrease in the average sample analysis and data recording time for the first batch of soil samples on the second day of the demonstration suggested that the field technicians became more familiar with the EnSys Petro Test System analysis procedures as the demonstration progressed.

The EnSys Petro Test System disassembly time was estimated to be 10 minutes on each day, or a total of 20 minutes for the entire demonstration. Disassembly included packing the reusable items of the EnSys Petro Test System required for TPH measurement. The disassembly time was not separately measured during the demonstration but was estimated based on field observations. Specifically, this estimate was based on the device setup time, excluding the time required for (1) differential photometer and digital balance calibration checks and (2) organization of extraction, analysis, and waste disposal supplies.

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 EnSys Petro Test System in terms of the secondary objectives stated in Section 4.1. The secondary objectives were addressed based on (1) observations of the EnSys Petro Test System's performance during the demonstration and (2) information provided by SDI.

7.2.1 Skill and Training Requirements for Proper Device Operation

The EnSys Petro Test System is easy to operate, requiring one field technician with basic wet chemistry skills acquired on the job or in a university. Because the sample extraction time may need to be adjusted based on soil type, basic knowledge of soil types is also recommended so that the technician can differentiate among sand, silt, and clay soil types and adjust the extraction time accordingly. For the demonstration, SDI chose to conduct sample analyses using either two or three technicians in order to increase the sample throughput. One or two technicians performed sample extraction while one technician concurrently performed multiple analyses.

To simplify sample analysis for the user, SDI customizes the EnSys Petro Test System to include dilution ampules that allow the user to obtain semiquantitative results in order to meet project-specific requirements. SDI has 20 preset dilution ampules readily available for gasoline and diesel analyses but develops nonstandard dilution ampules upon request. For the demonstration, SDI used 100- and 1,000-mg/kg preset dilution ampules to analyze gasoline- and diesel-containing soil samples.

Each item in the EnSys Petro Test System is labeled to assist the user with sample analysis activities. Containers that are similar in appearance but contain different reagents are color-coded. For example, dilution ampules used for gasoline-containing soil samples are color-coded blue and green for 100- and 1,000-mg/kg dilutions, respectively. Also, the labels on the 15-mL bottles containing chromogen, substrate, and stop solution are color-coded yellow, green, and red, respectively. Methanol for use in sample extraction and extract dilution is provided in premeasured, sealed ampules. In addition, items included in the Sample Extraction Kit and the 12T Soil Test Kit are kept organized within the foam workstation provided in the Common Accessory Kit. As a result, the likelihood of user error during sample analysis is minimized.

Each foam workstation has the capacity to allow five samples to be analyzed in one batch at up to three dilution levels. More than five samples can be analyzed at a given time by setting up multiple workstations, but the advisability of doing so depends on the user's experience with the EnSys Petro Test System. Because the SDI field technicians have extensive experience with the EnSys Petro Test System, SDI used up to three workstations, at any given time, during the demonstration.

The sample analysis procedure for the EnSys Petro Test System can be learned in the field with a few practice attempts. The system contains user guides that must be followed to properly operate the system. In addition, during regular business hours, SDI provides technical support over the telephone at no additional cost. According to SDI, the user guides supplemented by technical support over the telephone are adequate for a user to learn the sample analysis procedure. However, SDI also offers a 1-day, on-site training program for $999, which includes the cost of instructor travel and per diem and the cost of one EnSys Petro Test System for training purposes. SDI does not provide a training video for the system.

With the EnSys Petro Test System, the user can easily estimate TPH concentrations by measuring the difference in color intensities between the reference standard and the sample extract or multiple dilutions of the sample extract. During the demonstration, SDI analyzed each sample at three detection levels by diluting the sample extract twice using the 100- and 1,000-mg/kg dilution ampules. The resulting TPH concentration ranges used to estimate sample concentrations were <10; >10 to <100; >100 to <1,000; and >1,000 mg/kg for GRO-containing samples and <15; >15 to <100; >100 to <1,000; and >1,000 mg/kg for EDRO-containing samples. No calculations are required to compensate for the extract dilutions.

After the demonstration, SDI made minimal revisions to the TPH results reported in the field. Specifically, of the 203 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 data entry errors.

7.2.2 Health and Safety Concerns Associated with Device Operation

Sample analysis using the EnSys Petro Test System requires handling of small quantities of multiple, potentially hazardous reagents supplied in sealed containers. These reagents include methanol (100 percent); N,N-dimethylformamide (2 percent), the hazardous component of tetramethylbenzidine; and sulfuric acid (0.5 percent). Therefore, the user should employ good laboratory practices during sample analysis. 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).

During the demonstration, SDI field technicians operated the EnSys Petro Test System in modified Level D personal protective equipment (PPE) to prevent eye and skin contact with reagents. The PPE included safety glasses, disposable gloves, and work boots as well as work clothes with long sleeves and long pants. Sample analyses were performed outdoors in a well-ventilated area; therefore, exposure to volatile reagents through inhalation was not a concern. Health and safety information for reagents in the EnSys Petro Test System is included in material safety data sheets available from SDI.

The user should also exercise caution when handling the dilution ampules, which are made of glass. During the demonstration, one SDI field technician received a minor cut on a finger after accidentally touching the sharp edge of an open dilution ampule.

7.2.3 Portability of the Device

The EnSys Petro Test System is easily transported between sampling areas in the field. As stated in Table 2-2, the system consists of three kits: the (1) Sample Extraction Kit, (2) 12T Soil Test Kit, and (3) Common Accessory Kit. Each Sample Extraction Kit weighs about 3 pounds and is housed in a cardboard box that is 19 inches long, 7.25 inches wide, and 5 inches high. Each 12T Soil Test Kit weighs about 5 pounds and is housed in a cardboard box that is 18.5 inches long, 7.5 inches wide, and 5 inches high. Each Common Accessory Kit weighs about 19 pounds and is housed in a hard-plastic carrying case that is 19.5 inches long, 15 inches wide, and 6 inches high. The differential photometer, which is included in the Common Accessory Kit, weighs 0.8 pound and is 5.3 inches long, 3.4 inches wide, and 2.6 inches high. The differential photometer, digital balance, and digital timer are battery-operated. Because no AC power source is required, the system can be easily transported between sampling areas.

To operate the EnSys Petro Test System, a shaded sample preparation and analysis area is required. The area must be large enough to accommodate the items in one Sample Extraction Kit and one Common Accessory Kit. Disposable items in the 12T Soil Test Kit have designated positions in the foam workstation included in the Common Accessory Kit. According to SDI, the sample preparation and analysis area must be shaded because the chromogen (tetramethylbenzidine) and substrate (hydrogen peroxide) added during the color development step are photosensitive and should be kept out of direct sunlight. A staging area may also be required to store Sample Extraction Kits and 12T Soil Test Kits; the size of the staging area depends on the number of samples to be analyzed and is thus project-specific. For the demonstration, SDI performed sample preparation and analysis under one 8- by 8-foot tent that housed two 8-foot-long, folding tables; three folding chairs; one 20-gallon laboratory pack for flammable waste; and one 55-gallon drum for general refuse.

7.2.4 Durability of the Device

The Common Accessory Kit of the EnSys Petro Test System contains several reusable items, including the Artel DP™ differential photometer, ACCULAB® digital balance, Gilson M-25 Microman® positive displacement pipettor, and Eppendorf™ repeater pipettor. Based on observations made during the demonstration, the EnSys Petro Test System is a durable field measurement device; none of the system's reusable items malfunctioned or was damaged. These items are manufactured or distributed by established scientific equipment suppliers and are housed by SDI in a hard-plastic carrying case to prevent damage to the items during transport of the Common Accessory Kit. The items were also unaffected by the varying temperature and humidity conditions encountered between 8:00 a.m. and 5:00 p.m. on any given day of the demonstration. During the daytime, the temperature ranged from about 17 to 24 °C, while the relative humidity ranged from 53 to 88 percent. During sample analysis, the light, disposable items in the system were housed in the foam workstation, so wind speeds up to 20 miles per hour also did not affect system operation.

7.2.5 Availability of the Device and Spare Parts

During the demonstration, none of the reusable items in the EnSys Petro Test System required replacement. Had one of these items required replacement, it would not have been available in local stores. A replacement item can be obtained from SDI by overnight courier service if the order is placed by 2:00 p.m. eastern time. If the need for a replacement item is identified after 2:00 p.m. eastern time and the item is needed the next day, the item might be obtained from various scientific equipment suppliers, depending on their shipping procedures and locations. Spare parts for reusable items such as the differential photometer are not included in the EnSys Petro Test System. SDI recommends that malfunctioning reusable items be returned to SDI for service; according to SDI, repairs should not be attempted in the field by the user. Because SDI provides a 1-year warranty for reusable items, SDI will replace such items and supply them to the user by overnight courier service at no additional cost during the warranty period.

The power supply for the differential photometer consists of four rechargeable, nickel-cadmium batteries. The batteries require 8 to 10 hours to achieve a full recharge after discharge, and they supply enough power for about 500 readings between recharges. Because the batteries are hard-wired into the differential photometer, it should be returned to SDI for service if the batteries malfunction. The power supplies for the digital balance (one 9-volt battery) and digital timer (one G-13 cell button battery) can be purchased from local stores and replaced in the field if necessary.

Disposable items in the EnSys Petro Test System should be obtained from SDI. All the disposable items, including the antibody-coated test tubes, are manufactured only by SDI. The disposable items provided to a given user on a given occasion all come from the same lot. Because SDI conducts QC checks for each lot individually, if the user performs analyses with items from more than one lot or uses reagents obtained from a scientific supply store, SDI assumes no responsibility for the quality of the sample analysis results.

Chapter 8
Economic Analysis

As discussed throughout this ITVR, the EnSys Petro Test System 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 EnSys Petro Test System.

During the demonstration, the EnSys Petro Test System 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 EnSys Petro Test System and then compare this cost to that for the reference method. The cost per analysis was not estimated for the EnSys Petro Test System 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 EnSys Petro Test System (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 EnSys Petro Test System 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 EnSys Petro Test System unless otherwise stated.

8.1.1   Capital Equipment Cost

The capital equipment cost was the cost associated with the rental of the Common Accessory Kit, one of the three primary components of the EnSys Petro Test System used during the demonstration. The Common Accessory Kit is available for purchase or rental from SDI; the kit can be rented from SDI on a daily, weekly, or monthly basis. The kit can be rented on a daily basis for 9 percent of the purchase price; as a result, the break-even point between the purchase price and the daily rental cost is 12 days. Because the kit was used for 2 days during the demonstration, the capital equipment cost was the cost associated with the rental of the kit for 2 days, the less expensive alternative. The purchase price and rental cost information was obtained from a standard price list provided by SDI.

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8.1.2 Cost of Supplies

The cost of supplies was estimated based on the supplies required to analyze all demonstration samples using the EnSys Petro Test System that were not included in the capital equipment cost category. Supplies used by SDI during the demonstration included the disposable items of two primary components of the EnSys Petro Test System: the Sample Extraction Kit and 12T Soil Test Kit. During the demonstration, the quantities of kits used by SDI were noted each day. The purchase price of each kit was obtained from a standard price list provided by SDI. Because a user cannot 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

Because the EnSys Petro Test System contains photosensitive reagents (chromogen and substrate), SDI required a shelter such as a tent to perform sample analyses. In addition, because of the large number of samples analyzed during the demonstration, the EPA provided support equipment, including tables and chairs, for the field technicians' 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 EnSys Petro Test System 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 SDI. The measurement of the time required for SDI 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 technicians 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 EnSys Petro Test System. 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, SDI 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, residual solvent from sample extractions and dilutions, used EnCores, and unused chemicals that could not be returned to SDI were disposed of in a laboratory pack. SDI was required to provide any containers necessary to containerize individual wastes prior to their placement in a laboratory pack; however, SDI did not need additional containers.

During the demonstration, SDI generated an additional 4 gallons of liquid waste. This waste, which consisted of spent sample extract, detergent solution, tetramethylbenzidine, hydrogen peroxide, and sulfuric acid, was collected in a 5-gallon bucket provided by the demonstration site representatives. Because the liquid waste was determined to be noncorrosive, the contents of the bucket were disposed of on site in accordance with demonstration site waste disposal guidelines, and the cost for disposing of this waste was not included in the IDW disposal cost estimate.

Items such as used plastic weigh boats, wooden spatulas, and PPE were disposed of with municipal garbage in accordance with demonstration site waste disposal guidelines; the associated waste disposal cost 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 EnSys Petro Test System 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-specific and were not device- or reference method-dependent.

Shipping. Costs for shipping (1) the EnSys Petro Test System 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 EnSys Petro Test System Costs

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

8.2.1 Capital Equipment Cost

The capital equipment cost was the cost associated with the rental of the Common Accessory Kit (Item No. 6997020) for 2 days. Table 2-2 lists the items in the Common Accessory Kit, which are reusable. The Common Accessory Kit can be purchased for $1,999 or rented on a daily ($175), weekly ($450), or monthly

($800) basis. Because daily rental was the cheapest option in the context of the demonstration, the daily rental cost was used to calculate the capital equipment cost for the kit. Thus, the capital equipment cost of the Common Accessory Kit for the demonstration was $350.

Items in the Common Accessory Kit that can be purchased separately from SDI if additional quantities are needed include the Artel DP™ Differential Photometer ($1,000), ACCULAB® digital balance ($135), digital timer ($29), Eppendorf™ repeater pipettor ($507), and Gilson M-25 Microman® positive displacement pipettor ($325). During the demonstration, the photometer batteries required recharging. Because the batteries could not be recharged when the photometer was in use, SDI used a spare photometer to complete TPH measurements. Because the initial photometer was not damaged and did not require repair, the cost of the spare photometer was not included in the economic analysis. Also, during the demonstration, SDI used three foam workstations to conduct sample analyses, but only one foam workstation is included in the Common Accessory Kit. Because SDI provides spare foam workstations to users at no additional cost, no cost for the two additional workstations was included in the economic analysis.

8.2.2 Cost of Supplies

The cost of supplies was associated with the purchase of Sample Extraction Kits (Item No. 7042301EA) and 12T Soil Test Kits (Item No. 7042301). Table 2-2 lists the items in the Sample Extraction Kit and 12T Soil Test Kit, which are disposable. During the demonstration, SDI used 18 Sample Extraction Kits at $120 each and 15 12T Soil Test Kits at $366 each. Thus, the total cost of the supplies used by SDI during the demonstration was $7,650.

Of the items in the Sample Extraction Kit and 12T Soil Test Kit, only a few items in the 12T Soil Test Kit can be purchased separately if additional quantities are needed. Items in the 12T Soil Test Kit that can be purchased separately include the 5- and 12.5-mL Combitips® for the repeater pipettor at $1.20 each and the 50- to 250-μL Microman® positive displacement pipettor tips, which can be purchased in packages of 12 ($10), 24 ($15), 60 ($25), and 200 ($70). During the demonstration, no additional quantities of these items were required; all items required to perform TPH measurements were included in the Sample Extraction Kits and 12T Soil Test Kits used.

Table 8-1. EnSys Petro Test System Cost Summary

Item	Quantity	Unit Cost ($)	Itemized Cost ($)
Capital equipment			
Rental of Common Accessory Kit	1 unit for 2 days	175/day	350
Supplies			
Sample Extraction Kit	18 units	120	2,160
12T Soil Test Kit	15 units	366	5,490
Support equipment			
Tent	1 unit	159	159
Tables and chairs (two each)	1 set for 1 week	39	39
Labor			
Field technicians	5 person-days	332.60	1,663
Investigation-derived waste disposal	1 20-gallon container	345.00	345
Total Cost[a]			**$10,210**

Note:

[a] The total dollar amount was rounded to the nearest $10.

8.2.3 Support Equipment Cost

SDI was provided with one 8- by 8-foot tent to prevent decomposition of photosensitive reagents (chromogen and substrate) and to protect the EnSys Petro Test System and the field technicians from inclement weather during the demonstration. SDI was also provided 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

To complete all sample analyses and prepare the summary data package, three field technicians were required during the first day of the demonstration, and two field technicians were required during the second day. Based on a daily labor rate of $332.60 per person, the total labor cost for the EnSys Petro Test System was $1,663.

8.2.5 Investigation-Derived Waste Disposal Cost

SDI used one laboratory pack to collect flammable hazardous waste generated during the demonstration. The IDW disposal cost included the purchase cost of the laboratory pack ($38) and the cost associated with disposal of the laboratory pack in a landfill ($307) (Means 2000). The total IDW disposal cost was $345.

8.2.6 Summary of EnSys Petro Test System Costs

The total cost for performing more than 200 TPH analyses using the EnSys Petro Test System and for preparing a summary data package was $10,210 (rounded to the nearest $10). The TPH analyses were performed for 66 soil environmental samples, 89 soil PE samples, and 36 liquid PE samples. In addition to these 191 samples, 12 extract duplicates were analyzed for specified soil environmental samples. When SDI performed multiple dilutions or reanalyses for a sample, these were not included in the number of samples analyzed.

During the demonstration, SDI analyzed five samples in a given analytical batch at three detection levels. Five samples were the maximum number that could be analyzed using one foam workstation. In addition to analyzing all demonstration samples in such a manner, SDI reanalyzed seven sample extracts. Collectively, these activities required SDI to use one additional Sample Extraction Kit and 10 additional 12T Soil Test Kits, or 6 and 200 percent more of these components, respectively, than would otherwise have been needed. The additional Sample Extraction Kit was required only to reanalyze the seven sample extracts, whereas the additional 12T Soil Test Kits were required to perform all the TPH measurement activities.

The total cost of $10,210 for analyzing the demonstration samples using the EnSys Petro Test System included $350 for capital equipment; $7,650 for supplies; $198 for support equipment; $1,663 for labor; and $345 for IDW disposal. Of these five costs, the two largest were the cost of supplies (75 percent of the total cost) and the labor cost (16 percent of the total cost).

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 EnSys Petro Test System and reference method costs, the reference method costs were estimated for the same number of samples as was analyzed by SDI. 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 SDI 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 $41,290. 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 EnSys Petro Test System ($10,210) and the reference method ($41,290) are listed in Tables 8-1 and 8-2, respectively. The total TPH measurement cost for the EnSys Petro Test System was 75 percent less than that for the reference method. Although the EnSys Petro Test System analytical results did not have the same level of detail (for example, quantitative data) as the reference method analytical results or comparable QA/QC data, the EnSys Petro Test System provided semiquantitative TPH analytical results on site at significant cost savings. In addition, use of the EnSys Petro Test System 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 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.

Table 8-2. Reference Method Cost Summary

Item	Number of Samples Analyzed	Cost per Analysis ($)	Itemized Cost ($)
Soil environmental samples			
GRO	56	111	6,216
Extract duplicates	10	55.50	555
EDRO	66	142	9,372
Extract duplicates	12	71	852
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
Total Cost[a]			**$41,290**

Note:

[a] The total dollar amount was rounded to the nearest $10.

Chapter 9
Summary of Demonstration Results

As discussed throughout this ITVR, the EnSys Petro Test System was demonstrated by using it to analyze 66 soil environmental samples, 89 soil PE samples, and 36 liquid PE samples. In addition to these 191 samples, 12 extract duplicates prepared using the environmental samples were analyzed. The environmental samples were collected from four 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 EnSys Petro Test System.

The EnSys Petro Test System 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 (± 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 EnSys Petro Test System 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 EnSys Petro Test System exhibited the following desirable characteristics of a field TPH measurement device: (1) good precision and (2) high sample throughput. In addition, the EnSys Petro Test System exhibited moderate measurement costs.

A significant number of the EnSys Petro Test System TPH results were determined to be inconclusive because the detection level used by SDI were not appropriate to address the demonstration objectives. Overall, the device's results did not compare well with those of the reference method; in general, the device exhibited a high positive bias. In addition, the device showed a significant response to several interferents that are not PHCs—for example, >25 percent to PCE; >24 percent to turpentine; and >28 percent to 1,2,4-trichlorobenzene. These findings indicated that the accuracy of TPH measurement using the device will likely be impacted by the presence of halogenated solvents, naturally occurring oil and grease, and chlorinated semivolatile organic contaminants such as chlorinated pesticides and PCBs in soil samples. Collectively, the demonstration findings indicated that the user should exercise caution when considering the device for a site-specific field TPH measurement application.

Table 9-1. Summary of EnSys Petro TestSystem Results for the Primary Objectives

Primary Objective	Evaluation Basis	Performance Results	
		EnSys Petro Test System	Reference Method
P1 Determine the method detection limit	Method detection limit based on TPH analysis of seven low-concentration-range diesel soil PE samples	The device's TPH concentation ranges for six of seven samples overlapped the reference method results.	6.32 mg/kg
P2 Evaluate the accuracy and precision of TPH measurement	Pairwise comparison of EnSys Petro Test System and reference method TPH results for (1) 66 soil environmental samples collected from four areas; (2) 28 soil PE samples, including blank, weathered gasoline, and diesel soil samples; and (3) 6 liquid PE samples consisting of neat weathered gasoline and diesel	The EnSys Petro Test System results for 16 of 66 soil environmental samples were inconclusive. Of the remaining 50 results, the device's TPH concentration ranges overlapped the reference method results for only 8 samples (16 percent); 36 EnSys Petro Test System results were biased high, and 6 results were biased low. The EnSys Petro Test System results for 12 of 28 soil PE samples were inconclusive. Of the remaining 16 results, the device's TPH concentration ranges overlapped the reference method results for only 5 samples (31 percent); 9 EnSys Petro Test System results were biased high, and 2 results were biased low. The EnSys Petro Test System results for all 6 liquid PE samples were inconclusive.	
	Comparison of project-specific action level conclusions of the EnSys Petro Test System with those of the reference method for 66 soil environmental and 34 soil PE samples	The EnSys Petro Test System results for 3 of 66 soil environmental samples were inconclusive. Of the remaining 63 results, the device's conclusions agreed with those of the reference method for 41 samples (65 percent); 21 EnSys Petro Test System conclusions were false positives, and 1 was a false negative. The EnSys Petro Test System results for 14 of 34 soil PE samples were inconclusive. Of the remaining 20 results, the device's conclusions agreed with those of the reference method for 15 samples (75 percent); 3 EnSys Petro Test System conclusions were false positives, and 2 were false negatives.	
	Overall precision for soil environmental, soil PE, and liquid PE sample replicates	Soil environmental samples (11 triplicate sets) 　The TPH concentration ranges were the same for each field triplicate set.	Soil environmental samples (11 triplicate sets) 　RSD range: 4 to 39 percent 　Median RSD: 16 percent
		Soil PE samples (8 replicate sets) 　The TPH concentration ranges were the same for 6 of the 8 sets of replicates. Of the remaining 2 replicate sets, only one sample TPH concentration range in each set was different from the others.	Soil PE samples (7 replicate sets) 　RSD range: 5 to 13 percent 　Median RSD: 8 percent
		Liquid PE samples (2 triplicate sets) 　The TPH concentration ranges were the same for each triplicate set.	Liquid PE samples (2 triplicate sets) 　RSDs: 5 and 6 percent 　Median RSD: 5.5 percent
	Analytical precision for extract duplicates for soil environmental samples (12 for the EnSys Petro Test System and 12 for the reference method)	The TPH concentration ranges were the same for each extract duplicate set.	RPD range: 0 to 11 Median RPD: 3

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Table 9-1. Summary of EnSys Petro Test System Results for the Primary Objectives (Continued)

Primary Objective	Evaluation Basis	Performance Results	
		EnSys Petro Test System	Reference Method
P3 Evaluate the effect of interferents 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)	MTBE: 0 percent PCE: >25 percent Stoddard solvent: >26 percent Turpentine: >24 percent 1,2,4-Trichlorobenzene: >28 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
	Comparison of TPH results (simple, nonstatistical comparison for the EnSys Petro Test System and one-way analysis of variance for the reference method) for weathered gasoline and diesel soil PE samples without and with interferents at two levels Interferents for weathered gasoline soil PE samples: MTBE, PCE, Stoddard solvent, and turpentine Interferents for diesel soil PE samples: Stoddard solvent; turpentine; 1,2,4-trichlorobenzene; and humic acid	The TPH results were inconclusive for all interferents.	MTBE, a petroleum hydrocarbon, did not cause statistically significant interference at either of the two levels.
			PCE caused statistically signficant interference only at the high level.
			Stoddard solvent, a petroleum hydrocarbon, caused statistically significant interference at both levels for weathered gasoline and diesel samples.
			Turpentine caused statisticallysignificant interference (1) at both levels for weathered gasoline samples and (2) only at the high level for diesel samples.
			1,2,4-Trichlorobenzene causedstatistically significant interference only at the high level.
			Humic acid results were inconclusive.
P4 Evaluate the effect of soil moisture content on TPH measurement	Comparison of TPH results (simple, nonstatistical comparison for the EnSys Petro Test System and two-sample Student's t-test for the reference method) 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	The TPH results were inconclusive for both weathered gasoline and diesel soil PE samples.	Soil moisture content did not have a statistically significant impact.
P5 Measure the time required for TPH measurement (sample throughput)	Total time from sample receipt through preparation of the draft data package	39 hours, 35 minutes, for TPH measurement of 66 soil environmental samples, 89 soil PE samples, 36 liquid PE samples, and 12 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, andIDW disposal) for TPH measurement of 66 soil environmental samples, 89 soil PE samples, 36 liquid PE samples, and 12 extract duplicates	$10,210 (including the daily rental cost of the EnSys/EnviroGard Common Accessory Kit, which can be purchased for $1,999)	$41,290

Table 9-1. Summary of EnSys Petro Test System Results for the Primary Objectives (Continued)

Notes:

>	=	Greater than	PCE	=	Tetrachloroethene
IDW	=	Investigation-derived waste	PE	=	Performance evaluation
mg/kg	=	Milligram per kilogram	RPD	=	Relative percent difference
MTBE	=	Methyl-tert-butyl ether	RSD	=	Relative standard deviation

[a]   All statistical comparisons were made at a significance level of 5 percent.

Table 9-2. Summary of EnSys Petro Test System Results for the Secondary Objectives

Secondary Objective	Performance Results
S1 Skill and training requirements for proper device operation	The device can be operated by one person with basic wet chemistry skills. The device's user guides 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. Minimal effort is required to estimate a TPH concentration range using the device; the sign (negative or positive) associated with the differential photometer reading allows the user to determine the TPH concentration range for a given sample. At the end of the demonstration, SDI reported 203 TPH results. Of these, fewer than 5 percent required corrections, which primarily involved data entry errors.
S2 Health and safety concerns associated with device operation	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.
S3 Portability of the device	The device is battery-operated and requires no alternating current power source. The device can be easily moved between sampling areas in the field, if necessary.
S4 Durability of the device	The device is housed in a hard-plastic carrying case to prevent damage to the device. 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.
S5 Availability of device and spare parts	All items in the device are available from SDI. During a 1-year warranty period, SDI will supply replacement parts for the device by overnight courier service at no cost unless the reason for a part failure involves misuse of the device.

Chapter 10
References

AEHS. 1999. "State Soil Standards Survey." *Soil & Groundwater*. December 1999/January 2000.

API. 1994. Interlaboratory Study of Three Methods for Analyzing Petroleum Hydrocarbons in Soils. API Publication Number 4599. March.

API. 1996. "Compilation of Field Analytical Methods for Assessing Petroleum Product Releases." Publication Number 4635. December.

API. 1998. "Selecting Field Analytical Methods: A Decision-Tree Approach." Publication Number 4670. August.

ASTM. 1998. "Standard Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water." Designation: D 3586-95. *Annual Book of ASTM Standards*. Volume 11.01.

California Environmental Protection Agency. 1999. Memorandum Regarding Guidance for Petroleum Hydrocarbon Analysis. From Bart Simmons, Chief, Hazardous Materials Laboratory. To Interested Parties. October 21.

Dryoff, George V. Editor. 1993. "Manual of Significance of Tests for Petroleum Products." 6th Edition. American Society for Testing and Materials. ASTM Manual Series: MNL 1.

EPA. 1983. "Methods for Chemical Analysis of Water and Waste." Revision. Environmental Monitoring and Support Laboratory. Cincinnati, OH. EPA 600-4-79-020. March.

EPA. 1996. "Test Methods for Evaluating Solid Waste." Volumes 1A through 1C. SW-846. Third Edition. Update III. OSWER. Washington, DC. December.

EPA. 2000. "Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil Demonstration Plan." Office of Research and Development. Washington, DC. EPA/600/R-01/060. June.

Florida Department of Environmental Protection. 1996. "FL-PRO Laboratory Memorandum." Bureau of Waste Cleanup. Accessed on April 21. On-Line Address: www.dep.state.fl.us/labs/docs/flpro.htm

Fritz, James S., and George H. Schenk. 1987. *Quantitative Analytical Chemistry*. Allyn and Bacon, Inc. Boston, Massachusetts. Fifth Edition.

Gary, J.H., and G.E. Handwerk. 1993. *Petroleum Refining: Technology and Economics*. Marcel Dekker, Inc. New York, New York.

Massachusetts Department of Environmental Protection. 2000. "VPH/EPH Documents." Bureau of Waste Site Cleanup. Accessed on April 13. On-Line Address: www.state.ma.us/dep/bwsc/vp_eph.htm

Means. 2000. *Environmental Remediation Cost Data-Unit Price*. Kingston, Massachusetts.

Provost, Lloyd P., and Robert S. Elder. 1983. "Interpretation of Percent Recovery Data." *American Laboratory*. December. Pages 57 through 63.

Rittenburg, James H. 1990. *Development and Application of Immunoassay for Food Analysis*. Elsevier Applied Science. London, England, and New York, New York.

SDI. 1999. "PETRO Soil Test Technical Guide."

SDI. 2000. "Harnessing the Antibody—The Fundamentals of Enzyme Immunoassay."

Speight, J.G. 1991. *The Chemistry and Technology of Petroleum*. Marcel Dekker, Inc. New York, New York.

Texas Natural Resource Conservation Commission. 2000. "Waste Updates." Accessed on April 13. On-Line Address: www.tnrcc.state.tx.us/permitting/wastenews.htm#additional

Zilis, Kimberly, Maureen McDevitt, and Jerry Parr. 1988. "A Reliable Technique for Measuring Petroleum Hydrocarbons in the Environment." Paper Presented at the Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater. National Waste Water Association. Houston, Texas.

Appendix
Supplemental Information Provided by the Developer

This appendix contains supplemental information provided by SDI. After the introduction, this appendix discusses sample screening and device specificity.

Introduction

The EnSys Petro Test System used in the SITE demonstration is one of 10 distinctly different devices that SDI offers for on-site TPH measurement. The selection of the "best" device for a particular application depends on the type of contamination present, the contaminant concentrations expected, the data quality objective (such as semiquantitative or quantitative data), the number of samples to be analyzed, cost, and other considerations. Usually most of these variables are known before on-site analysis begins, and an SDI representative assists the user in selecting the appropriate device.

For the demonstration, the EnSys Petro Test System was chosen because it responds well to a variety of fuel types, particularly gasoline and diesel. The EnSys Petro Test System does not detect heavier fuels or measure aliphatic hydrocarbon compounds. The device has a wide dynamic range and is listed in EPA SW-846 Method 4030.

Sample Screening (Erring on the Positive Side)

The EnSys Petro Test System is a semiquantitative device that rapidly screens soil samples for the presence of petroleum fuel compounds; the device effectively detects the presence of PHCs. Because the antibody employed in this device has a different sensitivity to each of the various petroleum products, if the device is calibrated using a "typical" fuel calibrator, the device will not quantitatively report results for a specific petroleum product. Where there are mixtures of fuels, such as in the samples used in the SITE demonstration, the EnSys Petro Test System is calibrated to the least reactive fuel known to be present in order to ensure that all PHCs are detected. This approach can lead to elevated results for those PHCs to which the device is most sensitive. To perform a quantitative determination for a petroleum product, the fuel type present must be known and the device must be calibrated accordingly.

The EnSys Petro Test System is set up to have a positive bias of about 30 percent in order to ensure that even when the device is calibrated with the specific petroleum product of interest, the concentrations present will not be underreported. This is particularly important in screening scenarios where a nondetect or low-level result could have serious consequences; an elevated result is clearly a positive and at worst will trigger additional testing. Not all SDI measurement devices are biased high; however, it is important to be conservative with a device frequently employed in screening for hot spots.

Device Specificity

The ORO or heavy-range petroleum products will probably not be detected with the EnSys Petro Test System. The device is used almost exclusively for GRO and DRO measurement.

If a site contains a mixture of gasoline and diesel compounds, a simple correlation between device and laboratory results for the same samples will allow appropriate device calibration prior to field analysis.

The liquid samples analyzed in the demonstration clearly had high TPH concentrations. Despite the high TPH concentrations, the device could not detect PHCs in some samples. Until SDI understands the exact nature of these samples, it cannot address the device's performance during the demonstration.

During the demonstration, SDI used three detection levels to estimate the TPH concentration ranges for all samples. These detection levels were not always consistent with the project-specific action levels, which varied depending on sample source and type. As a result, many TPH results that were reported as >1,000 mg/kg were determined to be inconclusive when compared to the action levels

(1,500 and 2,000 mg/kg) that were above the highest detection level (1,000 mg/kg).

For several samples analyzed during the demonstration, the EnSys Petro Test System exhibited a more consistent response than the reference method, as was indicated by the precision associated with the replicate sample TPH measurements.

Soil samples analyzed during the demonstration were collected from different locations around the country and thus were not typical of a single site. A preliminary comparison of EnSys Petro Test System and reference method TPH results would allow the user to develop a conversion factor that would take into account site-specific factors, including soil type and contamination weathering. Application of such a conversion factor would result in better comparability between the device and reference method TPH results.