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Office of Research and
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Washington, DC 20460

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September 2001

EPA

Innovative Technology Verification Report

Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil

Wilks Enterprise, Inc. Infracal® TOG/TPH Analyzer

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Innovative Technology Verification Report

Wilks Enterprise, Inc.
Infracal® TOG/TPH Analyzer

Prepared by

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Contract No. 68-C5-0037

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Notice

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

ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM
VERIFICATION STATEMENT

TECHNOLOGY TYPE:	**FIELD MEASUREMENT DEVICE**
APPLICATION:	**MEASUREMENT OF TOTAL PETROLEUM HYDROCARBONS**
TECHNOLOGY NAME:	**Infracal® TOG/TPH ANALYZER**
COMPANY:	**WILKS ENTERPRISE, INC.**
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VERIFICATION PROGRAM DESCRIPTION

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

PROGRAM OPERATION

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

DEMONSTRATION DESCRIPTION

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

The Infracal® TOG/TPH Analyzer was demonstrated by using it to analyze 74 soil environmental samples, 91 soil performance evaluation (PE) samples, and 50 liquid PE samples. The environmental samples were collected in five areas contaminated with gasoline, diesel, lubricating oil, or other petroleum products, and the PE samples were obtained from a commercial provider. Collectively, the environmental and PE samples provided the different matrix types and the different levels and types of petroleum hydrocarbon (PHC) contamination needed to perform a comprehensive evaluation of the Infracal® TOG/TPH Analyzer. During the demonstration, Wilks analyzed most of the samples using the device equipped with one of two sample stages: Model CVH or Model HATR-T. Only 8 percent of the samples were analyzed using both models.

The accompanying notice is an integral part of this verification statement. September 2001

In general, Model CVH was used to analyze samples containing gasoline range organics (GRO) and Model HATR-T was used to analyze samples that did not contain GRO. For this reason, the performance of the Infracal® TOG/TPH Analyzer as a whole was evaluated, but that of each model was not. A complete description of the demonstration and a summary of its results are available in the "Innovative Technology Verification Report: Field Measurement Devices for Total Petroleum Hydrocarbons in Soil—Wilks Enterprise, Inc., Infracal® TOG/TPH Analyzer" (EPA/600/R-01/088).

TECHNOLOGY DESCRIPTION

The Infracal® TOG/TPH Analyzer developed by Wilks is based on infrared analysis. The device can be operated as either Model CVH or Model HATR-T simply by switching sample stages. Model CVH uses a sample stage that contains a quartz cuvette, and Model HATR-T uses the cubic zirconia horizontal attenuated total reflection sample stage. Model CVH is used when a sample contains GRO, extended diesel range organics (EDRO), or both, and Model HATR-T is used when a sample contains only EDRO. Because of the environmental hazards associated with chlorofluorocarbons, Model HATR-T, which uses Vertrel® MCA, is preferred over Model CVH, which uses Freon 113, a chlorofluorocarbon. However, according to Wilks, Model CVH is more sensitive and can achieve a lower detection limit than Model HATR-T.

The Infracal® TOG/TPH Analyzer includes a single-beam, fixed-wavelength, nondispersive infrared filter-based spectrophotometer with a dual detector system. In Model CVH, a pulsed beam of infrared radiation from a tungsten lamp is transmitted through a quartz cuvette that contains a sample extract. In Model HATR-T, which is based on an evaporation technique, an extract is placed directly on the sample stage. The radiation that passes through the extract enters the dual detector system, whose filters isolate a reference wavelength (2,500 nanometers) and an analytical wavelength (3,400 nanometers) to measure PHCs present in the extract.

During the demonstration, Wilks first dried a given soil sample by adding silica gel. Extraction of PHCs from the sample was typically performed by adding 20 milliliters of Freon 113 (for Model CVH) or Vertrel® MCA (for Model HATR-T) to 20 grams of the sample. The mixture was agitated by means of vigorous shaking, and the sample extract was decanted into an extraction reservoir. Using an air syringe, Wilks filtered the extract (1) into a quartz cuvette that was placed in Model CVH or (2) into a beaker and then transferred the extract to the center of the HATR-T sample stage using a microsyringe. Finally, Wilks read the TPH concentration in milligrams per kilogram on a digital display.

VERIFICATION OF PERFORMANCE

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

Method Detection Limit: Based on the TPH results for seven low-concentration-range diesel soil PE samples, the method detection limits were determined to be 76 and 4.79 milligrams per kilogram for the Infracal® TOG/TPH Analyzer (Model HATR-T) and reference method, respectively.

Accuracy and Precision: Seventy-two of 101 Infracal® TOG/TPH Analyzer results (71 percent) used to draw conclusions regarding whether the TPH concentration in a given sampling area or sample type exceeded a specified action level agreed with those of the reference method; 2 device conclusions were false positives, and 27 were false negatives.

Of 105 Infracal® TOG/TPH Analyzer results used to assess measurement bias, 22 were within 30 percent, 28 were within 30 to 50 percent, and 55 were not within 50 percent of the reference method results; 78 device results were biased low, and 27 were biased high.

For soil environmental samples, the Infracal® TOG/TPH Analyzer results were statistically (1) the same as the reference method results for one of the five sampling areas and (2) different from the reference method results for four sampling areas. For soil PE samples, the device results were statistically different from the reference method results for medium- and high-concentration-range weathered gasoline and diesel samples. For liquid PE samples, the device results were statistically different from the reference method results for both weathered gasoline and diesel samples.

The Infracal® TOG/TPH Analyzer results correlated highly with the reference method results for two of the five sampling areas and weathered gasoline soil PE samples (the square of the correlation coefficient [R^2] values ranged from 0.85 to 0.94, and F-test probability values were less than 5 percent). The device results correlated moderately with the reference method results for two sampling areas and diesel soil PE samples (R^2 values ranged from 0.59 to 0.68, and F-test probability values

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were less than 5 percent). The device results correlated weakly with the reference method results for one sampling area (the R^2 value was 0.14, and the F-test probability value was 35.32 percent).

Comparison of the Infracal® TOG/TPH Analyzer and reference method median relative standard deviations (RSD) showed that the device exhibited less overall precision than the reference method. Specifically, the median RSD ranges were 5 to 30 percent and 5.5 to 18 percent for the device and reference method, respectively.

Effect of Interferents: The Infracal® TOG/TPH Analyzer showed a mean response of less than 1 percent for neat tetrachloroethene (PCE); neat 1,2,4-trichlorobenzene; and soil spiked with humic acid. The device's mean responses for neat methyl-tert-butyl ether (MTBE), Stoddard solvent, and turpentine were 62, 120, and 77 percent, respectively. The reference method showed varying mean responses for MTBE (39 percent); PCE (17.5 percent); Stoddard solvent (85 percent); turpentine (52 percent); 1,2,4-trichlorobenzene (50 percent); and humic acid (0 percent). For the demonstration, MTBE and Stoddard solvent were included in the definition of TPH.

Effect of Moisture Content: Soil moisture content had a statistically significant impact on the Infracal® TOG/TPH Analyzer TPH results for diesel soil PE samples but not on those for weathered gasoline soil PE samples. Specifically, the device showed a three-fold increase in TPH results for diesel samples when the soil moisture content was increased from less than 1 percent to 9 percent. The reference method TPH results were unaffected when the soil moisture content was increased.

Measurement Time: From the time of sample receipt, Wilks required 35 hours, 30 minutes, to prepare a draft data package containing TPH results for 215 samples compared to 30 days for the reference method.

Measurement Costs: For the Infracal® TOG/TPH Analyzer, the TPH measurement cost for 215 samples was estimated to be $6,450 (including the monthly rental cost of the device, whose purchase price is $6,200) compared to $44,410 for the reference method.

Skill and Training Requirements: The Infracal® TOG/TPH Analyzer can be operated by one person with basic wet chemistry skills. The sample analysis procedure for the device can be learned in the field with a few practice attempts. During the demonstration, some of the items used during the sample preparation procedure made the TPH measurement procedure less simple and more time-consuming.

Portability: The Infracal® TOG/TPH Analyzer can be easily moved between sampling areas in the field, if necessary. It can be operated using a 110-volt alternating current power source or a direct current power source.

Durability and Availability of the Device: During a 1-year warranty period, if the infrared spectrophotometer or a sample stage malfunctions, Wilks will provide a replacement item within 48 hours on loan for a fee of $75 while the original item is being repaired. During the demonstration, Model CVH proved to be durable and did not malfunction or become damaged. However, the spectrophotometer malfunctioned when the Model CVH sample stage was replaced with the Model HATR-T sample stage. Wilks does not supply some items necessary for TPH measurement using the device (for example, extraction solvents). The availability of replacement or spare parts not supplied by Wilks depends on their manufacturer or distributor.

In summary, during the demonstration, the Infracal® TOG/TPH Analyzer exhibited the following desirable characteristics of a field TPH measurement device: (1) sensitivity to interferents that are PHCs (MTBE and Stoddard solvent), (2) lack of sensitivity to interferents that are not PHCs (PCE; 1,2,4-trichlorobenzene; and humic acid), (3) high sample throughput, and (4) low measurement costs. However, the device TPH results did not compare well with the reference method results. In addition, turpentine biased the device TPH results high, indicating that the accuracy of TPH measurement using the device will likely be impacted by naturally occurring oil and grease present in soil that are not removed by silica gel. Also, the device TPH results for diesel soil PE samples showed a three-fold increase when the soil moisture content was increased by 8 percentage points. Finally, the device results obtained using the two sample stages did not agree. Collectively, these demonstration findings indicated that the Infracal® TOG/TPH Analyzer may be considered for TPH screening purposes; however, the user should exercise caution when considering the device for a field TPH measurement application requiring definitive results.

Original
signed by

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Director
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Office of Research and Development

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

Foreword

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

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

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

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

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

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Abstract

The Infracal® TOG/TPH Analyzer developed by Wilks Enterprise, Inc. (Wilks), was demonstrated under the U.S. Environmental Protection Agency Superfund Innovative Technology Evaluation Program in June 2000 at the Navy Base Ventura County site in Port Hueneme, California. The purpose of the demonstration was to collect reliable performance and cost data for the Infracal® TOG/TPH Analyzer and six other field measurement devices for total petroleum hydrocarbons (TPH) in soil. In addition to assessing ease of device operation, the key objectives of the demonstration included determining the (1) method detection limit, (2) accuracy and precision, (3) effects of interferents and soil moisture content on TPH measurement, (4) sample throughput, and (5) TPH measurement costs for each device. The demonstration involved analysis of both performance evaluation (PE) samples and environmental samples collected in five areas contaminated with gasoline, diesel, lubricating oil, or other petroleum products. The performance and cost results for a given field measurement device were compared to those for an off-site laboratory reference method, "Test Methods for Evaluating Solid Waste" (SW-846) Method 8015B (modified). During the demonstration, Wilks required 35 hours, 30 minutes, for TPH measurement of 215 samples. The TPH measurement costs for these samples were estimated to be $6,450 for the Infracal® TOG/TPH Analyzer compared to $44,410 for the reference method. The method detection limits were determined to be 76 and 4.79 milligrams per kilogram for the device and reference method, respectively. During the demonstration, the device exhibited sensitivity to interferents that are petroleum hydrocarbons (methyl-tert-butyl ether and Stoddard solvent) and lack of sensitivity to interferents that are not petroleum hydrocarbons (tetrachloroethene; 1,2,4-trichlorobenzene; and humic acid). The device exhibited good precision for soil and liquid PE samples but not for environmental samples. The device TPH results (1) did not compare well with the reference method results and (2) were significantly impacted by soil moisture content (for diesel soil PE samples) and by turpentine, an interferent that is not a petroleum hydrocarbon. In addition, some of the items used during the sample preparation procedure made the TPH measurement procedure less simple and more time-consuming during the demonstration. Collectively, these demonstration findings indicated that the Infracal TOG/TPH Analyzer may be considered for TPH screening purposes; however, the user should exercise caution when considering the device for a field TPH measurement application requiring definitive results.

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Abbreviations, Acronyms, and Symbols

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

Abbreviations, Acronyms, and Symbols (Continued)

MMT	Monitoring and Measurement Technology
MS	Matrix spike
MSD	Matrix spike duplicate
MTBE	Methyl-tert-butyl ether
n-C_x	Alkane with “x” carbon atoms
NDIR	Nondispersive infrared
NERL	National Exposure Research Laboratory
NEX	Naval Exchange
ng	Nanogram
nm	Nanometer
ORD	Office of Research and Development
ORO	Oil range organics
OSWER	Office of Solid Waste and Emergency Response
PC	Petroleum company
PCB	Polychlorinated biphenyl
PCE	Tetrachloroethene
PE	Performance evaluation
PHC	Petroleum hydrocarbon
PPE	Personal protective equipment
PRA	Phytoremediation Area
PRO	Petroleum range organics
QA	Quality assurance
QC	Quality control
R^2	Square of the correlation coefficient
RPD	Relative percent difference
RSD	Relative standard deviation
SFT	Slop Fill Tank
SITE	Superfund Innovative Technology Evaluation
STL Tampa East	Severn Trent Laboratories in Tampa, Florida
SW-846	“Test Methods for Evaluating Solid Waste”
TOG	Total oil and grease
TPH	Total petroleum hydrocarbons
UST	Underground storage tank
VPH	Volatile petroleum hydrocarbon
Wilks	Wilks Enterprise, Inc.

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Chapter 1
Introduction

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

This innovative technology verification report (ITVR) presents demonstration performance results and associated costs for the Infracal® TOG/TPH Analyzer developed by Wilks Enterprise, Inc. (Wilks). 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 Wilks 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 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).

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 Infracal® TOG/TPH Analyzer is based and the field measurement device itself. Because TPH is a "method-defined parameter," the performance results for the device are compared to the results obtained using an off-site laboratory measurement method—that is, a reference method. Details on the selection of the reference method and laboratory are provided in Chapter 5.

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

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

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

1.3 Components and Definition of TPH

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

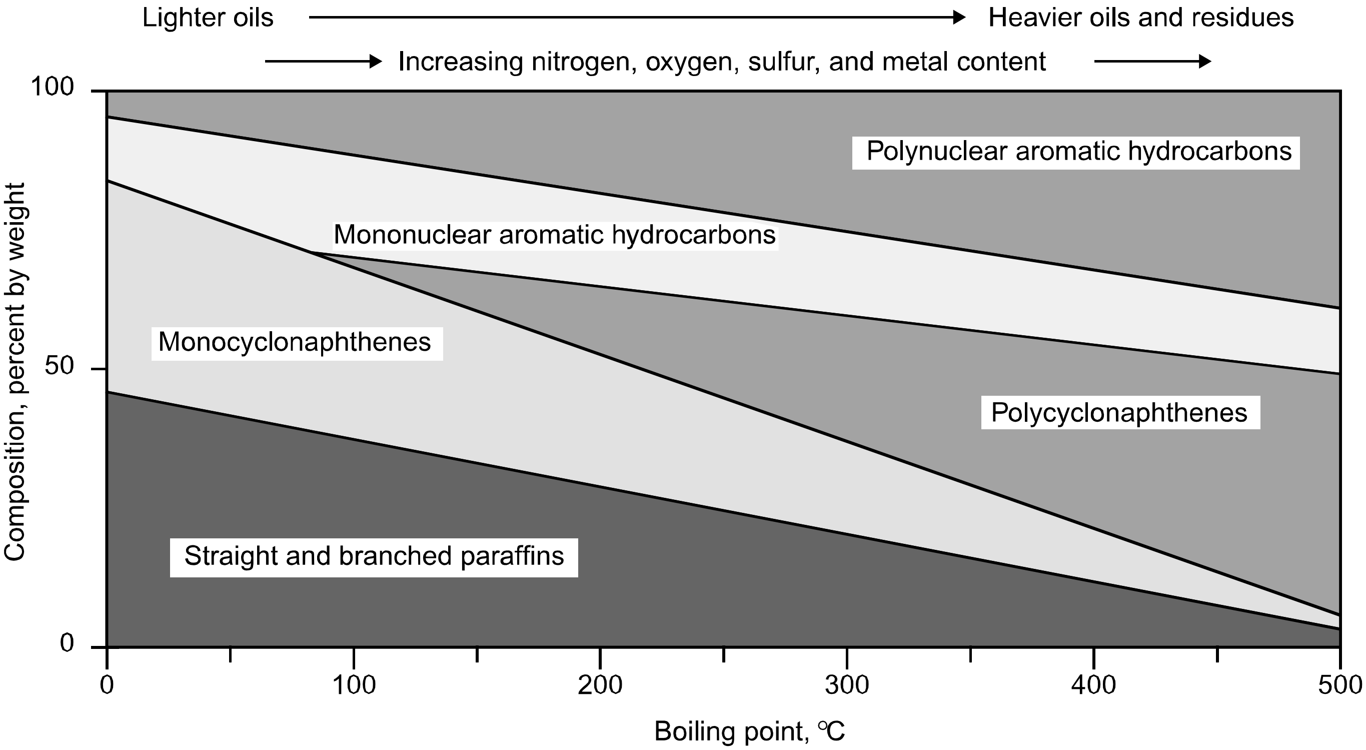
1.3.1 Composition of Petroleum and Its Products

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

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

The distribution of paraffins, naphthenes, and aromatic hydrocarbons depends on the source of crude oil. For example, Pennsylvania crude oil contains high levels of paraffins (about 50 percent), whereas Borneo crude oil contains less than 1 percent paraffins. As shown in Figure 1-1, the proportion of straight or branched paraffins decreases with increasing molecular weight or boiling point fraction for a given crude oil; however, this is not true for naphthenes or aromatic hydrocarbons. The proportion of monocyclonaphthenes decreases with increasing molecular weight or boiling point fraction, whereas the opposite is true for polycyclonaphthenes (for example, tetralin and decalin) and polynuclear aromatic hydrocarbons; the proportion of mononuclear aromatic hydrocarbons appears to be independent of molecular weight or boiling point fraction.

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



Source: Speight 1991

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

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

1.3.1.1 Gasoline

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

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

1.3.1.2 Naphthas

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

1.3.1.3 Kerosene

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

1.3.1.4 Jet Fuels

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

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 Infrared Analysis and the Infracal® TOG/TPH Analyzer, Models CVH and HATR-T

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

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

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

- A **quantitative measurement device** measures TPH concentrations ranging from its reporting limit through its linear range. The measurement result is reported as a single, numerical value that has an established precision and accuracy.

- A **semiquantitative measurement device** measures TPH concentrations above its reporting limit. The measurement result may be reported as a concentration range with lower and upper limits.

- A **qualitative measurement device** indicates the presence or absence of PHCs above or below a specified value (for example, the reporting limit or an action level).

The Infracal® TOG/TPH Analyzer is a field measurement device capable of providing quantitative TPH measurement results. Optical measurements made using the Infracal® TOG/TPH Analyzer are based on infrared analysis, which is described in Section 2.1. The Infracal® TOG/TPH Analyzer can be calibrated (1) at the factory by the developer using a standard hydrocarbon mixture specified by the user or (2) on site by the user using site-specific laboratory results or calibration standards. The device uses point-to-point calibration to correct for nonlinearity. During the demonstration, Wilks used calibration standards to calibrate the Infracal® TOG/TPH Analyzer.

Section 2.1 describes the technology upon which the Infracal® TOG/TPH Analyzer is based; Section 2.2 describes the device itself, and Section 2.3 provides Wilks 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 Infracal® TOG/TPH Analyzer. Detailed operating procedures for the device, including soil extraction, TPH measurement, and TPH concentration calculation procedures, are available from Wilks. Supplemental information provided by Wilks is presented in the appendix.

2.1 Description of Infrared Analysis

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

Infrared spectrophotometry generally covers the 1- to 15-µm wavelength region. All organic molecules and some inorganic ions absorb light energy in this region. Absorbance of infrared energy results in changes in vibrational motion in a molecule. The molecular vibrations observed may be divided into two types, stretching and bending. Stretching is the rhythmic movement of the atoms back and forth along the bond axis, whereas bending involves a change in bond angle between two atoms that are bonded to a third atom or the movement of a group of atoms with respect to the rest of the molecule. Based on the unique absorbance and vibrational motion associated with each compound, the type of compound in a sample can be identified using infrared analysis (Fritz and Schenk 1987).

The energy associated with shorter or near-infrared wavelengths (less than 4 µm) used for TPH measurement causes mostly stretching vibrations of bonds between hydrogen and heavier atoms. TPH measurement using infrared analysis involves absorbance measurement because the carbon-hydrogen bonds in the hydrocarbons absorb infrared light. During infrared analysis, absorbances associated with CH, CH_2, and CH_3 configurations are measured at a wavelength close to 3,400 nanometers (nm). Specifically, infrared devices that operate in the 3,380- to 3,500-nm wavelength range should be able to measure CH (3,380 nm), CH_2 (3,420 nm), and CH_3 (3,500 nm) configurations (Simard and others 1951).

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

Table 2-1. Absorbance Values of CH, CH_2, and CH_3 Groups

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

Source: Simard and others 1951

During infrared analysis using Model CVH, a sample extract is placed in a quartz cuvette that is then inserted into the spectrophotometer. A beam of infrared light is then passed through the sample extract. Infrared sources are generally continuum sources, which emit radiation at intensities that vary smoothly over ranges of wavelengths.

A typical example of an infrared source for near-infrared instruments used for TPH measurement is a tungsten lamp (Fritz and Schenk 1987; Ewing 1969).

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

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

where

A = Absorbance

I_0 = Intensity of light source

I = Intensity of light that passes through the sample extract

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

$$A = 0bc \qquad (2\text{-}2)$$

where

A = Absorbance

0 = Molar absorptivity (centimeter per mole per L)

b = Light path length (centimeter)

c = Concentration of absorbing species (mole per L)

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

During infrared analysis using Model HATR-T, a sample extract is transferred onto the center of the sample stage, which is made of cubic zirconia. Model HATR-T is based on the principle of horizontal attenuated total reflection of infrared radiation, whereas Model CVH is based on transmission of infrared radiation. In horizontal attenuated total reflection, when a beam of radiation encounters an interface between two media such as the cubic zirconia and sample extract, total reflection occurs if the beam is approaching the interface from the side with the higher refractive index and if the angle of incidence is greater than a critical angle that depends on the two refractive indices. Because some portion of the energy of the radiation crosses the interface in this process, the sample extract absorbs some radiation and reflects the rest. The reflected beam contains less energy than the incident beam, and a wavelength scan of the reflected beam produces an absorption spectrum that is a measure of the hydrocarbon concentration in the extract.

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

2.2 Description of Infracal® TOG/TPH Analyzer

The Infracal® TOG/TPH Analyzer was developed by Wilks. The device is identified according to the sample stage used. The device can be operated as either Model CVH or Model HATR-T simply by switching the sample stages. Model CVH uses the CVH sample stage, which contains a quartz cuvette, and Model HATR-T uses the cubic zirconia horizontal attenuated total reflection sample stage. Models CVH and HATR-T have been commercially available since 1996 and 1997, respectively. Model CVH is used when a sample contains GRO, EDRO, or both, and Model HATR-T is used when a sample contains only EDRO. Based on the hazards associated with the solvents used, Model HATR-T, which uses Vertrel® MCA, is preferred over Model CVH, which uses Freon 113, a chlorofluorocarbon (CFC). CFCs discharged to the atmosphere are primary contributors to depletion of the earth's stratospheric ozone layer. The United States, as a party to the Montreal Protocol on Substances that Deplete the Ozone Layer and as required by law under the Clean Air Act of 1990, is committed to controlling and eventually phasing out use of CFCs. However, Model CVH is more sensitive and can achieve a lower detection limit than Model HATR-T. This section describes both models of the Infracal® TOG/TPH Analyzer and summarizes their operating procedure.

2.2.1 Device Description

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

As stated in Section 2.2, the only difference between Models CVH and HATR-T involves the sample stage used. In Model CVH, infrared radiation from a tungsten lamp is captured using an elliptical source mirror and transmitted through a quartz cuvette containing a sample extract. The radiation that has passed through the extract enters a dual detector system containing filters that isolate a reference wavelength of 2,500 nm and an analytical wavelength of 3,400 nm. The reference wavelength stabilizes device response and automatically corrects absorbance values for fluctuations in ambient temperature and relative humidity. According to Wilks, Model CVH is suitable for analyzing sample extracts that have been extracted from soil using Freon 113 or other solvents, such as tetrachloroethene, that do not absorb light energy in the measurement range. Wilks used Freon 113 during the demonstration.

Model HATR-T, unlike Model CVH, is based on an evaporation technique and measures residual hydrocarbons after volatile organics evaporate from a sample extract. Therefore, analyses using Model HATR-T result in the loss of some volatile organics in the GRO range. Vertrel® MCA, a hydrochlorofluorocarbon extraction solvent manufactured by DuPont, is used with Model HATR-T. Although hexane can be used as the extraction solvent with Model HATR-T, Wilks recommends use of Vertrel® MCA because (1) it achieves measurement stability more quickly than hexane (in 1.5 to 2 minutes instead of 3 to 5 minutes); (2) it has a lower boiling point than hexane, which results in fewer light-end volatile organics being lost in the evaporation process; and (3) it is less flammable than hexane, resulting in fewer disposal concerns. In addition, Model HATR-T does not require a cuvette to contain a sample extract. The extract is transferred directly to the sample stage.

According to the developer, both Models CVH and HATR-T can measure aromatic and aliphatic hydrocarbons. However, Model CVH can measure both GRO and EDRO, but Model HATR-T primarily measures EDRO. Wilks claims that Model CVH has (1) an method detection limit (MDL) of 3 mg/kg and is linear up to 5,000 mg/kg in soil; (2) a measurement accuracy of plus or minus (±) 1 percent; and (3) a measurement precision of ±1 percent. According to Wilks, Model HATR-T has an MDL of 20 mg/kg and is linear up to 5,000 mg/kg in soil. No information is currently available from Wilks regarding the accuracy or precision of Model HATR-T. An evaluation of the MDLs, accuracy, and precision achieved by both models during the demonstration is presented in Chapter 7.

According to Wilks, the Infracal® TOG/TPH Analyzer can operate in a temperature range of 4 to 43 °C and a relative humidity range of 10 to 60 percent. In addition, Wilks believes that when the device is not in operation, it can be stored in a temperature range of -18 to 52 °C.

Table 2-2 lists the components of the Infracal® TOG/TPH Analyzer, the components of a field sampling kit for measurement of TPH in soil called KIT-10410-S, and additional supplies required for measurement of TPH in soil using the device. The additional supplies are categorized according to whether they are available from Wilks.

Supplies associated with TPH measurement using the Infracal® TOG/TPH Analyzer may also be categorized as either expendable or reusable. KIT-10410-S contains both expendable and reusable supplies. Expendable kit components include silica gel; pipette tips to be used with the 50-microliter pipette; 40-milliliter (mL), volatile organic analysis vials; and extraction reservoirs. Other expendable supplies used during the demonstration

Table 2-2. Infracal® TOG/TPH Analyzer, Model CVH and HATR-T Components and Supplies

Spectrophotometer and accessories
- Infrared spectrophotometer
- CVH or HATR-T sample stage
- Dust cover
- Instruction manual

KIT-10410-S
- Timer (batteries included)
- Battery-powered balance (batteries included)
- Silica gel (60-200 mesh) (500 grams)
- Teflon™ wash bottle (125 milliliters)
- Glass funnel
- 10-milliliter, graduated cylinder
- 100-milliliter, graduated cylinder with stopper
- Air syringe
- 20-milliliter, glass beaker
- Spatula
- 50-microliter pipette with pipette tips (pack of 50)
- 10-microliter syringe
- 250-milliliter syringe
- 40-milliliter, volatile organic analysis vials (box of 50)
- Extraction reservoirs with filter frit and silica gel cartridge (box of 50)
- Reservoir sealer
- Extraction procedure instructions

Supplies available from Wilks
- 10-millimeter, quartz cuvette with Teflon™ cap
- 50-millimeter, quartz cuvette and holder

Supplies not available from Wilks
- Extraction solvent (Freon 113 or Vertrel® MCA)
- External battery pack
- Calibration standards (3-IN-ONE oil in Freon 113 for Model CVH and 3-IN-ONE oil in Vertrel® MCA for Model HATR-T)

included Freon 113 and Vertrel® MCA extraction solvents. The remaining supplies listed in Table 2-2 are reusable.

The Infracal® TOG/TPH Analyzer in its steel box is 7 inches long, 7 inches wide, and 5.5 inches high and weighs about 5 pounds. The device can be operated using a 110- or 220-volt alternating current (AC) power source. The device may also be operated using a direct current (DC) power source such as an external battery pack, which Wilks used during the demonstration.

The Infracal® TOG/TPH Analyzer presents results in units selected by the user during calibration, such as mg/kg in soil, mg/L in liquid, or absorbance values. During the demonstration, Wilks programmed the device to present results as mg/kg in soil. The Infracal® TOG/TPH Analyzer has a standard, nine-pin, female DB9 connector (RS232-C) for serial data communication. Wilks offers an optional software package, InfraWin, that allows the user to connect a personal computer to the device and automatically download, label, and save measurement results; remotely control measurement parameters; generate and store multiple calibration tables; and report measurement results in various numerical and graphical formats. Measurement results may be transferred via the serial communication interface to a serial printer or to an external personal computer. The software package was not used during the demonstration.

According to Wilks, the average sample extraction and analysis time for Models CVH and HATR-T is 10 to 15 minutes per sample. The sample analysis procedure for both models can be learned in the field with a few practice attempts. Wilks also offers a 1-day, on-site training program and provides technical support over the telephone during regular business hours.

According to Wilks, Models CVH and HATR-T are innovative TPH field measurement devices because their spectrophotometer uses a pulsed, infrared light source instead of a "chopper," which mechanically "chops" the light beam to turn the radiation signal on and off. The chopper, which is a primary component of most conventional spectrophotometers, requires more maintenance to prevent drift than does the pulsed, infrared light source. In addition, Model HATR-T does not use Freon 113, which is expensive and is being phased out of use.

2.2.2 Operating Procedure

The Infracal® TOG/TPH Analyzer can be calibrated using known standards. Wilks calibrated the device off site before the demonstration using known standards; specifically, Wilks performed a seven-point calibration for Model CVH and a five-point calibration for Model HATR-T. Calibration standards for Models CVH and HATR-T were prepared by dissolving 3-IN-ONE oil in Freon 113 and Vertrel® MCA, respectively. Model CVH was calibrated using seven standards purchased from a chemical supplier, whereas Model HATR-T was calibrated using five standards prepared by Wilks.

During the demonstration, Wilks first dried a given soil sample by adding silica gel. Extraction of the sample was typically performed by adding 20 mL of Freon 113 (for Model CVH) or Vertrel® MCA (for Model HATR-T) to 20 grams of the sample. The mixture was agitated by means of vigorous shaking. The sample extract was then decanted into an extraction reservoir. Using an air syringe, Wilks filtered the extract (1) into a quartz cuvette that was placed in Model CVH or (2) into a beaker and then transferred the extract to the center of the HATR-T sample stage using a microsyringe. Wilks then pressed the "Run" button and read the concentration on the digital display.

Calibration checks of Model CVH were completed during the demonstration by analyzing known calibration standards at the beginning and end of each day; these checks were performed to ensure that the device's results were within the developer's historical acceptance limits. Zero calibration checks using blank solvent were also conducted at the beginning and end of each day and after analysis of every 10 samples.

2.3 Developer Contact Information

Additional information about the Infracal® TOG/TPH Analyzer can be obtained from the following source:

Wilks Enterprise, Inc.
Ms. Sandy Rintoul
140 Water Street
South Norwalk, CT 06854
Telephone: (203) 855-9136
Fax: (203) 838-9868
E-mail: info@wilksir.com
Internet: www.wilksir.com

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 Infracal® TOG/TPH Analyzer developer, Wilks, at its facility. Wilks used reference laboratory and Infracal® TOG/TPH Analyzer 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 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}.

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 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-C5 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 from the developers and demonstration site representatives. The demonstration design is summarized below.

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

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

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

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

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

During the demonstration, a Wilks field technician operated the Infracal® TOG/TPH Analyzer, Models CVH and HATR-T, 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. Wilks chose to analyze all the demonstration samples.

During the demonstration, Wilks analyzed most of the samples using the Infracal® TOG/TPH Analyzer equipped with either the Model CVH sample stage or the Model HATR-T sample stage; only 8 percent of the samples were analyzed using both models. In general, Model CVH was used to analyze samples containing GRO, and Model HATR-T was used to analyze samples that did not contain GRO. For this reason, this ITVR evaluates the performance of the Infracal® TOG/TPH Analyzer as a whole, not that of each model.

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

4.2.1 *Approach for Addressing Primary Objectives*

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

Primary Objective P1: Method Detection Limit

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

Primary Objective P2: Accuracy and Precision

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

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

Site	Area	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	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.

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, the ratio of the TPH results of a given device to the TPH results of the reference method was calculated. The ratio was used to develop a frequency distribution in order to determine how many of the device and reference method results were within 30 percent, within 50 percent, and outside the 50 percent window.

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

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

To evaluate analytical precision, one set of blind field triplicate environmental samples was collected from each depth interval at one location in each demonstration area except the B-38 Area, where site conditions allowed collection of triplicates in the top depth interval only. Blind triplicate low-, medium-, and high-concentration-range PE samples were also used to evaluate analytical precision because TPH concentrations in environmental samples collected during the demonstration sometimes differed from the analytical results for predemonstration investigation samples. The low- and medium-range PE samples were prepared using Freon 113 as a carrier, which facilitated preparation of homogenous samples. To evaluate a given field measurement device's ability to precisely measure TPH, the relative standard deviation (RSD) of the device and reference method TPH results for triplicate samples was calculated.

Additional information regarding analytical precision was expected to be collected by having the developers and reference laboratory analyze extract duplicates. Extract duplicates were to be 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. However, Wilks did not analyze extract duplicates for soil samples that were designated as such during the demonstration. As a result, the analytical precision of the device was not calculated based on the relative percent difference (RPD) between the TPH results for extract duplicates.

Primary Objective P3: Effect of Interferents

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

(3) 1,2,4-trichlorobenzene and humic acid are similar to those of EDRO. The solubility, availability, and cost of the interferents were also considered during interferent selection. Specific reasons for the selection of the six interferents are presented below.

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

- PCE is not a petroleum product but is detected in the GRO analysis during TPH measurement using a GC. PCE may also be viewed as a typical halogenated solvent that may be present in some environmental samples.

- Stoddard solvent is an aliphatic naphtha compound with a carbon range of n-C_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.

Primary Objective P4: Effect of Soil Moisture Content

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

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

Primary Objective P5: Time Required for TPH Measurement

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

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

Primary Objective P6: Costs Associated with TPH Measurement

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

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

4.2.2 Approach for Addressing Secondary Objectives

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

- The skills and training required for proper device operation (secondary objective S1) were evaluated by observing and noting the skills required to operate the device and prepare the data package during the demonstration and by discussing necessary user training with developer personnel.

- Health and safety concerns associated with device operation (secondary objective S2) were evaluated by observing and noting possible health and safety concerns during the demonstration, such as the types of hazardous substances handled by developer personnel during analysis, the number of times that hazardous substances were transferred from one container to another during the analytical procedure, and direct exposure of developer personnel to hazardous substances.

- The portability of the device (secondary objective S3) was evaluated by observing and noting the weight and size of the device and additional equipment required for TPH measurement as well as how easily the device was set up for use during the demonstration.

- The durability of the device (secondary objective S4) was evaluated by noting the materials of construction of the device and additional equipment required for TPH measurement. In addition, EPA representatives noted likely device failures or repairs that may be

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	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[d]	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-trichlorobenzene 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
bgs = Below ground surface
BVC = Base Ventura County
FFA = Fuel Farm Area
mg/kg = Milligram per kilogram
MTBE = Methyl-tert-butyl ether
NEX = Naval Exchange
PC = Petroleum company
PCE = Tetrachloroethene
PE = Performance evaluation
PHC = Petroleum hydrocarbon
PRA = Phytoremediation Area
SFT = Slop Fill Tank

[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 cores were divided into two samples based on visual observations. The upper layer of the soil core made up one sample, and the lower layer of the soil core made up the second sample.

[d] 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.

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: (1) the FFA, NEX Service Station Area, and PRA at the Navy BVC site; (2) the B-38 Area at the Kelly AFB site; and (3) the SFT Area at the PC site. Samples were collected in all areas except the PRA using a Geoprobe®; in the PRA, samples were collected using a Split Core Sampler.

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

Each core sample section was then transferred to a stainless-steel bowl. The presence of any unrepresentative material such as sticks, roots, and stones was noted in a field logbook, and such material was removed to the extent possible using gloved hands. Any lump of clay in the sample that was greater than about 1/8 inch in diameter was crushed between gloved fingers before homogenization. Each soil sample was homogenized by stirring it for at least 2 minutes using a stainless-steel spoon or gloved hands until the sample was visibly homogeneous. During or immediately following homogenization, any free water was poured from the stainless-steel bowl containing the soil sample into a container designated for IDW. During the demonstration, the field sampling team used only nitrile gloves to avoid the possibility of phthalate contamination from handling samples with plastic gloves. Such contamination had occurred during the predemonstration investigation.

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

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

Table 4-3. Environmental Samples

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

Notes:

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

[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 Wilks.

[c] Wilks did not analyze extract duplicates for soil samples that were designated as such during the demonstration.

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

[e] Model HATR-T was used to analyze these samples.

[f] Model CVH was used to analyze these samples.

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 less than 100 mg/kg; a medium-range sample was spiked to correspond to a TPH concentration range of 100 to 1,000 mg/kg; and a high-range sample was spiked to correspond to a TPH concentration of more than 1,000 mg/kg. To spike each low- and medium-range soil sample, ERA used Freon 113 as a "carrier" to distribute the contaminant evenly throughout the sample. Soil PE samples were spiked with interferents at two different levels ranging from 50 to 500 percent of the TPH concentration expected to be present. Whenever possible, the interferents were added at levels that best represented real-world conditions. ERA analyzed the samples containing weathered gasoline before shipping them to the Navy BVC site. The analytical results were used to confirm sample concentrations.

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

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 Infracal® TOG/TPH Analyzer.

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 Wilks and Reference Laboratory	Number of MS/MSD[b] Pairs	Number of Analyses by Wilks	Number of Analyses by Reference Laboratory[c]	
					GRO	EDRO
Soil Samples (Ottawa Sand)						
Weathered gasoline[d]	Low	7	0	7	7	7
Diesel[e]		7	0	7	0	7
Soil Samples (Processed Garden Soil)						
Weathered gasoline[d]	Medium	3	0	3	3	3
	High	3	1	3	5	5
Diesel[e]	Medium	3	0	3	0	3
	High	3	1	3	0	5
Blank soil (control sample)[d,e]	Trace	3[f]	1	6	5	5
MTBE (1,100 mg/kg) and weathered gasoline[d]	High	3	0	3	3	3
MTBE (1,700 mg/kg) and weathered gasoline[d]		3	0	3	3	3
PCE (2,810 mg/kg) and weathered gasoline[d]		3	0	3	3	3
PCE (13,100 mg/kg) and weathered gasoline[d]		3	0	3	3	3
Stoddard solvent (2,900 mg/kg) and weathered gasoline[d]		3	0	3	3	3
Stoddard solvent (15,400 mg/kg) and weathered gasoline[d]		3	0	3	3	3
Turpentine (2,730 mg/kg) and weathered gasoline[d]		3	0	3	3	3
Turpentine (12,900 mg/kg) and weathered gasoline[d]		3	0	3	3	3
Stoddard solvent (3,650 mg/kg) and diesel[d]		3	0	3	3	3
Stoddard solvent (18,200 mg/kg) and diesel[d]		3	0	3	3	3
Turpentine (3,850 mg/kg) and diesel[d]		3	0	3	3	3
Turpentine (19,600 mg/kg) and diesel[d]		3	0	3	3	3
1,2,4-Trichlorobenzene (3,350 mg/kg) and diesel[e]		3	0	3	0	3
1,2,4-Trichlorobenzene (16,600 mg/kg) and diesel[e]		3	0	3	0	3
Humic acid (3,940 mg/kg) and diesel[e]		3	0	3	0	3
Humic acid (19,500 mg/kg) and diesel[e]		3	0	3	0	3
Humic acid (3,940 mg/kg)[e]	Trace	3	0	3	0	3
Humic acid (19,500 mg/kg)[e]		3	0	3	0	3
Weathered gasoline at 16 percent moisture[d]	High	3	1	3	5	5
Diesel at negligible moisture (less than 1 percent)[e]		3	1	3	0	5
Liquid Samples (Neat Material)						
Weathered gasoline[d]	High	3	1	3	5	5
Diesel[d,e]		3[g]	0	5	0	3
MTBE[d]		6	0	6	6	0

Table 4-4. Performance Evaluation Samples (Continued)

Sample Type	Typical TPH Concentration Range[a]	Total Number of Samples to Wilks and Reference Laboratory	Number of MS/MSD[b] Pairs	Number of Analyses by Wilks	Number of Analyses by Reference Laboratory[c]	
					GRO	EDRO
Liquid Samples (Neat Material) (Continued)						
PCE[d]	Not applicable	6	0	6	6	0
Stoddard solvent[d,e]	High	6[f]	0	12	6	6
Turpentine[d,e]	Not applicable	6[f]	0	12	6	6
1,2,4-Trichlorobenzene[e]		6	0	6	0	6
Total		**125[h]**	**6**	**142**	**90**	**125**

Notes:

mg/kg = Milligram per kilogram

MS/MSD = Matrix spike and matrix spike duplicate

MTBE = Methyl-tert-butyl ether

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.

[d] Model CVH was used to analyze these samples.

[e] Model HATR-T was used to analyze these samples.

[f] Both Models CVH and HATR-T were used to analyze these samples.

[g] Model CVH was used to analyze three samples and Model HATR-T was used to analyze only two of the samples.

[h] The total number of samples to Wilks is 142 (both models CVH and HATR-T).

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

				Holding Time (days)	
Parameter[a]	Medium	Container	Preservation	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.

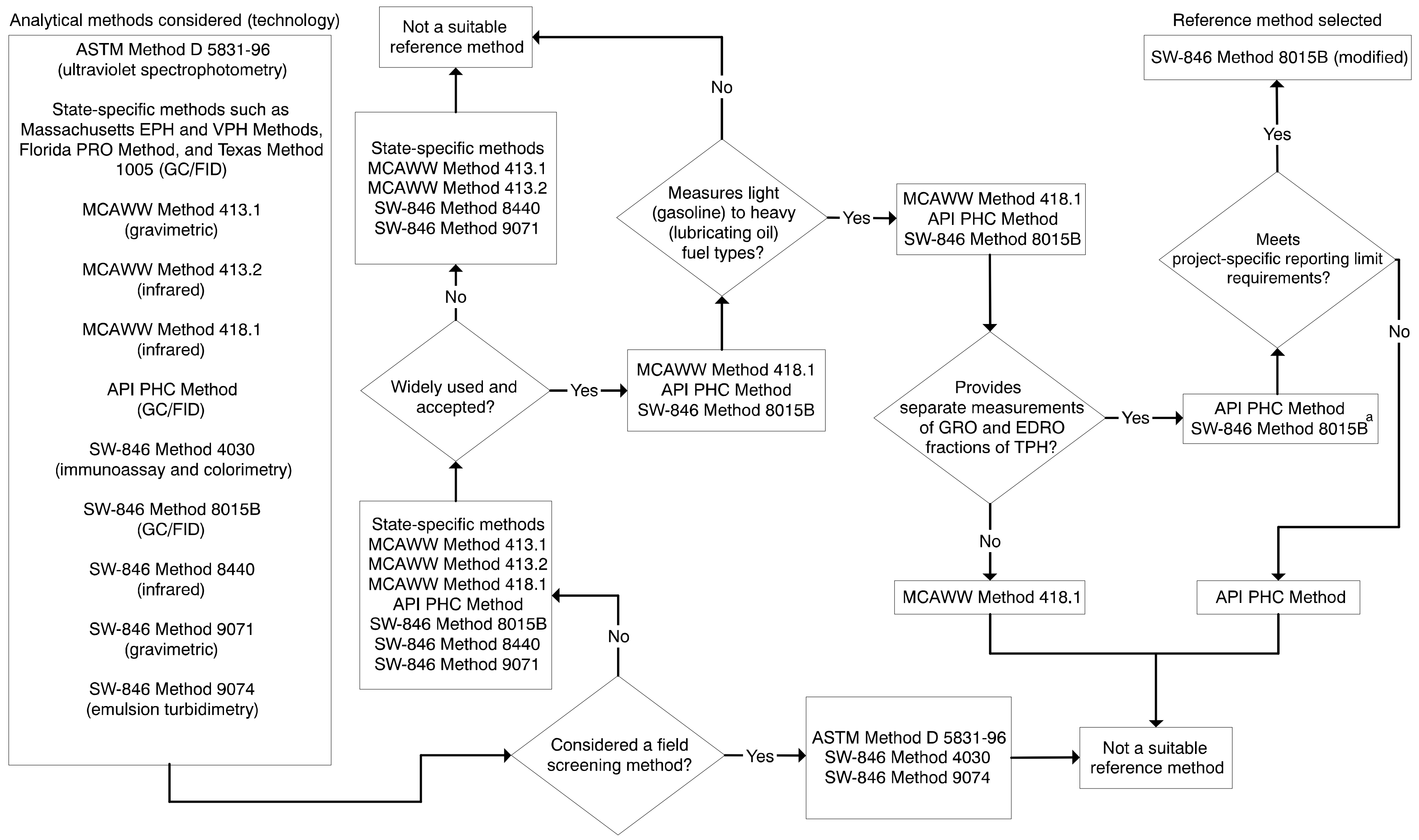
The reference method used was selected based on the following criteria:

- 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 CFC, and use of CFCs will eventually be phased out under the Montreal Protocol. However, because several states still accept the use of MCAWW Method 418.1 for measuring TPH, the method was retained for further consideration in the selection process (AEHS 1999).



Notes:

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

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

5.2 Reference Laboratory Selection

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

5.3 Summary of Reference Method

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

Table 5-1. Laboratory Sample Preparation and Analytical Methods

Parameter	Method Reference (Step)	Method Title
GRO	Based on SW-846 Method 5035 (extraction)	Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples
	Based on SW-846 Method 5030B (purge-and-trap)	Purge-and-Trap for Aqueous Samples
	Based on SW-846 Method 8015B (analysis)	Nonhalogenated Volatile Organics by Gas Chromatography
EDRO	Based on SW-846 Method 3540C (extraction)	Soxhlet Extraction
	Based on SW-846 Method 8015B (analysis)	Nonhalogenated Volatile Organics by Gas Chromatography
Percent moisture	Based on MCAWW Method 160.3[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.

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 5-2. 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.

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

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

SW-846 Method Reference (Step)	Project-Specific Procedures
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
GC = Gas chromatograph
ICV = Initial calibration verification
LCS = Laboratory control sample
LCSD = Laboratory control sample duplicate
min = Minute
mL = Milliliter
MS = Matrix spike
MSD = Matrix spike duplicate
$n\text{-}C_x$ = Alkane with “x” carbon atoms
ng = Nanogram
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 selected 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 relative percent difference (RPD) less than or equal to 20. All laboratory duplicate results met this criterion. The results for the laboratory duplicates are not separately discussed in this ITVR because soil sample TPH results were compared on a wet weight basis except for those used to address primary object P4 (effect of soil moisture content).

6.1.1 GRO Analysis

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

Method Blanks

Method blanks were analyzed to verify that steps in the analytical procedure did not introduce contaminants that affected analytical results. Ottawa sand and deionized water were used as method blanks for soil and liquid samples, respectively. These blanks underwent all the procedures required for sample preparation. The results for all method blanks met the acceptance criterion of being less than or equal to the required project-specific reporting limit (5 mg/kg). Based on method blank results, the GRO analysis results were considered to be valid.

Surrogates

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

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

The surrogate recoveries for 16 of the 56 samples did not meet the acceptance criterion. In each case, the surrogate was recovered at a concentration above the upper limit of the acceptance criterion. Examination of the gas chromatograms for the 16 samples revealed that some PHCs or naturally occurring 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 less than or equal to 25. When the MS/MSD percent recovery acceptance criterion was not met, instead of attributing the failure to meet the criterion to an 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 less than or equal to 25. Two or more environmental samples collected in each demonstration area whose samples were analyzed for GRO (the NEX Service Station, B-38, and SFT Areas) were designated as extract duplicates. A total of 10 samples designated as extract duplicates were analyzed for GRO. The RPDs for these samples ranged from 0.5 to 11. Therefore, the RPDs for all the extract duplicates met the acceptance criterion. Based on the extract duplicate results, the GRO analysis results were considered to be valid.

Laboratory Control Samples and Laboratory Control Sample Duplicates

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

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

Summary of Quality Control Check Results

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

The project-specific percent recovery acceptance criteria were met for most environmental samples and all PE samples. As expected, the percent recovery ranges were broader for the environmental samples than for the PE samples. As indicated by the mean and median percent recoveries, the QC check results generally indicated a slight negative bias (up to 20 percent) in the GRO concentration measurements; the exceptions were the surrogate recoveries for environmental samples and the LCS/LCSD recoveries for soil PE samples. The observed bias did not exceed the generally acceptable bias (±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

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.

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.

Surrogates

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

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

A total of 190 surrogate measurements were made during analysis of soil PE and associated QC samples. Five of these samples did not meet the percent recovery acceptance criterion. In each case, the surrogate was recovered at a concentration below the lower limit of the acceptance criterion. Three of the five samples were soil PE samples, and the remaining two samples were LCS/LCSDs. The reference laboratory reanalyzed the three soil PE samples and the LCS/LCSD pair as well as all the other samples in the QC lot associated with the LCS/LCSDs; during the reanalyses, all surrogate recoveries met the acceptance criterion. The surrogate recoveries for all results reported ranged from 46 to 143 percent with mean and median recoveries of 76 percent, indicating an overall negative bias. The surrogate recoveries for all reported sample results met the acceptance criterion. Based on the surrogate results for soil PE and associated QC samples, the EDRO analysis results were considered to be valid.

Matrix Spikes and Matrix Spike Duplicates

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

For environmental samples, a total of 13 MS/MSD pairs were analyzed. Two sample pairs collected in the FFA were designated as MS/MSDs. The sample matrix in this area primarily consisted of medium-grained sand. The percent recoveries for the MS/MSD samples ranged from 0 to 183 with RPDs of 0 and 19. One of the two sample pairs exhibited percent recoveries less than the lower acceptance limit. In the second sample pair, one sample exhibited a percent recovery less than the lower acceptance limit, and one sample exhibited a percent recovery greater than the upper acceptance limit. For both sample pairs, the RPD acceptance criterion for the MS/MSDs and the percent recovery and RPD acceptance criteria for the LCS/LCSDs associated with the analytical 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 less than or equal to 45. One or more environmental samples collected in each demonstration area were designated as extract duplicates. A total of 13 samples designated as extract duplicates were analyzed for EDRO. The RPDs for these samples ranged from 0 to 11 except for one extract duplicate pair collected in the SFT Area that had an RPD equal to 34. The RPDs for all the extract duplicates met the acceptance criterion. Based on the extract duplicate results, all EDRO results were considered to be valid.

Laboratory Control Samples and Laboratory Control Sample Duplicates

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

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

Summary of Quality Control Check Results

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

The project-specific percent recovery acceptance criteria were met for all surrogates and LCS/LCSDs. About one-half of the MS/MSDs did not meet the percent recovery acceptance criterion. As expected, the MS/MSD percent recovery range was broader for environmental samples than for PE samples. The mean and median percent recoveries for all the QC check samples indicated a negative bias (up to 33 percent) in the EDRO concentration measurements. Although the observed bias was slightly greater than the generally acceptable bias (±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

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

			Accuracy (Percent Recovery)					Precision (Relative Percent Difference)				
QC Check[a]	Matrix Associated with QC Check	No. of Measurements Used to Evaluate Data Quality	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.

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 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 Infracal® TOG/TPH Analyzer's performance, which is discussed in Chapter 7. Soil PE samples were prepared by adding weathered gasoline or diesel to Ottawa sand or processed garden soil. For each sample, an amount of weathered gasoline or diesel was added to the sample matrix in order to prepare a PE sample with a low (less than 100 mg/kg), medium (100 to 1,000 mg/kg), or high (greater than 1,000 mg/kg) TPH concentration. Liquid PE samples consisted of neat materials. Triplicate samples of each type of PE sample were analyzed by the reference laboratory except for the low-concentration-range PE samples, for which seven replicate samples were analyzed.

As described in Section 4.2, some PE samples also contained interferents. Section 6.2 does not discuss the reference method results for PE samples containing interferents because the results address a specific demonstration objective. To facilitate comparisons, the reference method results that directly address demonstration objectives are discussed along with the Infracal® TOG/TPH Analyzer 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.

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

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

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	14.7 mg/kg	39
Soil Samples (Processed Garden Soil)					
Weathered gasoline	Medium	196 to 781	550 mg/kg	344 mg/kg	62
	High	1,110 to 4,430	3,120 mg/kg	2,030 mg/kg	65
Weathered gasoline at 16 percent moisture	High	992 to 3,950	2,780 mg/kg	1,920 mg/kg	69
Diesel	Medium	220 to 577	454 mg/kg	281 mg/kg	62
	High	1,900 to 4,980	3,920 mg/kg	2,720 mg/kg	69
Diesel at less than 1 percent moisture	High	2,100 to 5,490	4,320 mg/kg	2,910 mg/kg	67
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.

results for the low-range diesel samples were within the 99 percent confidence interval of 10.8 to 54.6 mg/kg, indicating that the reference method results met the control limits but not the warning limits. Collectively, these observations indicated a negative bias in TPH measurements for low-range diesel samples.

As noted above, Table 6-3 presents ratios of the reference method mean TPH concentrations to the certified values for PE samples. The ratios for weathered gasoline-containing soil samples ranged from 62 to 69 percent and did not appear to depend on whether the samples were medium- or high-range samples. The ratio for neat, weathered gasoline (liquid sample) was 80 percent, which was 11 to 18 percentage points greater than the ratios for the soil samples. The difference in the ratios may be attributed to (1) potential loss of volatiles during soil sample transport and storage and during soil sample handling when extractions were performed and (2) lower analyte recovery during soil sample extraction. The less than 100 percent ratios observed indicated a negative bias in TPH measurement for soil and liquid samples containing weathered gasoline. The observed bias for the liquid samples did not exceed the generally acceptable bias (±30 percent) stated in SW-846 for most organic analyses. However, the bias for soil samples exceeded the acceptable bias by up to 8 percentage points.

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

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

Because the reference method results exhibited a negative bias for soil PE samples when compared to ERA-certified values, ERA's historical data on percent recoveries and RSDs from multiple laboratories were examined. Table 6-4 compares ERA's historical percent recoveries and RSDs to the reference method percent recoveries and RSDs obtained during the demonstration. Table 6-4 shows that ERA's historical recoveries also exhibited a negative bias for all sample types except weathered gasoline in water and that the reference method recoveries were less than ERA's historical recoveries for all sample types except diesel in water. The ratios of reference method mean recoveries to ERA historical mean recoveries for

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	65	74	8
Diesel in soil	87.7	19.6	59	68	7
Weathered gasoline in water	109	22.0	80	73	5
Diesel in water	78.5	22.8	128	163	6

Notes:

ERA = Environmental Resource Associates

[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.

weathered gasoline-containing samples indicated that the reference method TPH results were 26 percent less than ERA's historical recoveries. The reference method recoveries for diesel-containing (1) soil samples were 32 percent less than the ERA historical recoveries and (2) water samples were 63 percent greater than the ERA historical recoveries. In all cases, the RSDs for the reference method were significantly lower than ERA's historical RSDs, indicating that the reference method achieved significantly greater precision. The greater precision observed for the reference method during the demonstration may be associated with the fact that the reference method was implemented by a single laboratory, whereas ERA's historical RSDs were based on results obtained from multiple laboratories that may have used different analytical protocols.

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

6.3 Data Quality

Based on the reference method's performance in analyzing the QC check samples and selected PE samples, the reference method results were considered to be of adequate quality for the following reasons: (1) the reference method was implemented with acceptable accuracy (±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 31 percentage points for low-range and 8 percentage points for medium-range samples. The reference method recoveries observed were typical of the recoveries obtained by most organic analytical methods for environmental samples.

Chapter 7
Performance of the Infracal® TOG/TPH Analyzer

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 Infracal® TOG/TPH Analyzer 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 Infracal® TOG/TPH Analyzer based on primary objectives P1 through P5, which are listed below.

P1. Determine the MDL

P2. Evaluate the accuracy and precision of TPH measurement for a variety of contaminated soil samples

P3. Evaluate the effect of interferents on TPH measurement

P4. Evaluate the effect of soil moisture content on TPH measurement

P5. Measure the time required for TPH measurement

To address primary objectives P1 through P5, samples were collected from five different sampling areas. In addition, soil and liquid PE samples were prepared and distributed to Wilks and the reference laboratory. The numbers and types of environmental samples collected in each sampling area and the numbers and types of PE samples prepared are discussed in Chapter 4. Primary objectives P1 through P4 were addressed using statistical and nonstatistical approaches, as appropriate. The statistical tests performed to address these objectives are illustrated in the flow diagram in Figure 7-1. Before a parametric test was performed, the Wilk-Shapiro test was used to determine whether the Infracal® TOG/TPH Analyzer results and reference method results or, when appropriate, their differences were normally distributed at a significance level of 5 percent. If the results or their differences were not normally distributed, the Wilk-Shapiro test was performed on transformed results (for example, logarithm and square root transformations) to verify the normality assumption. If the normality assumption was not met, a nonparametric test was performed. Nonparametric tests are not as powerful as parametric tests because the nonparametric tests do not account for the magnitude of the difference between sample results. Despite this limitation, when the normality assumption was not met, performing a nonparametric test was considered to be a better alternative than performing no statistical comparison.

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

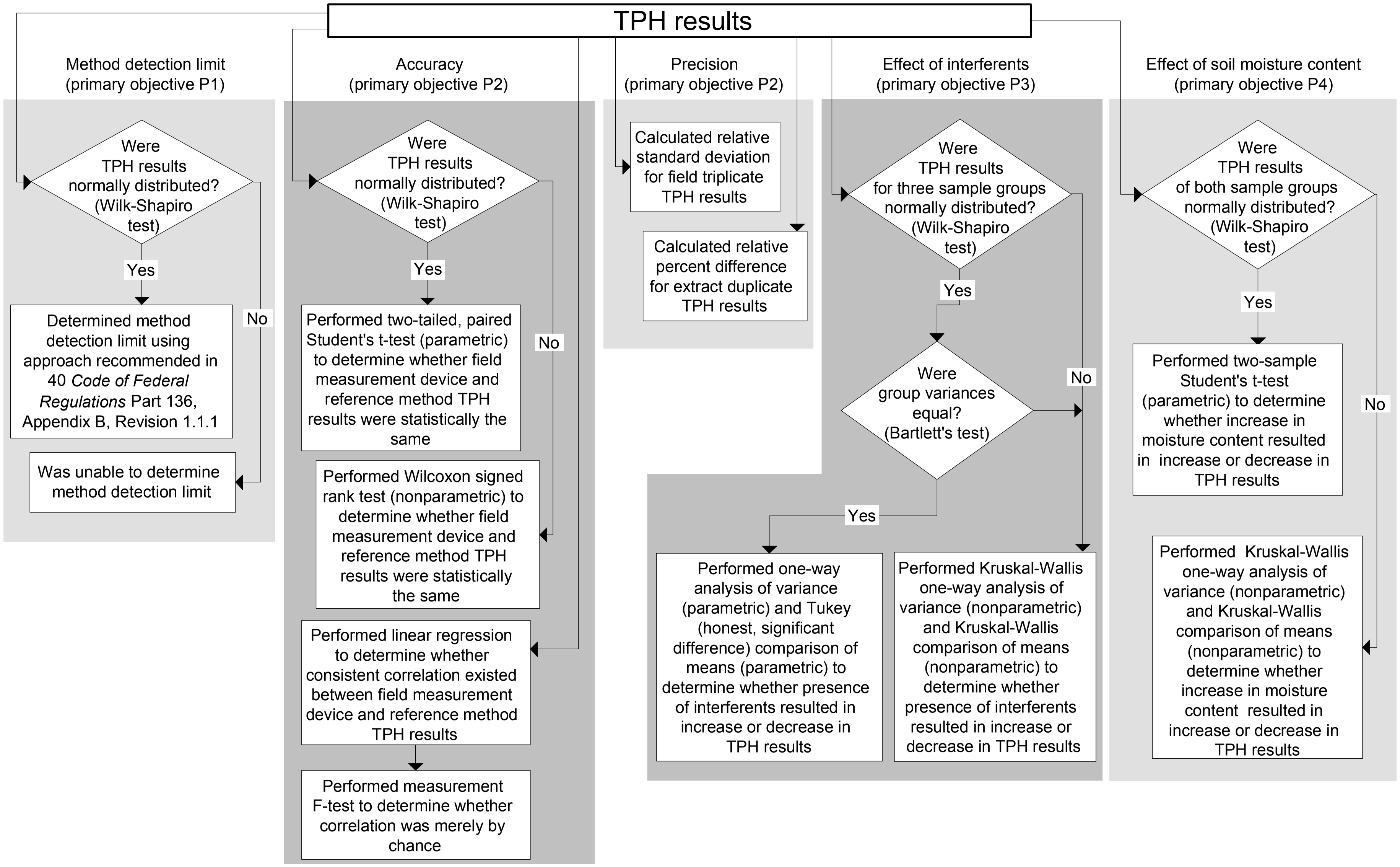


Figure 7-1. Summary of statistical analysis of TPH results.

The reference method GRO results were adjusted for solvent dilution associated with the soil sample moisture content because the method required use of methanol, a water-miscible solvent, for extraction of soil samples. In addition, based on discussions with Wilks, a given TPH result for the Infracal® TOG/TPH Analyzer was rounded to the nearest integer when it was less than or equal to 99 mg/kg or 99 mg/L and to the nearest 10 when it was greater than 99 mg/kg or 99 mg/L. Similarly, based on discussions with the reference laboratory, all TPH results for the reference method were rounded to three significant figures.

During the demonstration, Wilks analyzed all the samples except blank soil PE samples and neat diesel, Stoddard solvent, and turpentine liquid PE samples using the Infracal® TOG/TPH Analyzer equipped with either the Model CVH sample stage or the Model HATR-T sample stage. The blank soil PE samples and the neat diesel, Stoddard solvent, and turpentine liquid PE samples were analyzed using both sample stages. In general, Wilks used Model CVH to analyze samples containing GRO and Model HATR-T to analyze samples that did not contain GRO. Because only 8 percent of the samples were analyzed using both models, this chapter evaluates the performance of the Infracal® TOG/TPH Analyzer as a whole, not that of each model. However, in cases where TPH results were available for both models, the results are separately discussed for each model.

7.1.1 *Primary Objective P1: Method Detection Limit*

To determine the MDLs for the Infracal® TOG/TPH Analyzer and reference method, both Wilks and the reference laboratory analyzed seven low-concentration-range soil PE samples containing weathered gasoline and seven low-concentration-range soil PE samples containing diesel. Wilks analyzed the low-range weathered gasoline samples using Model CVH and the low-range diesel soil PE samples using Model HATR-T. 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. Thus, the MDL could be calculated for Model HATR-T of the Infracal® TOG/TPH Analyzer but not for Model CVH.

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 Model HATR-T 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

	Model HATR-T Result (mg/kg)	Reference Method Result (mg/kg)
	0[a]	16.4
	14	16.4
	7	13.2
	42	16.0
	0[a]	14.2
	49	14.1
	7	12.8
MDL	76	4.79

Notes:

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

[a] This result was not used to calculate the MDL for Model HATR-T.

When the Model HATR-T results for all seven soil PE samples containing diesel were considered, the results were found not to be normally distributed. However, the results were found to be normally distributed when only the five non-zero values were used to verify the distribution. For the reference method, all seven diesel soil PE sample results were normally distributed. Therefore, five of seven Model HATR-T results and all seven reference method results were used for MDL determination. 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.

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

where

S = Standard deviation of replicate TPH results

$t_{(n-1,1-\alpha=0.99)}$ = Student's t-value appropriate for a 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom (3.747 for n = 5 replicates; 3.143 for n = 7 replicates)

Based on the TPH results for the low-concentration-range diesel soil PE samples, the MDLs were determined to be 76 and 4.79 mg/kg for Model HATR-T and the reference method, respectively. Because the ORO concentrations in all these samples were below the reference laboratory's estimated reporting limit (5.1 mg/kg), the MDL for the reference method was also calculated using only DRO results. The MDL for the reference method based on the DRO results was 4.79 mg/kg, which was the same as the MDL for the reference method based on the EDRO results, indicating that the ORO concentrations below the reporting limit did not impact the MDL for the reference method.

The MDL of 76 mg/kg for Model HATR-T was greater than the MDL of 20 mg/kg claimed by Wilks for this model. For the purposes of reporting the demonstration results, Wilks used an MDL of (1) 10 mg/kg for Model CVH (Wilks claimed an MDL of 3 mg/kg for this model before the demonstration) and (2) 50 mg/kg for Model HATR-T. The MDL of 4.79 mg/kg for the reference method compared well with the MDL of 4.72 mg/kg published in SW-846 Method 8015C for diesel samples extracted using a pressurized fluid extraction method and analyzed for DRO.

7.1.2 Primary Objective P2: Accuracy and Precision

This section discusses the ability of the Infracal® TOG/TPH Analyzer to accurately and precisely measure TPH concentrations in a variety of contaminated soils. The Infracal® TOG/TPH Analyzer 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 Infracal® TOG/TPH Analyzer measurement of TPH was assessed by determining

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

During examination of these four factors, the data quality of the reference method and Infracal® TOG/TPH Analyzer 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 Infracal® TOG/TPH Analyzer and reference method results, particularly those for low- and medium-range diesel soil samples. Caution was also exercised during interpretation of statistical test conclusions drawn based on a small number of samples. For example, only three samples were used for each type of PE sample except the low-range diesel samples; the small number of samples used increased the probability that the results being compared would be found to be statistically the same.

As discussed in Chapter 2, during the demonstration, Models CVH and HATR-T were calibrated using standards that consisted of 3-IN-ONE oil in Freon 113 and Vertrel® MCA, respectively. The following sections discuss how the results of Model CVH, Model HATR-T, or both compared with the reference method results by addressing each of the four factors identified above.

Action Level Conclusions

Table 7-2 compares action level conclusions reached using the Infracal® TOG/TPH Analyzer and reference method results for environmental and soil PE samples. Section 4.2 of this ITVR explains how the action levels were selected

Table 7-2. Action Level Conclusions

Sampling Area or Sample Type		Action Level (mg/kg)	Total Number of Samples Analyzed	Percentage of Samples for Which Infracal® TOG/TPH Analyzer and Reference Method Conclusions Agreed	When Conclusions Did Not Agree, Were Infracal® TOG/TPH Analyzer Conclusions Conservative or Not Conservative?[a]
Fuel Farm Area		100	10[b]	90[b]	Not conservative
Naval Exchange Service Station Area		50	20[c]	95[c]	
Phytoremediation Area		1,500	8[b]	50[b]	
B-38 Area		100	8[c]	100[c]	
Slop Fill Tank Area		500	28[c]	71[c]	Not conservative (six of eight conclusions)
PE sample	Blank soil (9 percent moisture content)	10	3[c,d]	33[c]	Not conservative
PE sample	Blank soil and humic acid (9 percent moisture content)	200	6[b]	100[b]	
Soil PE sample containing weathered gasoline in	Medium-concentration range (9 percent moisture content)	200	3[c]	0[c]	Not conservative
	High-concentration range (9 percent moisture content)	2,000	3[c]	33[c]	
	High-concentration range (16 percent moisture content)	2,000	3[c]	67[c]	
Soil PE sample containing diesel in	Low-concentration range (9 percent moisture content)	15	7[b,e]		
	Medium-concentration range (9 percent moisture content)	200	3[b]	0[b]	Not conservative
	High-concentration range (less than 1 percent moisture content)	2,000	3[b]	67[b]	
	High-concentration range (9 percent moisture content)	2,000	3	0[b]	
Total			108	71	

Notes:

mg/kg = Milligram per kilogram
PE = Performance evaluation

[a] A conclusion was considered to be conservative when the Infracal® TOG/TPH Analyzer 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.

[b] Model HATR-T was used to analyze these samples.

[c] Model CVH was used to analyze these samples.

[d] Blank soil PE samples were also analyzed using the Model HATR-T; however, the TPH results were inconclusive because they were reported as "less than the detection limit," which was greater than the action level.

[e] The TPH results for these samples were inconclusive because the results were reported as "less than the detection limit," which was greater than the action level.

for the demonstration. Of the environmental samples, the percentage of samples for which the conclusions agreed ranged from 50 to 100. Of the PE samples, the percentage of samples for which the conclusions agreed ranged from 0 to 100. Overall, the conclusions were the same for 71 percent of the samples. No conclusions could be drawn for seven samples analyzed using Model CVH and three samples analyzed using Model HATR-T because of the high MDLs associated with the two models relative to the action levels.

The least agreement observed for the environmental samples was that for samples collected from the PRA (50 percent). Regarding the PE samples, none of the Infracal® TOG/TPH Analyzer action level conclusions agreed with those of the reference method for the medium-concentration-range weathered gasoline and diesel samples and the high-concentration-range (9 percent moisture content) diesel samples. The low percent agreements observed did not appear to depend on contamination type, contamination level, or the sample stage used for TPH measurement.

When the action level conclusions did not agree, the TPH results were further interpreted to assess whether the Infracal® TOG/TPH Analyzer conclusion was conservative. The device conclusion was considered to be conservative when the device 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. Of the 29 device conclusions for environmental and soil PE samples that did not agree with reference method conclusions, 27 (93 percent) were not conservative.

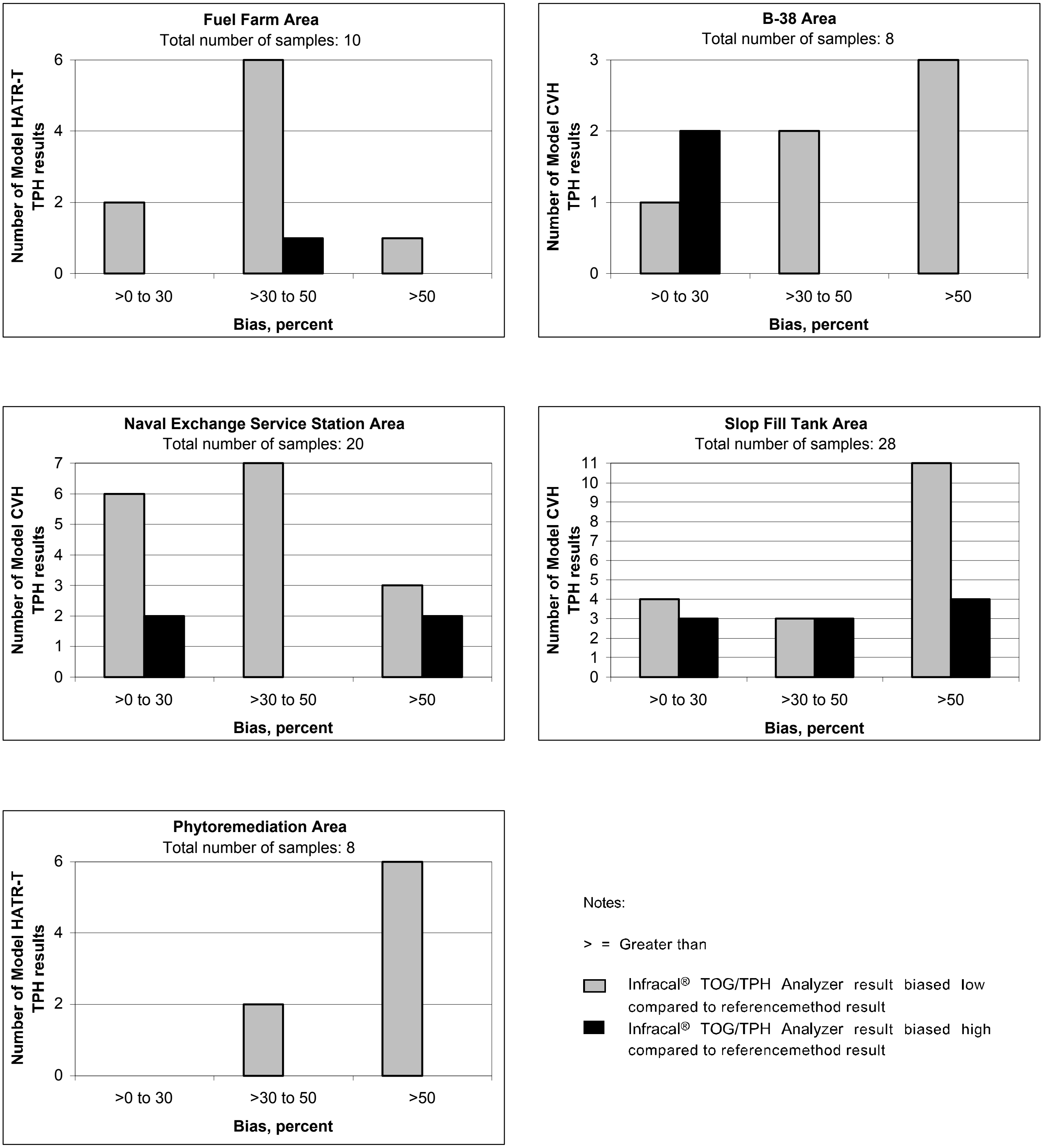
Measurement Bias

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

Figure 7-2 shows the distribution of measurement bias for the environmental samples. Of the five sampling areas, the best agreement between the Infracal® TOG/TPH Analyzer and reference method results was observed for samples collected from the FFA; for these samples, 90 percent of the device results were within 50 percent of the reference method results. Moderate agreement between the device and reference method results was observed for samples collected from the NEX Service Station Area and B-38 Area; for these samples, 75 and 62 percent of the device results, respectively, were within 50 percent of the reference method results. For samples collected from the SFT Area and PRA, 46 and 25 percent of the device results, respectively, were within 50 percent of the reference method results. Of 74 Infracal® TOG/TPH Analyzer results for the environmental samples, 57 (77 percent) were biased low. The observed bias did not appear to be a function of contamination type, contamination level, or the sample stage used for TPH measurement.

Figure 7-3 shows the distribution of measurement bias for selected soil PE samples. Of the five sets of samples containing PHCs and the one set of blank samples, moderate agreement between the Infracal® TOG/TPH Analyzer and reference method results was observed for the high-concentration-range diesel samples; for these samples, 50 percent of the device results were within 50 percent of the reference method results. For the blank soil samples analyzed using Model CVH and the high-range weathered gasoline samples, 33 percent of the device results were within 50 percent of the reference method results. All the remaining device results, including those for the blank soil samples analyzed using Model HATR-T, exhibited a bias of greater than 50 percent. The device results were biased low for all the PE samples except the blank soil samples and the low-range diesel samples analyzed using Model HATR-T.

The distributions of measurement bias for the blank soil samples analyzed using Models CVH and HATR-T and the low-concentration-range diesel soil PE samples were considered to be approximations because for these samples, all the Infracal® TOG/TPH Analyzer results were reported to be below the detection limits. For example, for the blank soil samples analyzed using Model CVH, if the measurement bias was calculated using the full detection limit (maximum bias), compared to the reference method, two sample results would be biased less than 30 percent low and one sample result would be biased greater than 50 percent high. When the Infracal® TOG/TPH Analyzer results reported to be below the detection limits were not considered, 18 of 18 soil PE sample results for the device



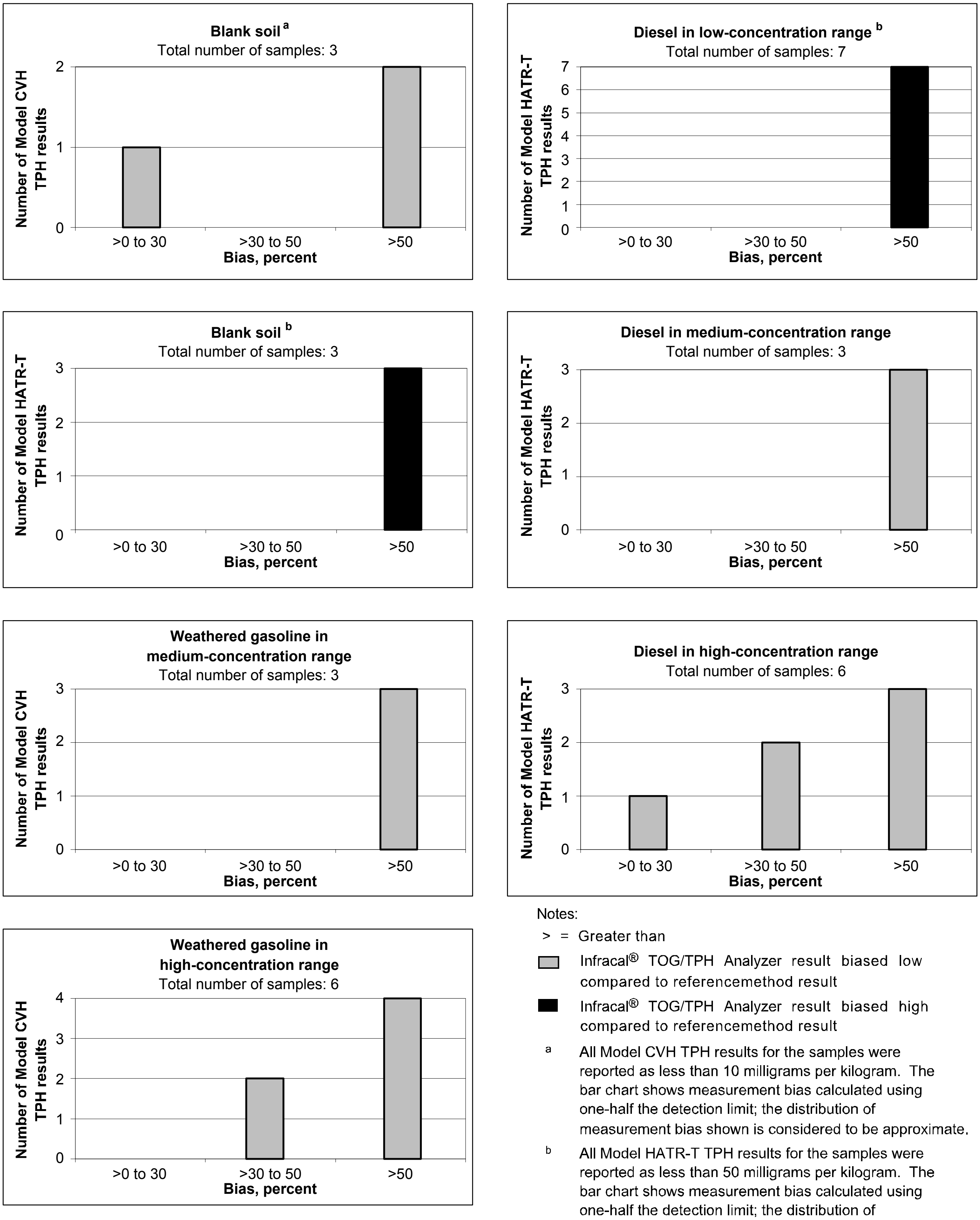
Notes:

> = Greater than

▨ Infracal® TOG/TPH Analyzer result biased low compared to referencemethod result

■ Infracal® TOG/TPH Analyzer result biased high compared to referencemethod result

Figure 7-2. Measurement bias for environmental samples.



Notes:

> = Greater than

▢ Infracal® TOG/TPH Analyzer result biased low compared to referencemethod result

■ Infracal® TOG/TPH Analyzer result biased high compared to referencemethod result

[a] All Model CVH TPH results for the samples were reported as less than 10 milligrams per kilogram. The bar chart shows measurement bias calculated using one-half the detection limit; the distribution of measurement bias shown is considered to be approximate.

[b] All Model HATR-T TPH results for the samples were reported as less than 50 milligrams per kilogram. The bar chart shows measurement bias calculated using one-half the detection limit; the distribution of measurement bias shown is considered to be approximate.

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

were found to be biased low compared to the reference method results.

Pairwise Comparison of TPH Results

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

Table 7-3 shows that the Infracal® TOG/TPH Analyzer and reference method results were statistically different at a significance level of 5 percent for all sampling areas except the B-38 Area. Based on a simple comparison of the results, this conclusion appeared to be reasonable because compared to the reference method results, the Infracal® TOG/TPH Analyzer results were biased low for (1) 9 of 10 samples from the FFA by up to 99 percent, (2) 16 of 20 samples from the NEX Service Station Area by up to 69 percent, (3) 8 of 8 samples from the PRA by up to 68 percent, and (4) 18 of 28 samples from the SFT Area by up to 88 percent.

Table 7-4 shows that the Infracal® TOG/TPH Analyzer and reference method results were statistically different at a significance level of 5 percent for all PE samples except blank soil samples, low-concentration-range diesel soil samples, and neat diesel samples analyzed using Model HATR-T. Because all Infracal® TOG/TPH Analyzer results for the blank soil and low-range diesel soil samples were reported as below the detection limits, these results were not used to make a statistical comparison. For the neat diesel samples analyzed using Model HATR-T, the two pairs of sample results reported were inadequate to perform a statistical comparison. Based on a simple comparison of the results, the statistical conclusions appeared to be reasonable for all PE sample types.

Of the Infracal® TOG/TPH Analyzer PE sample results that were statistically different from the reference method results, on average the device results for soil samples containing (1) high-concentration-range weathered gasoline (9 percent and 16 percent moisture content) were biased low by a factor of two; (2) medium-concentration-range weathered gasoline, medium-concentration-range diesel, and high-concentration-range diesel (9 percent moisture content) were biased low by a factor of four; and (3) high-concentration-range diesel (less than 1 percent moisture content) were biased low by up to 29 percent. Similar to the soil PE sample results, all the liquid PE sample results for the device were biased low compared to the reference method results. Specifically, on average, the device results for (1) neat weathered gasoline samples were biased low by 12 percent, (2) neat diesel samples analyzed using Model CVH were biased low by 23 percent, and (3) neat diesel samples analyzed using Model HATR-T were biased low by 60 percent.

Finally, when compared to the sample densities, the Infracal® TOG/TPH Analyzer results were biased low by 30 percent for neat weathered gasoline and by 51 percent for neat diesel analyzed using Model HATR-T. The device results for neat diesel analyzed using Model CVH were within 7 percent of the neat diesel density. These findings suggested that the low bias observed for environmental and soil PE samples analyzed using (1) Model CVH might have been attributable to low extraction efficiency and (2) Model HATR-T might have been attributable to low extraction efficiency and the low analytical accuracy of Model HATR-T itself.

Correlation of TPH Results

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

Table 7-3. Statistical Comparison of Infracal® TOG/TPH Analyzer and Reference Method TPH Results for Environmental Samples

Sampling Area	TPH Result (mg/kg)		Statistical Analysis Summary		
	Infracal® TOG/TPH Analyzer	Reference Method	Statistical Test and Null Hypothesis	Were Infracal® TOG/TPH Analyzer and Reference Method Results Statistically the Same or Different?	Probability of Null Hypothesis Being True (percent)
Fuel Farm Area[a]	54	68.2	Statistical Test Wilcoxon signed rank test (nonparametric) Null Hypothesis The median of the differences between the paired observations (Infracal® TOG/TPH Analyzer and reference method results) is equal to zero.	Different	0.58
	8,500	15,000			
	54	90.2			
	7,370	12,000			
	61	44.1			
	88	13,900			
	790	1,330			
	4,210	8,090			
	67	93.7			
	7,970	12,300			
Naval Exchange Service Station Area[b]	20	28.8	Statistical Test Two-tailed, paired Student's t-test (parametric) Null Hypothesis The mean of the differences between the paired observations (Infracal® TOG/TPH Analyzer and reference method results) is equal to zero.	Different	3.66
	220	144			
	1,120	617			
	260	293			
	250	280			
	710	1,870			
	1,070	1,560			
	Less than 10	9.56			
	150	270			
	1,060	881			
	990	1,120			
	Less than 10	14.2			
	130	219			
	1,040	1,180			
	900	1,390			
	18	15.2			
	45	54.5			
	1,550	2,570			
	2,260	3,030			
	Less than 10	15.9			
Phytoremediation Area[a]	740	2,140	Statistical Test Two-tailed, paired Student's t-test (parametric) Null Hypothesis The mean of the differences between the paired observations (Infracal® TOG/TPH Analyzer and reference method results) is equal to zero.	Different	0.01
	610	1,790			
	800	1,390			
	820	1,420			
	430	1,130			
	710	1,530			
	500	1,580			
	460	1,300			

Table 7-3. Statistical Comparison of Infracal® TOG/TPH Analyzer and Reference Method TPH Results for Environmental Samples (Continued)

Sampling Area	TPH Result (mg/kg)		Statistical Analysis Summary		
	Infracal® TOG/TPH Analyzer	Reference Method	Statistical Test and Null Hypothesis	Were Infracal® TOG/TPH Analyzer and Reference Method Results Statistically the Same or Different?	Probability of Null Hypothesis Being True (percent)
B-38 Area[b]	38	79.0	Statistical Test Two-tailed, paired Student's t-test (parametric) Null Hypothesis The mean of the differences between the paired observations (Infracal® TOG/TPH Analyzer and reference method results) is equal to zero.	Same	14.22
	33	41.5			
	24	61.4			
	37	67.3			
	220	193			
	88	69.4			
	16	43.8			
	32	51.6			
Slop Fill Tank Area[b]	140	105	Statistical Test Two-tailed, paired Student's t-test (parametric) Null Hypothesis The mean of the differences between the paired observations (Infracal® TOG/TPH Analyzer and reference method results) is equal to zero.	Different	0.57
	570	269			
	340	397			
	100	339			
	14	6.16			
	Less than 10	37.1			
	11	43.9			
	34	52.4			
	1,670	3,300			
	1,370	1,270			
	540	588			
	470	554			
	1,180	834			
	430	501			
	370	280			
	23	185			
	1,250	1,090			
	170	544			
	77	503			
	30	146			
	1,040	938			
	230	517			
	660	369			
	66	253			
	290	151			
	1,690	3,960			
	210	1,210			
	75	121			

Notes:

mg/kg = Milligram per kilogram

[a] Model HATR-T was used to analyze samples collected from this area.

[b] Model CVH was used to analyze samples collected from this area.

Table 7-4. Statistical Comparison of Infracal® TOG/TPH Analyzer and Reference Method TPH Results for Performance Evaluation Samples

Sample Type		TPH Result		Statistical Analysis Summary		
		Infracal® TOG/TPH Analyzer	Reference Method	Statistical Test and Null Hypothesis	Were Infracal® TOG/TPH Analyzer and Reference Method Results Statistically the Same or Different?	Probability of Null Hypothesis Being True (percent)
Soil Samples (Processed Garden Soil) (TPH Results in Milligram per Kilogram)						
Blank (9 percent moisture content)[a,b]		Less than 50[a]; less than 10[b]	5.12	Statistical Test Two-tailed, paired Student's t-test (parametric) Null Hypothesis The mean of the differences between the paired observations (Infracal® TOG/TPH Analyzer and reference method results) is equal to zero.	Not applicable[c]	
		Less than 50[a]; less than 10[b]	13.1			
		Less than 50[a]; less than 10[b]	13.5			
Weathered gasoline[b]	Medium-concentration range (9 percent moisture content)	80	350		Different	0.09
		87	346			
		93	336			
	High-concentration range (9 percent moisture content)	890	1,880		Different	0.68
		1,010	2,020			
		910	2,180			
	High-concentration range (16 percent moisture content)	1,020	1,740		Different	2.15
		780	1,980			
		900	2,050			
Diesel[a]	Low-concentration range (9 percent moisture content)	Less than 50	16.4		Not applicable[c]	
		Less than 50	16.4			
		Less than 50	13.2			
		Less than 50	16.0			
		Less than 50	14.2			
		Less than 50	14.1			
		Less than 50	12.8			
	Medium-concentration range (9 percent moisture content)	61	276		Different	0.24
		91	273			
		88	295			
	High-concentration range (9 percent moisture content)	820	2,480		Different	0.81
		610	2,890			
		750	2,800			
	High-concentration range (less than 1 percent moisture content)	2,060	2,700		Different	1.43
		1,990	2,950			
		2,140	3,070			
Liquid Samples (Neat Materials) (TPH Results in Milligram per Liter)						
Weathered gasoline[b]		591,440	656,000	Statistical Test Two-tailed, paired Student's t-test (parametric) Null Hypothesis The mean of the differences between the paired observations (Infracal® TOG/TPH Analyzer and reference method results) is equal to zero.	Different	3.86
		554,960	611,000			
		571,540	677,000			
Diesel[a,b]		423,760[a]; 810,330[b]	1,090,000		Different[b,d]	0.37[b]
		412,420[a]; 793,750[b]	1,020,000			
		902,090[b]	1,160,000			

Table 7-4. Statistical Comparison of Infracal® TOG/TPH Analyzer and Reference Method TPH Results for Performance Evaluation Samples (Continued)

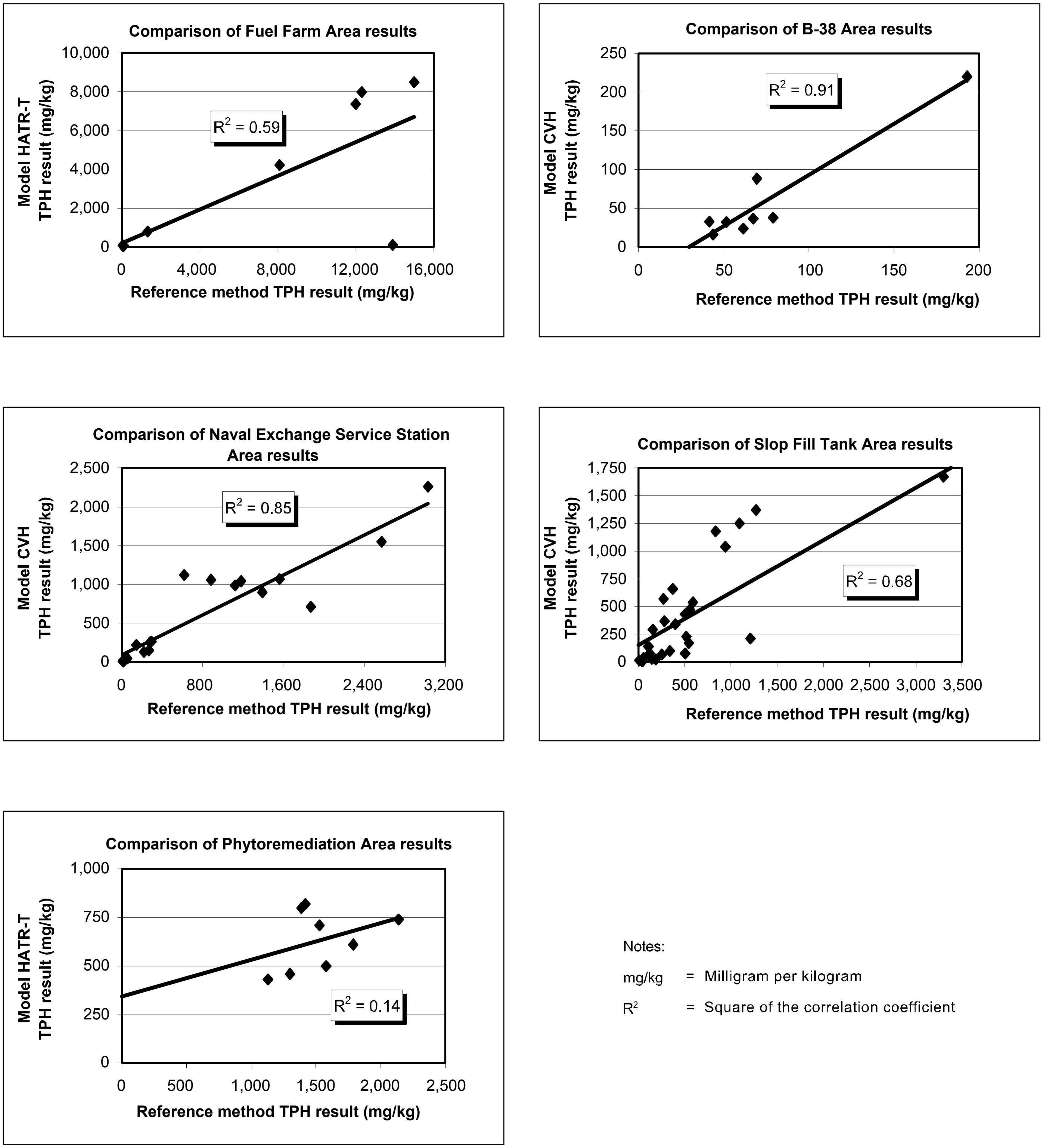
Notes:

[a] Model HATR-T was used to analyze the samples.

[b] Model CVH was used to analyze the samples.

[c] A statistical comparison of the results was not performed because all the Infracal® TOG/TPH Analyzer results for the samples were reported as below the detection limit.

[d] For Model HATR-T, the sample size was inadequate to perform a statistical comparison of results.

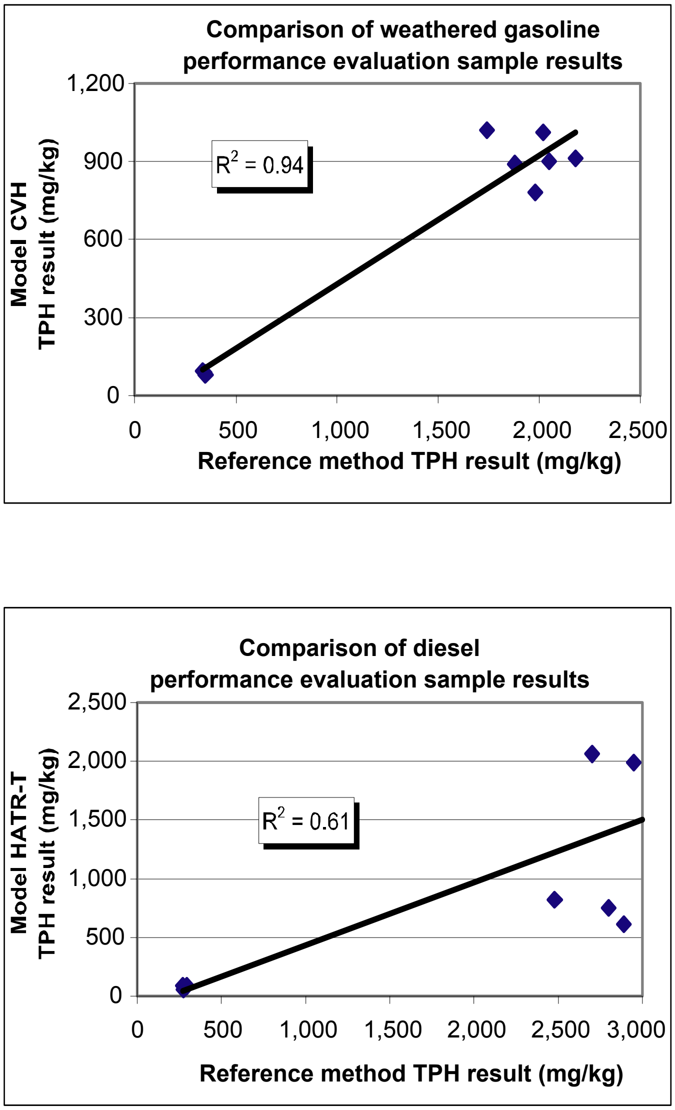


Notes:

mg/kg = Milligram per kilogram

R^2 = Square of the correlation coefficient

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



Notes:

mg/kg = Milligram per kilogram

R^2 = Square of the correlation coefficient

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

Table 7-5 shows that R^2 values for (1) environmental samples except PRA samples ranged from 0.59 to 0.91 and (2) weathered gasoline and diesel soil PE samples were 0.94 and 0.61, respectively. The R^2 value for the PRA samples was 0.14. For environmental samples, the probabilities of the slopes of the regression lines being equal to zero were 0.00 percent for the NEX Service Station Area and SFT Area, 0.02 percent for the B-38 Area, 0.99 percent for the FFA, and 35.32 percent for the PRA. For the soil PE samples, the probabilities of the slopes of the regression lines being equal to zero were 0.00 percent for the weathered gasoline samples and 1.32 percent for the diesel samples. These probabilities indicated that there were (1) a less than 5 percent probability for the FFA, NEX Service Station Area, B-38 Area, and SFT Area samples and for weathered gasoline and diesel soil PE samples and (2) a greater than 5 percent probability for the PRA samples that the Infracal® TOG/TPH Analyzer and reference method results correlated only by chance.

Based on the R^2 and probability values, the Infracal® TOG/TPH Analyzer and reference method results were considered to be (1) highly correlated for the NEX Service Station Area, B-38 Area, and weathered gasoline soil PE samples; (2) moderately correlated for the FFA, SFT Area, and diesel soil PE samples; and (3) weakly correlated for the PRA samples.

7.1.2.2 Precision

Both environmental and PE samples were analyzed to evaluate the precision associated with TPH measurements using the Infracal® TOG/TPH Analyzer 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. Wilks did not analyze any extract duplicates, which were to be used to evaluate the analytical precision of the device. Additional information on field triplicate preparation is included in Chapter 4.

Table 7-6 presents the Infracal® TOG/TPH Analyzer and reference method results for 12 sets of field triplicates. Precision was estimated using the RSDs for the field triplicates. For the Infracal® TOG/TPH Analyzer, the RSDs ranged from 7 to 86 percent with a median of 30 percent. The RSDs for the reference method ranged from 4 to 39 percent with a median of 18 percent. Comparison of the Infracal® TOG/TPH Analyzer and reference method median RSDs showed that the device exhibited less overall precision than the reference method. The device and reference method RSDs did not exhibit consistent trends based on the sample stage used to analyze samples, soil type, PHC contamination type, or TPH concentration.

Table 7-5. Summary of Linear Regression Analysis Results

Sampling Area or Sample Type	Regression Model (y = Infracal® TOG/TPH Analyzer TPH result, x = reference method TPH result)	Square of Correlation Coefficient	Probability That Slope of Regression Line Was Equal to Zero (percent)
Environmental Samples			
Fuel Farm Area[a]	y = 0.43x + 189.31	0.59	0.99
Naval Exchange Service Station Area[b]	y = 0.65x + 88.22	0.85	0.00
Phytoremediation Area[a]	y = 0.19x + 343.90	0.14	35.32
B-38 Area[b]	y = 1.32x - 39.07	0.91	0.02
Slop Fill Tank Area[b]	y = 0.47x + 152.59	0.68	0.00
Soil Performance Evaluation Samples			
Weathered gasoline[b]	y = 0.50x - 67.91	0.94	0.00
Diesel[a,c]	y = 0.54x - 100.11	0.61	1.32

Notes:

[a] Model HATR-T was used to analyze the samples.

[b] Model CVH was used to analyze the samples.

[c] Because all the Infracal® TOG/TPH Analyzer results for low-concentration-range diesel soil performance evaluation samples were reported as below the detection limit, these results were excluded from the linear regression analysis.

Performance Evaluation Samples

Table 7-7 presents the Infracal® TOG/TPH Analyzer and reference method TPH results and RSDs for eight sets of replicates for soil PE samples and two sets of triplicates for liquid PE samples.

For the Infracal® TOG/TPH Analyzer, the RSDs for the blank soil samples and low-concentration-range diesel soil samples were not considered in evaluating the device's precision because the device's results for these samples were reported as below detection limits. The RSDs for the remaining six replicate sets ranged from 4 to 21 percent with a median of 10 percent. The RSDs for the two triplicate sets of liquid samples analyzed using Model CVH were 3 and 7 percent with a median of 5 percent. For neat diesel samples analyzed using Model HATR-T, RPD was used to evaluate the precision because only two sample results were reported; the RPD for these samples was 3.

For the reference method, the RSD calculated for the blank soil samples was not considered in evaluating the method's precision because one of the three blank soil sample results (5.12 mg/kg) was estimated by adding one-half the reporting limits for the GRO, DRO, and ORO components of TPH measurement. The RSDs for the remaining seven replicate sets ranged from 2 to 10 percent with a median of 7 percent. The RSDs for the two triplicate sets of liquid samples were 5 and 6 percent with a median of 5.5 percent. Comparison of the Infracal® TOG/TPH Analyzer and reference method median RSDs showed that the device and reference method exhibited about the same level of precision for soil and liquid PE samples.

7.1.3 Primary Objective P3: Effect of Interferents

The effect of interferents on TPH measurement using the Infracal® TOG/TPH Analyzer 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 Infracal® TOG/TPH Analyzer and the reference method. Liquid interferent samples were submitted for analysis as blind triplicate samples. Wilks 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 Infracal® TOG/TPH Analyzer and reference

Table 7-6. Summary of Infracal® TOG/TPH Analyzer and Reference Method Precision for Field Triplicates of Environmental Samples

		Infracal® TOG/TPH Analyzer		Reference Method	
Sampling Area	Field Triplicate Set	TPH Result (milligram per kilogram)	Relative Standard Deviation (percent)	TPH Result (milligram per kilogram)	Relative Standard Deviation (percent)
Fuel Farm Area[a]	1	54	7	68.2	34
		54		90.2	
		61		44.1	
	2	8,500	86	15,000	11
		7,370		12,000	
		88		13,900	
Naval Exchange Service Station Area[b]	3	250	36	280	13
		150		270	
		130		219	
	4	710	21	1,870	39
		1,060		881	
		1,040		1,180	
	5	1,070	9	1,560	16
		990		1,120	
		900		1,390	
	6	Less than 10	80	9.56	23
		Less than 10		14.2	
		18		15.2	
Phytoremediation Area[a]	7	740	14	2,140	21
		610		1,790	
		800		1,390	
B-38 Area[b]	8	38	24	79	13
		24		61.4	
		37		67.3	
Slop Fill Tank Area[b]	9	1,180	9	834	14
		1,250		1,090	
		1,040		938	
	10	430	49	501	4
		170		544	
		230		517	
	11	370	79	280	29
		77		503	
		660		369	
	12	23	58	185	28
		30		146	
		66		253	

Notes:

[a] Model HATR-T was used to analyze samples collected from this area.

[b] Model CVH was used to analyze samples collected from this area.

Table 7-7. Comparison of Infracal® TOG/TPH Analyzer and Reference Method Precision for Replicate Performance Evaluation Samples

			Infracal® TOG/TPH Analyzer		Reference Method	
Sample Type		Replicate Set	TPH Result	Relative Standard Deviation (percent)	TPH Result	Relative Standard Deviation (percent)
Soil Samples (Processed Garden Soil) (TPH Results in Milligram per Kilogram)						
Blank (9 percent moisture content)[a,b]		1	Less than 50[a]; less than 10[b]	Not calculated[c]	5.1	45
			Less than 50[a]; less than 10[b]		13.1	
			Less than 50[a]; less than 10[b]		13.5	
Weathered gasoline[b]	Medium-range TPH concentration (9 percent moisture content)	2	80	8	350	2
			87		346	
			93		336	
	High-range TPH concentration (9 percent moisture content)	3	890	7	1,880	7
			1,010		2,020	
			910		2,180	
	High-range TPH concentration (16 percent moisture content)	4	1,020	13	1,740	8
			780		1,980	
			900		2,050	
Diesel[a]	Low-range TPH concentration (9 percent moisture content)	5	Less than 50	Not calculated[c]	16.4	10
			Less than 50		16.4	
			Less than 50		13.2	
			Less than 50		16.0	
			Less than 50		14.2	
			Less than 50		14.1	
			Less than 50		12.8	
	Medium-range TPH concentration (9 percent moisture content)	6	61	21	276	4
			91		273	
			88		295	
	High-range TPH concentration (9 percent moisture content)	7	820	15	2,480	8
			610		2,890	
			750		2,800	
	High-range TPH concentration (less than 1 percent moisture content)	8	2,060	4	2,700	6
			1,990		2,950	
			2,140		3,070	
Liquid Samples (Neat Materials) (TPH Results in Milligram per Liter)						
Weathered gasoline[b]		9	591,440	3	656,000	5
			554,960		611,000	
			571,540		677,000	
Diesel[a,b]		10	423,760[a]; 810,330[b]	3[a,d]; 7[b]	1,090,000	6
			412,420[a]; 793,750[b]		1,020,000	
			902,090[b]		1,160,000	

Notes:

[a] Model HATR-T was used to analyze the samples.

[b] Model CVH was used to analyze the samples.

[c] The relative standard deviation was not calculated because all the results were reported as below the detection limit.

[d] The relative percent difference was used to evaluate the precision for neat diesel samples analyzed using Model HATR-T because only two sample results were reported.

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

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 Infracal® TOG/TPH Analyzer 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 Infracal® TOG/TPH Analyzer ranged from 0 to 126 percent for liquid interferent samples; the mean response for humic acid was 0 percent. The TPH results for a given triplicate set and between the triplicate sets showed good agreement except for turpentine. The mean response for MTBE (62 percent) indicated that MTBE can be measured as TPH using the Infracal® TOG/TPH Analyzer. The mean responses for Stoddard solvent (120 percent for Model CVH and 0.5 percent for Model HATR-T) indicated that Stoddard solvent can be measured as TPH using CVH but not Model HATR-T. The mean responses for turpentine (77 percent for Model CVH and 0.5 percent for Model HATR-T) indicated that turpentine would result in false positives during TPH measurement using Model CVH but not Model HATR-T. The mean response of 0 percent for PCE and humic acid indicated that these compounds would not result in either false positives or false negatives during TPH measurement. Similarly, the mean response of 0.5 percent for 1,2,4-trichlorobenzene indicated that 1,2,4-trichlorobenzene would likely not result in either false positives or false negatives during TPH measurement. Comparison of the mean responses observed for liquid interferent samples analyzed using both sample stages suggested that Model HATR-T may have malfunctioned during the demonstration. Specifically, Model HATR-T showed less than 1 percent response for neat Stoddard solvent and turpentine, which would be expected to have strong absorption in the infrared region based on their chemical structures (carbon-hydrogen bonds); the mean responses observed for Model CVH appeared to be reasonable.

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 Infracal® TOG/TPH Analyzer and reference method. A parametric or nonparametric test was selected for statistical evaluation of the results using the approach presented in Figure 7-1.

TPH results for samples with and without interferents, statistical tests performed, and statistical test conclusions for both the Infracal® TOG/TPH Analyzer and 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 statistical results for each interferent are discussed below.

Effect of Methyl-Tert-Butyl Ether

The effect of MTBE was evaluated for soil PE samples containing weathered gasoline. Based on the liquid PE

Table 7-8. Comparison of Infracal® TOG/TPH Analyzer and Reference Method Results for Interferent Samples

	Infracal® TOG/TPH Analyzer			Reference Method		
Interferent and Concentration[a]	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)[c]	430,040	463,940	63	309,000	284,000	38
	496,370			272,000		
	465,420			270,000		
	431,620	443,470	60	303,000	299,000	40
	448,840			313,000		
	449,960			282,000		
Tetrachloroethene (1,621,000 milligrams per liter)[c]	Less than 4,010	2,000	0	269,000	272,000	17
	Less than 4,010			270,000		
	Less than 4,010			277,000		
	Less than 810	410	0	290,000	295,000	18
	Less than 810			288,000		
	Less than 810			307,000		
Stoddard solvent (771,500 milligrams per liter)[c,d]	973,950[c]; less than 20,100[d]	968,790[c]; 10,050[d]	126[c]; 1[d]	561,000	598,000	78
	954,050[c]; less than 20,100[d]			628,000		
	978,370[c]; less than 20,100[d]			606,000		
	827,250[c]; less than 4,100[d]	869,420[c]; 2,050[d]	113[c]; 0[d]	703,000	708,000	92
	909,100[c]; less than 4,100[d]			Not reported		
	871,900[c]; less than 4,100[d]			713,000		
Turpentine (845,600 milligrams per liter)[c,d]	748,420[c]; less than 20,100[d]	731,470[c]; 10,050[d]	86[c]; 1[d]	504,000	468,000	55
	725,210[c]; less than 20,100[d]			459,000		
	720,790[c]; less than 20,100[d]			442,000		
	615,160[c]; 4,880[d]	578,370[c]; 5,550[d]	68[c]; 0[d]	523,000	408,000	48
	611,440[c]; 5,880[d]			353,000		
	508,500[c]; 5,880[d]			349,000		
1,2,4-Trichlorobenzene (1,439,000 milligrams per liter)[d]	Less than 20,100	10,050	1	711,000	688,000	48
	Less than 20,100			620,000		
	Less than 20,100			732,000		
	Less than 4,100	2,050	0	754,000	754,000	52
	Less than 4,100			756,000		
	Less than 4,100			752,000		
Interferent Samples (Processed Garden Soil) (TPH Results in Milligram per Kilogram)						
Humic acid at 3,940 milligrams per kilogram[d]	Less than 50	25	0	8.99	9.00	0
	Less than 50			8.96		
	Less than 50			8.12		
Humic acid at 19,500 milligrams per kilogram[d]	Less than 50	25	0	69.3	76.0	0
	Less than 50			79.1		
	Less than 50			78.5		

Table 7-8. Comparison of Infracal® TOG/TPH Analyzer and Reference Method Results for Interferent Samples (Continued)

Notes:

[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] Model CVH was used to analyze the samples.

[d] Model HATR-T was used to analyze the samples.

Table 7-9. Comparison of Infracal® TOG/TPH Analyzer and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents

Sample Matrix and Interferent[a]		Infracal® TOG/TPH Analyzer					Reference Method				
		TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)
Soil Samples Without Interferents											
Weathered gasoline[b]		890	940	Not applicable			1,880	2,030	Not applicable		
		1,010					2,020				
		910					2,180				
Diesel[c]		820	730	Not applicable			2,480	2,720	Not applicable		
		610					2,890				
		750					2,800				
Soil Samples With Interferents											
Weathered gasoline	MTBE (1,100 mg/kg)[b]	710	860	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Same	5.82	1,900	1,950	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Same	11.21
		1,040					1,750				
		840					2,210				
	MTBE (1,700 mg/kg)[b]	660	620				2,150	2,340			
		470					2,320				
		740					2,560				
	PCE (2,810 mg/kg)[b]	1,040	950		Same	51.11	2,540	2,380		Mean with interferent at high level was different from means without interferent and with interferent at low level	0.00
		870					2,160				
		950					2,450				
	PCE (13,100 mg/kg)[b]	1,030	1,010				4,740	4,450			
		1,060					4,570				
		930					4,040				

Table 7-9. Comparison of Infracal® TOG/TPH Analyzer and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents (Continued)

Sample Matrix and Interferent[a]		Infracal® TOG/TPH Analyzer					Reference Method				
		TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)
Soil Samples With Interferents (Continued)											
Weathered gasoline (Continued)	Stoddard solvent (2,900 mg/kg)[b]	2,630	2,700	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00	4,350	4,410	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00
		2,770					4,760				
		2,710					4,110				
	Stoddard solvent (15,400 mg/kg)[b]	16,760	20,050				10,300	11,900			
		20,570					14,300				
		22,820					11,000				
Diesel	Stoddard solvent (3,650 mg/kg)[b]	2,950	2,620		All three means (with and without interferents) were significantly different from one another	0.00	4,390	4,520		All three means (with and without interferents) were significantly different from one another	0.00
		2,180					4,640				
		2,720					4,520				
	Stoddard solvent (18,200 mg/kg)[b]	13,530	13,000				8,770	7,880			
		8,580					6,580				
		16,900					8,280				
Weathered gasoline	Turpentine (2,730 mg/kg)[b]	1,740	1,470		Mean with interferent at high level was different from means without interferent and with interferent at low level	0.00	4,410	4,240		All three means (with and without interferents) were significantly different from one another	0.00
		1,390					3,870				
		1,290					4,440				
	Turpentine (12,900 mg/kg)[b]	14,800	16,600				12,800	12,900			
		24,150					11,200				
		10,840					14,600				

Table 7-9. Comparison of Infracal® TOG/TPH Analyzer and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents (Continued)

		Infracal® TOG/TPH Analyzer					Reference Method				
Sample Matrix and Interferent[a]		TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)
Soil Samples With Interferents (Continued)											
Diesel	Turpentine (3,850 mg/kg)[b]	2,860	2,860	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00	5,860	5,760	Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis pairwise comparison of means (nonparametric)	Mean without interferent was same as mean with interferent at low level; mean with interferent at low level was same as mean with interferent at high level	2.65
		2,760					5,810				
		2,960					5,610				
	Turpentine (19,600 mg/kg)[b]	14,800	14,760				15,000	13,900			
		17,160					13,300				
		12,320					13,300				
	1,2,4-Trichloro-benzene (3,350 mg/kg)[c]	590	870	Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis pairwise comparison of means (nonparametric)	Same	100	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
		930					3,750				
		1,080					3,550				
	1,2,4-Trichloro-benzene (16,600 mg/kg)[c]	Not analyzed[d]	940				7,940	7,060			
		750					6,560				
		1,130					6,690				

Table 7-9. Comparison of Infracal® TOG/TPH Analyzer and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents (Continued)

Sample Matrix and Interferent[a]		Infracal® TOG/TPH Analyzer					Reference Method				
		TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)
Soil Samples With Interferents (Continued)											
Diesel (Continued)	Humic acid (3,940 mg/kg)[c]	920	820	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Same	86.91	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				
		540					2,360				
	Humic acid (19,500 mg/kg)[c]	800	790				2,660	2,450			
		520					2,420				
		1,060					2,270				

Notes:

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

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

[b] Model CVH was used to analyze the samples.

[c] Model HATR-T was used to analyze the samples.

[d] The sample was not analyzed because the vial containing the sample and solvent broke during the sample extraction step.

sample (neat material) analytical results, MTBE was expected to bias both the Infracal® TOG/TPH Analyzer and reference method results high.

For the Infracal® TOG/TPH Analyzer, at the interferent levels used, MTBE was expected to bias the TPH results high by 73 percent (low level) and 110 percent (high level). The expected bias would be lower (31 and 48 percent, respectively) if MTBE in soil samples was assumed to be extracted as efficiently as weathered gasoline in soil samples. However, as shown in Table 7-9, 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 Infracal® TOG/TPH Analyzer's precision (7 percent).

For the reference method, at the interferent levels used, MTBE was expected to bias the TPH results high by 21 percent (low level) and 33 percent (high level). The expected bias would be lower (17 and 27 percent, respectively) if MTBE in soil samples was assumed to be extracted as efficiently as weathered gasoline in soil samples. However, no effect on TPH measurement was observed for soil PE samples analyzed during the demonstration. A significant amount of MTBE, a highly volatile compound, may have been lost during PE sample preparation, transport, storage, and handling, thus lowering the MTBE concentrations to levels that would not have increased the TPH results beyond the reference method's precision (7 percent).

Effect of Tetrachloroethene

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

Table 7-9 shows that PCE did not affect the Infracal® TOG/TPH Analyzer TPH results for soil PE samples containing weathered gasoline, which confirmed the conclusions drawn from the analytical results for neat PCE.

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

Effect of Stoddard Solvent

The effect of Stoddard solvent was evaluated for weathered gasoline and diesel soil PE samples. Based on the liquid PE sample (neat material) analytical results, Stoddard solvent was expected to bias both the Infracal® TOG/TPH Analyzer and reference method results high.

For the Infracal® TOG/TPH Analyzer, at the interferent levels used, Stoddard solvent was expected to bias the TPH results high by 370 percent (low level) and 1,970 percent (high level) for weathered gasoline soil PE samples and by 600 percent (low level) and 2,990 percent (high level) for diesel soil PE samples. The expected bias would be lower (160 and 840 percent, respectively, for weathered gasoline soil PE samples and 120 and 580 percent, respectively, for diesel soil PE samples) if Stoddard solvent in soil samples was assumed to be extracted as efficiently as weathered gasoline and diesel in soil samples. The statistical tests showed that the mean TPH results with and without the interferent were different for weathered gasoline and diesel soil PE samples, which confirmed the conclusions drawn from the analytical results for neat Stoddard solvent.

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

Effect of Turpentine

The effect of turpentine was evaluated for weathered gasoline and diesel soil PE samples. Based on the liquid PE sample (neat material) analytical results, turpentine was expected to bias both the Infracal® TOG/TPH Analyzer and reference method results high.

For the Infracal® TOG/TPH Analyzer, at the interferent levels used, turpentine was expected to bias the TPH results high by 220 percent (low level) and 1,060 percent (high level) for weathered gasoline soil PE samples and by 410 percent (low level) and 2,070 percent (high level) for diesel soil PE samples. The expected bias would be lower (96 and 450 percent, respectively, for weathered gasoline soil PE samples and 79 and 400 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. For weathered gasoline soil PE samples, the statistical tests showed that the mean TPH result with the interferent at the high level was different from the mean TPH results without the interferent and with the interferent at the low level, indicating that turpentine at the low level did not affect the TPH results for the weathered gasoline soil PE samples but that turpentine at the high level did affect the TPH results. For diesel soil PE samples, the statistical tests showed that the mean TPH results with and without the interferent were different, which confirmed the conclusions drawn from the analytical results for neat turpentine. The conclusion reached for the interferent at the low level in weathered gasoline soil PE samples was unexpected and did not seem reasonable based on a simple comparison of means that differed by a factor of almost two. However, the conclusion drawn from the statistical test was justified when the variabilities associated with the mean TPH concentrations were taken into consideration.

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 have no effect on the TPH results of the Infracal® TOG/TPH Analyzer; however, it was expected to bias the reference method results high.

Table 7-9 shows that 1,2,4-trichlorobenzene did not affect the Infracal® TOG/TPH Analyzer TPH results for diesel soil PE samples, which confirmed the conclusions drawn from the results of the neat 1,2,4-trichlorobenzene analysis.

For the reference method, at the interferent levels used, 1,2,4-trichlorobenzene was expected to bias the TPH results high by 62 percent (low level) and 305 percent (high level). The expected bias would be lower (33 and

164 percent, respectively) if 1,2,4-trichlorobenzene in soil samples was assumed to be extracted as efficiently as diesel in soil samples. The statistical tests showed that the probability of three means being equal was less than 5 percent. However, the tests also showed that when the interferent was present at the high level, TPH results were biased high. The effect observed at the high level confirmed the conclusions drawn from the analytical results for neat 1,2,4-trichlorobenzene. The statistical tests indicated that the mean TPH result with the interferent at the low level was not different from the mean TPH result without the interferent, indicating that the low level of 1,2,4-trichlorobenzene did not affect TPH measurement. However, a simple comparison of the mean TPH result 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 Infracal® TOG/TPH Analyzer and reference method.

Table 7-9 shows that humic acid did not affect the Infracal® TOG/TPH Analyzer TPH results for diesel soil PE samples, which confirmed the conclusions drawn from the analytical results for soil PE samples containing humic acid.

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 Infracal® TOG/TPH Analyzer and the reference method to accurately measure TPH, high-concentration-range soil PE samples containing weathered gasoline or diesel at two moisture levels were analyzed. The device and reference method results were converted from a wet weight basis to a dry weight basis in order to evaluate the effect of moisture content on the sample TPH results. The device and reference method dry weight TPH results for weathered gasoline samples and diesel samples were normally distributed; therefore, a two-tailed, two-sample Student's t-test was performed to determine whether these device and reference method results were impacted by soil moisture content—that is, to determine whether an increase in soil moisture content resulted in an increase or decrease in the TPH concentrations measured. 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 moisture levels were the same, and the probability of the null hypothesis being true.

Table 7-10 shows that Infracal® TOG/TPH Analyzer results for weathered gasoline soil samples at different moisture levels were statistically the same at a significance level of 5 percent, indicating that the increase in soil moisture content from 9 to 16 percent did not impact the TPH results. However, a statistical comparison of the device results for diesel soil samples showed that there was a less than 5 percent probability that the TPH results were the same at the two moisture levels (less than 1 percent and 9 percent), indicating that soil moisture content had a statistically significant impact on the device results. Based on a simple comparison of the results, the statistical test conclusions appeared to be reasonable.

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 Infracal® TOG/TPH

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

	Infracal® TOG/TPH Analyzer				Reference Method			
Sample Type and Moisture Level	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]	Probability of Null Hypothesis Being True[b] (percent)	TPH Result on Dry Weight Basis (milligram per kilogram)	Mean TPH Result (milligram per kilogram)	Were Mean TPH Results at Different Moisture Levels the Same or Different?[a]	Probability of Null Hypothesis Being True[b] (percent)
Weathered gasoline at 9 percent moisture level[c]	980	1,030	Same	64.75	2,070	2,230	Same	66.52
	1,110				2,220			
	1,000				2,400			
Weathered gasoline at 16 percent moisture level[c]	1,210	1,070			2,070	2,300		
	940				2,390			
	1,070				2,440			
Diesel at less than 1 percent moisture level[d]	900	797	Different	0.01	2,740	3,000	Same	71.95
	670				3,180			
	820				3,070			
Diesel at 9 percent moisture level[d]	2,080	2,080			2,720	2,930		
	2,000				2,970			
	2,160				3,100			

Notes:

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

[b] 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.

[c] Model CVH was used to analyze the samples.

[d] Model HATR-T was used to analyze the samples.

Analyzer setup, sample extraction, sample analysis, device disassembly, and data package preparation, was measured. During the demonstration, one field technician performed the TPH measurement activities using the device. Time measurement began at the start of each demonstration day when the technician began to set up the device and ended when she disassembled the device. Time not measured included (1) the time spent by the technician verifying that she had received all the demonstration samples indicated on chain-of-custody forms, (2) the times when she took breaks, and (3) the time that she 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 extract and analyze the first and last analytical batches of soil samples was measured. The number and type of samples in a batch were selected by Wilks.

The time required to complete TPH measurement activities using the Infracal® TOG/TPH Analyzer is shown in Table 7-11. The time required for each activity was rounded to the nearest 5 minutes.

Overall, Wilks required 35 hours, 30 minutes, for TPH measurement of 74 soil environmental samples (56 using Model CVH and 18 using Model HATR-T), 91 soil PE samples (52 using Model CVH, 33 using Model HATR-T, and 3 using both Models CVH and HATR-T), and 50 liquid PE samples (16 using Model CVH, 6 using Model HATR-T, and 14 using both Models CVH and HATR-T). Information regarding the time required for each measurement activity during the entire 5-day demonstration and for extraction and analysis of the first and last batches of soil samples is provided below. The times recorded for the first and last batches were for Models CVH and HATR-T, respectively.

The setup time for the Infracal® TOG/TPH Analyzer was measured at the beginning of each day during the 5-day demonstration period. Setup activities included device setup; analysis of QC check standards; and organization of extraction, dilution, analysis, and decontamination supplies. Device setup required a total of 1 hour, 50 minutes, during the 5-day demonstration, or an average of 22 minutes per day. The total setup time did not include a 5-hour period during which Wilks was away from the demonstration site obtaining another infrared spectrophotometer and Model HATR-T sample stage; the original spectrophotometer malfunctioned when the Model CVH sample stage was replaced with the Model HATR-T sample stage, and the spectrophotometer and Model HATR-T sample stage had to be replaced. Device setup on the first and last days of the demonstration required 25 and 15 minutes, respectively, or an average of 20 minutes per day. The decrease in the setup time between the first and last days suggested that the field technician became more familiar with the device setup procedure as the demonstration progressed.

Table 7-11. Time Required to Complete TPH Measurement Activities Using the Infracal® TOG/TPH Analyzer

	Time Required[a]		
Measurement Activity	First Soil Sample Batch[b]	Last Soil Sample Batch[c]	5-Day Demonstration Period
Infracal® TOG/TPH Analyzer setup[d]	25 minutes	15 minutes	1 hour, 50 minutes
Sample extraction	20 minutes	15 minutes	17 hours, 20 minutes
Sample analysis	5 minutes	20 minutes	14 hours, 20 minutes
Infracal® TOG/TPH Analyzer disassembly[d]	10 minutes	5 minutes	40 minutes
Data package preparation	Not measured	Not measured	1 hour, 20 minutes
Total	**1 hour**	**55 minutes**	**35 hours, 30 minutes**

Notes:

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

[b] The times recorded for the first soil sample batch were for Model CVH. The batch consisted of two samples.

[c] The times recorded for the last soil sample batch were for Model HATR-T. The batch consisted of four samples.

[d] The Infracal® TOG/TPH Analyzer setup and disassembly times were measured at the beginning and end of each day, respectively. The times recorded (1) for the first soil sample batch were for Model CVH the first day and (2) for the last soil sample batch were for Model HATR-T on the last day of the 5-day demonstration period.

Extraction of all 165 soil samples in 74 analytical batches required 17 hours, 20 minutes, resulting in average extraction times of 6.3 minutes per sample and 14 minutes per batch. However, the field technician also completed other activities during the demonstration, such as decontaminating glassware. Thus, the average extraction times included the time required to complete additional activities.

The time required for extraction of the first and last batches of soil samples was also recorded. During the first 4 days of the 5-day demonstration period, Wilks designated two samples for each analytical batch. The number of samples was based on the fact that the field technician performed sample extraction by manually agitating two vials of soil-solvent mixture at a time, one in each hand. On the last day of the demonstration, the technician chose to agitate two vials in each hand. As a result, four samples were designated for each of the last nine analytical batches. The first batch of two samples and the last batch of four samples required 20 and 15 minutes, respectively, for extraction. The decrease in the sample extraction time between the first and last batches of soil samples suggested that the technician became more familiar with the extraction procedure as the demonstration progressed. The average extraction time for all the batches (14 minutes) is close to the extraction time for the last batch (15 minutes), indicating that the technician became familiar with the extraction procedure during the early stages of the demonstration.

A total of 14 hours, 20 minutes, was required to report 215 TPH results, or an average of 4 minutes per sample. In addition to performing the 215 analyses required to report 215 TPH results, the field technician performed extract dilutions and reanalyses for the high-concentration-range samples. The average analysis time did not include the time taken to perform these additional activities.

The time required to analyze the first and last batches of soil samples was also recorded. A total of 5 minutes was required to analyze the first batch of samples using Model CVH. The first batch required two TPH analyses; therefore, an average of 2.5 minutes was required to complete one analysis. A total of 20 minutes was required to analyze the last batch of samples using Model HATR-T. The last batch required four TPH analyses; therefore, an average of 5 minutes was required to complete one analysis. The increase in the average analysis time between the first and last batches of soil samples may have been attributable to the additional time required to obtain a stable reading from Model HATR-T compared to Model CVH.

The disassembly time for the Infracal® TOG/TPH Analyzer was measured at the end of each day during the 5-day demonstration period. Disassembly included packing up the device and associated supplies required for TPH measurement. Device disassembly required a total of 40 minutes during the 5-day demonstration, or an average of 8 minutes per day. Device disassembly on the first and last days of the demonstration required 10 and 5 minutes, respectively, or an average of 7.5 minutes per day. The decrease in the disassembly time between the first and last days suggested that the field technician became more familiar with the disassembly procedure as the demonstration progressed.

Preparation of the data package required 1 hour, 20 minutes, in the field. Preparation of the data package submitted to the EPA at the end of the demonstration involved (1) photocopying Wilks' log sheets, which included sample identification numbers, the mass of soil and volume of solvent used, and TPH results, and (2) rechecking the number of samples analyzed against chain-of-custody forms. When extract dilutions had been performed, the TPH concentration calculations had been recorded on the log sheets. During the weeks following the demonstration, Wilks spent additional time revising the data package to address EPA comments. The revisions included correcting calibration, calculation, and typographical errors. The amount of additional time that Wilks spent finalizing the data package could not be quantified and was not included as part of the time required for TPH measurement.

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

7.2 Secondary Objectives

This section discusses the performance results for the Infracal® TOG/TPH Analyzer, Models CVH and HATR-T, in terms of the secondary objectives stated in

Section 4.1. The secondary objectives were addressed based on (1) observations of the Infracal® TOG/TPH Analyzer's performance during the demonstration and (2) information provided by Wilks.

7.2.1 Skill and Training Requirements for Proper Device Operation

Based on observations made during the demonstration, TPH measurement using the Infracal® TOG/TPH Analyzer requires one field technician with basic wet chemistry skills acquired on the job or in a university. Because the amount of sample drying agent (silica gel) used and the sample extraction time may need to be adjusted based on soil type and moisture content, basic knowledge of soil types is also recommended so that the technician can differentiate among sand, silt, and clay soil types and modify the sample drying and extraction steps accordingly. During the demonstration, Wilks chose to conduct sample analyses using one technician.

The sample analysis procedure for the Infracal® TOG/TPH Analyzer can be learned in the field with a few practice attempts. In addition, during regular business hours, Wilks provides technical support over the telephone at no additional cost. Wilks offers a 1-day, on-site training program for $750, which includes the cost for one instructor and one Infracal® TOG/TPH Analyzer for training purposes. The user would also have to pay an additional cost to cover the instructor's travel and per diem for 1 day.

As stated in Chapter 2, to minimize the use of Freon 113, Wilks recommends using Model CVH for TPH measurement of samples containing gasoline (the volatile portion of PHCs) and Model HATR-T for TPH measurement of samples containing diesel (the semivolatile portion of PHCs). Following the recommendation, the user would have to switch between the Model CVH and HATR-T sample stages when some samples contain gasoline and some contain diesel.

During the demonstration, the infrared spectrophotometer malfunctioned when the Model CVH sample stage was replaced with the Model HATR-T sample stage, and the spectrophotometer and Model HATR-T sample stage had to be replaced; the cause of the malfunction was not determined in the field. Based on demonstration observations, switching sample stages may require some skill.

With the Infracal® TOG/TPH Analyzer, minimal effort is generally required to calculate a TPH concentration because a one-to-one ratio between the mass of soil and volume of solvent used during sample extraction is programmed into the device, and the concentration can be read from the digital display in units of mg/kg TPH on a wet weight basis. For a diluted sample extract, the user must multiply the digital display reading by an appropriate dilution factor.

Based on demonstration results, Wilks had difficulty calculating TPH concentrations for diluted sample extracts, primarily due to use of incorrect dilution factors. After the demonstration, Wilks made revisions to the TPH results calculated in the field, including correcting calibration, calculation, and typographical errors. Of the 215 TPH results reported by Wilks during the demonstration, 90 TPH results were corrected after the demonstration was completed. The corrections were associated with incorrect calibration of Model HATR-T, use of an incorrect dilution factor while using Model CVH, and data entry errors.

During the demonstration, Wilks used supplies and took steps that significantly increased the time and effort associated with sample preparation and analysis activities. For example, Wilks had to carefully place a measured amount of each soil sample in a narrow-mouthed, 40-mL vial and then use a graduated cylinder to measure the volume of extraction solvent to be added. These steps took a significant amount of the field technician's time (an average of 5 minutes per sample). Use of vials with wider mouths and autopipettes would have made it easier and less time-consuming to weigh soil and measure extraction solvent, respectively. In addition, use of autopipettes would have allowed more accurate volumetric measurements. Wilks also used a large air syringe to filter the extraction solvent. This item proved difficult to use over a long period of time because it required considerable strength to operate. Disposable, filter syringes would have been equally effective and easier to use.

7.2.2 Health and Safety Concerns Associated with Device Operation

The primary health and safety hazard associated with using the Infracal® TOG/TPH Analyzer involves using Freon 113 extraction solvent with Model CVH. The two other chemicals required for use of the device are silica gel and Vertrel® MCA extraction solvent, both of which are nontoxic.

During the demonstration, the Wilks field technician operated the Infracal® TOG/TPH Analyzer in modified Level D personal protective equipment (PPE) to prevent eye and skin contact with Freon 113. The PPE included safety glasses, disposable gloves, work boots, and work clothes with long sleeves and long pants. Sample analyses were performed outdoors in a well-ventilated area; therefore, exposure to Freon 113 through inhalation was not a concern. Health and safety information for the Freon 113 used during sample extraction, extract dilution, and glassware decontamination is included in material safety data sheets available from Wilks.

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

7.2.3 Portability of the Device

The Infracal® TOG/TPH Analyzer comes in a cardboard box and weighs about 5 pounds. The box is 10 inches long, 10 inches wide, and 14 inches high. According to Wilks, an optional carrying case for the device is available for purchase by the user. The device is operated using a 110-volt AC power source or DC power from a battery pack. Because the Infracal® TOG/TPH Analyzer comes in a small box, and because an AC power source is not required to operate the device, it is easily transported between sampling areas in the field.

Except for the extraction solvents, supplies required to perform TPH measurements using the Infracal® TOG/TPH Analyzer are provided in KIT-10410-S. The components of KIT-10410-S are contained in a cardboard box that weighs 11 pounds and is 14 inches long, 14 inches wide, and 12 inches high. The Freon 113 and Vertrel® MCA extraction solvents have to be purchased from chemical suppliers in the quantities required. For the demonstration, Wilks brought Freon 113 and Vertrel® MCA extraction solvents in 2-liter and 1-liter bottles, respectively.

To operate the Infracal® TOG/TPH Analyzer, a sample preparation and analysis area is required. The area must be large enough to accommodate the infrared spectrophotometer, its sample stage or stages, and supplies required for sample preparation and analysis. The size of the area depends on the number of samples to be analyzed and is thus project-specific. During the demonstration, Wilks performed sample preparation and analysis under one 8- by 8-foot tent that housed two 8-foot-long, folding tables; two folding chairs; one 20-gallon laboratory pack for flammable waste; and one 55-gallon drum for general refuse.

7.2.4 Durability of the Device

According to Wilks, the infrared spectrophotometer contains no mechanical or electronic parts that could potentially malfunction during sample analysis. Based on observations made during the demonstration, Model CVH proved to be durable and did not malfunction or become damaged. However, the infrared spectrophotometer malfunctioned when the Model CVH sample stage was replaced with the Model HATR-T sample stage, and the spectrophotometer and Model HATR-T sample stage had to be replaced; the cause of the malfunction was not determined in the field.

A battery-powered A&D Weighing balance included in KIT-10410-S contains electronic parts that could potentially malfunction, but the balance did not malfunction during the demonstration. Wilks used an egg timer instead of the timer provided in KIT-10410-S during the demonstration; as a result, the timer included in the kit could not be evaluated in terms of its durability.

The Infracal® TOG/TPH Analyzer is manufactured and distributed by Wilks. The components of KIT-10410-S are available from a variety of manufacturers; Wilks supplies them to users in one package. The Infracal® TOG/TPH Analyzer and KIT-10410-S are each housed in a padded, cardboard box.

The cause of the malfunction of Model HATR-T described above remains unknown. However, based on observations made during the demonstration, the operation of the Infracal® TOG/TPH Analyzer was generally unaffected by the varying temperature and humidity conditions encountered between 8:00 a.m. and 5:00 p.m. on any given day. During the daytime, the temperature ranged from about 17 to 24 °C, and the relative humidity ranged from 53 to 88 percent. During sample analysis, wind speeds up to 20 miles per hour did not affect device operation.

7.2.5 Availability of the Device and Spare Parts

When the Infracal® TOG/TPH Analyzer is purchased, Wilks provides a 1-year warranty for the device. A warranty is also provided when the device is rented. If an infrared spectrophotometer or sample stage that has been purchased or rented malfunctions in the field and is still under warranty, Wilks will provide the replacement item within 48 hours on loan for a fee of $75 while the original item is being repaired. Spare parts for the Infracal® TOG/TPH Analyzer, such as a cuvette or bulb, are not included with the device when it is purchased or rented. Replacement parts can be purchased from Wilks or a scientific equipment supplier. During the demonstration, Model HATR-T required replacement. Wilks replaced the malfunctioning infrared spectrophotometer and the Model HATR-T sample stage with another unit borrowed from a local Wilks customer at no charge. However, this option would not have been available to a typical user. Wilks recommends that a malfunctioning Infracal® TOG/TPH Analyzer or sample stage be returned to Wilks for service.

Wilks does not provide a warranty for KIT-10410-S. Replacement components for KIT-10410-S and additional quantities of its components can be purchased from scientific equipment suppliers. The Freon 113 and Vertrel® MCA extraction solvents have to be purchased from chemical suppliers in the quantities required.

Chapter 8
Economic Analysis

As discussed throughout this ITVR, the Infracal® TOG/TPH Analyzer was demonstrated by using both Models CVH and HATR-T 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 Infracal® TOG/TPH Analyzer.

During the demonstration, the Infracal® TOG/TPH Analyzer 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 device and then compare this cost to that for the reference method. The cost per analysis was not estimated for the Infracal® TOG/TPH Analyzer 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 Infracal® TOG/TPH Analyzer (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 device 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 Infracal® TOG/TPH Analyzer unless otherwise stated.

8.1.1 Capital Equipment Cost

The capital equipment cost was the cost associated with the rental of Infracal® TOG/TPH Analyzer Models CVH and HATR-T used during the demonstration. The Infracal® TOG/TPH Analyzer is available for purchase or rental from Wilks. The device can be rented on a monthly basis for 15 percent of the purchase price; as a result, the break-even point between the purchase price and the rental cost is about 7 months. Because the Infracal® TOG/TPH Analyzer was used for 5 days during the demonstration, the capital equipment cost was the cost associated with the rental of the device for 1 month, the less expensive alternative. The purchase price and rental cost information was obtained from a standard price list provided by Wilks.

During the demonstration, the infrared spectrophotometer malfunctioned when the Model CVH sample stage was replaced with the Model HATR-T sample stage. Wilks replaced the malfunctioning infrared spectrophotometer and the Model HATR-T sample stage with another unit borrowed from a local Wilks customer at no charge. Because the cost of the replacement could not be accurately estimated, this cost was not included in the economic analysis.

8.1.2 Cost of Supplies

The cost of supplies was estimated based on the supplies required to analyze all demonstration samples using the Infracal® TOG/TPH Analyzer that were not included in the capital equipment cost category. The supplies that Wilks used during the demonstration fall into three categories: (1) KIT-10410-S, (2) additional KIT-10410-S components, and (3) other supplies not included in the kit. The supplies may be further classified as expendable and reusable. Examples of expendable supplies include chemicals (such as solvent for extracting PHCs from soil and for cleaning glassware) and disposable gloves. Examples of reusable supplies include 10-millimeter, quartz cuvettes and Freon calibration standards. During the demonstration, the types and quantities of all supplies used by Wilks were noted each day.

For supplies provided by Wilks during the demonstration, Wilks' costs were used to estimate the cost of supplies. The costs for supplies not provided by Wilks were estimated based on price quotes from independent sources. Because a user cannot typically return unused supplies, no salvage value for supplies that were not used during the demonstration was included in the cost of supplies.

8.1.3 Support Equipment Cost

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

8.1.4 Labor Cost

The labor cost was estimated based on the time required for Infracal® TOG/TPH Analyzer 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 Wilks. The measurement of the time required for Wilks to complete all analyses and submit the data package to the EPA was rounded to the nearest half-hour. For the economic analysis, it was assumed that a field technician who had worked for a fraction of a day would be paid for an entire 8-hour day. Based on this assumption, a daily rate for a field technician was used in the analysis.

During the demonstration, EPA representatives evaluated the skill level required for the field technician to complete analyses and calculate TPH concentrations. Based on the field observations, a field technician with basic wet chemistry skills acquired on the job or in a university and a few hours of device-specific training was considered to be qualified to operate the Infracal® TOG/TPH Analyzer. 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, Wilks was provided with two 20-gallon laboratory packs for collecting hazardous wastes generated (one for flammable wastes and one for corrosive wastes) and was charged for each laboratory pack used. Unused samples and sample extracts, used EnCores, and unused chemicals that could not be returned to Wilks or an independent vendor were disposed of in a laboratory pack. Spent Freon 113 extraction solvent, which cannot be disposed of in a landfill because of regulatory constraints, was collected in an empty Freon 113 solvent bottle to be sent to a certified solvent reclaimer. Items such as used PPE and disposable glassware were disposed of with municipal garbage in accordance with demonstration site waste disposal guidelines. Wilks was required to provide any containers necessary to containerize individual wastes prior to their placement in a laboratory pack. The cost for these containers was not included in the IDW disposal cost estimate.

8.1.6 Costs Not Included

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

Oversight of Sample Analysis Activities. A typical user of the Infracal® TOG/TPH Analyzer 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 Infracal® TOG/TPH Analyzer and necessary supplies to the demonstration site, (2) sample coolers to the reference laboratory, and (3) spent Freon 113 extraction solvent to a certified solvent reclaimer 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 Infracal® TOG/TPH Analyzer Costs

This section presents information on the individual costs of capital equipment, supplies, support equipment, labor, and IDW disposal for the Infracal® TOG/TPH Analyzer as well as a summary of these costs. Additionally, Table 8-1 summarizes the Infracal® TOG/TPH Analyzer costs.

8.2.1 Capital Equipment Cost

The capital equipment cost was the cost associated with the rental of Infracal® TOG/TPH Analyzer Models CVH and HATR-T. The device is available for rental on a monthly basis for 15 percent of the purchase price. A user incurs at least a 1-month rental cost even if the device is needed for only a few days. Thus, although Wilks used the device for only 5 days during the demonstration, a 1-month rental cost was used for the economic analysis.

The Infracal® TOG/TPH Analyzer consists of an infrared spectrophotometer and the Model CVH or Model HATR-T sample stage. The device also contains an instruction manual. The Infracal® TOG/TPH Analyzer, including the Model CVH sample stage, can be purchased for $4,975; the Model HATR-T sample stage can be purchased for an additional $1,225. Alternatively, a user can purchase the Infracal® TOG/TPH Analyzer with the Model HATR-T sample stage for $5,800 and then purchase the Model CVH sample stage for an additional $475. Because the former option–that is, the purchase of the device with the Model CVH sample stage and the separate purchase of the Model HATR-T sample stage–is $75 cheaper, this option was used to calculate the rental cost of the device for the economic analysis. Thus, the rental cost for the Infracal® TOG/TPH Analyzer and both sample stages was $930.

8.2.2 Cost of Supplies

During the demonstration, Wilks used (1) supplies in KIT-10410-S (which are listed in Section 2.2.1), (2) additional KIT-10410-S components, and (3) other supplies not included in the kit that were needed to analyze the samples. The kit contains the supplies required to perform 50 soil analyses and can be purchased from Wilks for $865.

Table 8-1 lists all supplies that Wilks used during the demonstration, including KIT-10410-S, additional KIT-10410-S components, and other supplies not included in the kit. KIT-10410-S contains both expendable and reusable supplies. Because of the large number of samples analyzed, Wilks used additional quantities of expendable kit components, including silica gel, 40-mL volatile organic analysis vials, and extraction reservoirs. Other expendable supplies used during the demonstration included disposable, latex gloves and Freon 113 and Vertrel® MCA extraction solvents, which were used with Models CVH and HATR-T, respectively, for extracting PHCs from soil and for cleaning glassware. Reusable supplies used during the demonstration included 10-millimeter, quartz cuvettes with Teflon™ caps and Freon calibration standards for Model CVH and an external battery pack for both Models CVH and HATR-T.

Cost information for all the supplies used during the demonstration is presented in Table 8-1. The total cost of the supplies used by Wilks during the demonstration was

Table 8-1. Infracal® TOG/TPH Analyzer Cost Summary

Item	Quantity	Unit Cost ($)	Itemized Cost[a] ($)
Capital equipment			
Rental of infrared spectrophotometer and Models CVH and HATR-T sample stages	1 unit for 5 days	930/month[b]	930
Supplies[c]			
KIT-10410-S	1 unit	865	865
Additional KIT-10410-S components			
Silica gel, 60-200 mesh (500-gram bottle)	2 units	49.50	99
40-milliliter volatile organic analysis vials (72 per box)	3 units	62.50	188
Extraction reservoirs (50 per box)	3 units	176	528
Other supplies			
Freon 113 extraction solvent (2-liter bottle)[d]	2 units	210	420
Vertrel® MCA extraction solvent (1-liter bottle)[e]	2 units	45	90
Disposable, latex gloves (100 per box)	1 unit	20.50	21
10-millimeter, quartz cuvettes with Teflon™ caps (set of four)[d]	1 unit	575	575
External battery pack	1 unit	210	210
Freon calibration standards (set of seven)[d]	1 unit	295	295
Support equipment			
Tent	1 unit	159	159
Tables and chairs (two each)	1 set for 1 week	39	39
Labor			
Field technician	5 person-days	332.60	1,663
Investigation-derived waste disposal			
Spent Freon 113 extraction solvent	13 pounds	2	26
Laboratory pack	1 20-gallon container	345	345
Total Cost[f]			**$6,450**

Notes:

[a] Itemized costs were rounded to the nearest $1.

[b] A user incurs a 1-month rental cost even if the device is needed for only a few days.

[c] Unless otherwise specified, each item was used during sample analysis with both Models CVH and HATR-T.

[d] This item was used during sample analysis with Model CVH.

[e] This item was used during sample analysis with Model HATR-T.

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

$3,291 (the cost of each item was rounded to the nearest $1). All these supplies are available from Wilks except the Freon 113 and Vertrel® MCA extraction solvents and the disposable, latex gloves, which must be purchased from a retail vendor of laboratory supplies.

During the demonstration, Wilks also used the following supplies that cost less than $10 each: (1) a 280-count box of Kimwipes® ($3.60) for wiping the quartz cuvettes and (2) a 3-ounce bottle of 3-IN-ONE oil ($3.29) for calibrating Model HATR-T.

8.2.3 Support Equipment Cost

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

8.2.4 Labor Cost

One field technician was required for 5 days during the demonstration to complete all sample analyses and prepare the summary data package. Based on a labor rate of \$332.60 per day, the total labor cost for the Infracal® TOG/TPH Analyzer was \$1,663.

8.2.5 Investigation-Derived Waste Disposal Cost

Wilks used one laboratory pack to collect flammable hazardous waste, including unused soil and liquid samples that contained PHCs and used EnCores and ampules, generated during the demonstration. Wilks collected all the unused and spent Freon 113 extraction solvents in different bottles. At the end of the demonstration, Wilks took these solvents back to its laboratory. In California, spent Freon 113 solvent is disposed of by sending the solvent to a reclaimer that has been certified by the EPA. Random querying of five EPA-certified solvent reclaimers in California revealed that spent Freon 113 is accepted for a fee ranging from \$1.52 to \$2.39 per pound, or an average of about \$2 per pound. About 4 liters or 13 pounds of spent Freon 113 solvent was generated during the demonstration. Therefore, the IDW disposal cost included the purchase cost of the laboratory pack (\$38), the cost associated with disposal of the laboratory pack in a landfill (\$307), and the cost associated with sending the spent Freon 113 solvent to a reclaimer (\$26) (Means 2000). The total IDW disposal cost was \$371.

8.2.6 Summary of Infracal® TOG/TPH Analyzer Costs

The total cost for performing more than 200 TPH analyses using the Infracal® TOG/TPH Analyzer and for preparing a summary data package was \$6,450 (rounded to the nearest \$10). The TPH analyses were performed for 74 soil environmental samples (56 using Model CVH and 18 using Model HATR-T), 91 soil PE samples (52 using Model CVH, 33 using Model HATR-T, and 3 using both Models CVH and HATR-T), and 50 liquid PE samples (16 using Model CVH, 6 using Model HATR-T, and 14 using both Models CVH and HATR-T). When Wilks performed multiple extractions, dilutions, or reanalyses for a sample, these were not included in the number of samples analyzed. During the demonstration, the multiple extractions, dilutions, and reanalyses did not require more supplies than would otherwise have been needed. The total cost included \$930 for capital equipment; \$3,291 for supplies; \$198 for support equipment; \$1,663 for labor; and \$371 for IDW disposal. Of these five costs, the two largest were the cost of supplies (51 percent of the total cost) and the cost of labor (26 percent of the total cost). If a user anticipates needing the Infracal® TOG/TPH Analyzer for more than 7 months, which is the break-even point between the purchase price and the rental cost for the device, it would be more cost-effective to purchase the device.

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 Infracal® TOG/TPH Analyzer and reference method costs, the reference method costs were estimated for the same number of samples as was analyzed by Wilks. 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 Wilks 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 \$44,410. 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 Infracal® TOG/TPH Analyzer (\$6,450) and the reference method (\$44,410) are listed in Tables 8-1 and 8-2, respectively. The total TPH measurement cost for the device was 85 percent less than that for the reference method. Although the Infracal® TOG/TPH Analyzer analytical results did not have the same level of detail (for example, carbon ranges) as the reference method analytical results or comparable QA/QC

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
EDRO	74	142	10,508
Soil performance evaluation samples			
GRO	55	111	6,105
EDRO	91	142	12,922
Liquid performance evaluation samples			
GRO	30	111	3,330
EDRO	50	106.50	5,325
Total Cost[a]			**$44,410**

Note:

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

data, the device provided TPH analytical results on site at significant cost savings. In addition, use of the Infracal® TOG/TPH Analyzer 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.

Chapter 9
Summary of Demonstration Results

As discussed throughout this ITVR, the Infracal® TOG/TPH Analyzer was demonstrated by using it to analyze 74 soil environmental samples, 91 soil PE samples, and 50 liquid PE samples. The environmental samples were collected from five individual areas at three contaminated sites, and the PE samples were obtained from a commercial provider, ERA. Collectively, the environmental and PE samples provided the different matrix types and the different levels and types of PHC contamination needed to perform a comprehensive evaluation of the Infracal® TOG/TPH Analyzer.

During the demonstration, Wilks analyzed most of the samples using the Infracal® TOG/TPH Analyzer equipped with either the Model CVH sample stage or the Model HATR-T sample stage; only 8 percent of the samples were analyzed using both models. In general, Model CVH was used to analyze samples containing GRO, and Model HATR-T was used to analyze samples that did not contain GRO. For this reason, this ITVR evaluates the performance of the Infracal® TOG/TPH Analyzer as a whole, not that of each model.

The Infracal® TOG/TPH Analyzer 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 Infracal® TOG/TPH Analyzer 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 Infracal® TOG/TPH Analyzer exhibited the following desirable characteristics of a field TPH measurement device: (1) sensitivity to interferents that are PHCs (MTBE and Stoddard solvent), (2) lack of sensitivity to interferents that are not PHCs (PCE; 1,2,4-trichlorobenzene; and humic acid), (3) high sample throughput, and (4) low measurement costs. The device exhibited good precision for soil and liquid PE samples but not for environmental samples.

Overall, the Infracal® TOG/TPH Analyzer TPH results did not compare well with the reference method results. In addition, turpentine biased the device TPH results high, indicating that the accuracy of TPH measurement using the device will likely be impacted by naturally occurring oil and grease present in soil that are not removed by silica gel. Also, the device results for diesel soil PE samples were significantly impacted by soil moisture content; an 8 percentage point increase in soil moisture content resulted in a three-fold increase in TPH results. Finally, the results obtained using the two sample stages (Models CVH and HATR-T) did not agree. Specifically, for neat Stoddard solvent, Model CVH showed a mean response of 120 percent, whereas Model HATR-T showed a mean response of less than 1 percent. Similarly, for neat diesel, the Model HATR-T TPH results were only one-half the Model CVH TPH results. Collectively, these demonstration findings indicated that the Infracal®

Table 9-1. Summary of Infracal® TOG/TPH Analyzer Results for the Primary Objectives

Primary Objective	Evaluation Basis[a]	Performance Results	
		Infracal® TOG/TPH Analyzer	Reference Method
P1 Determine the method detection limit	Method detection limit based on TPH analysis of seven low-concentration-range diesel soil PE samples	76 mg/kg	4.79 mg/kg
P2 Evaluate the accuracy and precision of TPH measurement	Comparison of project-specific action level conclusions of the Infracal® TOG/TPH Analyzer with those of the reference method for 74 soil environmental and 34 soil PE samples	Of the 108 Infracal® TOG/TPH Analyzer results, 7 were inconclusive. Of the 101 device conclusions, 72 (71 percent) agreed with those of the reference method; 2 device conclusions were false positives, and 27 were false negatives.	
	Comparison of Infracal® TOG/TPH Analyzer TPH results with those of the reference method for 74 soil environmental and 31 soil PE samples	22 of 105 Infracal® TOG/TPH Analyzer results (21 percent) were within 30 percent of the reference method results; 15 device results were biased low, and 7 were biased high. 28 of 105 Infracal® TOG/TPH Analyzer results (27 percent) were within 30 to 50 percent of the reference method results; 24 device results were biased low, and 4 were biased high. 55 of 105 Infracal® TOG/TPH Analyzer results (52 percent) were not within 50 percent of the reference method results; 39 device results were biased low, and 16 were biased high.	
	Pairwise comparison of Infracal® TOG/TPH Analyzer and reference method TPH results for (1) soil environmental samples collected from five areas; (2) soil PE samples, including blank, weathered gasoline, and diesel soil samples; and (3) liquid PE samples consisting of neat weathered gasoline and diesel	For soil environmental samples, the Infracal® TOG/TPH Analyzer results were statistically (1) the same as the reference method results for one of the five sampling areas and (2) different from the reference method results for four sampling areas. For soil PE samples, the Infracal® TOG/TPH Analyzer results were statistically different from the reference method results for medium- and high-concentration-range weathered gasoline and diesel samples; the device results for blank samples and low-concentration-range diesel samples could not be compared with the reference method results because the device results were below detection limits. For liquid PE samples, the Infracal® TOG/TPH Analyzer results were statistically different from the reference method results for both weathered gasoline and diesel samples.	
	Correlation (as determined by linear regression analysis) between Infracal® TOG/TPH Analyzer and reference method TPH results for (1) soil environmental samples collected from five areas and (2) soil PE samples, including weathered gasoline and diesel soil samples	The Infracal® TOG/TPH Analyzer results correlated highly with the reference method results for two of the five sampling areas and weathered gasoline soil PE samples (R^2 values ranged from 0.85 to 0.94, and F-test probability values were less than 5 percent). The Infracal® TOG/TPH Analyzer results correlated moderately with the reference method results for two sampling areas and diesel soil PE samples (R^2 values ranged from 0.59 to 0.68, and F-test probability values were less than 5 percent). The Infracal® TOG/TPH Analyzer results correlated weakly with the reference method results for one sampling area (the R^2 value was 0.14, and the F-test probability value was 35.32 percent).	

Table 9-1. Summary of Infracal® TOG/TPH Analyzer Results for the Primary Objectives (Continued)

Primary Objective	Evaluation Basis[a]	Performance Results	
		Infracal® TOG/TPH Analyzer	Reference Method
P2 Evaluate the accuracy and precision of TPH measurement (continued)	Overall precision (RSD) for soil environmental, soil PE, and liquid PE sample replicates	Soil environmental samples (12 triplicates) RSD range: 7 to 86 percent Median RSD: 30 percent	Soil environmental samples (12 triplicates) RSD range: 4 to 39 percent Median RSD: 18 percent
		Soil PE samples (6 replicates) RSD range: 4 to 21 percent Median RSD: 10 percent	Soil PE samples (7 replicates) RSD range: 2 to 10 percent Median RSD: 7 percent
		Liquid PE samples (2 triplicates) RSDs: 3 and 7 percent Median RSD: 5 percent	Liquid PE samples (2 triplicates) RSDs: 5 and 6 percent Median RSD: 5.5 percent
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: 62 percent PCE: 0 percent Stoddard solvent: 120 percent[b] Turpentine: 77 percent[b] 1,2,4-Trichlorobenzene: 0.5 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 (one-way analysis of variance) 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	MTBE, a petroleum hydrocarbon, did not cause statistically significant interference at either of the two levels.	MTBE, a petroleum hydrocarbon, did not cause statistically significant interference at either of the two levels.
		PCE did not cause statistically significant interference at either of the two levels.	PCE caused statistically significant interference only at the high level.
		Stoddard solvent, a petroleum hydrocarbon, caused statistically significant interference at both levels for weathered gasoline and diesel samples.	Stoddard solvent, a petroleum hydrocarbon, caused statistically significant interference at both levels for weathered gasoline and diesel samples.
		Turpentine caused statistically significant interference (1) only at the high level for weathered gasoline samples and (2) at both levels for diesel samples.	Turpentine caused statistically significant interference (1) at both levels for weathered gasoline samples and (2) only at the high level for diesel samples.
		1,2,4-Trichlorobenzene did not cause statistically significant interference at either of the two levels.	1,2,4-Trichlorobenzene caused statistically significant interference only at the high level.
		Humic acid did not cause statistically significant interference at either of the two levels.	Humic acid results were inconclusive.
P4 Evaluate the effect of soil moisture content on TPH measurement	Comparison of TPH results (two-sample Student's t-test) for weathered gasoline and diesel soil PE samples at two moisture levels: 9 and 16 percent for weathered gasoline samples and less than 1 and 9 percent for diesel samples	Soil moisture content had a statistically significant impact on diesel sample results but not on weathered gasoline sample results.	Soil moisture content did not have a statistically significant impact.

Table 9-1. Summary of Infracal® TOG/TPH Analyzer Results for the Primary Objectives (Continued)

Primary Objective	Evaluation Basis[a]	Performance Results	
		Infracal® TOG/TPH Analyzer	Reference Method
P5 Measure the time required for TPH measurement (sample throughput)	Total time from sample receipt through preparation of the draft data package	35 hours, 30 minutes, for TPH measurement of 74 soil environmental samples, 91 soil PE samples, and 50 liquid PE samples	30 days for TPH measurement of 74 soil environmental samples, 89 soil PE samples, 36 liquid PE samples, and 13 extract duplicates
P6 Estimate TPH measurement costs	Total cost (costs of capital equipment, supplies, support equipment, labor, and IDW disposal) for TPH measurement of 74 soil environmental samples, 91 soil PE samples, and 50 liquid PE samples	$6,450 (including the monthly rental cost of the Infracal® TOG/TPH Analyzer, which can be purchased for $6,200)	$44,410

Notes:

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

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

[b] These mean responses were observed when Model CVH was used for TPH measurements. The mean responses observed for neat Stoddard solvent and turpentine were less than 1 percent when Model HATR-T was used for TPH measurement.

Table 9-2. Summary of Infracal® TOG/TPH Analyzer 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 instruction manual is considered to be adequate training material for proper device operation. The sample analysis procedure for the device can be learned in the field with a few practice attempts. The device's digital display provides a sample's TPH concentration in milligrams per kilogram TPH on a wet weight basis; minimal effort is required to calculate a TPH concentration when a soil to solvent mass ratio other than one is used or when a sample extract dilution is involved. However, after the demonstration, 90 of 215 TPH results had to be corrected; the corrections were associated with incorrect calibration of Model HATR-T, use of incorrect dilution factors during use of Model CVH, and data entry errors. Some of the items used during the sample preparation procedure, including the narrow-mouth vials used for weighing and extracting soil samples, the graduated cylinder used for measuring the volume of extraction solvent, and the large air syringe used for extract filtration, made the TPH measurement procedure less simple and more time-consuming.
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, work clothes with long sleeves and long pants) should be adequate for safe device operation.
S3 Portability of the device	The device can be easily moved between sampling areas in the field, if necessary. The device can be operated using a 110-volt alternating current power source or a direct current power source.
S4 Durability of the device	The device is provided in a padded, cardboard box to prevent damage to its components. During the demonstration, Model CVH proved to be durable and did not malfunction or become damaged. However, the infrared spectrophotometer malfunctioned when the Model CVH sample stage was replaced with the Model HATR-T sample stage, and the spectrophotometer and Model HATR-T sample stage had to be replaced; the cause of the malfunction was not determined in the field. 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	During a 1-year warranty period, if the infrared spectrophotometer or a sample stage malfunctions, Wilks will provide a replacement item within 48 hours on loan for a fee of $75 while the original item is being repaired. Wilks does not supply some items necessary for TPH measurement using the device (for example, extraction solvents). The availability of replacement or spare parts not supplied by Wilks depends on their manufacturer or distributor.

TOG/TPH Analyzer may be considered for TPH screening purposes; however, the user should exercise caution when considering the device for a field TPH measurement application requiring definitive results.

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." 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 3856-95. *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." ASTM Manual Series: MNL 1. 6th Edition.

EPA. 1983. "Methods for Chemical Analysis of Water and Waste." Revision. Environmental Monitoring and Support Laboratory. Cincinnati, Ohio. 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." ORD. Washington, DC. EPA/600/R-01/060. June.

Ewing, Galen W. 1969. *Instrumental Methods of Chemical Analysis*. Third Edition. McGraw-Hill Book Company. New York.

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.

Simard, R.G., Ichiro Hasegawa, William Bandaruk, and C.E. Headington. 1951. "Infrared Spectrophotometric Determination of Oil and Phenols in Water." *Analytical Chemistry*. Volume 23, No. 10. October. Pages 1384 to 1387.

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 Water Well Association (Now Known as National Ground Water Association). Houston, Texas.

Appendix
Supplemental Information Provided by the Developer

This appendix contains supplemental information provided by Wilks. After the introduction, this appendix discusses updates on improvements to the Infracal® TOG/TPH Analyzer and comments on the SITE demonstration. Although Model CVH could have been used to analyze all the demonstration samples, Wilks did not analyze all the samples using Model CVH because of time constraints. Wilks chose to demonstrate Model HATR-T because many customers want to reduce Freon use and prefer to use hexane as a solvent for sample extraction.

Introduction

Freon extraction and infrared analysis for TPH and total oil and grease (TOG) have been widely used both in laboratory settings and in the field over the past 25 years. Wilks chose to demonstrate two models of the Infracal® TOG/TPH Analyzer during the demonstration: Models CVH and HATR-T. Model CVH uses infrared radiation transmission with a hydrocarbon-free solvent. Model HATR-T uses a hydrocarbon-containing solvent that is evaporated; the residual film is measured using attenuated total reflection. With transmission (Model CVH), more sample can be processed during analysis, making TPH measurement more sensitive; also, because there is no evaporation step, volatile components remain in the solvent for measurement. Model HATR-T uses evaporation; therefore, a sample with light hydrocarbon fractions or a high proportion of volatiles cannot be analyzed using this technique. The lower sensitivity makes Model HATR-T appropriate for analyses for high concentrations of heavy oils.

During the demonstration, Wilks used Freon with Model CVH because of this chemical's proven reliability as an extraction solvent. Although use of Freon has been extended to 2005, its price has increased substantially, making it less appealing. Carbon tetrachloride, chloroform, and PCE are potential replacements, although carbon tetrachloride and chloroform are rarely used because of their toxicity. In addition to its analytical uses, Freon is widely used for metal part cleaning. There is a large demand for a replacement solvent, and new, hydrocarbon-free solvents are coming into the market. One example is Asahiklin AK 225. ASTM currently has a technical committee developing a new extraction solvent and a new infrared analysis method for TOG and TPH in soil and water. Wilks believes that more inexpensive, infrared-friendly solvents will be available in the future, thus extending the viability of Model CVH.

Updates on Improvements to the Infracal® TOG/TPH Analyzer

Since the completion of the SITE demonstration, Wilks has made calibration and sample filtering improvements to the Infracal® TOG/TPH Analyzer, as discussed below.

Calibration

Wilks' experience during the demonstration revealed that calibration was the most difficult aspect of TPH measurement in the field. As a result, Wilks has developed an extensive calibration program. Users of the Infracal® TOG/TPH Analyzer now have the following calibration options:

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

- **Prepackaged Standards.** Wilks has contracted with a registered International Standards Organization (ISO)-9001 chemical reference material manufacturer to prepare standards now available from Wilks for Models CVH and HATR-T.

- **Certified Laboratory Calibration.** Wilks has contracted with a certified laboratory to calibrate the Infracal® TOG/TPH Analyzer with standards made using either the user's own oil sample or a heavy oil.

- **Noncertified Factory Calibration.** Because there are several methods for measuring TOG or TPH, and because one method does not necessarily match another, the Infracal® TOG/TPH Analyzer can be calibrated based on a particular laboratory method. Wilks technical support staff will assist device users interested in this option.

Because Wilks was unable to obtain samples of known TPH concentrations from the off-site laboratory used for the demonstration, Wilks used calibration standards that it had itself prepared. In retrospect, because GC was used as the reference method, Wilks believes that its results would have matched the reference method results more closely if Wilks had been able to calibrate its device based on the reference method.

Sample Extract Filtering

During the demonstration, Wilks used a Luer Lock to pressurize the extraction reservoir and force the sample extract through a filter frit and cartridge. The Luer Lock tended to be stiff, making the filtering a bit awkward. A stand is included with the filter setup. This stand greatly improves the ease of using the Luer Lock.

Comments on the SITE Demonstration

The demonstration site was very well organized, and the setup was comfortable to work in. Wilks' only comment involves the large number of samples that Wilks was required to test—over 250 in 5 days. Wilks has never had an application of the Infracal® TOG/TPH Analyzer in which analysis of 50 samples per day was expected. Typical on-site analysis is usually limited to 10 to 20 samples per day. Nonetheless, Wilks was pleased to be able to analyze such a large number of samples.

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