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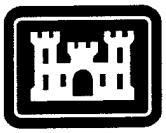

US Army Corps
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Cold Regions Research &
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Evaluating the Hanby Test Kits for Screening Soil and Groundwater for Total Petroleum Hydrocarbons

Field Demonstration

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PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, Geological Sciences Division, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

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CONTENTS

TABLES

Table

Evaluating the Hanby Test Kits for Screening Soil and Groundwater for Total Petroleum Hydrocarbons

Field Demonstration

ALAN D. HEWITT

INTRODUCTION

This report covers the results of a technology demonstration designed to assess the capabilities of the Hanby Test Kits, in conjunction with three methods of analysis, to estimate the amount of total petroleum hydrocarbon (TPH) contamination in environmental samples. This kit was evaluated under the guidelines of the *Rapid Commercialization Initiative*, with additional oversight from the California Environmental Technology Certification Program (California Environmental Protection Agency 1998), at the Naval Construction Battalion Center, Port Hueneme, California, an Advance Fuel Hydrocarbon National Environmental Technology Test Site. The test plans for this field exercise were prepared by the Naval Facilities Engineering Service Center that is located on this base (U.S. Navy 1999). For this evaluation, 90 samples were distributed over a 2.5-day period for on-site analysis and data reduction.

The field and quality assurance (QA) samples used in this evaluation included both soils and groundwater matrices. Field contaminated soil samples were obtained from three different locations and groundwater samples were collected at two of these locations. Each place represented a different range of TPH contamination. One sampling location was within a contaminant plume resulting from an underground release of gasoline. The hydrocarbons at this site are gasoline range organic (GRO) compounds. Another location was within a plume resulting from leaks in the plumbing and the unlined sumps at an above-ground fuel farm, where diesel and bunker C fuel had been stored. The hydrocarbons at this site are, for the most part, diesel range organic (DRO) compounds. The remaining sampling locations were two test plots in an on-going remediation program. The contamination that remains in these biopile and phytoremediation test plots is principally the petroleum hydrocarbons that are classified as residual range organics (RRO). At these two locations, only soil samples were collected. The QA samples consisted of matrix blanks, sample duplicates, matrix spike samples, and performance evaluation (PE) samples.

The Hanby Test Kits use the Friedel-Crafts alklyation reactions with hydrocarbons, principally aromatic hydrocarbons, to produce a color on the surface of a catalyst that can be interpreted by visual inspection or by instrumental analysis. For this study, the resultant color for each sample was quantified by a visual comparison to a set of photographs and by two different field-portable spectrophotometers, i.e., the H.E.L.P. Mate 2010 and 2000 (HM 2010 and HM 2000). Here the accuracy, precision, and reliability of these technologies are evaluated.

TECHNOLOGY DESCRIPTION

All three analytical methods developed for use with the Hanby Test Kits measure the intensity of visible colors that form when aromatic compounds have an alkylhalide group attached to them through the Friedel-Crafts alkylation reaction process. Because petroleum-based fuels, oils, and solvents contain aromatic compounds, the resultant reaction products can be used to estimate the TPH concentration in contaminated samples. The reagents used in the Hanby Test Kits are aluminum trichloride ($AlCl_3$) as the catalyst and carbon tetrachloride (CCl_4) as the source of alkyl (alkylhalide) groups that are attached to the aromatic hydrocarbons (e.g., benzene, toluene, xylenes, phenan-

threne, asphaltines, etc.). Carbon tetrachloride also serves as a solvent to quantitatively remove the hydrocarbons from soil and water sample matrices. The team that prepared and analyzed the field samples for this technology demonstration was made up of John Hanby, the developer of the Hanby Test Kits and three methods of measurement, and one of his employees. Henceforth, this team will be called the "technology developer." The following steps were used to prepare soil and water samples for sequential analysis by the visual and spectrophotometric methods.

For soils contaminated with GRO compounds, 5.0 ± 0.2 g was transferred to a VOA vial containing 10 mL of an extraction solvent composed of 20% carbon tetrachloride/80% n-heptane (v/v). For the DRO and RRO contamination, 5.0 ± 0.2 g of soil was first transferred to an empty VOA vial and then the extraction solvent was added. The sample vial was agitated until the sample was completely dispersed. In the case of a clay that would not disperse by manual shaking, the cap of the VOA vial was removed and a clean metal spatula was used to break apart the soil matrix, exposing as much surface area as possible. Extraction was performed over a 4- to 5-minute period, then the sample was allowed to sit until 4.2 mL of a clear solvent layer could be decanted into a specially designed optical cuvette (a mark on the wall of the vessel denoted the 4.2-mL volume that was required). Then, 0.5 g of $AlCl_3$ (a strong Lewis acid catalyst) was added to the cuvette containing the sample extract. The cuvette was capped and shaken repeatedly for periods of 15 seconds, over a 2- to 3-minute span, to fully develop the color resulting from the Friedel-Crafts alkylation reaction.

For water samples, a separatory funnel was filled to a 500-mL mark, and 5 mL of carbon tetrachloride was added. The capped separatory funnel was then agitated to completely intersperse this immiscible solvent throughout the aqueous sample, while any pressure buildup was periodically vented. This extraction step took 2 to 3 minutes, after which the denser solvent was allowed to settled to the bottom of the funnel. While the carbon tetrachloride was separating, the drain tube of the separatory funnel was dried with a clean, rolled-up piece of paper towel, then the clear solvent layer was drained into a cuvette, filling it to the 4.2-mL mark. After the cuvette was checked for water droplets clinging to the walls (if they were present, the solvent was transferred to a second optical tube), 0.5 g of $AlCl_3$ was added, the tube was capped, and then it was shaken repeatedly for periods of 15 seconds, over a 2- to 3-minute span, to fully develop the color.

The TPH concentration was visually interpreted by comparing the intensity of color to the appropriate color chart (i.e., GRO, DRO, or RRO, for a soil or water matrix), about 4 minutes after the catalyst had been added to the solvent extract. The technology developer prepared these color charts using commercial petroleum products that represented the different hydrocarbon ranges (i.e., GRO, DRO, etc.) and taking them through the various preparation steps for either a soil or water sample. However, because each sample was also to be analyzed by the HM 2010 and 2000, a correction factor was necessary for the visual determinations because both of the spectrophotometric methods specify that only 0.5 g of the catalyst be used to produce the color. This is half the amount that was used when the visual color charts were produced. To correct for the decreased volume of catalyst, which remains as a separate phase, the concentrations indicated by the photo charts were divided by two after the sample's color intensity was matched to the chart.

The HM 2010 and HM 2000 are both in the early stages of development, and this field exercise was a beta test. For spectral analysis, the developer claims that the HM 2010 transmits (by reflectance) a single wavelength of energy through the 1- to 2-cm layer of catalyst, and that the amount of transmitted energy is inversely proportional to the concentration of TPH present in the sample. In its current design, the light source is located above the cuvette and the detector is centered beneath the cuvette. For the light energy to pass through the sample, the cap of the cuvette must be removed before it is placed in the optical cell. The HM 2000 measures reflectance in the visible region (400–750 nm) of the energy spectrum, using a charged-couple device (CCD) array detector. In a way that is similar to the single wavelength system, the developer claims that the amount of reflectance is inversely proportional to the TPH concentration. A tungsten-halogen continuum light is focused on the catalyst and the energy that is not absorbed by the sample is reflected back to the detector for measurement. Both the light source and detector are located beneath the cuvette in this spectrophotometer. As the detector is capable of measuring an energy spectrum, the developer may include, in the future, a qualitative analysis of the unique spectrums of chromophoric (color-producing) Friedel-Crafts reaction products that are created for different petroleum fuels, oils, and solvents.

Currently, both spectrophotometric instruments are only capable of reporting TPH values relative to calibration curves that are developed in the same fashion as for the visual method of analysis. Therefore, the calibration models consisted of instrumental responses to standards prepared from commercial petroleum products using either soil or water sample matrix procedures. These calibration models can currently be stored as an

application on the HM 2000 system, allowing for the direct readout of the TPH concentration in a sample. During this field exercise, the HM 2010 was only capable of producing voltage responses, which had to be manually interpreted to generate sample TPH concentrations. Samples were measured with the HM 2010 about 5 minutes after the catalyst was added, and about 3 minutes later, the same cuvette was placed in the HM 2000. Samples can be prepared and analyzed by all three methods within 15 minutes.

The reported detection limits for TPH in environmental matrices for all three methods of analysis are about 10 mg/kg for soil samples and 0.1 mg/L for water samples. With all of these measurement systems, the upper end of the calibration range is 1000 mg TPH/kg for soil and 50 mg TPH/L for water. Samples that exceeded these ranges were reanalyzed by diluting a small quantity of the sample extract. The technology developer claims that, by following the recommended sample preparation and analytical procedures, TPH concentration estimated with these three methods are within ±25% or better of the values established by standard laboratory methods (Hanby 1998).

Independent of which method of analysis is used, the cost of purchasing the matrix-appropriate Hanby Test Kit, for performing the Friedel-Crafts alkylation reaction, is approximately $1000. It comes with enough reagents for 15 samples, and includes photographic charts for a visual analysis. Reagent supply kits for an additional 15 samples can be purchased for $250. The HM 2010 and HM 2000 are currently projected to sell for about $800 and approximately $8000 (laptop computer included), respectively. To bring the cost per sample analyzed below $100, the approximate cost of a TPH laboratory analysis, one Hanby Test Kit ($1000, 15 analyses) would have to be purchased for a visual analysis, one Hanby Test Kit and one reagent supply kit (approximately $2000, 30 analyses) would be necessary for analysis with the HM 2010, and one Hanby Test Kit and six reagent supply kits ($10,000, 105 analyses) would be necessary for analysis with the HM 2000.

EXPERIMENTAL DESIGN

As mentioned earlier, these three methods of estimating TPH concentrations on-site were evaluated with samples contaminated by petroleum products. Both soil and groundwater matrices were evaluated for GRO and DRO/bunker C, while RRO was only assessed in soil samples (Table 1). All of the participants helped develop the sampling plan for this field exercise. This was necessary to ensure that the number and type of samples anticipated could be processed in the time allotted, and so that the sample integrity would not be compromised. This second requirement means that the samples are representative of the in-situ conditions. More importantly, it attempts to eliminate potential sources of determinant error, with respect to the handling and distribution of samples, so that the different methods of preparing and estimating TPH concentrations can be validly compared.

The protocol developed used a single and double blind format for both the technology developer and the reference laboratory. Therefore, aside from knowing the range of hydrocarbons representative of contamination present in a given sample (i.e., GRO range) and matrix (i.e., soil or groundwater) it was often impossible to distinguish a field sample from a matrix spike, matrix blank, or a PE sample. This was accomplished on-site

Table 1. Samples collected and prepared for on-site analysis.

	Field		*Matrix*			
	Samples	*Duplicate*	*Blank*	*Spike duplicate*	*PE**	*Total*
Gasoline range organics (GRO; b.p. 60–170°C)						
Soil	9	2	1	2 (4)†	4	20
Water	6	1	1	2 (4)	4	16
Diesel range organics (DRO; b.p. 160–400°C)						
Soil	12	2	1	2 (4)	8	27
Water	12	1	1	2 (4)	—	18
Residual (motor oil) range organics (RRO; b.p. 315–540°C)						
Soil	6	1	—	1 (2)	—	9

*Performance evaluation samples.
†Number in parenthesis are the total number of matrix spike samples.

by having all of the sample distribution activities inside a trailer, while the technology developer was set up outside under a canopy. Samples were delivered to the technology developer in a vessel labeled with only a sample number, and, in the case of soil, its weight. At the same time that samples were collected and prepared for on-site analysis, 90 co-located samples or sample splits were taken for off-site analysis by the reference laboratory. Two additional samples were taken as trip blanks, which consisted of the MeOH extraction solvent that was used to prepare all of the GRO soil samples sent off-site. In addition, the State of New Mexico Environmental Laboratory, which served as the QA laboratory for this technology demonstration, received 23 samples, 17 of soil and 6 of groundwater. This QA laboratory received field, PE, and matrix blank samples contaminated with GRO compounds, and field samples contaminated with the DRO/bunker C and RRO compounds. In addition to the samples that were sent to these two laboratories, an entire set of soil and groundwater samples contaminated with GRO compounds was sent to the CRREL for analysis. The sample identity was known by both the QA and CRREL laboratories prior to analysis. All of the samples sent off-site were refrigerated during storage and transportation.

The technology demonstration plan (U.S. Navy 1999) gives a detailed description of the techniques used to collect bulk samples of soil and water, along with the sampling locations, and the historical background information concerning the use of petroleum products on this site. For both the GRO and DRO/bunker C plumes, a Geoprobe® (Geoprobe Systems, Inc., Sulina, Kansas) sampler was used to obtain the soil and groundwater samples. Bulk soil samples were obtained using a closed-piston sampler, with a plastic core barrel liner, that had a 1.75-in. (4.45-cm) diameter and a 3-ft (0.9-m) length. A Geoprobe sampler was also used to obtain a sample of background material (uncontaminated soil matrix). For the locations where RRO contamination exists, bulk soil samples were obtained using a drop hammer sampler after hand auguring to the depth of interest. The drop hammer sampler had a core barrel liner, consisting of a brass sleeve, with a 2-in. (5.1-cm) diameter and 6-in. (15.2-cm) length. After each end of these sampling vessels (plastic tubes and brass sleeves) was retrieved, their ends were sealed with plastic caps (the tops of the plastic tubes were trimmed leaving no headspace), they were labeled, and then they were promptly delivered to the trailer for processing.

Groundwater samples were collected from within the GRO and DRO/bunker C contaminant plumes, and uncontaminated groundwater samples were taken from a background location. All of the groundwater samples were co-located with the borehole used to obtain the bulk soil samples for this field exercise. With the exception of the background sample, groundwater was obtained using a sipper push point attached to the end of a Geoprobe push rod. The sipper point consists of a 4-in. (10.1-cm) section screened with stainless steel wire mesh, to which a new piece of polyethylene tubing was attached for each sampling point (depth of 10 to 19 ft [3 to 6 m]). The groundwater was pumped from the depth of interest using a peristaltic pump set at a rate of approximately 500 mL/min, when possible. The background groundwater sample was collected via the peristaltic pump system from a permanent monitoring well.

The following sections describe the subsampling and handling protocols used by the sample distribution team for both types of environmental matrices, and the preparation of the matrix spikes and PE samples (Tables 2 and 3). With the exception of two sets of PE samples, all of the other QA samples were fortified (spiked) on-site using reference standards purchased in sealed glass ampoules containing 1-mL quantities. Once these ampoules were opened, aliquots were transferred, in every case but one, with glass microliter syringes (Hamilton). With exception of the water taken from the background monitoring well, all of the containers used for sample collection and distribution were clean glass bottles with Teflon-lined septum caps. Samples of the background water were initially held in plastic 4-L jugs.

GRO compounds in soil

The high vapor pressures (i.e., low boiling points) of many of the hydrocarbons in gasoline make the matrices contaminated with this product, particularly soils, susceptible to volatilization losses (Hewitt et al. 1995). In addition, several GRO compounds are susceptible to biological degradation if not properly preserved between collection and analysis (Hewitt 1997). Because of these concerns, soil samples taken from the locations contaminated by GRO compounds were handled with a different procedure than the samples of the less volatile and less biological labile DRO/bunker C and RRO compounds.

Subsamples of GRO-contaminated soils were placed directly into VOA vials that contained either a binary solvent mixture of carbon tetrachloride and n-heptane or methanol (MeOH). Special precautions to limit exposure were taken that were consistent with guidance given in Method 5035 and D 4547-98 (EPA 1986, ASTM 1998). The VOA vials containing the binary solvent were prepared by the technology developer, while those containing MeOH were prepared at CRREL. In addition, all of the VOA vials containing MeOH had been spiked with two surrogate compounds, p-Bromofluorobenzene and trifluorotoluene, each at a concentration of 2 µg/mL.

Table 2. Matrix spike samples.

Matrix	Standard Name (ID)*	Standard Concentration (mg TPH/mL)	Spike vol. (mL)	Sample wt. or vol. (g or mL)	Target concentration
Gasoline range organics (GRO; b.p. 60–170°C)					
Soil	AK-101.0-GCS	5.0	0.100	5.0 ± 0.2 g	100 mg TPH/kg
Soil	AK-101.0-GCS	5.0	0.500	5.0 ± 0.2 g	500 mg TPH/kg
Water	AK-101.0-GCS	5.0	0.100	1050 mL	0.48 mg TPH/L
Water	AK-101.0-GCS	5.0	5.00	1050 mL	24 mg TPH/L
Diesel range organics (DRO; b.p. 160–400°C)					
Soil	AK-102.0-DCS	5.0	0.250	5.0 ± 0.2 g	250 mg TPH/kg
Soil	AK-102.0-DCS	5.0	1.00	5.0 ± 0.2 g	1000 mg TPH/kg
Soil	AK-102.0-DCS	5.0	1.00	20.0 ± 0.2 g	250 mg TPH/kg
Soil	AK-102.0-DCS	5.0	4.00	20.0 ± 0.2 g	1000 mg TPH/kg
Water	AK-102.0-DCS	5.0	0.200	1050 mL	0.95 mg TPH/L
Water	AK-102.0-DCS	5.0	5	1050 mL	24 mg TPH/L
Residual range organics (RRO; b.p. 315–540°C)					
Soil	MO-Comp-D-40x	5.0	1.00	5.0 ± 0.2 g	1000 mg TPH/kg
Soil	MO-Comp-D-40x	5.0	4.00	20.0 ± 0.2 g	1000 mg TPH/kg

*Manufacturer's (AccuStandard, Inc., New Haven, Connecticut) sample identification code.

For GRO compounds in soil, the test plan specified that 20 samples be distributed for analysis (Table 1). Discrete soil samples were taken from the plastic core barrel liners immediately after they were opened, which was within a couple of minutes of their arrival at the trailer. The bulk sample was exposed for subsampling by removing the end caps and approximately one-third of vertical wall of the plastic liner using a specially designed tool containing two knife blades (Geoprobe). Samples of 5.0 ± 0.2 g, which were both composited and co-located, were obtained for on-site and off-site analysis by using a modified (tip and plunger removed) 5-mL plastic syringe (Hewitt et al. 1995). These samples were composited by pushing the syringe into the freshly exposed surface twice, at predetermined depth intervals, and acquiring approximately 2.5 g of soil (about

Table 3. Performance evaluation samples.

Matrix	Standard Name (ID)	Standard Concentration (mg TPH/mL)	Spike vol. (mL)	Sample wt. or vol. (g or mL)	Target conc. or certified conc. (and perf. acc.)†
Gasoline range organics (GRO; b.p. 60–170°C)					
Soil	AK-101.0-GCS*	5.0	0.200	5.00 ± 0.02 g	200 mg TPH/kg
Water	Cat. No. 762** Lot. No. 50017	1.03	1.00	1000 mL	1.03 mg TPH/L (0.689 to 1.57)
Diesel range organics (DRO; b.p. 160–400°C)					
Soil	Cat. No. 765** Lot. No. 40018	—	—	20 g	401 mg TPH/kg (194 to 509)
Soil	Cat. No. 765** Lot. No. 40016	—	—	20 g	2480 mg TPH/kg (1200 to 3160)

*AccuStandard Inc., New Haven, Connecticut.
†Performance acceptance limits.
**Certified Standards purchased from Environmental Resources Associates, Arvada, Colorado.

1.5 cm^3) with each push. Samples were co-located by making these pushes at diagonal corners of a small square (3.8 × 3.8 cm). Therefore, subsamples from two diagonal corners were composited for on-site analysis, and the other two corners were composited for off-site analysis. To transfer the prescribed weight of soil, the syringe was tared before use and then weighed again after collection. The samples were adjusted to ensure that each weighed 5.0 ± 0.2 g by slightly over-filling (more than 5 g), then shaving excess soil off the end with a spatula, to attain the desired weight. Once it was obtained, the 5.0 ± 0.2-g sample was immediately extruded into a VOA vial that contained 10 mL of extraction solvent.

To take sample duplicates, the same location in the plastic core barrel liner was sampled by pushing the modified syringe to a greater depth in each of the four corners of the square. As above, samples from diagonal corners were obtained by pushing the syringe into soil surface twice, before the weight was adjusted and the sample extruded into the prepared VOA vials.

The soil matrix blank was initially obtained from a core barrel liner as a bulk sample by transferring about 300 g to a 250-mL bottle. This background sample was obtained 2 days before the technology demonstration began. The same modified syringe was used to obtain 5.0 ± 0.2 g of soil from this bottle. These matrix blank samples were then transferred to a VOA vial containing 10 mL of solvent. This same process was used when the matrix spike samples (Table 2) were prepared, except that an aliquot of a commercial standard was added.

Performance evaluation samples for GRO compounds were prepared by spiking soil (silty clay) that had been sieved, autoclaved, and air dried in a class 100 clean air station (Table 3). For these samples, 5.00 ± 0.02 g of soil was transferred to a 5-mL glass ampoule at CRREL, then shipped to the site where it was immediately sealed with a propane torch after spiking, 2 days prior to the start of the technology demonstration. These samples were stored in a freezer until they were used. In preparation for analysis, a sealed ampoule was placed inside of a VOA vial containing 10 mL of solvent, the VOA vial was capped, and the ampoule was broken open and its contents completely dispersed by shaking. Several brief episodes of manual shaking were necessary to ensure that all of the soil was dispersed into the solvent phase.The presence of broken glass in these sample vials allowed them to be distinguished from the others that were analyzed on-site.

All of the soil samples placed into the VOA vials for on-site analysis were delivered to the technology developer within 1 hour. Soil samples placed into the VOA vials containing 10 mL of MeOH were initially dispersed, then allowed to sit overnight before aliquots of the extract were decanted off. Up to three separate aliquots of the MeOH extract were removed from each VOA vial by pouring a portion of the clear solvent layer directly into small 1.9-mL vials. A complete set of these MeOH extracts, including two trip blanks (VOA vials containing only MeOH and the surrogates compounds), was sent to the reference laboratory and also returned to CRREL for analysis, and several sample aliquots and two trip blanks were sent to the QA laboratory.

GRO compounds in water

For aqueous matrices contaminated with GRO compounds, 16 bulk water samples (Table 1) were obtained from within the gasoline contaminant plume by completely filling either a 1- or 4-L amber glass bottle. The larger sized bottle was only used when the volume necessary for the sample duplicate was collected. Soon after these bottles were delivered to the sample distribution trailer, they were gently swirled. Then two to four VOA vials were completely filled and capped, and a 500-mL aliquot was slowly decanted into a separatory funnel (two in the case of the sample duplicate).

Matrix blank samples were prepared by decanting water directly from one of the plastic jugs filled with background water into 40-mL VOA vials or into a separatory funnel. Matrix spike samples were prepared by filling four 1-L bottles with 1050 mL of the background water, then spiking (Table 2). These matrix spike samples were prepared 1 day prior to use, and were stored in a refrigerator. Subsamples were decanted from these bottles in the same way used for the discrete groundwater samples. Four PE samples were prepared by spiking 1.00 L of HPLC grade water, held in four separate 1-L glass bottles (Table 3). These samples were also prepared and distributed using the same procedure as used for the discrete groundwater samples.

Immediately after a water sample was decanted into a separatory funnel, it was returned to the technology developer for extraction. A complete set of the water samples contained in the 40-mL VOA vials was sent to the reference laboratory and also to CRREL for analysis, and a few VOA vials were sent to the QA laboratory.

DRO compounds in soil

For soil samples contaminated with DRO/bunker C, the test plan specified that 27 samples be distributed for analysis (Table 1). After the core barrel liners were opened as described before, bulk soil samples of about 200 g were removed from the depths of interest using a stainless steel spatula and placed into a 250-mL glass bottle. The contents of the bottle were then briefly homogenized (mixed) with a spatula. After mixing, two different plastic syringe sampling tools were used to

transfer samples to empty VOA vials. One or more 40-mL VOA vials were filled to capacity (approximately 60 g) using the EasyDraw syringe™ (U.S. Oil Company) for the off-site laboratories, and 5.0 ± 0.2 g of soil was placed into a VOA vial with a modified 5-mL syringe for on-site preparation and analysis. As described previously, the soil sample obtained in the 5-mL syringe was handled so that only 5.0 ± 0.2 g was delivered. Soil sample duplicates were prepared by taking two rounds of samples from the same bulk sample bottle.

Matrix blank samples were prepared by transferring the above two quantities (5.0 ± 0.2 g and approximately 60 g) from a bottle containing background soil. This same soil was also used to prepare the matrix spike samples (Table 2). Two reference materials, supplied as 20.0 ± 0.2-g quantities in a sealed glass ampoule, were purchased to serve as the PE samples (Table 3). For on-site analysis, one ampoule of each concentration was opened and 5.0 ± 0.2-g quantities were transferred to four VOA vials. Four intact ampoules of the low level certified standard and two of the high level were sent to the reference laboratory for analysis. Prior to shipping these ampoules, all of the reference sample information was removed and they were relabeled.

VOA vials containing 5.0 ± 0.2 g of soil were delivered for on-site analysis soon after preparation. A complete set of the VOA vials that were filled to capacity was shipped to the reference laboratory and a few were sent to the QA laboratory. According to the protocols used by the QA and reference laboratory, only 10- or 20-g quantities, respectively, of the soil present in these VOA vials were removed for extraction and analysis. Since the matrix spike and PE samples only contained 20 g of soil per container, the reference laboratory was asked to analyze the entire contents of the vessel.

DRO compounds in water

For groundwater contaminated with DRO/bunker C, the test plan specified that 18 samples be distributed (Table 1). Bulk water samples were obtained in clean 4-L amber glass bottles by filling them to capacity, when possible. Soon after being delivered to the trailer, these bottles were gently swirled, then water was slowly decanted into a separatory funnel, filling it up to the 500-mL volume mark. Then, one or more 1-L amber glass bottles were filled to capacity for the off-site laboratories. For the groundwater sample duplicate, two separatory funnels and two 1-L amber glass bottles were filled from a single 4-L bottle.

The matrix blank was prepared by filling a separatory funnel with 500 mL and a 1-L glass bottle to capacity with background water. Matrix spike samples were prepared by filling four 1-L amber glass bottles with 1050 mL of background water, then spiking (Table 2). The high level matrix spike was prepared by decanting the entire contents of five ampoules filled with approximately 1.0 mL of standard reference solution into a bottle containing 1050 mL of water. Because this commercial standard was prepared in methylene chloride, which is not soluble in water, it was necessary to add 2 mL of MeOH to the low level matrix spike bottles, and to shake them vigorously for several minutes, before the spike went into solution. To get the high level matrix spike into solution, the majority of the water had to be poured into a clean bottle, then 10 mL of MeOH was added to the methylene chloride spike in the presence of only about 15 mL of water. After vigorous shaking, the methylene chloride went into solution and the water that had been removed was added back to the bottle. Aliquots from each one of these bottles were decanted into the separatory funnel, filling it to the 500-mL mark, then the remainder (550 mL) was sent for reference laboratory analysis.

RRO compounds in soil

For the soil contaminated with RRO compounds, the test plans specified that nine samples be distributed (Table 1). After the cap was removed from one end of the brass core barrel liner, approximately 200 g of soil was transferred to a 250-mL glass bottle and mixed with a stainless steel spatula. After mixing, subsamples were removed using the same procedure as used for the soil samples with DRO/bunker C range contamination. For the soil matrix spikes, either 5.0 ± 0.2 g or 20 g of the background soil was transferred to VOA vials that were then spiked (Table 2). Only one matrix spike sample was prepared for the reference laboratory.

LABORATORY ANALYSES

To eliminate variations that could potentially exist among different sources of commercial standards, a set of the reference standards that had been used for making the matrix spike samples was distributed to all of the off-site laboratories. Each laboratory was asked to use these reference standards to calibrate their instruments prior to analyzing the field and QA samples. The reference laboratory was asked to use the analytical methods listed in Table 4, and to establish the TPH concentration within certain hydrocarbon ranges.

In addition to the reference laboratory, CRREL analyzed all of the samples contaminated with GRO compounds. CRREL used Methods 5021/8021 for sample preparation and quantification, which specify a headspace system coupled to a gas chromatograph equipped with a photo ionization detector. The deter-

Table 4. Methods of analysis used by the reference laboratory.

TPH fraction	Sample location	EPA SW-846 method	Quantitation range	Approx. boiling point range
BTEX*	GRO plume	8020	NA	NA
GRO	GRO plume	8015B	C6 to C12	60 to 170°C
DRO/RRO	DRO/bunker C plume and plots	8015B**	C10 to C40	160 to 540°C

*Benzene, toluene, ethyl-benzene, and the xylenes.
**Methylene chloride extraction.

minative method used by the QA laboratory was similar to that used by the reference laboratory, i.e., Methods 8020 and 8015 (U.S EPA 1986).

RESULTS

Table 5 gives the TPH results for this technology demonstration. The results presented for the technology developer only include the values reported for the visual and HM 2000 measurement methods because the HM 2010 system is not ready for evaluation. Prior to recording the reference laboratory results given in Table 5a, the data had to be manipulated to change the units and to address the presence of surrogate compounds. This alteration was necessary for the methanol extracts, because the reference laboratory had not been informed of the volume of extraction solvent used, and that two surrogate compounds were present. As a result, they initially reported TPH values on a mg/L basis and had concentrations (low) for the matrix blank and trip blanks that were in reality the surrogate compounds. All of the values were changed to mass per mass basis by multiplying the reported value by the volume of methanol divided by the weight of the soil sample (a default value of 5.0 g was used for all QA samples). To address the surrogate contribution to the TPH values reported, an average concentration based on the two trip blanks and soil matrix blank was subtracted from samples that were prepared and analyzed with the same dilution factor. This latter correction affected only two samples. All of the other samples were diluted further by at least a factor of 10×, thereby making this correction unnecessary. Failure to inform the reference laboratory of the sample preparation procedure was an oversight by the technology demonstration program.

Another problem, which resulted from inadequate communication, was that some of the samples sent to the QA laboratory were not analyzed for the appropriate parameters. No TPH values were reported by the QA laboratory for the samples contaminated with GRO. Instead, this laboratory only reported concentrations for the benzene, toluene, ethyl-benzene, and the xylenes (BTEX). The reference laboratory and CRREL also reported the total BTEX concentration in all the samples contaminated with GRO compounds. The BTEX values determined by these three laboratories are shown in Table 6.

Lastly, the values reported in these tables for the soil samples are based on moist weight and all values were rounded to two significant figures, or less. A single significant figure value was reported when it was limited by the instrument display on the HM 2000 or by the concentration provided with the visual comparison chart. For completeness, the percent dry weights determined for the all of the soil samples and the background soil used for the matrix spike samples are presented in Table 7.

A close inspection of the values for the water samples contaminated with GRO compounds shows that these samples may not have had stable analyte concentrations. These samples were handled following the procedure recommended by the State of California; therefore, they were not preserved by acidification. The holding times for the majority of these samples, with the exception of WG-11, -10, -12, and -13, which were analyzed after 6 days, was 9 to 14 days, or longer. Moreover, three water samples that were apparently misplaced by the reference laboratory were held for 29 days prior to analysis (Table 5b), while those analyzed by the QA laboratory were held for about 40 days (Table 6). As a results, all of the matrix spike recoveries were lower than expected and, in general, there is a trend showing that the samples held for longer periods had lower determined analyte concentrations. So, all of the groundwater samples, with the exception of the PE samples, may have lost analytes from biodegradation during refrigerated storage. The PE samples were not affected by this loss mechanism because HPLC grade water is abiotic.

Table 5. Demonstration results for total petroleum hydrocarbons in soil and water.

a. Concentrations (mg/kg) of TPH in soil samples contaminated with GRO compounds.

Sample no./ID	CRREL	Ref. lab	Technology developer: Visual	Technology developer: HM2000
SG-1/PE (200)*	200	220	200	740
SG-2/PE (200)	180	220	500	750
SG-3/PE (200)	220	240	400	740
SG-4/PE (200)	190	220	170	270
SG-6/Matrix-Spike (100)	86	120	200	160
SG-7/Matrix-Spike (100)	90	200	140	160
SG-20/Matrix-Spike (500)	450	440	250	720
SG-21/Matrix-Spike (500)	460	480	730	510
SG-5/Matrix-Blank	<1	<1	10	2.2
SG-8/Sample	19	80	50	72
SG-18/Sample Duplicate (SG-8)	20	53	80	79
SG-10/Sample	<1	180	20	14
SG-19/ Sample Duplicate (SG-10)	<1	690	10	11
SG-9/Sample	4400	6300	8300	11000
SG-11/Sample	5800	4800	5100	9200
SG-12/Sample	13000	7500	12000	12000
SG-13/Sample	14	240	49	30
SG-14/Sample	<1	<1	21	21
SG-15/Sample	980	720	360	720
SG-16/Sample	<1	6	5	18

*Values in parenthesis are the spiked concentration in mg TPH/kg or the sample duplicate.

Table 5 (cont'd).

b. Concentrations (mg/L) of TPH in water samples contaminated with GRO compounds. The reference laboratory analyzed GW-10, 11, 12, and 13 after 6 days, GW 14, 15 and 16 after 29 days, and the rest after 14 days of refrigerated storage. Samples were analyzed at CRREL after 9 days of refrigerated storage.

Sample no./ID	CRREL	Ref. lab	Technology developer: Visual	Technology developer: HM2000
WG-1/PE (1.0)*	0.93	0.88	4.3	4.8
WG-2/PE (1.0)	0.99	1.0	5.0	4.8
WG-3/PE (1.0)	1.0	1.1	1.0	IF**
WG-4/PE (1.0)	1.1	1.1	7.0	IF
WG-6/Matrix Spike (0.48)	0.29	0.25	0.5	IF
WG-7/Matrix Spike (0.48)	0.22	0.19	2.5	5.2
WG-15/Matrix Spike (24)	18	11	SL†	SL
WG-16/Matrix Spike (24)	21	11	SL	SL
WG-11/Sample	1.2	1.3	1.0	1.0
WG-14/Sample Duplicate (WG-11)	1.2	1.6	4.0	5.3
WG-5/Matrix Blank	<0.05	<0.05	<0.1	<0.05
WG-8/Sample	37	130	30	22
WG-9/Sample	11	12	5.0	7.0
WG-10/Sample	7.7	8.6	>30	>50
WG-12/Sample	3.6	4.4	10	11
WG-13/Sample	0.95	0.61	2.0	2.0

*Values in parenthesis are the spiked concentration in mg TPH/kg or the sample duplicate.
**Instrument failure.
†Sample lost during preparation.

Table 5 (cont'd). Demonstration results for total petroleum hydrocarbons in soil and water.

c. Concentrations (mg/kg) of TPH in soil samples contaminated with DRO/bunker C.

Sample no./ID	Ref. lab	QA lab	Technology developer	
			Visual	HM2000
SDM-1/PE (401)*	520	NA**	810	900
SDM-2/PE (401)	510	NA	1500	950
SDM-3/PE (401)	570	NA	2000	580
SDM-4/PE (401)	590	NA	690	2000
SDM-25/PE (2480)	4900	NA	6800	7700
SDM-26/PE (2480)	3900	NA	9000	8500
SDM-27/PE (2480)	NA	NA	4900	3500
SDM-28/PE (2480)	NA	NA	6000	9000
SDM-6/Matrix Spike (250)	190	NA	480	740
SDM-7/Matrix Spike (250)	200	NA	400	820
SDM-23/Matrix Spike (1000)	900	NA	2500	1300
SDM-24/Matrix Spike (1000)	400	NA	2500	1900
SDM-12/Sample	27000	NA	7500	19000
SDM-21/Sample Dup. (SDM-12)	19000	NA	7500	26000
SDM-15/Sample	18000	NA	15000	17000
SDM-22/Sample Dup. (SDM-15)	22000	NA	18000	20000
SDM-5/Matrix Blank	NR†	56	48	20
SDM-8/Sample	<10††	NA	<10	150
SDM-9/Sample	59000	24000	26000	43000
SDM-10/Sample	<10	NA	<10	89
SDM-11/Sample	1300	NA	400	170
SDM-13/Sample	<10	NA	48	65
SDM-14/Sample	<10††	390	99	210
SDM-16/Sample	<10	NA	10	31
SDM-17/Sample	86	190	260	310
SDM-18/Sample	<10	NA	50	30
SDM-19/Sample	17	NA	52	52

*Values in parenthesis are the spiked concentration in mg TPH/kg or the sample duplicate.
**Not analyzed.
†Not reported.
††21 mg TPH/kg found in motor oil range organic compounds.

Aside from all of the laboratory results perhaps being biased low for the groundwater samples, there are several additional concerns that pertain to the reference laboratory results:

- Failure to yield an average TPH value that was within the certified range of acceptance for DRO in soil PE samples (Table 5c, SDM-1, -2, -3, and -4, 548 ± 39 mg TPH/kg vs. certified range of acceptance 194 to 509 mg TPH/kg; SDM-25 and 26, 4400 ± 707 mg TPH/kg vs. certified range of acceptance 1200 to 3160 mg TPH/kg).
- Matrix spike values that were either twice or half the target concentration (Table 5a, SG-7, 200 mg TPH/kg reported vs. a 100 mg TPH/kg spiked; Table 5c, SDM-24, 400 mg TPH/kg vs. a 1000 mg TPH/kg spiked; Table 5e, M1, 430 mg TPH/kg vs. a 1000 mg TPH/kg spiked).
- Samples held beyond the contracted analysis period of 14 days. WG-14, -15, and -16 were held for 29 days prior to analysis. Two of these samples were matrix spikes that had reported TPH concentrations less than half the target concentration (Table 5b, WG-16, 11 mg TPH/L vs. 24 mg TPH/L spiked).
- Failure to report values for samples that were supposedly distributed. No values were reported for SDM-5, WDM-1, WDM-16, WDM-17, WDM-10, and WDM-11.
- Poor agreement with the TPH values reported by the QA laboratory (Tables 5c, d, and e), and for BTEX in Table 6, while there was good agreement

Table 5 (cont'd).

d. Concentrations (mg/L) of TPH in water samples contaminated with DRO/ bunker C.

Sample no./ID	Ref. lab	QA lab	Technology developer	
			Visual	HM2000
WDM-1/Matrix Spike (0.98)*	NR**	NA†	0.84	<0.05
WDM-2/Matrix Spike (0.98)	0.87	NA	0.5	<0.05
WDM-16/Matrix Spike (24)	NR	NA	30	8.6
WDM-17/Matrix Spike (24)	NR	NA	50	>50
WDM-4/Sample	8	NA	13	33
WDM-18/Sample Dup. (WDM-4)	15	NA	17	26
WDM-15/Matrix Blank	<0.5	NA	<1	<0.05
WDM-3/Sample	120	NA	8.4	40
WDM-5/Sample	14	29	22	64
WDM-6/Sample	32	NA	8.4	22
WDM-7/Sample	19	NA	5	13
WDM-8/Sample	19	NA	6.7	19
WDM-9/Sample	2.6	NA	2.9	1.4
WDM-10/Sample	NR	23	2.2	3.2
WDM-11/Sample	NR	NA	5	8
WDM-12/Sample	38	NA	5.9	13
WDM-13/Sample	3	8.1	1.7	<0.05
WDM-14/Sample	0.66	NA	0.5	<0.05

*Values in parenthesis are the spiked concentration in mg TPH/kg or the sample duplicate.
**Not analyzed.
†Not reported.

Table 5 (cont'd).

e. Concentrations (mg/kg) of TPH in soil samples contaminated with RRO compounds.

Sample no./ID	Ref. lab	QA lab	Technology developer	
			Visual	HM2000
M1/Matrix Spike (1000)	430	NA*	1000	630
M9/Matrix Spike (1000)	NS**	NA	900	560
M7/Sample	380	NA	12000	22000
M8/Sample duplicate (M7)	400	NA	24000	22000
M2/Sample	300	1800	7900	11000
M3/Sample	250	NA	10000	7500
M4/Sample	<10†	NA	480	990
M5/Sample	320	2500	5100	8600
M6/Sample	52	NA	6100	6500

*Not analyzed.
**No sample.
†110 mg TPH/kg as diesel range organic compounds.

Table 6. Concentrations of benzene, toluene, ethyl-benzene, and the xylenes (BTEX) in selected soil and water samples contaminated with GRO compounds.

Sample no./ID	CRREL	QA lab	Reference lab
a. Soil (mg total BTEX/kg)			
SG-1	48	36	33
SG-2	47	41	31
SG-3	48	26	34
SG-4	46	40	30
SG-8	3.2	2.6	2.1
SG-11	1400	1400	740
SG-15	140	150	32
SG-18	3.4	8.0	2.8
b. Water* (mg total BTEX/L)			
WG-2**	0.22	0.23	0.10
WG-8	12.0	8.7	22.5
WG-11	0.34	0.29	0.27

*The QA laboratory analyzed these water samples after about 40 days of refrigerated storage, while the aliquots of the same samples were analyzed at CRREL after 9 days of refrigerated storage.
**Certified BTEX value 0.22 mg/L, performance acceptance range 0.17–0.30 mg/L.

Table 7. Percent dry weight of soil samples.

Sample	% dry wt.	Sample	% dry wt.
SG-1, 2, 3, 4	100	SDM-8	93.5
SG-5, 6, 7	93.8	SDM-9	86.0
SG-8	86.3	SDM-10	72.7
SG-9	89.7	SDM-11	90.1
SG-10	83.2	SDM-12	84.6
SG-11	81.6	SDM-13	72.1
SG-12	84.7	SDM-14	87.4
SG-13	86.1	SDM-15	85.7
SG-14	82.4	SDM-16	75.9
SG-15	85.7	SDM-17	82.0
SG-16	87.3	SDM-18	74.5
SG-18	85.7	SDM-19	84.0
SG-19	83.7	M-2	86.5
SG-20, 21	86.0	M-3	85.7
		M-4	79.4
		M-5	84.0
		M-6	80.3
		M-7	88.7

between the QA laboratory and CRREL for the determination of BTEX concentrations (Table 6).

- Failure to yield a total BTEX value within the certified range of acceptance for a PE water sample (Table 6, WG-2, 0.10 mg BTEX/L vs. certified range of acceptance 0.17 to 0.30 mg BTEX/L).
- High values for a sample duplicate, and a large discrepancy among these values, while repeated analysis at CRREL of an aliquot of extract from the same sample showed that the TPH was likely to be near or below the practical quantitation limits (Table 5a, SG-10 and SG-19, 180 and 690 mg TPH/kg).
- Failure to supply chromatograms with the data package that were legible or that were labeled with the test plan sample numbers.

The combination of these concerns diminishes the credibility of the reference laboratory data. The following evaluation, therefore, only applies to those samples with target or with certified TPH concentrations, i.e., the matrix spikes and PE samples. One exception will be the use of values for the sample duplicates to evaluate precision.

Independent of using either the visual or the HM 2000 measurement method for estimating TPH concentrations, the values reported for the PE samples were biased high, on average, by a factor of 3× relative to the certified or the expected value (Table 8). In particular, the values reported for the PE water sample were high (4× to 5× greater) compared to the certified value of 1.0 mg TPH/L. For the matrix spike samples, both on-site analysis methods were able, for a few samples, to report average TPH values that fell within ±25% of the expected concentration (Table 9). This level of agreement between expected and estimated values was attained by the visual method, for two out of eight matrix spike duplicates analyzed, and by the HM 2000 method, for one out of seven matrix spike duplicates analyzed. Unlike the PE samples, the values reported by these two methods of analysis for the matrix spike samples were both greater than and less than the expected concentrations.

The percent relative standard deviations (%RSD) achieved by the HM 2000 for the sets of PE samples ranged from 35 to 56%, and were on the average greater than 40% (Table 8). At this level of precision (40% RSD), the range of values established varied by at least a factor of 2.5× from the lowest to the highest reported TPH concentration. The relative percent differences (%RPD) achieved by the HM 2000 for the matrix spike duplicates and the sample duplicates were also used to assess precision. The %RPDs ranged up to 140%

Table 8. Percent recoveries and relative standard deviations estimated by the off-site laboratories and on-site by the technology developer for the performance evaluation materials.

			Hanby	
Sample no./ID	*CRREL % Recov. (% RSD)*	*Ref. Lab % Recov. (% RSD)*	*Visual % Recov.*	*HM 2000 % Recov (% RSD)*
GRO				
SG-1, 2, 3, 4 (200 mg TPH/kg)	99 (8.6)	112 (4.4)	160	310 (38)
WG-1, 2, 3, 4 (1.0 mg TPH/L)	100 (7.0)	102 (10.2)	430	480
DRO				
SDM-1, 2, 3, 4 (401 mg TPH/kg)	NA	134 (7.0)	300	270 (56)
SDM-25, 26, 27, 28 (2480 mg TPH/kg)	NA	177 (22.7)*	270	290 (35)

* Only two of the four replicates were analyzed.

(Tables 9 and 10) and were on average 35% for the HM 2000 method. The precision of the visual method was not assessed because estimates arise from a discontinuous scale and are subjective.

The sampling team distributed 90 samples for on-site analysis during the 2.5-day exercise. On the first day, 20 soil and 16 water samples contaminated with GRO compounds were distributed. On the second day, 36 soil samples and 16 water samples were distributed. Of the soils distributed on day two, 27 were contaminated by DRO/bunker C and 9 were contaminated by RRO compounds. All 16 water samples were contaminated with DRO/bunker C. On the morning of the last day, two water samples with DRO contamination were distributed. The technology developer agreed to analyze the large number of samples on the second day of the field exercise.

The technology developer analyzed all of the 20 soil samples distributed on the first day; however, while analyzing the 16 water samples, the HM 2000 instrument developed a software problem that required off-site assistance. When it became clear that the HM 2000 would be unable to continue, the technology developer chose to hold some of the sample extracts overnight, prior to adding the catalyst and forming the Friedel-Crafts reaction products. Because of this interruption, five water samples were not analyzed by the HM 2000 system. On the morning of the second day, the HM 2000 system was brought back on-line and the analysis of the water samples that had been distributed on the first day was continued. Visual and HM 2010 measurements were made on 34 of the 36 samples distributed.

On the second day of the field exercise, the HM 2000 experienced another software failure after the 16 water samples contaminated with DRO/bunker C had been analyzed. This could not be corrected during the technology demonstration. At about the same time the HM 2000 failed, the HM 2010 also failed because of a low battery charge. The combination of these two problems forced the technology developer to treat 38 samples (36 soil samples and 2 water matrix spikes) by taking them through the solvent extraction step, then shipping them off-site prior to adding the catalyst and completing the analysis.

The large amount of time spent to address these problems limited the time available to prepare a data report. As a result, no TPH values were reported during the technology demonstration; however, a preliminary data report was made available on the following Monday (the technology demonstration finished on a Friday). This initial data report showed that of the 90 samples distributed, 52 samples (58%) were analyzed on-site by the visual comparison and the HM 2010 methods, and 47 samples (53%) had been analyzed by the HM 2000. Preliminary TPH values were reported at this time for the visual and HM 2000 methods of analysis; however, none were reported for the HM 2010. During this field exercise, the HM 2010 was only capable of producing voltage responses because of an integrated circuit failure, and calibration models for the

Table 9. Percent recoveries and relative percent differences estimated by the off-site laboratories and on-site by the technology developer for the matrix spike duplicates.

			Hanby	
Sample no./ID	*CRREL % Recov. (% RPD)*	*Ref. Lab % Recov. (% RPD)*	*Visual % Recov.*	*HM 2000 %Recov. (% RPD)*
GRO				
SG-6, 7	88	160	170	160
(100 mg TPH/kg)	(4.5)	(50)		(0)
SG-20, 20	91	92	97	123
(500 mg TPH/kg)	(2.2)	(8.7)		(34)
WG-6, 7	53	46	310	IF*
(0.48 mg TPH/kg)	(28)	(27)		IF
WG-15, 16	81	46	SL**	SL
(24 mg TPH/kg)	(15)	(0)	SL	SL
DRO				
SDM-6, 7	NA†	78	180	310
(250 mg TPH/kg)	NA	(5.1)		(10)
SDM-21, 22	NA	65	250	160
(1000 mg TPH/kg)	NA	(77)		(38)
WDM-1, 2	NA	91.6*	70	< 5
(0.98 mg TPH/kg)	NA	—		
WDM-16, 17	NA	NR†	170	OR††
(24 mg/kg TPH/kg)	NA	NR		OR
RRO				
M1, M9	NA	43*	95	60
(1000 mg TPH/kg)	NA	—		(12)

* Instrument failure.
** Sample lost.
† NA= not analyzed; NR = not reported.
†† Greater than value reported.

different hydrocarbon ranges and matrices still had to be developed. Sample analysis was completed after the HM 2000 was serviced by the company that had developed the software program, in which all of the software and applications were reloaded back onto the laptop computer that had been furnished with the HM 2000 analyzer. A final data report was available 12 days after the end of the field exercise. Soon after sending in this final data report, the technology developer recommended that the TPH values yielded by HM 2010 be omitted from this evaluation.

DISCUSSION

The Hanby Test Kits and the visual method of analysis are currently recognized by the U.S. Environmental Protection Agency as a reliable field screening method for TPH in environmental matrices (EPA 1993). The highest data-quality level that has been assigned to this technique states that it is capable of producing TPH values that are within an order of magnitude of the true or accepted concentration (EPA 1997). The performance of the visual method of analysis for the QA samples distributed during this field exercise supports this classification, as there were no TPH values outside of this range. Indeed, there were only a couple of values yielded (Table 5b, WG-2, WG-4, and WG-7) by the visual method of analysis that were a factor of 5× or slightly greater than the expected concentration. One of the features of the HM 2000 is its ability to provide a digital-readout of a discrete TPH value following sample analysis. This feature removes the subjectivity associated with a visual comparison of colors between samples and a

Table 10. Relative percent differences estimated by the off-site laboratories and on-site by the technology developer for the sample duplicates.

Sample no./ID	*CRREL (% RPD)*	*Ref. lab (% RPD)*	*HM 2000 (% RPD)*
GRO			
SG-8, 18	5.1	65	46
SG-10, 19	0	120	67
WG-11, 14	0	21	140
DRO			
SDM-12, 21	NA*	35	31
SDM-15, 22	NA	20	16
WDM-4, 18	NA	52	24
RRO			
M7, M8	NA	5.1	0

*Not analyzed.

limited number of photographs that represent different TPH concentrations. Therefore, one would expect that an increase in accuracy would accompany this more sophisticated measurement technology. In comparison to the visual method of analysis, however, the HM 2000 yielded some values that were false negatives (Table 5d, WDM-1 and -2) and one that was greater than the expected value by more than 10× (Table 5b, WG-7). Therefore, about 10% of the values (3 out of 29) estimated for QA samples by the HM 2000 failed to meet the criterion that is currently applied to the visual method of analysis.

The samples that the HM 2000 had the most difficulty with were background and HPLC water samples spiked to between 0.48 and 1 mg TPH/L (Tables 5c and d). The reported detection limit for both the visual and HM 2000 methods is stated to be 0.1 mg TPH/L (Hanby 1998). The inability of the HM 2000 to estimate values that were at least within an order of magnitude for waters spiked at 0.48 or 0.98 mg TPH/L shows that this detection limit cannot always be achieved. Furthermore, even when comparing the values yielded for a PE sample (Table 5c, SDM-1 through 4) with a TPH concentration close to the mid-point of the calibration range (500 mg TPH/kg), the HM 2000 failed to distinguished itself as being superior to the visual method of analysis.

It has been stated that these on-site methods of estimating TPH in environmental matrices are capable of producing concentrations within ±25% or better of the concentration established by accepted methods of analysis, when the specific contaminant of concern is known (U.S. Navy 1999, Hanby 1998). Here, two independent laboratories established concentrations for PE water and soil samples contaminated with GRO (Tables 5a and b) that were within 12% of the certified or expected concentration. In addition, two certified PE samples of DRO compounds in soil were distributed for analysis. The average value reported by the technology developer for these same PE samples was, in one case, 59% higher, while in the other seven cases it was more than 250% higher than the concentrations verified by the reference laboratory. Looking at the values estimated for the matrix spike samples shows that, in only two cases, was the visual method, and in one case, was the HM 2000 method, able to yield an average value within ±25% of the expected concentrations (Table 9). In one instance, for the visual method, this was clearly fortuitous, since the two values were separated by a factor of 2.9 (Table 5a, SG-20 and SG-21).

One of the other reasons for developing a spectrophotometric method of analysis with a digital-readout was that this approach would allow for an assessment of precision. Looking at the relative standard deviations established for the PE samples shows that the HM 2000 was incapable of achieving a high-degree of precision. That is, this method cannot achieve the levels of accuracy (i.e., ±25%) and precision (i.e., 15% RSD) that are associated with the more rigorous statistical analyses that are applied to field and laboratory analytical methods for the analysis of PE samples.

The analysis problems experienced with the HM

2000 during the field exercise clearly show that this approach to estimating TPH requires further development. Indeed, because of the instrumental complications with both the HM 2000 and HM 2010, no TPH values were reported during the technology demonstration, and many of the measurements had to be made off-site. Overall, because of the instrumental failures, and the false negative values, the HM 2000 method of analysis was found to be less reliable and less accurate than the visual method.

SUMMARY

The planning for this technology demonstration began only about 2 months before the actual field exercise. This short timetable limited the amount of oversight that was possible. By far the largest problem stemming from this short planning period was the lack of a thorough evaluation of a reference laboratory prior to its selection. Failure to use a laboratory with a current state certification to perform TPH analyses of environmental matrices, and one that lacked the proper documentation of its standard operating procedures for this class of compounds, undermined the credibility of the data established for the field samples. Furthermore, the reference laboratory failed to produce properly labeled chromatograms that perhaps could have been used to subjectively qualify suspect results. The large number of QA samples included in this study, however, could be used to judge performance, since they either had certified or expected values, and the matrices chosen for creating the matrix spike samples were determined to be relatively clean.

The performance of three different methods of measuring the Friedel-Crafts reaction products, produced by the Hanby Test Kits, were evaluated for reliability and for providing accurate and precise TPH concentrations in environmental matrices. The HM 2010, which is designed to measure the transmission of light (via reflectance) through the colored catalyst, failed to produce reliable TPH concentrations and requires further development before formal testing. The HM 2000, which measures reflectance over the entire visible spectrum, experienced two instrumental failures during the field exercise, and, therefore, is not currently capable of routine use. The visual method of analysis, although subjective, was found to be reliable for the identification of TPH contamination and for estimating concentration within an order of magnitude of the expected or certified value. This same level of data quality, however, was not consistently achieved with the HM 2000, which reported two false negative values and one that was greater than the expected value by more than order of magnitude.

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14. ABSTRACT

This report evaluates the methods of analysis that can be used with the Hanby Test Kits for assessing the total petroleum hydrocarbon (TPH) contamination in environmental matrices. This field screening technique is based on the colorimetric analysis of petroleum products in soil and water matrices, following a solvent extraction and a Friedel-Crafts reaction. The methods include visually comparing the sample to reference photographs, and two spectrophotometric (H.E.L.P. Mate 2010, and 2000) systems designed to establish discrete values. To test these field screening techniques, 90 field and quality assurance (QA) samples were obtained. Both of the spectrophotometric methods experienced instrumental problems, so that fewer than 60% of the samples distributed could be analyzed on-site. Ultimately, the H.E.L.P. Mate 2010 was dropped from the evaluation altogether. Furthermore, because of these complications, no TPH values were reported during the field exercise. The results yielded by the visual and H.E.L.P. Mate 2000 methods were compared for the QA samples; the visual technique was more reliable for showing the presence and estimating the quantity of TPH contamination.

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