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Innovative Technology Verification Report

Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil

Wilks Enterprise, Inc. Infracal ® TOG/TPH Analyzer

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**

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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.

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 mediumconcentration-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 highconcentration-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 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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