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Environmental Protection
Agency

Office of Research and
Development
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Innovative Technology Verification Report

Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil

Dexsil ® Corporation PetroFlag ™ System

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: **PetroFLAG™ SYSTEM**

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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 PetroFLAG™ System developed by Dexsil® Corporation (Dexsil).

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 PetroFLAG™ System and six other field measurement devices for TPH in soil. This verification statement focuses on the PetroFLAG™ System; a similar statement has been prepared for each of the other six devices. The performance and cost of the PetroFLAG™ System were compared to those of an off-site laboratory reference method, "Test Methods for Evaluating Solid Waste" (SW-846) Method 8015B (modified). To verify a wide range of performance attributes, the 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 PetroFLAG™ System was demonstrated by using it to analyze 66 soil environmental samples, 79 soil performance evaluation (PE) samples, and 36 liquid PE samples. In addition to these 181 samples, 10 extract duplicates prepared using the environmental samples were analyzed. The environmental samples were collected in four areas contaminated with gasoline, diesel, or other petroleum products, and the PE samples were obtained from a commercial provider. Dexsil chose not to analyze soil samples collected in a fifth area because Dexsil believed that the natural organic material in the area would adversely impact the PetroFLAG™ System's ability to accurately measure TPH. In addition, Dexsil chose not to analyze low- and medium-concentration-range weathered gasoline soil PE samples because according to Dexsil, the PetroFLAG™ System was not sensitive to weathered gasoline concentrations of less than 1,000 milligrams per kilogram.

Collectively, the environmental and PE samples provided the different matrix types and the different levels and types of petroleum hydrocarbon contamination needed to perform a comprehensive evaluation of the PetroFLAG™ System. A complete description of the demonstration and a summary of its results are available in the "Innovative Technology Verification Report: Field Measurement Devices for Total Petroleum Hydrocarbons in Soil—Dexsil® Corporation PetroFLAG™ System" (EPA/600/R-01/092).

TECHNOLOGY DESCRIPTION

The PetroFLAG™ System manufactured by Dexsil is based on emulsion turbidimetry, which involves measurement of the light scattered by an emulsion. With the PetroFLAG™ System, a proprietary, nonpolar, organic solvent mixture composed of alcohols, primarily methanol, is used to extract petroleum hydrocarbons from soil samples. A proprietary developer solution that is polar in nature and that acts as an emulsifier is added to a sample extract in order to precipitate the aromatic and aliphatic hydrocarbons and form uniformly sized micelles. Light at a wavelength of 585 nanometers is passed through the emulsion, and the amount of light scattered by the emulsion at a 90-degree angle is measured using a turbidimeter. The TPH concentration in the emulsion is then determined by comparing the turbidity reading for the emulsion to that for a reference standard or to a standard calibration curve. According to Dexsil, the TPH concentration thus measured is a function of the mean molecular weight of the hydrocarbons present in the sample.

During the demonstration, extraction of petroleum hydrocarbons in a given soil sample was typically completed by adding 10 milliliters (mL) of proprietary methanol mixture extraction solvent to 10 grams of the sample. To form an emulsion, 2 mL of sample extract was then decanted into a vial containing 4 mL of developer solution. The emulsion was analyzed using the PetroFLAG™ Analyzer (turbidimeter) to obtain a direct measurement of the TPH concentration in the soil sample.

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 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 20 and 6.32 milligrams per kilogram for the PetroFLAG™ System and reference method, respectively.

Accuracy and Precision: Seventy-one of 97 PetroFLAG™ System results (73 percent) used to draw conclusions regarding whether the TPH concentration in a given sampling area or sample type exceeded a specified action level agreed with those of the reference method; 26 PetroFLAG™ System conclusions were false positives. There were no false negatives.

Of 91 PetroFLAG™ System results used to assess measurement bias, 11 were within 30 percent, 9 were within 30 to 50 percent, and 71 were not within 50 percent of the reference method results; 82 PetroFLAG™ System results were biased high, and 9 were biased low.

For soil environmental samples, the PetroFLAG™ System results were statistically (1) the same as the reference method results for one of the four sampling areas and (2) different from the reference method results for three of the sampling areas.

For soil PE samples, the PetroFLAG™ System results were statistically (1) the same as the reference method results for highconcentration- range diesel samples and (2) different from the reference method results for blank samples, high-concentrationrange weathered gasoline samples, and low- and medium-concentration-range diesel samples. For liquid PE samples, thePetroFLAG™ System results were statistically different from the reference method results for both weathered gasoline and diesel samples.

The PetroFLAG™ System results correlated highly with the reference method results for one of the four sampling areas and diesel soil PE samples (the square of the correlation coefficient [R_2] values were greater than 0.90, and F-test probability values were less than 5 percent). The PetroFLAG™ System results correlated moderately with the reference method results for two of the four sampling areas (R_2 values were 0.84 and 0.86, and F-test probability values were less than 5 percent). The PetroFLAG™ System results correlated weakly with the reference method results for one of the four sampling areas and

weathered gasoline soil PE samples (R_2 values were 0.42 and 0.10, respectively, and F-test probability values were greater than 5 percent).

Comparison of the PetroFLAG™ System and reference method median relative standard deviations (RSD) showed that the PetroFLAG™ System and the reference method exhibited similar overall precision. Specifically, the median RSD ranges were 6 to 19 percent and 5.5 to 16 percent for the PetroFLAG™ System and reference method, respectively. The analytical precision was about the same for the PetroFLAG™ System (a median relative percent difference of 5) and reference method (a median relative percent difference of 4).

Effect of Interferents: The PetroFLAG™ System showed a mean response of less than 5 percent for neat methyl-tert-butyl ether (MTBE) and tetrachloroethene (PCE) and for soil spiked with humic acid. The device's mean responses for neat Stoddard solvent; turpentine; and 1,2,4-trichlorobenzene were 42.5, 103, and 16 percent, respectively. The reference method showed varying mean responses for MTBE (39 percent); PCE (17.5 percent); Stoddard solvent (85 percent); turpentine (52 percent); 1,2,4-trichlorobenzene (50 percent); and humic acid (0 percent). For the demonstration, MTBE and Stoddard solvent were included in the definition of TPH.

Effect of Moisture Content: The PetroFLAG™ System showed a statistically significant decrease (17 percent) in TPH results when the soil moisture content was increased from 9 to 16 percent for weathered gasoline soil PE samples; the reference method TPH results were unaffected. Both PetroFLAG™ System and reference method TPH results were unaffected when the soil moisture content was increased from less than 1 to 9 percent for diesel soil PE samples.

Measurement Time: From the time of sample receipt, Dexsil required 50 hours, 40 minutes, to prepare a draft data package containing TPH results for 181 samples and 10 extract duplicates compared to 30 days for the reference method, which was used to analyze 199 samples and 13 extract duplicates.

Measurement Costs: The TPH measurement cost for 181 samples and 10 extract duplicates was estimated to be $6,390, including the capital equipment purchase cost of $695, for the PetroFLAG™ System compared to $38,560 for the reference method.

Key demonstration findings are summarized below for the secondary objectives.

Skill and Training Requirements: The PetroFLAG™ System 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.

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

Durability and Availability of the Device: All items in the PetroFLAG™ System are available from Dexsil. During a 6-month warranty period, Dexsil will supply replacement parts for the device by overnight courier service at no cost. During the demonstration, none of the device's reusable items malfunctioned or was damaged.

In summary, during the demonstration, the PetroFLAG™ System exhibited the following desirable characteristics of a field TPH measurement device: (1) good precision, (2) lack of sensitivity to interferents that are not petroleum hydrocarbons (PCE and humic acid), (3) low measurement costs, and (4) ease of use. In addition, the PetroFLAG™ System exhibited moderate sample throughput. Based on action level conclusions and statistical correlations, the PetroFLAG™ System TPH results compared well with those of the reference method; however, the device exhibited a high bias, and its TPH results were determined to be statistically different from those of the reference method. In addition, turpentine and 1,2,4-trichlorobenzene

biased the device's TPH results high. Moreover, an increase in soil moisture content biased the device's TPH results low for weathered gasoline soil PE samples. Collectively, the demonstration findings indicated that the user should exercise caution when considering the device for a specific field TPH measurement application.

Original
signed by

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