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Agency

Office of Research and
Development
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Innovative Technology Verification Report

Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil

Environmental Systems Corporation Synchronous Scanning Luminoscope

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: **SYNCHRONOUS SCANNING LUMINOSCOPE**

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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 Synchronous Scanning Luminoscope (Luminoscope) developed by the Oak Ridge National Laboratory in collaboration with Environmental Systems Corporation (ESC).

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 Luminoscope and six other field measurement devices for TPH in soil. This verification statement focuses on the Luminoscope; a similar statement has been prepared for each of the other six devices. The performance and cost of the Luminoscope 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 Luminoscope was demonstrated by using it to analyze 74 soil environmental samples, 89 soil performance evaluation (PE) samples, and 36 liquid PE samples. In addition to these 199 samples, 12 extract duplicates prepared using the environmental samples were analyzed. 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 contamination needed to perform a comprehensive evaluation of the Luminoscope. 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—Environmental Systems Corporation Synchronous Scanning Luminoscope" (EPA/600/R-01/083).

TECHNOLOGY DESCRIPTION

The Luminoscope uses a xenon lamp to produce a multiwavelength ultraviolet light beam that passes through an excitation monochromator before irradiating a sample extract held in a quartz cuvette. When the sample extract is irradiated, aromatic hydrocarbons in the extract emit light at a longer wavelength than does the light source. The light emitted from the sample extract passes through another monochromator, the emission monochromator, and is detected using a photomultiplier tube. The photomultiplier tube detects and amplifies the emitted light energy and converts it into an electrical signal. This signal is used to determine the intensity of the light emitted and generate a spectrum for the sample.

The components of the Luminoscope are structured to maintain a constant wavelength interval between the excitation and emission monochromators. This modification of classical fluorescence technology is called synchronous fluorescence and takes advantage of the overlap between the excitation and emission spectra for a sample to produce more sharply defined spectral peaks.

During the demonstration, extraction of petroleum hydrocarbons in a given soil sample was completed by adding 10 milliliters of methanol to 2 grams of the sample. The mixture was agitated using a test tube shaker and centrifuged. The sample extract was then decanted into a quartz cuvette that was placed in the Luminoscope. The extract was analyzed over a wavelength range of 250 to 400 nanometers. A laptop computer with Grams/32 software was used to control the Luminoscope, integrate the area under the peaks of the sample spectrum in order to report a TPH concentration for the sample, and manage data collected by the device.

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-range diesel soil PE samples, the method detection limits were determined to be 36 and 6.32 milligrams per kilogram for the Luminoscope and reference method, respectively.

Accuracy and Precision: Seventy-five of 108 Luminoscope results (69 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; 10 Luminoscope conclusions were false positives, and 23 were false negatives.

Of 102 Luminoscope results used to assess measurement bias, 19 were within 30 percent, 13 were within 30 to 50 percent, and 70 were not within 50 percent of the reference method results; 64 Luminoscope results were biased low, 37 were biased high, and 1 showed no bias.

For soil environmental samples, the Luminoscope results were statistically different from the reference method results for all five sampling areas. For soil PE samples, the Luminoscope results were statistically (1) the same as the reference method results for blank and high-range weathered gasoline samples and (2) different from the reference method results for mediumrange weathered gasoline samples and low-, medium-, and high-range diesel samples. For liquid PE samples, the

Luminoscope results were statistically different from the reference method results for both weathered gasoline and diesel samples.

The Luminoscope results correlated highly with the reference method results for two of the five sampling areas, weathered gasoline soil PE samples, and diesel soil PE samples (the square of the correlation coefficient [R_2] values were greater than or equal to 0.90, and F-test probability values were less than 5 percent). The Luminoscope results correlated moderately with the reference method results for two of the five sampling areas (R_2 values were 0.57 and 0.65, and F-test probability values were less than 5 percent). The Luminoscope results correlated weakly with the reference method results for one sampling area (the R_2 value was 0.52, and the F-test probability value was near 5 percent).

Comparison of the Luminoscope and reference method median relative standard deviations (RSD) showed that the Luminoscope exhibited greater overall precision than the reference method. Specifically, the median RSD ranges were 8 to 12 percent and 5.5 to 18 percent for the Luminoscope and reference method, respectively. The analytical precision was about the same for the Luminoscope (a median relative percent difference of 5) and reference method (a median relative percent difference of 4).

Effect of Interferents: The Luminoscope showed a mean response of less than 5 percent for neat materials, including methyltert-butyl ether (MTBE); tetrachloroethene (PCE); Stoddard solvent; turpentine; and 1,2,4-trichlorobenzene, and soil spiked with humic acid. The reference method showed varying mean responses for MTBE (39 percent); PCE (17.5 percent); Stoddard solvent (85 percent); turpentine (52 percent); 1,2,4-trichlorobenzene (50 percent); and humic acid (0 percent). For the demonstration, MTBE and Stoddard solvent were included in the definition of TPH.

Effect of Moisture Content: Both Luminoscope and reference method TPH results were unaffected when the moisture content was increased from (1) 9 to 16 percent for weathered gasoline soil PE samples and (2) less than 1 to 9 percent for diesel soil PE samples.

Measurement Time: From the time of sample receipt, ESC required 67 hours, 30 minutes, to prepare a draft data package containing TPH results for 199 samples and 12 extract duplicates compared to 30 days for the reference method, which was used to analyze 1 additional extract duplicate.

Measurement Costs: The TPH measurement cost for 199 samples and 12 extract duplicates was estimated to be $7,460 for ESC's on-site sample analysis service option using the Luminoscope compared to $42,430 for the reference method. The estimated cost was much higher ($34,950) for the Luminoscope purchase option because of the significant capital equipment cost ($26,500).

Key demonstration findings are summarized below for the secondary objectives.

Skill and Training Requirements: The Luminoscope can be operated by one person with analytical chemistry skills. The 3-day, device-specific training offered by ESC should assist the user in acquiring necessary skills, including preparation of calibration curves, calculation of TPH results, and proper use of the Grams/32 software required for device operation. During the demonstration, the experienced ESC technician noted a software error; subsequently, 77 percent of the spectra generated required correction. After the demonstration, 107 of 211 TPH results had to be corrected; the corrections were associated with use of an incorrect calibration slope factor, use of an incorrect dilution factor, and data entry errors.

Portability: The device 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 such as a 12-volt power outlet in an automobile.

Durability and Availability of the Device: ESC offers a 1-year warranty for the Luminoscope. During the warranty period, ESC will supply replacement parts for the device by overnight courier service at no cost. ESC does not supply some equipment necessary for TPH measurement using the device, including a test tube shaker, centrifuge, and digital balance; the availability of replacement or spare parts not supplied by ESC depends on their manufacturer or distributor. During the demonstration, a sensitivity chip in the Luminoscope required replacement; all other device components functioned properly.

In summary, during the demonstration, the Luminoscope exhibited the following desirable characteristics of a field TPH measurement device: (1) good precision, (2) lack of sensitivity to moisture content and to interferents that are not petroleum hydrocarbons (PCE; turpentine; and 1,2,4-trichlorobenzene), and (3) low measurement costs. In addition, the Luminoscope exhibited moderate sample throughput. However, the Luminoscope TPH results did not compare well with those of the reference method, indicating that the user should exercise caution when considering the device for a specific field TPH measurement application. In addition, field observations indicated that operation of the device may prove challenging unless

the operator has significant analytical chemistry skills and device-specific training.

Original
signed by

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