Standard Practice for Cone Penetrometer Technology Characterization of Petroleum Contaminated Sites with Nitrogen Laser-Induced Fluorescence[1]

This standard is issued under the fixed designation D6187; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers the method for delineating the subsurface presence of petroleum hydrocarbons and other hydrocarbons using a fiber optic based nitrogen laser-induced fluorescence sensor system.

1.2 The petroleum hydrocarbon sensing scheme utilizes a fluorescence technique in which a nitrogen laser emits pulsed ultraviolet light. The laser, mounted on the cone penetrometer platform, is linked via fiber optic cables to a window mounted on the side of a penetrometer probe. Laser energy emitted through the window causes fluorescence in adjacent contaminated media. The fluorescent radiation is transmitted to the surface via optical cables for real-time spectral data acquisition and spectral analysis on the platform.

1.3 This sensor responds to any material that fluoresces when excited with ultraviolet wavelengths of light, largely the polycyclic aromatic, aromatic, and substituted hydrocarbons, along with a few heterocyclic hydrocarbons. The excitation energy will cause all encountered fluorophores to fluoresce, including some minerals and some non-petroleum organic matter. However, because the sensor collects full spectral information, discrimination among the fluorophores may be distinguished using the spectral features associated with the data. Soil samples should be taken to verify recurring spectral signatures to discriminate between fluorescing petroleum hydrocarbons and naturally occurring fluorophores.

1.4 This practice is used in conjunction with a cone penetrometer of the electronic type, described in Test Method D5778.

1.4.1 The direct push LIF described in this practice can provide accurate information on the characteristics of the soils and contaminants encountered in the vadose zone and the saturated zone, although it does not make a distinction between dissolved and sorbed contamination in the saturated zone.

1.5 This practice describes rapid, continuous, in-situ, real-time characterization of subsurface soil.

1.6 Direct push LIF is limited to soils that can be penetrated with the available equipment. The ability to penetrate strata is based on carrying vehicle weight, density of soil, and consistency of soil. Penetration may be limited; or, damage to sensors can occur in certain ground conditions.

1.7 This practice does not address the installation of any temporary or permanent soil, groundwater, soil vapor monitoring, or remediation devices; although, the devices described may be left in-situ for the purpose of on-going monitoring.

1.8 The values stated in inch-pound units are to be regarded as the standard. The SI units given in parentheses are for information only.

1.9 Direct push LIF environmental site characterization will often involve safety planning, administration, and documentation. This practice does not purport to address the issues of operational or site safety.

1.10 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D653 Terminology Relating to Soil, Rock, and Contained Fluids
D1129 Terminology Relating to Water
D3650 Test Method for Comparison of Waterborne Petroleum Oils By Fluorescence Analysis
D4657 Test Method for Polynuclear Aromatic Hydrocarbons

---

[1] This practice is under the jurisdiction of ASTM Committee D18 on Soil and Rock and is the direct responsibility of Subcommittee D18.21 on Groundwater and Vadose Zone Investigations.

Current edition approved July 1, 2010. Published September 2010. Originally approved in 1997. Last previous edition approved in 2003 as D6187–97(2003). DOI: 10.1520/D6187-97R10.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

in Water (Withdrawn 2005)[3]

D5088 Practice for Decontamination of Field Equipment Used at Waste Sites

D5730 Guide for Site Characterization for Environmental Purposes With Emphasis on Soil, Rock, the Vadose Zone and Groundwater (Withdrawn 2013)[3]

D5778 Test Method for Electronic Friction Cone and Piezocone Penetration Testing of Soils

D6001 Guide for Direct-Push Groundwater Sampling for Environmental Site Characterization

D6067 Practice for Using the Electronic Piezocone Penetrometer Tests for Environmental Site Characterization

E131 Terminology Relating to Molecular Spectroscopy

E169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis

E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

E388 Test Method for Wavelength Accuracy and Spectral Bandwidth of Fluorescence Spectrometers

E578 Test Method for Linearity of Fluorescence Measuring Systems

E579 Test Method for Limit of Detection of Fluorescence of Quinine Sulfate in Solution

E924 Guide for Quality Assurance of Laboratories Using Molecular Spectroscopy (Withdrawn 2003)[3]

E1614 Guide for Procedure for Measuring Ionizing Radiation-Induced Attenuation in Silica-Based Optical Fibers and Cables for Use in Remote Fiber-Optic Spectroscopy and Broadband Systems

3. Terminology

3.1 *Definitions:*

3.1.1 Terminology used within this practice is in accordance with Terminologies D653, D1129, and E131, and Practice D3415 with the addition of the following:

3.1.2 *calibration*—the process by which the relationship of instrumental response to changes in the nature and concentration of reference materials is determined.

3.1.3 *Fluorophore*—a material that produces, undergoes, or exhibits fluorescence.

3.1.4 *Laser-induced fluorescence (LIF)*—the rapid emission of light from an atom or molecule after it has absorbed radiation from collimated and polarized monochromatic light source.

3.1.5 *TPH*—total petroleum hydrocarbons.

3.1.6 *TRPH*—total recoverable petroleum hydrocarbons.

3.1.7 *vadose zone*—the hydrogeological region extending from the soil surface to the top of the principal water table; commonly referred to as the "unsaturated zone" or "zone of aeration". However, these alternate names are inadequate as they do not take into account locally saturated regions above the principal water table (for example, perched water zones).

3.2 *Definitions:*

3.2.1 *in-situ testing devices*—are sensors or samplers, used for obtaining mechanical or chemical test data, that are typically pushed, rotated or driven from the surface or below the bottom of a borehole following completion of an increment of drilling.

3.2.2 *push depth*—the depth below a ground surface to which the tip of the direct push water sampling device has penetrated.

3.3 *Definitions:*

3.3.1 Definitions in accordance with Test Method D6067:

3.3.2 *cone penetrometer*—a penetrometer in which the leading end of the penetrometer tip is a conical point designed for penetrating soil and for measuring the end-bearing component of penetration resistance.

3.3.3 *electronic cone penetrometer*—a friction cone penetrometer that uses force transducers, such as strain gauge load cells, built into a non-telescoping penetrometer tip for measuring, within the penetrometer tip, the components of penetration resistance.

3.3.4 *penetrometer*—an apparatus consisting of a series of cylindrical push rods with a terminal body (end section), called the penetrometer tip, and measuring devices for determination of the components of penetration resistance.

3.3.5 *penetrometer tip*—the terminal body (end section) of the penetrometer which contains the active elements that sense the components of penetration resistance. The penetrometer tip may include additional electronic instrumentation for signal conditioning and amplification.

3.3.6 *push rods*—the thick-walled tubes or rods used to advance the penetrometer tip.

4. Summary of Practice

4.1 This practice is based on a cone penetrometer deployed fiber optic-based, nitrogen laser-induced fluorescence sensor system. It is an in situ field screening technique for characterizing the subsurface distribution. This practice is not a replacement for these traditional methods; but is a means of reducing the number of borings and wells required to achieve site characterization. See Fig. 1 and Fig. 2

4.2 This practice provides semi-quantitative data on the subsurface distribution of POL products from the fluorescence response induced in the polycyclic aromatic hydrocarbon compounds that are components of petroleum products. It makes use of a laser excitation source that targets polycyclic aromatic hydrocarbons with three or more fused aromatic rings and detects them in the bulk soil matrix throughout the vadose, capillary fringe, and saturated zones. When the sensor is used in conjunction with an industry-standard 20 ton penetrometer push vehicle and subsurface conditions are favorable, measurements have been made to depths greater than 150 ft (45.7 m). The depth of push is influenced by many geological factors (that is, properties of soil) and may vary widely from site to site.

4.3 The spectral data provides a means of confirming that observed fluorescence events are consistent with the spectra from known petroleum products. It provides a field screening

---

[3] The last approved version of this historical standard is referenced on www.astm.org.

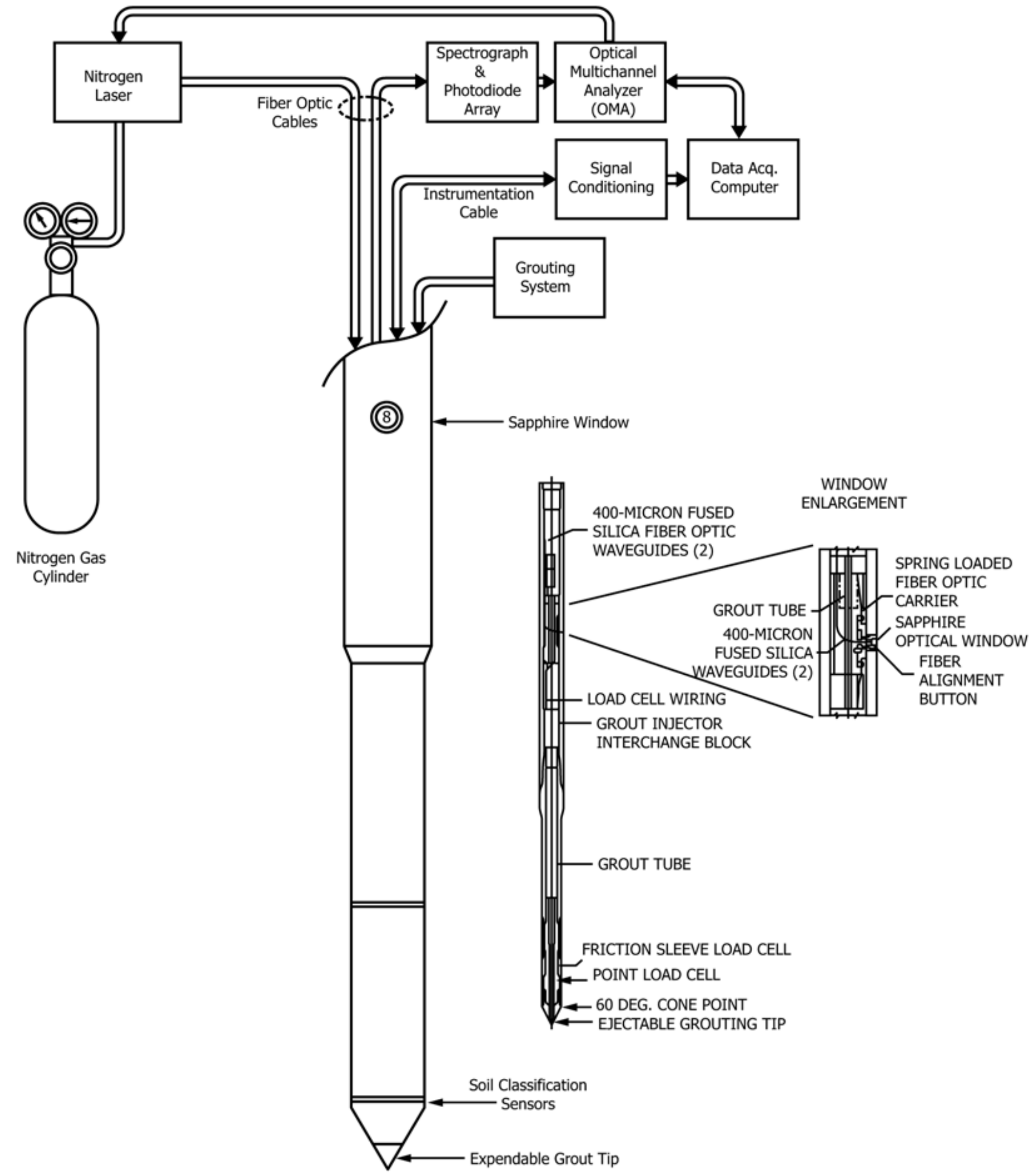

FIG. 1 Laser-Induced Fluorescence Petroleum, Oil, and Lubricant Sensor

capability that is proportional to contamination concentration and relative to a specified detection limit derived for a specific fuel product on a site specific soil matrix.

4.4 Although under ideal conditions detection limits are in the ppm range, the same contaminant in various matrices will have different levels of detection due to the influences of these matrices.

5. Significance and Use

5.1 Direct push LIF is used for site investigations where the delineation of petroleum hydrocarbons and other fluorophores is necessary. Generic terms for these investigations are site assessments and hazardous waste site investigations. Continuous LIF is used to provide information on the relative amounts of contamination and to provide a lithological detail of the subsurface strata. These investigations are frequently required in the characterization of hazardous waste sites.

5.2 This technology provides preliminary results within minutes following the completion of each test. This allows the number, locations, and depths of subsequent tests to be adjusted in the field. Field adjustment may increase the efficiency of the investigation program.

5.3 The rapid fluorescence data gathering provided by direct push LIF provides information necessary to assess the presence of contamination in soils and associated pore fluids in the field. This method allows for immediate determination of relative amounts of contamination. This allows the number, locations, and depths of subsequent activities to be adjusted in the field. Field adjustment may increase the efficiency of the investigation program.

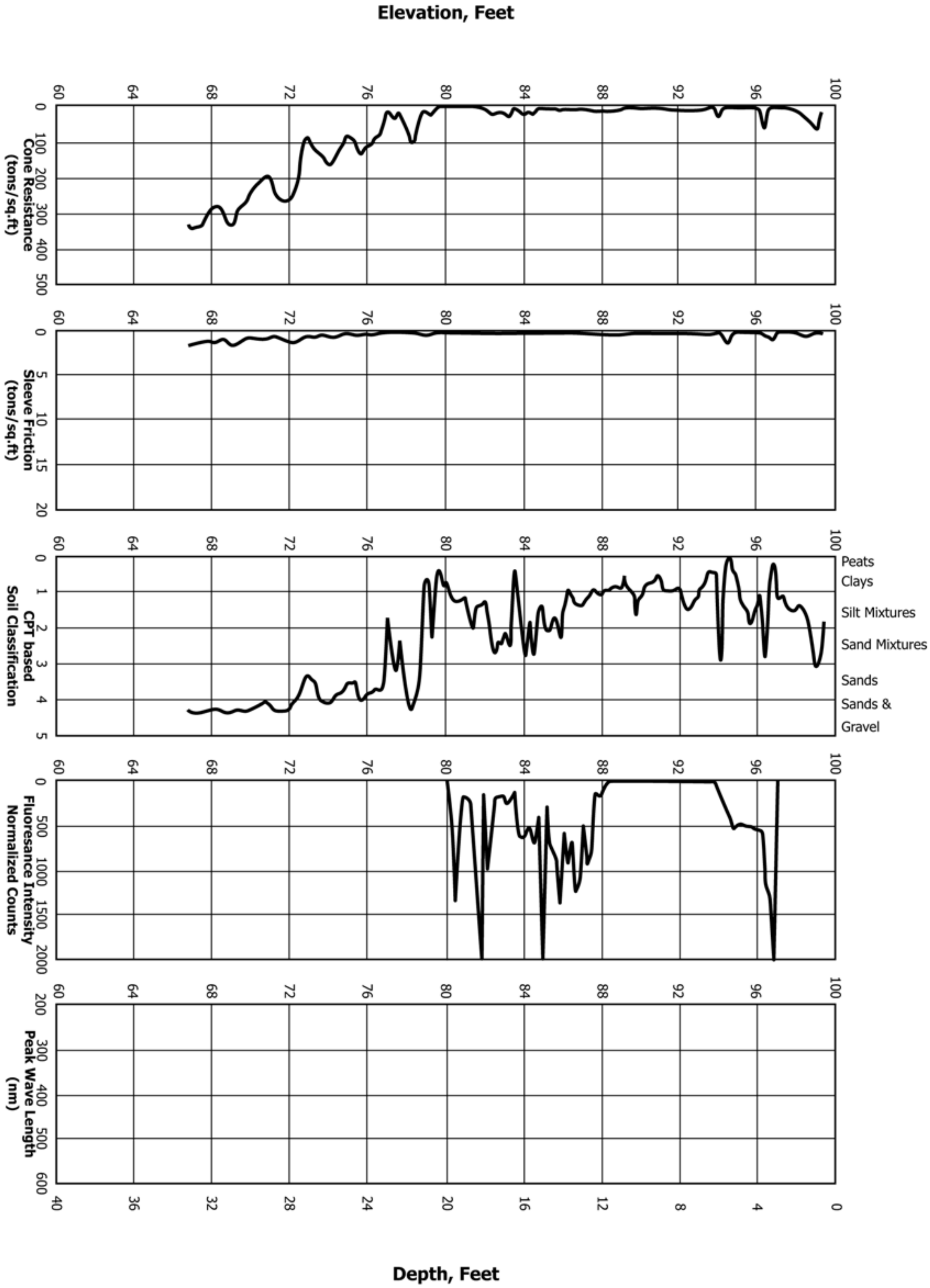

FIG. 2 Typical Panel Plot for POL and Geophysical Sensors

5.4 With appropriate sensors, the direct-push investigation program can provide information on soil stratigraphy and the distribution of petroleum and other fluorophores in the subsurface. This method results in minimum site disturbance and generates no cuttings that might require disposal (**1**).[4]

5.5 This practice is confirmed using soil samples collected at given depths to confirm the fluorescence readings using a field deployed EPA Method 418.1 (**2**) , EPA method 8015-modified, and a modified EPA 8270 Method (**3**), or equivalent methodologies, as compared to the fluorescence reading from the same depth from the sensor to verify that the fluorescence correlates with the contamination. The collected samples are also tested on the probe window in the truck to ensure the sample collected is representative of the region tested in situ.

5.6 This practice may not be the correct method for preliminary or supplemental investigations in all cases. Chemical and physical properties of site specific soil matrices may have an effect on site specific detection limits. Subsurface conditions affect the performance of the equipment and methods associated with the direct push method. Direct push methods are not effective in pushing in solid bedrock and are marginally effective in pushing in weathered formations. Dense gravelly tills where boulders and cobbles are present, stiff and hard clays, and cemented soil zones may cause refusal and potential probe breakage. Certain cohesive soils, depending on their moisture content, can create friction on the cone penetrometer probes which can eventually equal or exceed the static reaction force and/or the impact energy being applied. As with all direct push methods, precautions must be taken to prevent cross contamination of aquifers through migration of contaminants up or down the cone penetrometer hole.

5.7 The practicing of direct push techniques may be controlled by various government regulations governing subsurface explorations. Certification or licensing regulations, or both, may in some cases be considered in establishing performance criteria. For additional information see (**4-15**)

6. Apparatus

6.1 *General*—The main components of the LIF sensor are the laser, fiber optic cables, the fluorescence detection system, and the computer system. The nitrogen laser emits light of a known wavelength (337 nm) and passes it along a fiber optic cable. The laser light then is dispersed into the soil through a window mounted on the terminal end of a cone penetrometer probe. Induced fluorescence from the soil returns to the fluorescence detector along a second fiber optic cable. A detector (that is, photodiode array, charged coupled device) and signal processor (that is, optical multichannel analyzer) are used as the fluorescence detector and the data are processed by a computer system.

6.1.1 Most apparatus required is discussed in Test Method D5778 and Guide D6067.

6.2 *Laser*—Laser radiation excitation is produced by a pulsed nitrogen laser. The emitted laser radiation is focused through a lens and directed into the excitation fiber.

6.3 *Fiber Optic Cables,* should be capable of transmitting UV light at 337 nm. Maximum attenuation of the fiber optic cables should be 10 dB/km at approximately 820 nm. Both the excitation fiber and the return fiber, and the instrumentation cables are all protected by a neoprene shrink tubing jacket forming the sensor umbilical, that is passed through the center of each push rod. The excitation fiber is terminated at the window where the light passes onto the soil surface adjacent to the window. The return fiber passes the returned light from the soil into the detection system.

6.4 *Window,* located at the terminal end of the cone penetrometer. It should be scratch resistant and capable of transmitting UV light with minimal loss or sorption (that is, sapphire) and should be checked for fluorescence prior to use. The window should be removable to facilitate periodic replacement as necessary.

6.5 *Fluorescence Detection System*—The detector contains mirrors and a grating so that the returned light is diffracted into its component wavelengths. The signal processor receives the data from the detector and displays the spectra of the returned signal.

6.6 *Computer System,* may consist of two computers. One computer is the data acquisition computer and the second computer is the post-acquisition processing computer. The data acquisition computer communicates and transfers data from the signal processor. The data is then transferred to the post-processing computer where the data is manipulated and plotted.

7. Procedure

7.1 This sensor technology is calibrated using two types of standards.

7.1.1 A quality control standard (that is, Quinine Sulfate or Rhodamine 6G) (refer to Test Methods E578 and E579) is used to ensure that the system is functioning correctly and facilitates data normalization if the probe is changed during field operations.

7.1.2 A set of calibration standards is prepared to evaluate the sensitivity of the sensor to the soil type at the site and the contamination expected to be encountered. This set of standards is used to establish the level of base line noise in the measurements as well as the sensitivity of the sensor to the soil/contamination combination. An alternative method is to take multiple soil samples upon completion of LIF work and use the laboratory analysis of these samples as standards to evaluate the sensitivity of soil/contaminant combinations.

7.2 *Initial Calibration Procedures* (**4**)*:*

7.2.1 A time delay calibration shall be performed when operating the detector in gated mode to ensure optimum time gating of the detection system. This is performed because the detector setup is gated for the duration of fluorescence emission return at the detector. Although the purpose of LIF is not to resolve fluorescence lifetime information, a majority of the fluorescence compounds have lifetimes between 1 to 100 nanoseconds; therefore, an optimal gating time, triggered by the firing of the laser, is 100 nanoseconds. A plot intensity versus time delay is acquired and determines the optimum

---

[4] The boldface numbers given in parentheses refer to a list of references at the end of the text.

delay. The time delay varies solely as a function of the optical path length between the laser and the detector.

7.2.2 A wavelength calibration is performed to determine the intercept and slope of the line converting detector pixel number into wavelength. A mercury lamp is used to provide known wavelengths for calibration. A helium-neon laser may be used to verify the calibration. Another method to verify calibration is to excite a fluorescence standard and confirm the location of peaks associated with the standard and nitrogen laser. This is required after the spectrograph, the fiber input to the spectrograph, or the detector are changed. Recalibration is also required when the wavelength of the fluorescent standard is greater than 5 nanometers from the standard value.

7.2.3 A semi-quantitative concentration calibration may be performed using a set of calibration standards (spiked site-specific soil samples) prepared by the serial addition method. The accuracy of this procedure is dependent upon the correlation of standards versus site specific contaminants and representativeness of site specific soil samples. The calibration standards are run in triplicate at the beginning of each day and again when equipment is changed. These samples are sequentially presented to the window for measurement. Fluorescence intensity obtained during the calibration procedure should be equivalent to the concentration of contaminant in the sample based upon representativeness of the standard used and the soil sample collected. The average and relative standard deviation is computed for each sample. If the relative standard deviation exceeds 20 % for replicate analyses of any single sample, that sample is rerun. If the relative standard deviation remains excessive, the system check standard is measured. If the check standard is out of compliance, system checkout and debugging is required by checking the laser performance and output power, fiber optic cable alignment, fiber optic terminations, and window conditions should be checked.

7.2.4 Sample heterogeneity (from the site samples) may contribute to a large relative standard deviation. If this is the case, the number of measurements is doubled until the relative standard deviation falls within 20 %. A calibration curve is generated by plotting the average of maximum fluorescence peak intensity versus the concentration of fuel product added to the calibration soil sample. A linear fit is performed yielding slope, intercept, and correlation coefficient. The correlation coefficient must be greater than 0.90. The calibration curve will be regenerated if the correlation coefficient is less than 0.90.

7.2.5 The reference methods, TRPH by infrared spectrometry TPH by a gas chromatograph equipped with a flame ionization detector and semivolatile organic compounds by GC/MS, are EPA Method 418.1 (**2**) EPA Method 8015-Modified and EPA Method 8270-Modified (**3**) respectively. Singularly, these methods do not provide a direct correlation; however, the combination of these and others provide a proportional relationship to fluorescence generated spectra.

7.3 *Continuing Calibration Procedures* (**4**)*:*

7.3.1 A fluorescent standard (see 1.4.1) may be analyzed using the LIF system before and after each push. This measurement is a check of system performance and provides a means for normalizing measurements. If the fluorescent intensity changes by more than 20 % of the initial value determined during pre-push calibration, system trouble shooting procedures will be initiated.

7.4 *Direct Push LIF* (**1**)*:*

7.4.1 Procedures for the operation of the cone penetrometer are as described for cone penetrometers of the electronic type in Test Method D5778.

7.4.2 Pre-push operations consist of sensor probe setup, sensor probe calibrations, and initializing the data collection software.

7.4.3 Sensor data is collected using the LIF probe, during the procedure associated with the direct push method (see 7.1.1), via the computer data acquisition system on the cone penetrometer platform.

7.4.4 Data acquisition is completed using the LIF probe at the cone penetrometer probe termination depth.

7.4.5 No further calibrations are performed on the sensor unless anomalies (see 1.3) are observed in the collected data.

7.4.6 Immediate decisions are made on-site for additional push locations based on the information acquired.

7.5 *Obtaining Physical Samples for Confirmation* (**1**)*:*

7.5.1 The samples are obtained within 1 to 2 ft (0.3 to 0.6 m) of the original sensor push point. The data acquisition computer system is used to determine the target depth.

7.5.2 A typical site investigation is performed by recording LIF spectral signatures at various site locations. Soil samples are collected upon completion of LIF work, and each sample is split into three subsamples. Each soil subsample is placed against the LIF probe window and the spectrum recorded to verify that the soil sample produces a response similar to what was recorded during the LIF push. The subsamples of the original soil sample are analyzed using a field deployed EPA Method 418.1 (**2**), and representative samples are sent for analytical laboratory analysis. Soil samples are also analyzed from locations where no LIF response was observed to confirm that the locations are free of contamination.

8. Report

8.1 The data and calibration reports for the cone penetrometer should conform to the methods and information described in Test Method D5778 and Guide D6067.

8.2 Report the following data (**4**):

8.2.1 Field data plots from all pushes, cone pressure, sleeve friction, and soil classification, each with respect to depth. Field plots of peak fluorescence wavelength versus depth, and all push data displaying the raw fluorescence spectrum collected during the pushes,

8.2.2 System check and calibration sample concentrations; tabulated raw system check and calibration sample fluorescence data; average system check intensity and system check ratio for each push; background, noise, and sensitivity calculated from calibration data,

8.2.3 Borehole logs indicating soil sample collection information, including sample numbers, depth of samples, location of water table, and other relevant information concerning the collection of the soil samples; chain-of custody documentation associated with soil samples, and

8.2.4 Laboratory results for TPH and TRPH measurements of soil samples, including the standard analytical results and quality control data.

9. Keywords

9.1 coal tar; cone penetrometer; creosole; in-situ sensor; direct push; laser-induced fluorescence; petroleum contamination; site characterization

REFERENCES

(1) PRC Environmental Management, Inc.,“ Innovative Technology Evaluation Report on the Demonstration of the Site Characterization and Analysis Penetrometer System,” U.S. Environmental Protection Agency Superfund Innovative Technology Evaluation Program, Environmental Monitoring Systems Laboratory, Las Vegas, NV, 1995.

(2) United States Environmental Protection Agency, “Methods for Chemical Analysis of Water and Wastes,” *EPA-600/4-79-020* , revised March 1983.

(3) United States Environmental Protection Agency,“ Test Method for Evaluating Solid Waste,” *SW-846*, Third Edition. November 1983.

(4) Naval Command, Control and Ocean Surveillance Center Research, Development, Test, and Evaluation Division, “Laser Induced Fluorometry/Cone Penetrometer Technology Demonstration Plan,” U.S. Environmental Protection Agency Consortium for Site Characterization Technology, Environmental Monitoring Systems Laboratory, Las Vegas, NV, 1995.

(5) Davis, W.M., Karn, R., Porter, B., Jones, P., Lynch, A. “Field Portable Analysis for Validation of the Site Characterization and Analysis Penetrometer System Petroleum, Oil, and Lubricant Sensor,” *Technical Report*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, 1995.

(6) Naval Command, Control and Ocean Surveillance Center Research, Development, Test, and Evaluation Division, “Site Characterization and Analysis Penetrometer System (SCAPS) Laser Induced Fluorescence (LIF) Sensor for Rapid Field Screening of Petroleum, Oil and Lubricants (POL),” State of California-Environmental Protection Agency Department of Toxic Substances Control Certification Program (AB 2060) for Hazardous Waste Environmental Technologies, San Diego, CA 1994.

(7) G.D. Gillispie and St. Germain, R.W., “Performance Characterization of the Rapid Optical Screening Tool,” *Field Screening Methods for Hazardous Wastes and Toxic Chemicals*, In Press, 1995.

(8) St. Germain, R.W., and Gillispie, G.D., “Real-Time Continuous Measurement of Subsurface Petroleum Contamination with the Rapid Optical Screening Tool,” *Field Screening Methods for Hazardous Wastes and Toxic Chemicals*, In Press, 1995.

(9) Koester, J.P., Lee, L.T., Olsen, R.S., Douglas, D.H., Comes, G.D., Cooper, S. S., and Powell, J.F. “Field Trials of the Site Characterization and Analysis Penetrometer System at the Savannah River Site” *Technical Report GL-93-16*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, 1993.

(10) Apitz, S.E., Theriault, G.A., and Lieberman, S.H. “Optimization of the Optical Characteristics of a Fiber Optic Guided Fluorescence Technique for the In Situ Evaluation of Fuels in Soils,” In: *Environmental and Process Monitoring Technologies*, T. Vo Dinh, Editor, Proce. SPIE 1637, 1992, pp. 241 -254.

(11) Apitz, S.E., Borbridge, L.M., Bracchi, K., and Lieberman, S.H., “The Fluorescent Response of Fuels in Soils: Insights into Fuel-Soil Interactions,” In: *International Conference on Monitoring Toxic Chemicals and Biomarkers*, T. Vo Dinh, Editor, Proc. SPIE 1716, 1992.

(12) Apitz, S.E., Borbridge, L.M., Theriault, G.A., and Lieberman, S.H., “Remote In Situ Determination of Fuel Products in Soils: Field Results and Laboratory Investigations,” *Analysis*, 20, 1992, pp. 461-474.

(13) Inman, S.M., Thibado, P., Theriault, G., and Lieberman, S.H., “Development of a Pulsed-Laser, Fiber Optic-Based Fluorometer for Time-Resolved Measurements of Polycyclic Aromatic Hydrocarbons in Seawater.” *Anal. Chim. Acta,* 239, 1992, pp. 45-51.

(14) Miller, J.N., *Fluorescence Spectrometry by the Ultraviolet Spectrometry Group*, Chapman and Hall, New York, 1981.

(15) Hofstraat, J.W., and Latuhinin, M.J., “Corrections of Fluorescence Spectra in Applied Spectroscopy,” Vol, 48, 4, 1994, pp. 436-447