Designation: E 2143 – 01

Standard Practice for Using Field-Portable Fiber Optics Synchronous Fluorescence Spectrometer for Quantification of Field Samples for Aromatic and Polycyclic Aromatic Hydrocarbons[1]

This standard is issued under the fixed designation E 2143; 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 test method provides a rapid method for the screening of environmental samples for aromatic hydrocarbons (AHs) and polycyclic aromatic hydrocarbons (PAHs). The screening takes place in the field and provides immediate feedback on limits of contamination by substances containing AHs and PAHs. Quantification is obtained by the use of appropriately characterized, site-specific calibration curves. Remote sensing by use of optical fibers is useful for accessing difficult to reach areas or potentially dangerous materials or situations. When contamination of field personnel by dangerous materials is a possibility, use of remote sensors may minimize or eliminate the likelihood of such contamination taking place.

1.2 This test method is applicable to AHs and PAHs present in samples extracted from soils or in water. This test method is applicable for field screening or, with an appropriate calibration, quantification of total AHs and PAHs.

1.3 *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:*

D 1129 Terminology Related to Water[2]

D 4489 Practice for Sampling of Waterborne Oils[3]

D 5412 Test Method for Quantification of Complex Polycyclic Aromatic Hydrocarbon Mixtures or Petroleum Oils in Water[3]

E 131 Terminology and Symbols Related to Molecular Spectroscopy[4]

E 388 Test Method for Spectral Bandwidth and Wavelength Accuracy of Fluorescence Spectrometers[4]

E 578 Test Method for Linearity of Fluorescence Measuring Systems[4]

E 579 Test Method for Limit of Detection of Fluorescence of Quinine Sulfate[4]

3. Terminology

3.1 For definitions of terms used in this test method refer to Terminology D 1129 and E 131.

4. Summary of Test Method

4.1 This test method consists of extracting the AHs and PAHs from soil samples or preparation of water samples followed by synchronous fluorescence analysis with a field-portable instrument. The samples require serial dilutions of samples to establish a linear response. These measurements are made using standard fluorescence cuvettes. While some optimization of selectivity can be accomplished by varying the wavelength difference between excitation and emission monochromators, generally spectra generated from petroleum contaminants with a wavelength difference such as 6 or 18 nm provide good results and no preliminary spectra are required (see Test Method D 5412).

4.2 Different soils have varying partition coefficients. Therefore, representative samples of a subset of the extracts or the water samples should be analyzed by gas chromatography (GC) or other appropriate methods. The purpose is to establish a site-specific calibration curve to be used for quantification of total AHs and PAHs in the environmental samples of interest.

4.3 When desirable, determination of AHs and PAHs may be made remotely using an optical fiber.

5. Significance and Use

5.1 This technique is designed for on-site rapid screening and characterization of environmental soil and water samples resulting in significant cost savings for environmental remediation projects. Remote analysis can be made with optical fibers when situations warrant or demand use of this option.

5.2 Quantification of total AHs and PAHs in these environmental samples is accomplished by having a subset of the samples analyzed by an alternate technique and generating a site-specific calibration curve.

5.3 Synchronous fluorescence provides sufficient spectral

[1] This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and is the direct responsibility of Subcommittee E13.09 on Optical Fibers and Wave Lengths.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.02.

[4] *Annual Book of ASTM Standards*, Vol 03.06.

information to characterize the AHs and PAHs present as benzene, toluene, ethylbenzene and xylene(s) (BTEX), the aromatic portion of total petroleum hydrocarbons (TPH), or large aromatic ring systems up to at least seven fused rings, such as might be found in creosote.

6. Interferences

6.1 The synchronous fluorescence spectrum can be distorted or quantification may be affected if there is a contaminant present that produces a synchronous peak in the same vicinity as the material of interest. Often spectroquality solvents contain impurities that produce background signals. Solvent blanks should be used to verify a low fluorescence background so the background can be subtracted from the sample's spectrum.

6.2 There are naturally occurring compounds that fluoresce, which may interfere with the detection of petroleum compounds, present in the sample. Humic acid from leaf mold is an example of such a compound. Its strongest emission occurs in the near ultraviolet range.

6.3 Absorption of the exciting light by the sample itself (self-filtering effect) produces erroneous results. Analysis of serial dilutions of the sample detects this effect and ensures an accurate analysis is made. Once linearity is established, then integration of the spectrum produces accurate results.

6.4 Certain solvents used for extraction of the soil samples could quench or absorb the fluorescence and raise the limit of detection. Care should be taken to avoid halogenated solvents or solvents containing other quenchers. The user of this test method should bear this in mind when selecting an appropriate solvent.

NOTE 1—Storage of samples in improper containers, such as plastics other than polytetrafluoroethylene (or TFE-fluorocarbon), may result in contamination.

NOTE 2—This test method is normally used without an internal standard due to possible interference by the internal standard.

6.5 Certain optical fibers may generate a fluorescence background. These should be avoided whenever possible. If they must be used, a background spectrum should be generated and subtracted from any samples measured.

7. Apparatus

7.1 *Fluorescence Spectrometer*—An instrument recording in the spectral range of at least 250 to 650 nm is required for both excitation and emission spectrum measurements and capable of scanning both monochromators at a constant speed with a constant wavelength offset between them for synchronous scanning. The bandwidth of the monochromators should be less than one half the wavelength offset between the monochromators or smaller. The spectrometer should be capable of remote sensing via optic fiber. The detector should be a photomultiplier tube or a device with similar sensitivity and response time. Occasionally field work requires the spectrometer to be battery powered. The instrument should meet the specifications in Table 1.

7.2 *Excitation Source*—A pulsed (9.9 W) Xenon lamp or other source having sufficient intensity throughout the ultraviolet and visible regions can be used.

7.3 *Cuvette Sample Holder*—Sample holders should be fabricated to hold commercially available, fluorescence-free, fused silica cuvettes.

TABLE 1 Desirable Performance Standards of a Field Portable Fluorescence Spectrometer

Characteristic	Desirable Range	Typical
Monochromator		
Bandwidth	1–5 nm	3 nm
Wavelength accuracy	± 0.5–2 nm	± 1.0 nm
Reproducibility	± 0.1– 1 %	± 0.2 %
Interface		
Data collection	computerized	laptop PC
Instrument control	control and data	
Source		
Broad band	200–1000 nm	Xenon lamp
Low-power consumption	5–75 W	10 W

7.4 *Optical Fiber Holder*—A stage that allows correct positioning of the optical fiber with respect to the emission and excitation monochromators. The device may also be used to optically match each fiber and the respective monochromator.

7.5 *Computer System*—The instrument should be interfaced to a computer system that is compatible with the instrument and has suitable software for spectral data manipulation.

7.6 *Cuvette*—A standard 12 by 12 by 31 mm fluorescence-free fused silica cuvette. Four sides of the cuvette should be polished.

7.7 *Optical Fiber*—Fused silica fiber (preferably a high hydroxide) is required for transmission of the ultraviolet wavelengths required for accurate spectroscopic analysis. In general, this material has good thermal characteristics, can be obtained with low fluorescence background, and is readily available commercially.

7.8 *Glassware*—A 10 mL and 2 mL disposable pipet, both marked with 0.1 mL gradations. A glass disposable test tube, capable of holding volumes of liquid greater than 15 mL. The test tube caps should be polytetrafluoroethylene lined to reduce potential contamination.

7.9 *Scale*—A portable scale capable of measuring 2 g of soil to the nearest 0.1 g.

7.10 *Centrifuge*—A portable centrifuge, capable of holding the test tubes described in 7.8.

7.11 *Shaker*—A portable shaker, capable of mixing the soil and solvent in the test tubes described in 7.8.

7.12 *Filter Apparatus*—A syringe with disposable 100-µm glass detachable filters.

8. Reagents and Materials

8.1 *Purity of Reagents*—Spectroquality grade reagents should be used in all instances unless otherwise stated.

8.2 *Purity of Water*—ASTM Grade 3 or Grade 4 water should be used.

8.3 *Solvents*—High purity solvents should be used. Solvents should be of sufficient purity so as to not generate a background fluorescence spectrum when analyzed as a blank. Solvents such as hexane, cyclohexane and methylcyclohexane, ethanol, methanol, etc. must not absorb in the spectral region of interest.

9. Sampling and Sample Preparation

9.1 *Water Samples*—Collect water samples in accordance

with Practice D 4489, as applicable.

9.1.1 If the water samples contain visible particles, then the samples may be either centrifuged or filtered depending on the nature of the particles. Large, dense particles can usually be centrifuged to the bottom of the sample container, while finer particles must be filtered. The water samples should be centrifuged in the containers in which they are sampled, in order to avoid volatilization of the organic hydrocarbons. The water samples should be filtered into the cuvette for analysis.

9.1.2 Add approximately 2.5 mL of the water sample into the cuvette using a disposable pipet and place the cuvette into the instrument sample holder. The sample is ready for analysis.

9.2 *Soil Samples*—Collect the sample using accepted procedures already established by ASTM Committee D18.

9.2.1 Obtain a representative 2-g soil sample from the sample container. The sample should be weighed directly in the test tube.

9.2.2 Add 10 mL of the appropriate solvent to the soil sample in the test tube using a disposable pipet.

9.2.3 Shake the sample until greater than 90 % of the sample is suspended in the solvent. Follow this shaking process by centrifuging the sample in order to separate the solvent from the soil.

9.2.4 Pour the extract into a second test tube. At this point some particles may be present in the extract, thus filtration will be required to remove them.

9.2.5 If the quality check in 13.6 indicates a need for additional extraction, then the additional extraction will be performed at this time.

10. Preparation of Apparatus

10.1 Prior to mobilization for field use, set up and calibrate the fluorescence spectrometer according to the manufacturer's instructions and Test Methods E 388, E 578, and E 579. Once in the field, include in the calibration procedures, a check of the wavelength accuracy of the instrument using an appropriate line-source such as a mercury lamp or xenon lamp. In addition, check the baseline of the instrument by analyzing a solvent blank. Other options for calibration may include the use of plastic standards, sealed solutions of anthracene or other commercially available standards.

11. Procedure

11.1 *Water Samples*—Analyze the water sample over an appropriate wavelength region using a synchronous scan with a wavelength offset between the monochromators of 18 nm. Other wavelength offset between the monochromators values may be used when appropriate.

11.1.1 Subtract the spectrum of a distilled water blank from the spectrum of the water sample.

11.1.2 Integrate the area under the spectrum of the sample over the appropriate wavelength region to determine the relative value.

11.1.3 Determine if the sample is in the linear range. The determination of linear range is done by performing a 1:1 dilution. Subtract the spectrum of a distilled water blank from the spectrum of the 1:1 dilution. Integrate the area under the spectrum of the sample over the appropriate wavelength region. If the integrated value is half of the original value, then the sample is in the linear range; otherwise, perform subsequent dilutions until the linear range is established.

11.2 *Soil Samples*—Analyze the soil sample extract over the appropriate wavelength region using a synchronous scan with a wavelength offset between the monochromators of 18 nm.

11.2.1 Subtract the spectrum of a solvent blank from the spectrum of the soil sample.

11.2.2 Integrate the area under the spectrum of the sample over the appropriate wavelength region to determine the relative value.

11.2.3 Determine whether the sample is in the linear range according to 11.1.3.

11.3 *Quantitative Analysis*—After several soil or water samples have been analyzed by the instrument, pick several samples representing a range of concentrations (at least three: high, medium, and low) and include solvent blanks and samples of known composition. These samples should be analyzed by the laboratory using the appropriate method, such as total petroleum hydrocarbons using the Environmental Protection Agency (EPA), gasoline range organics (GRO), and diesel range organics (DRO) methods or total polycyclic aromatic hydrocarbons. Many of the approved EPA methods also include aliphatic hydrocarbons in the analysis. If the relative proportion of aromatic hydrocarbons to aliphatic hydrocarbons remains constant then the correlation graphs described in 11.3.1 can be developed.

11.3.1 For each sample analyzed by the laboratory, plot the laboratory concentration versus the instrument concentration on a scatter plot. Apply a trend line to the data set and perform linear regression. The equation of the trend line can be used to predict the value of future instrument analyses.[5] For further information, see Ref (*1*) in Appendix X1.

12. Calculations

12.1 Spectra collected may be smoothed prior to integration. For total AHs and PAHs content integration should be performed on a solvent blank (I_{bl}) and the sample (I_{sp}) over an identical wavelength region. The sample must be in the linear range of a dilution of sample versus signal intensity curve. The final result (R) will be as follows:

$$R = DF \times (I_{sp} - I_{bl}) \quad (1)$$

where:

DF = dilution factor of the sample.

12.2 The final results of the measurements are used in generating a site-specific calibration curve determined by an independent analysis of a subset of samples (R versus laboratory concentration). Subsequent samples' total AHs and PAHs content is determined from the calibration curve and the following conversion:

12.2.1 *For Soils*—Calculate the concentration of the original extract sample as:

$$\text{concentration in } \mu g/g = C_c\,(V_s/M_s) \quad (2)$$

where:

[5] Mendenhall, W., and Sinshick, T., *Statistics for Engineering and the Sciences*, 3rd ed., Dellen Publishing Co., 1992.

C_c = concentration from calibration curve, µg/mL,
V_s = volume of diluted extract, mL, and
M_s = weight of soil that was extracted, g.

12.2.2 *For Water*—Calculate the concentration of the original sample as:

$$\text{concentration in µg/mL} = C_c\,(V_s/V_t) \quad (3)$$

where:
C_c = concentration from calibration curve, µg/mL,
V_s = volume of diluted sample, mL, and
V_t = volume of water sample, mL.

12.3 If smoothing is done, the smoothing algorithm used shall be reported.

13. Quality Control Measures

13.1 Calibrate the wavelength accuracy and the spectral bandwidth of the field-portable spectrometer using Test Method E 388 prior to a field trip. On a daily basis, confirm the calibration utilizing an appropriate line source during field work. Also on a daily basis, confirm the calibration using an appropriate standard sample as described in 10.1.

13.2 Determine the linearity of the spectrometer and measure the instrument's limit of detection using Test Methods E 578 and E 579 at the beginning and again at the end of a field trip.

13.3 Run triplicate blanks through the entire sample preparation procedure at the beginning of a field effort and single blanks every 4 h throughout the field effort.

13.4 Frequently run a solvent blank and generate a blank spectrum to verify uncontaminated cuvettes and solvents and to provide a solvent spectrum that may be subtracted from sample spectra.

13.5 While in the field, run one sample in triplicate each day using separate aliquots of the same sample extract. Run these aliquots through identical preparation and analysis as the other samples. This will provide a reproducibility study for that field site.

13.6 Check the recovery of material by the extraction technique being used. This is done by performing a second extraction of a subset of the soil samples. If the second extract contains a significant percentage of material compared to the first extract (15 to 30 %) then a third extraction may be needed depending on the accuracy required for the field work. Combine all aliquots containing significant material for analysis.

13.7 All samples shall be diluted serially until linearity is established and results shall be determined from samples measured in the linear range of sample concentrations.

13.8 When characterizing a new site, or if the soil matrix/composition alters significantly, sufficient samples should be made in duplicate and the extractions or duplicate water samples analyzed by an independent method and a calibration curve generated. If possible, select samples that give a wide range of results and include solvent blanks and known composition samples in the subset of samples being independently evaluated.

14. Precision and Bias

14.1 *Precision*—The analytic technique is similar to that described in Test Method D 5412. The precision and bias of the analyses of soils are comparable to water that undergoes the extraction procedure.

14.2 *Bias*—The analysis of the water samples that do not undergo an extraction step reduces the negative bias.

14.3 Site-specific calibration curves are illustrated in Figs. 1-3. The three curves illustrated are for benzene, toluene, ethylebenzene, xylene (BTEX), naphthalene, and the aromatic component of total petroleum hydrocarbon (TPH). In comparing results from a field-portable fluorescent spectrometer against results determined by an analytic laboratory, the correlation coefficients are 0.90, 0.96, and 0.93 for BTEX, nahthalene, and TPH respectively. Instrument bias is reduced by splitting samples and running approved EPA-SW 846 Laboratory Methods.[6] Instrument precision is similarly established on a site specific basis by comparing field results to approved laboratory methods.

15. Keywords

15.1 fluorescence; PAH quantification; PAHs; synchronous fluorescence; ultraviolet-visible luminescence or fluorescence

[6] Available from U.S. Government Printing Office, Superintendent of Documents, 732 North Capitol Street, NW, Mail Stop: SDE, Washington, DC 20401 (Supplies *Code of Federal Regulations*), www.access.gpo.gov

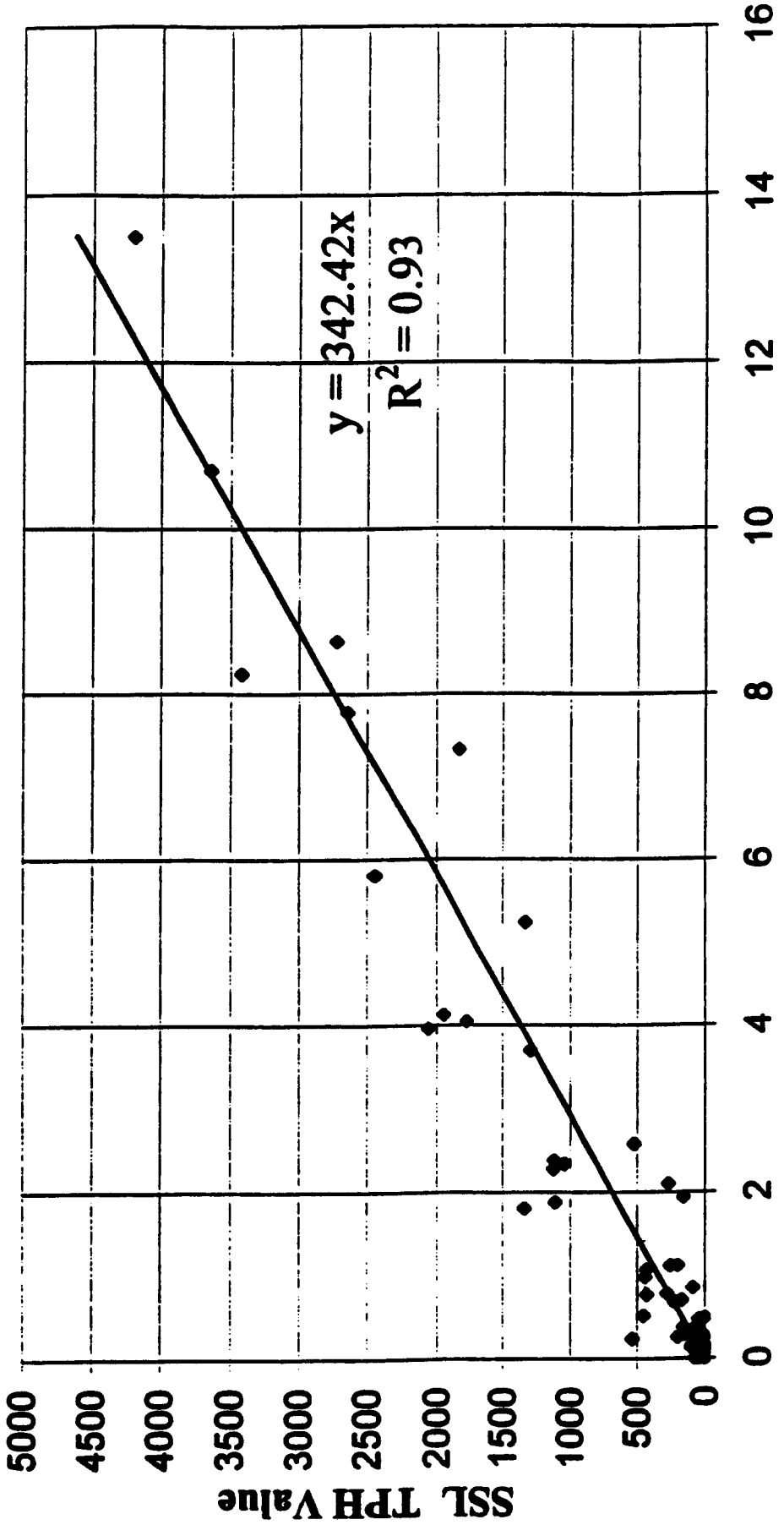

FIG. 1 TPH Comparison—Luminoscope Value Versus Laboratory

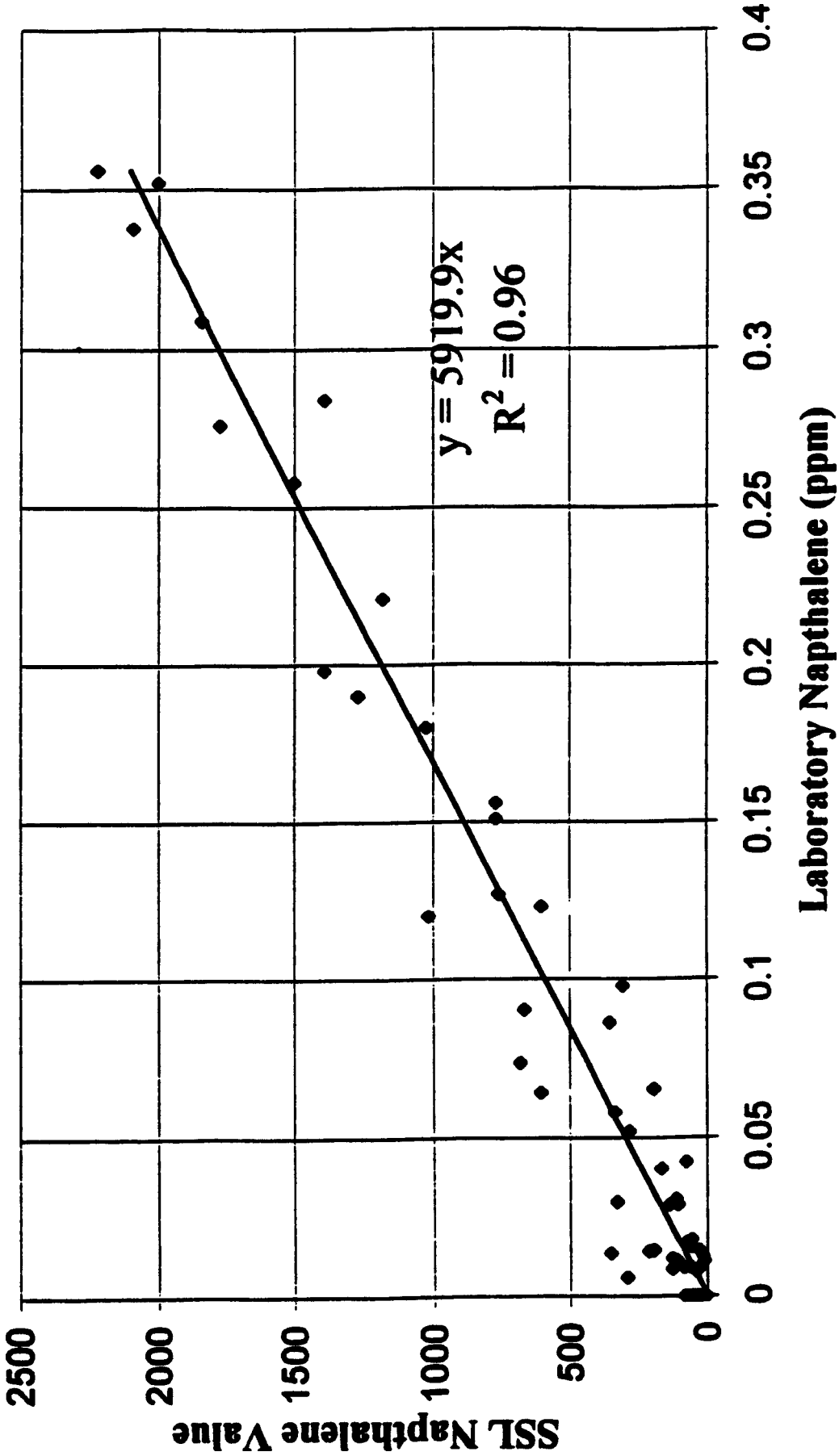

FIG. 2 Napthalene Comparison—Luminoscope Versus Laboratory

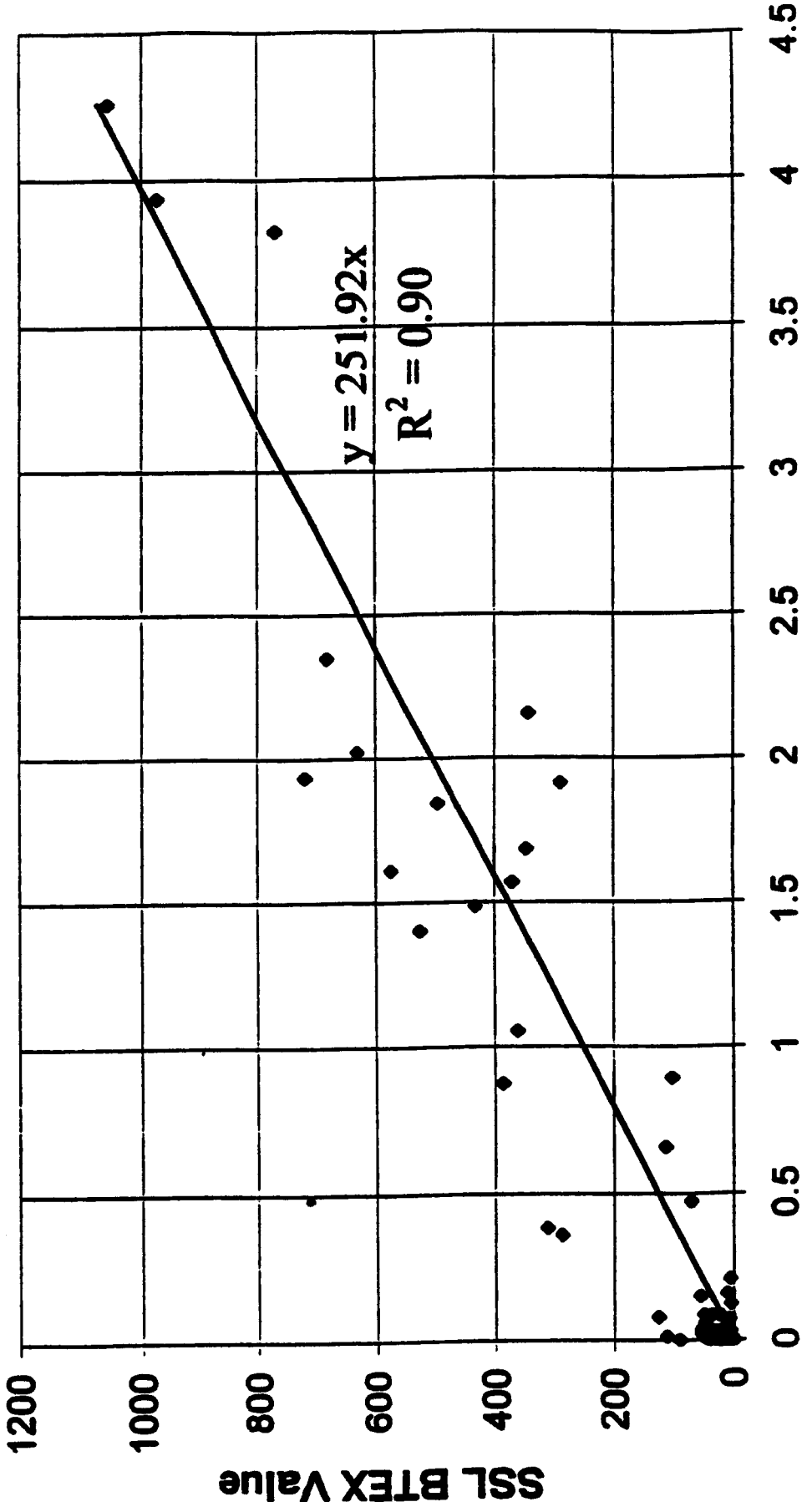

FIG. 3 BTEX Comparison—Luminoscope Value Versus Laboratory

APPENDIX

(Nonmandatory Information)

X1. ADDITIONAL INFORMATION

X1.1 The following is a list of additional references:

(*1*) Alarie, J. P., Vo-Dinh, T., Miller, G., Ericson, M. N., Maddox, S. R., and Watts, W., (Oak Ridge National Laboratories, Oak Ridge, TN), Eastwood, D., Lidberg, R., and Dominguez, M., (Lockheed Environmental Systems and Technologies Company, Las Vegas, NV), "Development of Battery-Operated Portable Synchronous Luminescence Spectrofluorometer," *Rev. Sci. Instrum*. Vol 64, No. 9, September 1993.

(*2*) Amick, E. N, and Pollard, J. E., ((Lockheed Environmental Systems and Technologies Company, Oak Ridge, TN), Engelmann, W. H., and Brown, K. W., (U.S. Environmental Protection Agency, Las Vegas, NV), Alarie, J. P., Watts, W., and Vo-Dinh, T., (Oak Ridge National Laboratory, Oak Ridge, TN), Akindele, F. M., (U.S. Environmental Protection Agency, Atlanta, GA) and Crockett, A. B., (Idaho National Engineering Laboratory, Idaho Falls, ID), "Polycyclic Aromatic Hydrocarbons from U.S. and Antarctic Sites Analyzed with Synchronous Fluorescence Spectrometry," *Proceedings of Field Analytical Conference* (sponsored by EPA), Las Vegas, NV, 1995.

(*3*) Siddiqui, K. J. and Eastwood, D., "Optimal Feature Section in the Classification of Synchronous Fluorescence of Petroleum Oils," *SPIE*, Vol 2505, 1996, pp. 2-13.

(*4*) Vo-Dinh, T., "Multicomponent Analysis by Synchronous Luminescence Spectrometry," *Analytical Chemistry*, Vol 50 No. 3, March 1976.

(*5*) Vo-Dinh, T., "Synchronous Excitation Spectroscopy," *Modern Fluorescence Spectroscopy*, Vol 4, Chapter 5, edited by E. L. Wehry, Plenum Publishing Corporation, 1981, pp. 167-191.

(*6*) Vo-Dinh, T., Pal, A., and Pal, T., "Photoactivated Luminescence Method for Rapid Screening of Polycholorinated Biphenyls," *Analytical Chemistry*, Vol 66, No. 8., April 15, 1994.