Designation: D5412 – 93 (Reapproved 2024)

Standard Test Method for Quantification of Complex Polycyclic Aromatic Hydrocarbon Mixtures or Petroleum Oils in Water[1]

This standard is issued under the fixed designation D5412; 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 covers a means for quantifying or characterizing total polycyclic aromatic hydrocarbons (PAHs) by fluorescence spectroscopy (Fl) for waterborne samples. The characterization step is for the purpose of finding an appropriate calibration standard with similar emission and synchronous fluorescence spectra.

1.2 This test method is applicable to PAHs resulting from petroleum oils, fuel oils, creosotes, or industrial organic mixtures. Samples can be weathered or unweathered, but either the same material or appropriately characterized site-specific PAH or petroleum oil calibration standards with similar fluorescence spectra should be chosen. The degree of spectral similarity needed will depend on the desired level of quantification and on the required data quality objectives.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3325 Practice for Preservation of Waterborne Oil Samples
D3326 Practice for Preparation of Samples for Identification of Waterborne Oils
D3415 Practice for Identification of Waterborne Oils
D3650 Test Method for Comparison of Waterborne Petroleum Oils By Fluorescence Analysis (Withdrawn 2018)[3]
D4489 Practices for Sampling of Waterborne Oils
D4657 Test Method for Polynuclear Aromatic Hydrocarbons in Water (Withdrawn 2005)[3]
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

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[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.

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

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129, Terminology E131, and Practice D3415.

4. Summary of Test Method

4.1 This test method consists of fluorescence analysis of dilute solutions of PAHs or petroleum oils in appropriate solvents (spectroquality solvents such as cyclohexane or other appropriate solvents, for example, ethanol, depending on polarity considerations of the sample). The test method requires an initial qualitative characterization step involving both fluorescence emission and synchronous spectroscopy in order to select appropriate calibration standards with similar fluorescence spectra as compared to the samples (see Annex A1 for the definition of spectral similarity). Intensities of peak maxima of suitable emission spectra are then used to develop calibration curves for quantification.

NOTE 1—Although some sections of the characterization part of this test method are similar to Test Method D3650, there are also significant differences (see Annex A1). Since the purpose and intent of the two test methods are different, one should not be substituted for the other.

5. Significance and Use

5.1 This test method is useful for characterization and rapid quantification of PAH mixtures including petroleum oils, fuels, creosotes, and industrial organic mixtures, either waterborne or obtained from tanks.

5.2 The unknown PAH mixture is first characterized by its fluorescence emission and synchronous scanning spectra. Then a suitable site-specific calibration standard with similar spectral characteristics is selected as described in Annex A1. This calibration standard may also be well-characterized by other independent methods such as gas chromatography (GC), GC-mass spectrometry (GC-MS), or high performance liquid chromatography (HPLC). Some suggested independent analytical methods are included in References **(1-7)**[4] and Test Method D4657. Other analytical methods can be substituted by an experienced analyst depending on the intended data quality objectives. Peak maxima intensities of appropriate fluorescence emission spectra are then used to set up suitable calibration curves as a function of concentration. Further discussion of fluorescence techniques as applied to the characterization and quantification of PAHs and petroleum oils can be found in References **(8-18)**.

5.3 For the purpose of the present test method polynuclear aromatic hydrocarbons are defined to include substituted polycyclic aromatic hydrocarbons with functional groups such as carboxyl acid, hydroxy, carbonyl and amino groups, and heterocycles giving similar fluorescence responses to PAHs of similar molecular weight ranges. If PAHs in the more classic definition, that is, unsubstituted PAHs, are desired, chemical reactions, extractions, or chromatographic procedures may be required to eliminate these other components. Fortunately, for the most commonly expected PAH mixtures, such substituted PAHs and heterocycles are not major components of the mixtures and do not cause serious errors.

6. Interferences

6.1 The fluorescence spectra may be distorted or quantification may be affected if the sample is contaminated with an appreciable amount of other fluorescent chemicals that are excited and which fluoresce in the same spectral regions with relatively high fluorescence yields. Usually the fluorescence spectra would be distorted at levels greater than 1 % to 2 % of such impurities before the quantification would be seriously affected. (**Warning—**Storage of samples in improper containers (for example, plastics other than TFE-fluorocarbon) may result in contamination.)

NOTE 2—*Spectroquality* solvents may not have low enough fluorescence background to be used as solvent blanks. Solvent lots vary in the content of fluorescent impurities that may increase with storage time even for unopened bottles.

NOTE 3—This test method is normally used without a matrix spike due to possible fluorescence interference by the spike. If a spike is to be used, it must fluoresce in a spectral region where it will not interfere with the quantification process. Compounds that could be used are dyes that fluoresce at longer wavelengths than the emission of the PAH mixture.

6.2 If the PAH mixture to be analyzed is a complex mixture such as an oil or creosote, it is assumed that a well-characterized sample of the same or similar material is available as a calibration standard so the fluorescent fraction of the mixture can be ratioed against the total mixture. Otherwise, since the samples and standards are weighed, the nonfluorescent portion of the mixture would bias the quantification although the characterization portion of the test method for PAHs given in Annex A1 would be unaffected.

7. Apparatus

7.1 *Fluorescence Spectrometer*—An instrument recording in the spectral range of 250 nm to at least 600 nm for both excitation and emission responses and capable of scanning both monochromators simultaneously at a constant speed with a constant wavelength offset between them for synchronous scanning. The instrument should meet the specifications in Table 1. (Also known as spectrofluorometer or fluorescence spectrophotometer.) Consult manufacturer's instrument manuals for specific operating instructions.

TABLE 1 Specifications for Fluorescence Spectrometers

Wavelength Reproducibility	
Excitation monochromator	±2 nm or better
Emission monochromator	±2 nm or better
Gratings (Typical Values)	
Excitation monochromator	minimum of 600 lines/mm blazed at 300 nm
Emission monochromator	minimum of 600 lines/mm blazed at 300 nm or 500 nm
Photomultiplier Tube	
S-20 or S-5 response or equivalent	
Spectral Resolutions	
Excitation monochromator	spectral bandpass of 2.5 nm or less
Emission monochromator	spectral bandpass 2.5 nm or less
Maximum bandpasses for both monochromators at least 10 nm	

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