Designation: D8431 – 22

Standard Test Method for Detection of Water-soluble Petroleum Oils by A-TEEM Optical Spectroscopy and Multivariate Analysis[1]

This standard is issued under the fixed designation D8431; 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 the *(1)* detection of trace level (µg/L range) of oil and petroleum (water-soluble fraction) pollutants in surface and ground drinking water sources, *(2)* identification of the compounds, and *(3)* alerting analysts with a contaminant concentration prediction. This test method facilitates identification and quantification from 20 to 1000 µg/L of target contaminants, including: water-soluble fraction of aromatic compounds from the BTEX family (benzene, toluene, ethylbenzene, and xylenes) and naphthalene from the polycyclic aromatic hydrocarbon (PAH) group, referred to as *BTEXN* in this test method, in water samples with up to 15 mg/L of dissolved organic carbon (DOC). The main approach involves analyzing and characterizing key water intake locations before the treatment and developing the contaminant library. The water-soluble (*BTEXN*) contaminants are associated with, but not limited to petroleum oils and fuels including commercial diesel fuel, gasoline, kerosene, heavy oil, fuel oil and lubricate oil, etc.

1.2 The data sets are analyzed using multivariate methods to test contaminant identification and quantification. The multivariate methods include classification and regression algorithms to analyze fluorescence EEM data acquired in the laboratory. The common goal of these algorithms is to reduce multidimensionality and eliminate noise of fluorescence and background signals. Automated identification-quantification methods linked directly to the instrument acquisition-analysis software are commercially available.

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
D3650 Test Method for Comparison of Waterborne Petroleum Oils By Fluorescence Analysis (Withdrawn 2018)[3]
D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D6046 Classification of Hydraulic Fluids for Environmental Impact
D6161 Terminology Used for Microfiltration, Ultrafiltration, Nanofiltration, and Reverse Osmosis Membrane Processes
E169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis
E2617 Practice for Validation of Empirically Derived Multivariate Calibrations
E2719 Guide for Fluorescence—Instrument Calibration and Qualification
E2891 Guide for Multivariate Data Analysis in Pharmaceutical Development and Manufacturing Applications

[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.

2.2 *U.S. EPA Standards:*[4]

Method 415.3 Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water[5]

Method 524.2 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectroscopy[6]

Method 8270D Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry[7]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *absorbance-transmittance and fluorescence excitation emission matrix (A-TEEM), n*—a spectroscopic technique that simultaneously measures the absorbance, transmission and fluorescence excitation-emission matrix spectra of samples in solution.

3.2.2 *colored dissolved organic matter (CDOM), n*—the optically measureable component of dissolved organic matter, also known as chromophoric dissolved organic matter, that strongly absorbs short wavelength light ranging from blue to ultraviolet (UV).

3.2.3 *dissolved organic matter (DOM), n*—the amount of organic matter in a water sample passing through a 0.45 µm filter, reported as percent or fraction. **D6161**

3.2.4 *fluorescent dissolved organic matter (FDOM), n*—the fraction of CDOM that fluoresces and strongly absorbs in the UV spectrum.

3.2.5 *raw water, n*—water that has not been treated. **D1129**

3.2.5.1 *Discussion*—Untreated water from wells, surface sources, or public drinking water supplies.

3.2.6 *water accommodated fraction (WAF), n*—the predominately aqueous portion of a mixture of water and a poorly water-soluble material which separates in a specified period of time after the mixture has undergone a specified degree of mixing and includes water, dissolved components, and dispersed droplets of the poorly water-soluble material. **D6046**

3.2.7 *water-soluble fraction (WSF), n*—water-soluble fluorescent low-molecular weight aromatic compounds that are typically present in oil and petroleum products. **D6046**

3.3 *Abbreviations:*

3.3.1 *AFU*—arbitrary fluorescence unit

3.3.2 *BTEX*—benzene, toluene, ethylbenzene, and xylenes

3.3.3 *DOC*—dissolved organic carbon

3.3.4 *EEM*—excitation emission matrix

3.3.5 *ISS*—intermediate stock solutions

3.3.6 *OD*—optical density

3.3.7 *PAH*—polycyclic aromatic hydrocarbon

3.3.8 *PCA*—principal components analysis

3.3.9 *PLS*—partial least squares analysis

3.3.10 *PLSDA*—partial least squares discriminant analysis

3.3.11 *PPE*—personal protective equipment

3.3.12 *PTFE*—polytetrafluoroethylene

3.3.13 *QC*—quality control

3.3.14 *RSU*—water Raman standard unit

3.3.15 *RU*—Raman unit

3.3.16 *SIMCA*—soft independent modeling by class analogy

3.3.17 *SSS*—standard stock solutions

3.3.18 *SVM*—support vector machine

3.3.19 *SVMDA*—support vector machine discriminant analysis

3.3.20 *XGB*—extreme gradient boosted tree

3.3.21 *XGBDA*—extreme gradient boosted tree discriminant analysis

4. Summary of Test Method

4.1 Fig. 1 provides a summary flow chart of this test method.

4.2 A sample of raw water between 3 mL to 10 mL is filtered with 0.45 µm membrane filter and analyzed by an A-TEEM instrument for WSF oil contamination identification and quantification.

4.3 Instrument calibration is achieved by first testing a negative control blank (either a sealed water standard per 13.2.2 or Type I water per 8.1), and then testing a set of target contamination component (*BTEXN*) standards and assessing them by multivariate analysis (see 12.2).

4.4 The classification or regression model is saved as a method in a predictor dashboard which then outputs reports of possible contaminant classification and or contaminant concentrations in the raw water sample (see 13.3 and Section 14).

5. Significance and Use

5.1 Source water protection calls for a rapid and reliable optical method to identify and quantify the oil spill contamination, such as water-soluble fraction of aromatic compounds from the BTEX family (benzene, toluene, ethylbenzene, and xylenes) and naphthalene from the polycyclic aromatic hydrocarbon (PAH) group.

5.2 This test method identifies the presence of contamination and quantifies the target contamination component(s) to provide a threshold-based alert signal.

5.3 This test method can be used by drinking water treatment plant operators and decision makers as a first line of defense for both initially detecting petroleum product spills, as well as tracking attenuation over time, in source water to

[4] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

[5] https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=525073&Lab=NERL

[6] https://www.epa.gov/sites/default/files/2015-06/documents/epa-524.2.pdf

[7] https://19january2017snapshot.epa.gov/sites/production/files/2015-12/documents/8270d.pdf