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

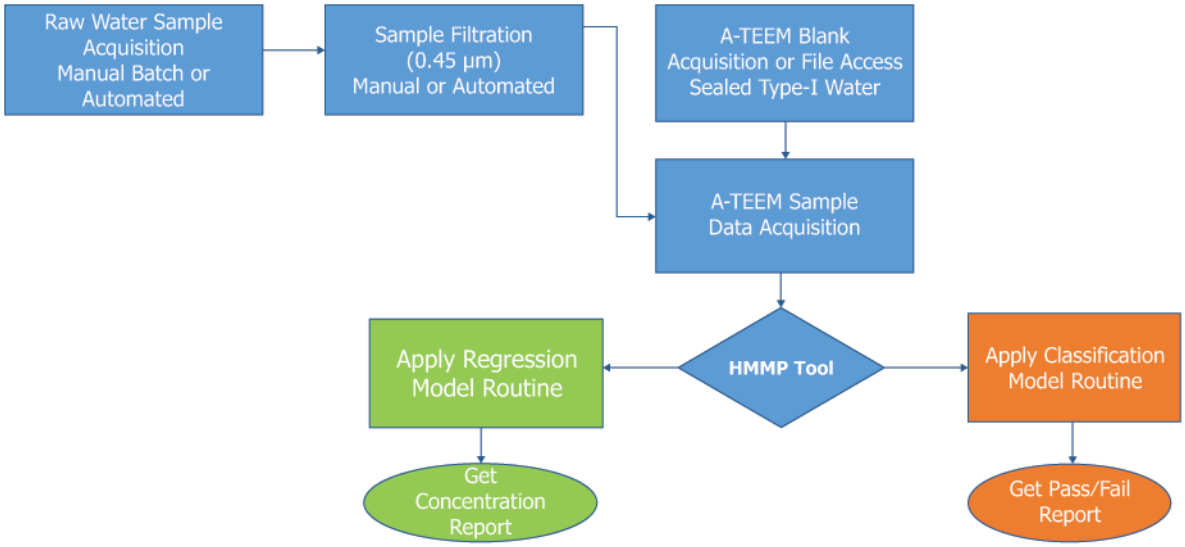

FIG. 1 Method Flowchart

prevent contaminant uptake into the processed water and treatment infrastructure.

6. Interferences

6.1 Naturally occurring fluorescing materials, such as humic/fulvic acids and protein-like components, may interfere with the identification of target chemicals with relatively low quantum yields especially those compounds with fluorescence exciting and emitting in the near ultraviolet (UV) region. A ruggedness study conducted prior to ILS determined the range of DOC up to 15 mg/L does not have a significant effect on the test results.

6.2 The typical upper limit of turbidity in drinking water sources is site-specific. High turbidity in source water may be expected to interfere with the fluorescence measurements because of the particulate light scattering effects that are enhanced at lower wavelengths (higher energies). This method is designed to alleviate the effects of turbidity on the water-soluble components detection by filtering out any particles greater than 0.45 µm. A ruggedness study conducted prior to ILS determined the range of turbidity up to 20 NTU does not have a significant impact on the test results.

6.3 Solvent or blank contamination, or issues due to improper glassware cleaning may cause interferences.

7. Apparatus

7.1 *Fluorescence Spectrophotometer (or Spectrofluorometer)*[8]—An instrument recording in the spectral range of 200 nm to at least 800 nm for both excitation and emission responses with Inner-filter effect correction function. Such an instrument should be capable of meeting the specifications outlined in Annex A1, Table A1.1. See Ref (**1**).[9]

7.2 *Fluorescence Cuvette Cells*—Quartz cells with 4 clear windows, made from fluorescence-free synthetic quartz glass with a path length of 10 mm and a height of 45 mm.

7.2.1 The UV transmittance range should be ideally in the operational range of 200 nm to 800 nm. The maximum operational temperature of the quartz material should be at least 600 °C.

7.2.2 Quartz flow cells with a path length of 10 mm are equipped with optional automatic sipper accessory which provides flow-through capability and does not require cell stirrer.

7.3 *Cuvette Cell Stirrer*—A small magnetic cell stirrer with a controller. Place stirrer into the bottom of the cell compartment. The cell is then placed on top of the magnet drive.

7.4 *Magnetic Stir Bars*—PTFE-coated magnetic stir bars with appropriate dimensions to fit within the quartz cuvette cells and provide rapid vertical and horizontal mixing.

7.5 *Water Bath*—A liquid circulating temperature controller. Includes all necessary tubing for connection to sample chamber using quick-release pipe couplings. Recommend setting experiment temperature at 25 °C.

7.6 *Syringe Filters*—0.45 µm membrane filters. EPA Method 415.3 (2.2) recommends two hydrophilic filter membrane materials, polyethersulfone and polypropylene.

8. Reagents

8.1 *Purity of Water*—The purity of reagent water should be checked by running a water blank prior to running samples (refer to Section 13, Procedure). Type I water is acceptable and preferred in this test method (Specification D1193).

[8] The sole source of supply of the apparatus known to the committee at this time is HORIBA Instruments Incorporated, 20 Knightsbridge Rd, Piscataway, NJ 08854. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

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

8.2 *BTEXN Standards*—Neat compounds or high purity standards are required. These may be purchased from commercial sources. The following *BTEXN* compounds are required:

8.2.1 Benzene (CAS # 71-43-2)
8.2.2 Toluene (CAS # 108-88-3)
8.2.3 Ethylbenzene (CAS # 100-41-4)
8.2.4 o-Xylene (CAS # 95-47-6)
8.2.5 m-Xylene (CAS # 108-38-3)
8.2.6 p-Xylene (CAS # 106-42-3)
8.2.7 Naphthalene (CAS # 91-20-3)

8.3 *Cleaning Reagent*—All glassware must be scrupulously clean. The necessary level of cleanliness can be achieved by performing all of the steps in Test Method D3650.

8.4 *Methanol*—Spectroscopic grade[10] methanol (preferred) shall be used in all tests unless otherwise stated.

NOTE 1—Every solvent has a UV-Vis absorbance cutoff wavelength. The solvent cutoff is the wavelength below which the solvent itself absorbs all of the light. When choosing a solvent be aware of its absorbance cutoff and where the compound under investigation is thought to absorb. If they are close, choose a different solvent. Refer to Practice E169 for a table of solvent cutoffs.

8.5 *Nitric Acid, 68 % to 70 %*—Concentrated nitric acid for cleaning cuvettes.

9. Hazards

9.1 The analytes in this test method are known carcinogens. Neat standards and stock solutions should be handled and prepared in a fume hood. The lab personnel should don appropriate PPE, such as safety glasses, gloves, and lab coat to minimize exposure to these chemicals used in this test method.

10. Sampling, Test Specimens, and Test Units

10.1 Collect samples in accordance with Practices D3694 as applicable.

10.2 Analyze samples within 2 h upon the time of collection (Practices D3694).

NOTE 2—Samples may be preserved and stored according to Practices D3694 and D4841.

10.3 For calibration samples, dilute *BTEXN* standards (see 8.2) then spike into raw water for calibration standards as described in Section 12.

10.4 The test unit of sample absorbance is in optical density (OD) in units of cm^{-1}. The test unit of sample fluorescence EEM is either in arbitrary fluorescence unit (AFU) or normalized to water Raman unit (RU) (see Section 13).

11. Preparation of Apparatus

11.1 Follow the manufacturer's instructions for instrument start-up and warm-up.

11.2 Start *water bath* and ensure it is at equilibrium at room temperature (22 °C to 25 °C).

11.2.1 Ensure the instrument's sample chamber is connected to the water bath.

12. Calibration and Standardization

12.1 *Instrument Calibration:*

12.1.1 Calibrate the instrument according to the manufacturer's instructions, Practice E169, and Guide E2719.

12.2 *Method Calibration:*

12.2.1 *Standard Solution Preparation:*

12.2.1.1 Prepare analyte stock solutions using spectroscopic grade methanol (see 8.4). Dilute the neat commercial analytical standards (see 8.2) to intermediate stock solutions (ISS) containing mixtures of compounds of interest in methanol (see 8.4). ISS should be prepared fresh the day when a new calibration is carried out.

12.2.1.2 Generally, prepare calibration standards using calibrated volumetric pipettes to dilute the ISS into disposable glass test tubes using methanol (see 8.4). Place a piece of Parafilm over the top of the test tubes and vortex vigorously for approximately 30 s to ensure mixing. Table 1 shows the example preparation of a *BTEXN* calibration standard with the final concentration of 100 µg/L for each analyte. The *BTEXN* standard stock solutions (SSS) are first prepared by spiking neat standards into methanol and diluting to 10 mL for each analyte. The SSS concentrations are calculated using spike volume and analyte density. A portion of SSS is spiked into another flask containing methanol and diluted with methanol to 10 mL to make intermediate standard solutions (ISS) with a concentration of 20 000 µg/L. Note that neat naphthalene is a solid. Weigh 0.05 g neat naphthalene and add to a flask containing 10 mL methanol. Dissolve and dilute to the 10-mL mark with methanol. A portion of this is diluted in methanol in a separate flask to achieve an ISS of naphthalene of 20 000 µg/L. The ISS is spiked into each sample tube and diluted to 9 mL with raw water. The final concentrations of analytes are 100 µg/L in the calibration standards.

[10] Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

TABLE 1 Example Preparation of Calibration Standards

Analyte	Density of neat solution (mg/µL)	Vol. of neat solution (µL)	SSS conc. (mg/L)	SSS conc. (µg/L)	Vol. of ISS (mL)	ISS conc. (µg/L)	Vol. of SSS to spiked to ISS (µL)	Vol. of ISS spiked to Calibration Standard (µL)	Vol. of Calibration Standard (µL)	Final Calibration Standard conc. (µg/L)
Benzene	0.8765	28	2454	2 454 000	10	20 000	81	45	9000	100
Toluene	0.87	38	3306	3 306 000	10	20 000	60	45	9000	100
Ethylbenzene	0.8665	38	3293	3 293 000	10	20 000	61	45	9000	100
Xylenes (total)	0.864	38	3283	3 283 000	10	20 000	61	45	9000	100
Naphthalene	–	–	5000	5 000 000	10	20 000	40	45	9000	100

12.2.1.3 See Table 2 of example sample *BTEXN* final concentrations.

12.2.1.4 Prepare a baseline sample by filtering 3 mL to 10 mL raw water with a 0.45 µm membrane filter. Use this as the 0 concentration sample (baseline). Insert the 0 concentration sample. Measure EEM spectra following steps in Section 13. An example is to start with 2.8 mL filtered raw water in a clean cuvette with a clean stir bar.

NOTE 3—To avoid cross-contamination or sample carryover problem, it is not recommended to use flowcell or flow-through system for performing calibration spiking samples. The flow-through system is suitable for routine monitoring of this test method as mentioned in Section 13, Procedure.

12.2.1.5 Prepare all calibration standards in the same manner as their position arises in the batch operation. All samples are spiked then filtered before data acquisition. Turn on the stirrer in the sample compartment to ensure thorough mixing of the sample. Allow to stir for 60 seconds prior to data acquisition to ensure homogenous mixing of the sample solution. The stirring speed was determined to be an insignificant factor in the ruggedness study.

12.2.1.6 When introducing solvent-based standard into water in cuvette, avoid diluting more than 3 % volume, (that is, 90 µL standard to 3000 µL water). To do this, use the smallest calibrated pipette volume practical.

NOTE 4—It is optimal to prepare each calibration standard in four aliquots and analyze each aliquot four times to ensure enough dataset for an accurate multivariate model.

NOTE 5—It is optimal to collect initial calibration dataset with different raw water samples that cover sufficient variations in DOC and turbidity characteristics to ensure model robustness. Once an initial calibration model is considered acceptable, and after testing, it should be subject to model validation before deployment (section 12.3).

NOTE 6—The absorbance $OD_{254\ nm}$ should be less than 1 cm^{-1} to be in the linear range with fluorescence. Dilute the sample if $OD_{254\ nm}$ is greater than 1 cm^{-1}. Use Type I water for the dilution process. Record the dilution factor.

12.2.2 *Calibration Classification and Regression Models:*

12.2.2.1 Export the absorbance and processed EEM data files to multivariate analysis software. The joined spectral data are used as X-block, and concentration data (if available) are used as Y-block. Save the multiblock model for combining the absorbance and EEM data.

NOTE 7—Data should be screened for outliers or errors that may lead to irrelevant correlations. The appropriate data preprocessing is critical and should be considered carefully. All the outlier exclusion and data preprocessing steps should be documented (Practice E2891).

12.2.2.2 Use classification techniques such as partial least square discriminant analysis (PLSDA), support vector machine discriminant analysis (SVMDA), soft independent modeling by class analogy (SIMCA), and extreme gradient boosted tree discriminant analysis (XGBDA). Build regression models using techniques such as principal component analysis (PCR), partial least squares analysis (PLS), support vector machine (SVM), and extreme gradient boosted tree (XGB) (**2-5**). The spectral (X-block) calibration dataset is further preprocessed using mean-centering and clutter removal using the full rank extended mixture model. Concentration (Y-block) calibration data is preprocessed using mean-centering. Evaluate the regression model effectiveness based on calibration, cross-validation, and validation set prediction correlation coefficients. Classification is based on the resulting confusion matrix parameters for both the strict ($p > 0.5$) and the most probable rule of the total number of positive identifications. Select the best-performing algorithm to be incorporated into the final method file.

12.3 *Models Validation:*

12.3.1 Refer to Practice E2617 for model validation. Model validation must be performed with an independent test set. No model is ready for deployment until a proper validation has been performed. In general, a minimum of 20 validation samples is recommended, and they should not contain the same raw water matrix or replicates from the calibration samples. Validation samples should span the ranges of the independent variable, that is, concentration values, over which the calibration will be used.

12.3.2 Revalidate when the instrument conditions change, such as hardware or software updates. Ongoing periodic revalidation should be monitored as more samples are collected, especially when there are potentially challenging samples, such as raw water samples with high DOC or high turbidity values.

12.4 *Models Maintenance:*

12.4.1 Refer to Guide E2891 for guidance on models maintenance. It is recommended to build routines that check the performance of the model over time as new data is collected. The model maintenance routine schedule could be based on a predefined time frequency, such as, lamp replacement schedule, or the laboratory's quality assurance schedule, whether quarterly, biannually, or annually; or change of events, such as change of raw water intake locations. Update the model when the accuracy or precision do not fall with the performance criteria of the test method.

12.5 *Creating a Multi-Model Predictor (HMMP) Method:*

TABLE 2 Example Calibration Standards Concentrations

Compound	Target Concentration (µg/L)								
	Raw Source Water	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
Benzene	0	1	10	25	45	110	225	5	0
Toluene	0	1	10	25	45	110	225	0	0
Ethylbenzene	0	1	10	25	45	110	225	0	0
Xylenes (total)	0	1	10	25	45	110	225	0	0
Naphthalene	0	0.5	1	2	20	60	100	0	10
Total *BTEXN*	0	4.5	41	102	200	500	1000	5	10

12.5.1 Load the multiblock model into the HMMP tool to create a new method that includes the validated classification and/or regression models.

12.5.2 This HMMP method is recommended to be source-specific and include the working range for *BTEXN* mixture and raw water DOC concentration determined in 12.2.

13. Procedure

13.1 *Sample Pretreatment:*

13.1.1 Bring the sample aliquots to room temperature.

13.1.2 Filter samples with 0.45 µm membrane filters.

13.1.3 Transfer enough amount of aliquots to the quartz cuvette for measurement. If using an automatic flow-through system, place the sample tube near extraction point for automatic measurement.

13.2 *Data Acquisition Procedure:*

13.2.1 Refer to Annex A2.1 for details on data acquisition procedure. Do not use this procedure until the method is calibrated and validated as described in 12.2 and 12.3. The method to be deployed is site-specific and the raw water DOC concentration should be within the specified working range.

13.2.2 Use the sealed water standard to perform Water Raman Standard Unit (RSU) test in order to normalize the signal to RSU. Refer to manufacturer's instructions on RSU test procedure. Record the normalization factor. The purpose of this test is to evaluate instrument signal throughput and verify wavelength calibration. This test provides a standardized intensity for EEM measurements which facilitates inter-lab comparison study.

13.2.3 Set up the method parameters and sample sequence to include a blank and number of samples to be measured. Set the scan conditions by following details described in Annex A2.1. Insert the blank sample. Collect and save blank file in the designated project folder. The sealed water standard can be used as the blank. Begin the sequence and load samples when prompted by the data acquisition software dialogue.

13.2.4 When sample acquisition is complete, check the corresponding Notes page to confirm no saturation warnings were observed. If No then proceed; if Yes then reevaluate sample integration time, rerun blank and normalization factor procedures, then rerun the sample.

NOTE 8—In case of saturation warning, rerun the sample with a shorter integration time until there is no saturation warning.

13.2.5 When all samples are complete, empty contents of the cuvettes down the drain. Clean cuvettes by aliquoting 3.5 mL concentrated nitric acid (see 8.4) into each cuvette and allow to sit for 1 h. Dispose of nitric acid in the sink with running tap water and rinse cuvettes >10 times with Type I water. Blot dry with lens tissue paper and allow cuvettes to air dry. The cuvettes shall be cleaned between each use. It is the analyst's responsibility to ensure that the cuvette is clean.

NOTE 9—It is recommended to use the commercially available and affordable cuvettes as single-use disposable quartz cuvettes to avoid cross contamination or carryover among samples. Refer to 7.2 for recommended cuvette specifications.

13.3 *Running Multi-model Predictor Procedure:*

13.3.1 Refer to Annex A2.2 for details on HMMP procedure. Fig. 1 describes a Method Flowchart (4.1).

13.3.2 Implement QC on the samples by following referenced EPA methods (2.2).

14. Report

14.1 Classification report includes a display of parameters, such as Class Pred Probability and Class Pred most probable as "pass" indicating no *BTEXN* contamination, or "fail" indicating possible *BTEXN* contamination above the threshold limit set in the method (Fig. 2).

14.2 Regression report includes a display of parameters, for example, predicted *BTEXN* concentrations in the sample (Fig. 3).

15. Precision and Bias

15.1 The interim repeatability study with one single laboratory validation was conducted in 2021.[11] A complete precision statement is expected to be available in five years from publication.

15.2 *Repeatability*—A preliminary repeatability for the model predicted concentrations was estimated based on Practice D2777, and the data collected from the single-lab characterization study. The calibration set included 560 spiked *BTEXN* samples and 12 raw water samples; the validation set included 80 spiked *BTEXN* samples and 48 raw water samples, respectively. Each *BTEXN* sample was prepared by spiking a given amount of *BTEXN* mixture into the raw water matrix and then filtered with 0.45 µm membrane filters (details described in 12.2). XGB regression models were developed and evaluated for each analyte to predict its concentration in the validation samples. These regression models were optimized to the extent possible, by achieving the lowest Root Mean Square Error sums for the Calibration set, the Cross-Validation set, and most importantly the Prediction dataset. Refer to Annex A3 for details on goodness-of-fit models. For each concentration in

[11] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-2002. Contact ASTM Customer Service at service@astm.org.

Method Name: BTEXN-Class
Method Created By: Ichen@JYUS-IT-DELLOAN
Report Date: 09-Feb-2021 16:26:23

Runtime: Tuesday December 01 2020 12:36:30 PM

Sample	Class Pred Probability Fail	Class Pred Probability Pass	Class Pred Strict	Class Pred Most Probable
2020-12-01-12-51-51-B1S1S3R0PEM.dat	0.054616	0.94538	pass	pass
2020-12-01-12-52-22-B1S1S3R1PEM.dat	0.054616	0.94538	pass	pass
2020-12-01-13-26-34-B1S4S8R0PEM.dat	0.98515	0.014848	fail	fail
2020-12-01-13-27-02-B1S4S8R1PEM.dat	0.98515	0.014848	fail	fail

FIG. 2 Example Classification Report Output

Method Name: btexn_regression
Method Created By: Ichen@JYUS-IT-DELLOAN
Report Date: 22-Jan-2021 17:54:02

Runtime: Thursday March 21 2019 3:47:23 PM

Sample	CCD Saturation	Y Predicted 1 Benzene (ppb)	Y Predicted 3 Ethylbenzene (ppb)	Y Predicted 5 Naphthalene (ppb)	Y Predicted 2 Toluene (ppb)	Y Predicted 4 Xylenes (ppb)
2019-03-21-15-47-28-B1S1H5R0PEM.dat	0	100	19.9997	1.0001	79.9993	19.9983
2019-03-21-15-55-48-B1S1H5R1PEM.dat	0	100	19.9997	1.0001	79.9993	19.9983
2019-03-21-16-03-47-B1S2H6R0PEM.dat	0	250.0006	75.0004	100	100.0001	74.9967
2019-03-21-16-12-02-B1S2H6R1PEM.dat	0	250.0006	75.0004	100	100.0001	74.9967
2019-03-21-16-22-11-B1S3H7R0PEM.dat	0	499.9994	749.9999	100	100.0001	750.0016
2019-03-21-16-30-04-B1S3H7R1PEM.dat	0	499.9994	749.9999	100	100.0001	750.0016

FIG. 3 Example Regression Report Output

the low (from 0 µg/L to 50 µg/L for *BTEX*, and 0 µg/L to 20 µg/L for Naphthalene) or high range (from 0 µg/L to 225 µ/L for *BTEX* and from 0 µg/L to 100 µg/L for Naphthalene), the pooled mean, pooled standard deviation, and pooled recovery were calculated for each *BTEXN* analyte, which are detailed in Tables 3-12.

15.3 *Detection Limit*—Based on Practice E2617, using the formula: $DL = 3.3\ s/S$, where s is the standard deviation of the Y-intercept and S is the slope of the linear relationship between the regression model predicted and the target concentration values, single-lab study determined the detection limits for target *BTEXN* analytes. The detection limits are detailed in Tables 13 and 14 for low and high ranges, respectively.

15.4 *Quantification Limit*—Based on Practice E2617, using the formula: $DL = 10\ s/S$, where s is the standard deviation of the Y-intercept and S is the slope of the linear relationship between the regression model predicted concentration and the target concentration values, single-lab study determined the quantification limits for target *BTEXN* analytes. The quantification limits are detailed in Tables 13 and 14 for low and high ranges, respectively.

15.5 *Reproducibility*—A full interlaboratory study will be completed within five years to determine the reproducibility of this test method.

TABLE 3 Repeatability Table for *Benzene* (<50 µg/L) based on the Single Lab Study

Concentration (µg/L)	N	Mean (µg/L)	*S* (µg/L)	*S*rel (%)	Recovery (%)
5	4	1.1	0.1	9.6	21.6
10	4	10.0	0.002	0.02	100.0
25	4	25.0	0.01	0.1	100.0
45	4	45.0	0.04	0.1	100.0

Concentration – target concentration of sample
N – number of samples
Mean – mean value
S – standard deviation
*S*rel – relative standard deviation
Recovery – percent recovery of sample

TABLE 4 Repeatability Table for *Benzene* (>50 µg/L) based on the Single Lab Study

Concentration (µg/L)	N	Mean (µg/L)	*S* (µg/L)	*S*rel (%)	Recovery (%)
110	4	109.3	0.1	0.1	99.4
225	4	224.8	0.1	0.04	99.9

Concentration – target concentration of sample
N – number of samples
Mean – mean value
S – standard deviation
*S*rel – relative standard deviation
Recovery – percent recovery of sample

TABLE 5 Repeatability Table for *Toluene* (<50 µg/L) based on the Single Lab Study

Concentration (µg/L)	N	Mean (µg/L)	*S* (µg/L)	*S*rel (%)	Recovery (%)
10	4	9.9	0.2	1.7	99.4
25	4	25.0	0.03	0.1	100.0

Concentration – target concentration of sample
N – number of samples
Mean – mean value
S – standard deviation
*S*rel – relative standard deviation
Recovery – percent recovery of sample

TABLE 6 Repeatability Table for *Toluene* (>50 µg/L) based on the Single Lab Study

Concentration (µg/L)	N	Mean (µg/L)	*S* (µg/L)	*S*rel (%)	Recovery (%)
110	4	110.0	0.1	0.1	100.0
225	4	224.8	0.1	0.1	99.9

Concentration – target concentration of sample
N – number of samples
Mean – mean value
S – standard deviation
*S*rel – relative standard deviation
Recovery – percent recovery of sample

16. Keywords

16.1 A-TEEM; CDOM; early warning; FDOM; oil spill detection and monitoring; surface water