Designation: D7485 – 23

Standard Test Method for Determination of Nonylphenol, *p-tert*-Octylphenol, Nonylphenol Monoethoxylate and Nonylphenol Diethoxylate in Environmental Waters by Liquid Chromatography/Tandem Mass Spectrometry[1]

This standard is issued under the fixed designation D7485; 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 determination of nonylphenol (NP), nonylphenol ethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), and octylphenol (OP), extracted from water utilizing solid phase extraction (SPE), separated using liquid chromatography (LC) and detected with tandem mass spectrometry (MS/MS). These compounds are qualitatively and quantitatively determined by this method. This method adheres to single reaction monitoring (SRM) mass spectrometry.

1.2 The method detection limit (MDL) and reporting limit (RL) for NP, NP1EO, NP2EO, and OP are listed in Table 1.

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

D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents

D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

D5905 Practice for the Preparation of Substitute Wastewater

2.2 *Other Documents:*[3]

40 CFR Part 136, Appendix B Definition and Procedure for the Determination of the Method Detection Limit

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 *environmental water, n*—shall refer to water tested using this method; see Section 5.

3.2.2 *nonylphenol, NP, n*—is a mixture of branched p-nonylphenol isomers; commercial NP is produced by the reaction of phenol with commercial nonene; commercial nonene is not simply a linear C9H18 alpha olefin; it is a complex mixture of predominantly nine-carbon olefins, called propylene trimer, containing no linear isomers; this synthesis results in a mixture of various branched nonylphenol isomers rather than a discrete chemical structure; the branched nonyl group is positioned predominantly in the *para* position on the phenol ring.

3.2.3 *octylphenol, OP, n*—commercial octylphenol is produced by the reaction of phenol and diisobutylene to produce predominantly the 4-(1,1,3,3-tetramethylbutyl)phenol isomer.

[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] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

TABLE 1 MDL and Reporting Limits

Analyte	MDL[A] (ng/L)	Reporting Range[B] (ng/L)
NP	33	100–2000
NP1EO	9	100–2000
NP2EO	9	100–2000
OP	24	100–2000

[A] MDL determined following The Code of Federal Regulations, 40 CFR Part 136, Appendix B.
[B] Lowest point of the reporting range is calculated from the LV 1 concentration calibration standard in Table 4.

3.2.4 *independent reference material, IRM, n*—a material of known purity and concentration obtained either from the National Institute of Standards and Technology (NIST) or other reputable supplier; the IRM must be obtained from a different lot of material than is used for calibration.

3.3 *Acronyms:*

3.3.1 *CCC, n*—Continuing Calibration Check

3.3.2 *IC, n*—Initial Calibration

3.3.3 *LC, n*—Liquid Chromatography

3.3.4 *LCS/LCSD, n*—Laboratory Control Sample/Laboratory Control Sample Duplicate

3.3.5 *MDL, n*—Method Detection Limit

3.3.6 *MeOH, n*—Methanol

3.3.7 *mM, n*—millimolar, 1×10^{-3} moles/L

3.3.8 *MRM, n*—Multiple Reaction Monitoring

3.3.9 *MS/MSD, n*—Matrix Spike/Matrix Spike Duplicate

3.3.10 *NA, adj*—Not Available

3.3.11 *ND, n*—non-detect

3.3.12 *NP1EO, n*—represents branched nonylphenol monoethoxylate.

3.3.13 *NP2EO, n*—represents branched nonylphenol diethoxylate.

3.3.14 *n-NP2EO, n*—represents normal straight chain nonylphenol diethoxylate. n-NP2EO is used in this method as a surrogate. It is not produced commercially and is not expected to be found in environmental waters.

3.3.15 *P&A, n*—Precision and Accuracy

3.3.16 *PPB, n*—parts per billion

3.3.17 *PPT, n*—parts per trillion

3.3.18 *QA, adj*—Quality Assurance

3.3.19 *QC, adj*—Quality Control

3.3.20 *RL, n*—Reporting Limit

3.3.21 *RSD, n*—Relative Standard Deviation

3.3.22 *RT, n*—Retention Time

3.3.23 *SDS, n*—Safety Data Sheets

3.3.24 *SRM, n*—Single Reaction Monitoring

3.3.25 *SS, n*—Surrogate Standard

3.3.26 *TC, n*—Target Compound

3.3.27 *μM, n*—micromolar, 1×10^{-6} moles/L

3.3.28 *VOA, n*—Volatile Organic Analysis

4. Summary of Test Method

4.1 This is a performance-based method and modifications are allowed to improve performance.

4.2 For NP, NP1EO, NP2EO, and OP analysis, solid phase extraction is used to extract water samples.

4.2.1 *Solid Phase Extraction*—250 mL volume of sample adjusted to pH 2 is extracted using a solid phase extraction cartridge. The acetonitrile/water extract is concentrated to a volume of 1.0 mL, and then analyzed by LC/MS/MS operated in the multiple reaction monitoring (MRM) mode.

4.3 The target compounds are identified by retention time and SRM transition and are quantitated using the SRM transition of the target compounds utilizing external calibration. The final report issued for each sample lists the concentration of NP, NP1EO, NP2EO, and OP.

5. Significance and Use

5.1 NP and OP have been shown to have toxic effects in aquatic organisms. The source of NP and OP is prominently from the use of common commercial surfactants. The most widely used surfactant is nonylphenol ethoxylate (NPEO) which has an average ethoxylate chain length of nine. The ethoxylate chain is readily biodegraded to form NP1EO, NP2EO, nonylphenol carboxylate (NPEC) and, under anaerobic conditions, NP. NP will also biodegrade, but may be released into environmental waters directly at trace levels. This method has been investigated and is applicable for environmental waters, including seawater.

6. Interferences

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other apparatus producing discrete artifacts or elevated baselines. All of these materials are routinely demonstrated to be free from interferences by analyzing laboratory reagent blanks under the same conditions as the samples.

6.2 All glassware is washed in hot water with detergent, rinsed in hot water and rinsed with distilled water. The glassware is then dried and heated in an oven at 250 °C for 15 min to 30 min. All glassware is subsequently cleaned with acetone and methanol. Detergents containing alkylphenolic compounds must not be used.

6.3 All reagents and solvents should be of pesticide residue purity or higher to minimize interference problems.

6.4 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences can vary considerably from sample source to sample source, depending on variations of the sample matrix.