



Designation: ~~D7065 – 11~~ D7065 – 17

Standard Test Method for Determination of Nonylphenol, Bisphenol A, *p*-tert- Octylphenol, Nonylphenol Monoethoxylate and Nonylphenol Diethoxylate in Environmental Waters by Gas Chromatography Mass Spectrometry¹

This standard is issued under the fixed designation D7065; 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 determination of nonylphenol (NP), nonylphenol ethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), octylphenol (OP), and bisphenol A (BPA) that are partitioned into organic solvent, separated using gas chromatography and detected with mass selective detection. These compounds or isomer mixtures are qualitatively and quantitatively determined by this test method. This test method adheres to selected ion monitoring mass spectrometry but full scan mass spectrometry has also been shown to work well under these conditions. Either analysis may be used.

1.2 The method detection limit (MDL) and reporting limit (RL) for NP, NP1EO, NP2EO, OP, and BPA 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 to 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](#)

[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](#)

[E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method](#)

2.2 *Other Publications:*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: Definitions of Terms Specific to This Standard:*

3.1.1 Nonylphenol, NP, n—nonylphenol is mixed isomers of branched p-nonylphenol.

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, Washington, DC 20401-0001, <http://www.access.gpo.gov>.

TABLE 1 MDL and Reporting Limits

Analyte	MDL ^A (µg/L)	Reporting Range ^B (µg/L)
NP	0.9	5.0-80.0
NP1EO	1.2	10.0-160.0
NP2EO	1.8	20.0-320.0
OP	0.2	1.0-16.0
BPA	0.3	1.0-16.0

3.1.1.1 *Discussion*—

TABLE 1 Method Detection Limit (MDL) and Reporting Limits

Analyte	MDL, ^A (µg/L)	Reporting Range, ^B (µg/L)
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NP1EO	1.2	10.0–160.0
NP2EO	1.8	20.0–320.0
OP	0.2	1.0–16.0
BPA	0.3	1.0–16.0

^A MDL Determined Following The determined following the Code of Federal Regulations, 40 CFR Part 136, Appendix B.

^B Lowest Pointpoint of the Reporting Rangereporting range is Calculatedcalculated from the LV1 Concentration Calibration Standardconcentration calibration standard in Table 4.

Commercial nonylphenol 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.

3.2.1 *bisphenol A, BPA, n*—represents 4,4'-dihydroxy-2,2-diphenylpropane.

3.2.1.1 *Discussion*—

Commercial bisphenol A is produced by the condensation reaction of phenol and acetone to produce predominantly the 4,4'-dihydroxy-2,2-diphenylpropane.

3.1.2 *Octylphenol, OP, n*—OP represents 4-(1,1,3,3-tetramethylbutyl)phenol.

3.1.2.1 *Discussion*—

Commercial octylphenol is produced by the reaction of phenol and diisobutylene to produce predominantly the 4-(1,1,3,3-tetramethylbutyl)phenol isomer.

3.2.2 *environmental water, n*—shall refer to water tested using this test method. See Section 5.

3.1.3 *Bisphenol A, BPA, n*—BPA represents 4,4'-dihydroxy-2,2-diphenylpropane.

3.1.3.1 *Discussion*—

Commercial bisphenol A is produced by the condensation reaction of phenol and acetone to produce predominantly the 4,4'-dihydroxy-2,2-diphenylpropane.

3.2.3 *nonylphenol, NP, n*—mixed isomers of branched p-nonylphenol.

3.2.3.1 *Discussion*—

Commercial nonylphenol 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.

3.1.4 *Environmental water, n*—it shall refer to water tested using this method. See Section 5.

3.2.4 *octylphenol, OP, n*—represents 4-(1,1,3,3-tetramethylbutyl)phenol.

3.2.4.1 *Discussion*—

Commercial octylphenol is produced by the reaction of phenol and diisobutylene to produce predominantly the 4-(1,1,3,3-tetramethylbutyl)phenol isomer.

3.3 Abbreviations:

3.2.1 NP1EO—branched nonylphenol monoethoxylate:

3.3.1 *n-NP*—normal straight chain nonylphenol

3.3.1.1 Discussion—

n-NP is used in this test method as a surrogate for NP, OP and BPA. *n-NP* is not produced commercially and is not expected to be found in environmental waters.

3.2.2 NP2EO—branched nonylphenol diethoxylate:

3.3.2 *n-NP1EO*—normal straight chain nonylphenol ethoxylate

3.3.2.1 Discussion—

n-NP1EO is used in this test method as a surrogate for NP1EO and NP2EO. *n-NP1EO* is not produced commercially and is not expected to be found in environmental waters.

3.2.3 *n-NP*—normal straight chain nonylphenol:

3.2.3.1 Discussion—

n-NP is used in this method as a surrogate for NP, OP and BPA. *n-NP* is not produced commercially and is not expected to be found in environmental waters:

3.3.3 *NP1EO*—branched nonylphenol monoethoxylate

3.2.4 *n-NP1EO*—normal straight chain nonylphenol ethoxylate:

3.2.4.1 Discussion—

n-NP1EO is used in this method as a surrogate for NP1EO and NP2EO. *n-NP1EO* is not produced commercially and is not expected to be found in environmental waters:

3.3.4 *NP2EO*—branched nonylphenol diethoxylate

4. Summary of Test Method

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

4.2 For NP, NP1EO, NP2EO, BPA, and OP analysis, continuous liquid-liquid extraction technique is used for water samples.

4.3 *Continuous Liquid-Liquid Extraction Technique*—A 1-L volume of sample adjusted to pH 2 is extracted with methylene chloride. The methylene chloride extract is dried using sodium sulfate if needed, concentrated to a volume of 0.5 mL, and then analyzed by GC/MS operated in the selected ion monitoring (SIM) or full scan mode.

4.4 The target compounds are identified by retention time and confirmed by comparing the sample mass spectrum to that of a known standard. The target compounds are quantitated using the quantitation ions of the target compounds utilizing the internal standards acenaphthene-d₁₀, and phenanthrene-d₁₀. The final report issued for each sample lists total concentration of NP, NP1EO, NP2EO, BPA, and OP, if detected, or MDLs, if not detected, in µg/L for water samples.

5. Significance and Use

5.1 Nonylphenol,⁴ octylphenol, and bisphenol A have been shown to have toxic effects in aquatic organisms. The source of nonylphenol and octylphenol is prominently from the use of common commercial surfactants. The most widely used surfactant is NPEO which has an average ethoxylate chain of 9 mol of ethoxylate. The ethoxylate chain is readily biodegraded to form NP1EO and NP2EO, nonylphenol carboxylate (NPEC) and, under anaerobic conditions, nonylphenol. Nonylphenol will also biodegrade, but may be released into environmental waters directly at trace levels. This test method has been investigated for use with surface water and waste treatment effluent samples and is applicable to these matrices. It has not been investigated for use with salt water or solid sample matrices.

⁴ Aquatic Life Ambient Water Quality Criteria—Nonylphenol Final, US EPA Office of Water Document Number EPA-822-R-05-005, December 2005. You can request a copy by sending an email (center.water.resource@epa.gov) or by conventional mail to EPA Water Resource Center, 4101F, 1200 Pennsylvania Avenue, N.W., Washington, DC 20460, U.S. EPA Office of Water, *Aquatic Life Ambient Water Quality Criteria — Nonylphenol Final*, Document Number EPA-822-R-05-005, December 2005. Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

5.2 The first reported synthesis of BPA was by the reaction of phenol with acetone by Zincke.⁵ BPA has become an important high volume industrial chemical used in the manufacture of polycarbonate plastics and epoxy resins. Polycarbonate plastic and resins are used in numerous products including electrical and electronic equipment, automobiles, sports and safety equipment, reusable food and drink containers, electrical laminates for printed circuit boards, composites, paints, adhesives, dental sealants, protective coatings, and many other products.⁶ The environmental source of BPA is predominantly from the decomposition of polycarbonate plastics and resins. BPA is not classified as bio-accumulative by the U.S. Environmental Protection Agency (EPA) and will biodegrade. BPA may be released into the environment waters directly at trace levels through landfill leachate and sewage treatment plant effluents.

6. Interferences

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other apparatus that lead to discrete artifacts or elevated baseline in the selected ion current profiles. 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 scrupulously cleaned. All glassware is washed in hot water with detergent such as powdered Alconox, ~~Deto-Jet~~, ~~Det-o-Jet~~, Luminox, or ~~Citrojet~~, ~~Citrajet~~,⁷ rinsed in hot water and rinsed with distilled water. The glassware is then dried and heated in an oven at 250°C for 15 to 30 min. All glassware is subsequently cleaned with acetone and methylene chloride. 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 will vary considerably from sample source to sample source, depending on variations of the sample matrix.

7. Apparatus

7.1 GC/MS System:

7.1.1 *Gas Chromatograph (GC) System*—An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, autosamplers, and gases. The injection port must be designed for split/splitless when using the capillary columns.

7.1.2 *Analytical Column*—An analytical column (DB-5MS 30-m × 0.25 mm i.d.; ID; film thickness—0.25 μm or equivalent; (5 %-phenyl)-methylpolysiloxane) suitable for the analysis of target alkylphenols.⁸

7.1.3 *Mass Spectrometer (MS) System*—An MS system capable of scanning 45 to 500 amu every 2 s or less, using 70 eV in the electron impact mode, and producing a mass spectrum which meets all the criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

7.2 CLLE Apparatus.

7.3 Organic Solvent Evaporation Device.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless indicated otherwise, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.⁹ Other reagent grades may be used provided it is first ascertained that they are of sufficiently high purity to permit their use without affecting the accuracy of the measurement.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type I of ~~specification~~ Specification D1193. It must be demonstrated that this water does not contain contaminants at concentrations sufficient to interfere with the analysis.

8.3 *Gases*—Research grade nitrogen or helium of highest purity are used.

8.4 *Methylene Chloride*, chromatography grade.

8.5 *Methanol*, purge and trap grade.

⁵ Zincke, T., 1905, "Mitteilungen aus dem chemischen Laboratorium der Universität Marburg," *Justus Leibigs Annals Chemie*, Vol. 343, pages 75-79. Zincke, T., 1905, "Mitteilungen aus dem chemischen Laboratorium der Universität Marburg," *Justus Leibigs Annals Chemie*, Vol. 343, pp. 75-79.

⁶ Additional information about BPA is available on the internet at <http://www.bisphenol-a.org> or <http://www.bisphenol-a.org>.

⁷ Alconox, Det-o-Jet, Luminox, and Citrajet are trademarks of Alconox, Inc., White Plains, NY.

⁸ The sole source of supply of the columns known to the committee at this time is J&W Columns, Agilent Technologies, Inc., 2850 Centerville Rd., Wilmington, DE 19808. 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,¹ which you may attend.

⁹ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. 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.

- 8.6 *Branched Nonylphenol Monoethoxylate (NP1EO)*, available as a high purity custom standard.
- 8.7 *Branched Nonylphenol Diethoxylate (NP2EO)*, available as a high purity custom standard.
- 8.8 *Branched Nonylphenol Ethoxylate Blend (NP1EO–NP3EO)*, where the composition is determined by gas chromatography.¹⁰
- 8.9 *Nonylphenol (NP)*, >95 % para isomer (CAS #84852-15-3); # 84852-15-3).
- 8.10 *Octylphenol (OP)*, 99+ % 4-(1,1,3,3-tetramethylbutyl)phenol (CAS #140-66-9); # 140-66-9).
- 8.11 *Bisphenol A (BPA)*, 99+ % 4,4'-isopropylidenediphenol (CAS #80-05-7); # 80-05-7).
- 8.12 *Concentrated H₂SO₄* (CAS #7664-93-9); (CAS # 7664-93-9)
- 8.13 *Internal Standard Mix*, containing acenaphthene-d₁₀ and phenanthrene-d₁₀.
- 8.14 *n-nonylphenol* (CAS #104-40-5); (CAS # 104-40-5).
- 8.15 *n-NP monoethoxylate (n-NP1EO, CAS #104-35-8); (n-NP1EO, CAS # 104-35-8).*
- 8.16 *Acetone, Reagent Grade* (CAS #67-64-1); (CAS # 67-64-1).
- 8.17 *Perfluorotributylamine, PFTBA* Perfluorotributylamine; (CAS PFTBA, (CAS# # 311-89-7).

9. Hazards

9.1 Normal laboratory safety applies to this test method. Analysts should wear safety glasses, gloves and lab coats when working with acids. Methylene chloride is used as an extraction solvent for this test method. Analysts should review the MSDS for all reagents used in this test method.

10. Sample Collection, Preservation, and Storage

10.1 Sampling:

10.1.1 Grab samples must be collected in glass sample containers. Conventional sampling practices should be followed. Refer to Guide **D3856** and Practice Practices D3694. Automatic sampling equipment should be as free as possible of Tygon tubing and other potential sources of contamination. Samples must be iced or kept at 0 to 4°C. Samples must be prevented from freezing.

10.2 Preservation:

10.2.1 Adjust to pH 2 with H₂SO₄. Store samples between 0 and 4°C from the time of collection until extraction. Extract the sample within 28 days of collection and completely analyze within 40 days of extraction.

10.2.2 Sample extracts may be stored in sealed glass containers at <0°C indefinitely.

<https://standards.iteh.ai/catalog/standards/sist/4d21d862-95ea-437c-8e47-f82daaed657f/astm-d7065-17>

11. Preparation of GC/MS

11.1 *Chromatograph Operating Conditions* (approximate values, your instrument may require different settings):

Carrier Gas:	Helium
Carrier Flow:	Variable (1.3 to 0.4 mL/min), Constant Pressure (11.16 psi approximately)
Average Velocity	42 cm/s
Injection Port Parameters:	Splitless Injection
Injection Pressure:	10 to 12 psi
Injection port temperature:	290°C
Injection Port Temperature:	290°C
Purge flow to split vent:	30mL/min at 0.75 min,
Purge Flow to Split Vent:	30mL/min at 0.75 min, Total Flow 34.2 mL/min
Column oven temperature:	50°C initially and hold 2 min
Column Oven Temperature:	50°C initially and hold 2 min 50 to 320°C at 10°C/min 320°C – hold 5 min
Injection Volume:	1 µL
Injection Liner:	Single taper liner
MS Transfer Line Temperature:	290°C

11.2 Mass Spectrometer Parameters:

¹⁰ The sole source of supply of the blend known to the committee at this time is Schenectady International, Inc., 2750 Balltown Road, Schenectady, NY 12309. 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,¹ which you may attend.

Mode:	Electron Ionization
Electron Multiplier:	Set electron multiplier to achieve optimal performance.
Tune:	Autotune using PFTBA masses 69, 219, and 502.
Dwell Time:	30 ms
SIM Ions:	Refer to Table 2 .

NOTE 1—For details regarding retention times and quantitation ions refer to [Table 2](#).

12. Calibration and Standardization

12.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test, the following procedures must be followed when performing ~~the~~this test method.

12.2 Calibration and Standardization:

12.2.1 To calibrate the instrument, analyze 5 calibration standards containing 5 increasing concentration levels of NP, NP1EO, NP2EO, BPA, OP, n-NP, and n-NP1EO prior to analysis of sample. The values in [Table 3](#) are shown as approximate concentrations. A calibration stock standard solution is prepared from standard materials or purchased as certified solutions. Stock standard ~~solution~~Solution A (Level 5) containing NP, NP1EO, NP2EO, BPA, OP, n-NP, and n-NP1EO is prepared at Level 5 concentration and aliquots of that solution are diluted to prepare Levels 1 through 4. There are many ways to accomplish this; the following steps

TABLE 2 Retention Time (RT) and Electron Impact Ions^A

Parameter	RT (Minutes)	Quantitation Ions	Confirmation Ions
Octylphenol	16.50	135	107, 91
Nonylphenol (NP)	17.58	121	107, 163, 220
Isomer Group 1			
Nonylphenol (NP)	17.58	121	107, 163, 220
Isomer Group 1			
NP Isomer Group 2	17.71	135	107, 121, 220
NP Isomer Group 3	17.80	149	135, 107, 220
NP Isomer Group 4	17.87	149	121, 220
NP Isomer Group 5	17.90	135	121, 107, 220
NP Isomer Group 6	17.94	149	121, 107, 220
NP Isomer Group 7	18.05	135	107, 163, 220
NP Isomer Group 8	18.16	149	121, 107, 220
NP Isomer Group 9	18.18	163	121, 107, 220
NP Isomer Group 10	18.28	135	107, 149, 220
NP Isomer Group 11	18.37	149	107, 121, 220
NP Isomer Group 12	18.39	135	149, 107, 220
NP1EO Isomer Group 1	20.45	165	207, 221, 264
NP1EO Isomer Group 2	20.58	179	135, 107, 264
NP1EO Isomer Group 3	20.66	179	193, 107, 264
NP1EO Isomer Group 4	20.71	179	193, 165, 264
NP1EO Isomer Group 5	20.78	179	193, 165, 264
NP1EO Isomer Group 6	20.91	179	207, 135, 264
NP1EO Isomer Group 7	20.97	193	179, 221, 264
NP1EO Isomer Group 8	21.05	207	165, 107, 264
NP1EO Isomer Group 9	21.12	179	135, 193, 264
NP1EO Isomer Group 10	21.22	193	179, 107, 264
Bisphenol A	22.82	213	228, 119
NP2EO Isomer Group 1	23.29	251	265, 209, 308
NP2EO Isomer Group 2	23.44	223	135, 308
NP2EO Isomer Group 3	23.49	237	223, 279, 308
NP2EO Isomer Group 4	23.53	223	135, 237, 308
NP2EO Isomer Group 5	23.59	223	135, 237, 308
NP2EO Isomer Group 6	23.63	237	209, 279, 308
NP2EO Isomer Group 7	23.78	237	223, 265, 308
NP2EO Isomer Group 8	23.84	251	237, 223, 308
NP2EO Isomer Group 9	23.92	223	135, 308
NP2EO Isomer Group 10	24.03	237	223, 149, 308
n-NP (Surrogate)	19.63	107	135, 220
n-NP1EO (Surrogate)	22.47	107	151, 264, 91
Acenaphthene-d ₁₀	15.04	164	140
(Internal Std.)			
Acenaphthene-d ₁₀	15.04	164	140
(Internal Std.)			
Phenanthrene-d ₁₀	18.86	188	94, 160
(Internal Std.)			
Phenanthrene-d ₁₀	18.86	188	94, 160
(Internal Std.)			

^A Refer to [Figs. 1-5](#), which will make the quantitation method more apparent.