Designation: D8310 – 20

Standard Test Method for Analysis of Target Phenols (TPs) in Soil by Multiple Reaction Monitoring Liquid Chromatography/Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation D8310; 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 analysis of nonylphenol (NP), nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), octylphenol (OP), and bisphenol A (BPA), referred to collectively as target phenols (TPs), in soil, sediments, and biosolids by extraction with acetone, filtration, dilution with water, and analysis by liquid chromatography/tandem mass spectrometry. The sample extracts are prepared in a solution of 75 % acetone and 25 % water because TPs have an affinity for surfaces and particles that is more pronounced at lower concentrations. The range of applicability of the test method is shown in Table 1. The method may be extended outside of these ranges depending on additional performance studies not undertaken here.

1.2 *Units*—The values stated in SI units are to be regarded as the standard. No other units of measurement are included in this standard.

1.3 *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.*

1.4 *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]

D1193 Specification for Reagent Water

D7858 Test Method for Determination of Bisphenol A in Soil, Sludge, and Biosolids by Pressurized Fluid Extraction and Analyzed by Liquid Chromatography/Tandem Mass Spectrometry

2.2 *Federal Standards:*[3]

29 CFR Part 1910 Occupational Safety and Health Standards

40 CFR Part 136, Appendix B Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *batch quality control, n*—all the quality control (QC) samples and standards included in an analytical procedure.

3.1.2 *bisphenol A, BPA*—defined in Test Method D7858.

3.1.3 *bisphenol A (propane-D6), BPA-D_6*—defined in Test Method D7858.

3.1.4 *2-bromo-4-(1,1,3,3-tetramethylbutyl)phenol, Br-OP, n*—used in this test method as a surrogate.

3.1.4.1 *Discussion*—2-bromo-4-(1,1,3,3-tetramethylbutyl) phenol is not produced commercially and is not expected to be found in the environment. It was reported that compounds in highly chlorinated, bromide-rich wastewaters could potentially interfere with the Br-OP surrogate. If this interference is encountered, n-nonylphenol is suggested as an alternative surrogate.

3.1.5 *nonylphenol, NP, n*—mixture of branched p-nonylphenol isomers.

3.1.5.1 *Discussion*—Commercial NP is produced by the reaction of phenol with commercial nonene. Commercial nonene is not simply a linear C_9H_{18} 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.

[1] This test method is under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.01.06 on Analytical Methods.

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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 Tested Method Parameters of the Standard

Analyte	ESI Mode	MDL (µg/kg)[A]	Reporting Range (µg/kg)
Bisphenol A	Negative	15.5	100–2500
Octylphenol	Negative	44.2	200–5000
Nonylphenol	Negative	30.4	100–2500
Nonylphenol Monoethoxylate	Positive	931.2	3000–45 000
Nonylphenol Diethoxylate	Positive	7.4	100–2500

[A] MDL is calculated based upon nine spiked samples.

3.1.6 *nonylphenol diethoxylate, NP2EO, n*—branched nonylphenol diethoxylate.

3.1.7 *nonylphenol monoethoxylate, NP1EO, n*—branched nonylphenol monoethoxylate.

3.1.8 *normal nonylphenol, n-NP, n*—normal straight chain nonylphenol.

3.1.8.1 *Discussion*—n-NP is used in this test method as a surrogate. It is not produced commercially and is not expected to be found in the environment.

3.1.9 *normal nonylphenol diethoxylate, n-NP2EO, n*—normal straight chain nonylphenol diethoxylate.

3.1.9.1 *Discussion*—n-NP2EO is used in this test method as a surrogate. It is not produced commercially and is not expected to be found in the environment.

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

3.1.11 *reporting limit check sample, RLCS, n*—this sample verifies that if the analyte was present at the reporting limit, it would be confidently identified.

3.1.12 *target phenols, TPs, n*—in this test method, NP, NP1EO, NP2EO, OP, and BPA, collectively.

3.2 *Abbreviations:*

3.2.1 *ADOC*—analyst demonstration of capability

3.2.2 *BPA*—bisphenol A

3.2.3 *Br-OP*—2-bromo-4-(1,1,3,3-tetramethylbutyl)phenol

3.2.4 *CAS*—chemical abstract service

3.2.5 *CCC*—continuing calibration check

3.2.6 *DL*—detection limit

3.2.7 *EPA*—U.S. Environmental Protection Agency

3.2.8 *IC*—initial calibration

3.2.9 *IDOC*—initial demonstration of capability

3.2.10 *LC*—liquid chromatography

3.2.11 *LCS*—laboratory control sample

3.2.12 *LCSD*—laboratory control sample duplicate

3.2.13 *LIMS*—relational laboratory information management system

3.2.14 *MDL*—method detection limit

3.2.15 *MI*—matrix interference

3.2.16 *MRM*—multiple reaction monitoring

3.2.17 *MS*—mass spectrometry

3.2.18 *MS/MSD*—matrix spike/matrix spike duplicate

3.2.19 *MSP*—method specific parameter

3.2.20 *NA*—not available

3.2.21 *NP1EO*—nonylphenol monoethoxylate

3.2.22 *NP2EO*—nonylphenol diethoxylate

3.2.23 *OP*—octylphenol

3.2.24 *P&A*—precision and accuracy

3.2.25 *PPB*—parts per billion

3.2.26 *PPM*—parts per million

3.2.27 *PPT*—parts per trillion

3.2.28 *PTFE*—polytetrafluoroethylene

3.2.29 *PVDF*—poly-vinylidene dichloride

3.2.30 *QA*—quality assurance

3.2.31 *QC*—quality control

3.2.32 *QMP*—quality management plan

3.2.33 *REC*—percent recovery

3.2.34 *RL*—reporting limit

3.2.35 *RLCS*—reporting limit check sample

3.2.36 *RSD*—relative standard deviation

3.2.37 *RT*—retention time

3.2.38 *RTS*—retention time shift

3.2.39 *SOP*—standard operating procedure

3.2.40 *SRM*—single reaction monitoring

3.2.41 *SS*—surrogate standard

3.2.42 *TC*—target compound

3.2.43 *TCL*—target compound limit

3.2.44 *TP*—target phenols

3.2.45 *UPLC*—ultra performance liquid chromatography

3.2.46 *VOA*—volatile organic analysis

4. Summary of Test Method

4.1 A sample (~2 g) is transferred to a VOA vial and spiked with surrogates (all samples) and TPs (laboratory control and matrix spike samples) and then extracted with 7.5 mL of acetone by tumbling on a rotator for 2 h. Any device may be used that mixes the sample; a rotator device was chosen in this case because it inverts the sample, allowing the soil to be in a constant fluid motion and not clumped. The samples are centrifuged at 1900 rpm for 10 min and then filtered through an Acrodisc GxF/0.2 µm PVDF membrane syringe-driven filter unit. Of Specification D1193 Type 1 water, 2.5 mL is added to the filtered extract and then analyzed by LC/MS/MS. All concentrations reported, only to the RL, using this method are based upon a dry-weight basis.

4.2 The TCs are identified by comparing the SRM transition and RT. BPA has a confirmatory SRM transition also. The confirmatory SRM transition will be correlated to the known standard SRM transition for identification of BPA (Table 2). The RT for the analyte of interest shall also agree with the RT of the mid-level standard by ±5 %. The TC is quantitated using the SRM transition of the TC using external calibration. As an additional QC measure, non-labeled surrogates (listed in 8.2)

TABLE 2 Variable Mass Spectrometer Parameters

Analyte	ESI Mode	Retention Time, min	SRM Mass Transition (Parent > Product)	Cone Voltage, V	Collision Energy, eV
BPA	negative	5.58	227.1 > 211.9	40	18
BPA confirmatory[A]	negative	5.58	227.1 > 132.7	40	25
OP	negative	8.53	205.1 > 132.7	40	24
NP	negative	9.70	219.3 > 133.1	40	28
NP1EO	positive	9.71	282.3 > 126.9	20	9
NP2EO	positive	9.65	326.3 > 182.9	25	11
BPA-D_6 (surrogate)	negative	5.57	233.3 > 214.9	40	19
BPA-D_6 confirmatory[A] (surrogate)	negative	5.57	233.3 > 137.8	40	25
Br-OP (surrogate)	negative	9.56	283.1 > 78.6	40	25
n-NP (surrogate)	negative	10.71	219.3 > 105.6	40	20
n-NP2EO (surrogate)	positive	10.69	326.4 > 88.8	25	15

[A] Confirmatory transitions are optional but should be included for added qualitative information.

recoveries are monitored; the percent recovery of each should fall within the control limits of the method. The final report issued for each sample lists concentration of TPs and surrogates, if detected, or non-detect at the RL if not detected, in microgram/kilogram on a dry-weight basis.

5. Significance and Use

5.1 This test method developed for the analysis of TPs in soil and sediment samples is based upon an LC/MS/MS analysis. Any type of coupled liquid chromatography/mass spectrometry system may be used that meets the study objectives of the individual project. These may include, but are not limited to: trap, single quadrupoles, time-of-flight, high resolution, and others not mentioned here.

5.2 The MDL and reporting range for TPs are listed in Table 1. This SOP has been tested on Ottawa sand, four ASTM soil types, biosolid sample, and one commercial soil. The P&A QC acceptance criteria are listed in Table 3. Tables 4-17 display the TC and surrogate recoveries in the various soil types. 40 CFR Part 136, Appendix B was used as a guide to determine the MDLs. The 40 CFR Part 136 MDL criteria were not met for NP2EO; this does not affect the method because the SOP only reports to the RL and is not a regulatory method. All site sample results are not reported below the RL using this method. RLCS concentrations may be reported below the RL because they are spiked at or near the RL.

5.3 The RL for a specific soil sample may differ from that listed depending on the nature of the interferences in the sample matrix. Variability in historical LCS spike recovery may be used to estimate uncertainty. The estimate of minimum laboratory contribution to measurement uncertainty of this test method for each analyte is listed in Table 3. These values are derived from P&A samples from the initial IDOC study for this test method. The uncertainty will be greater near the RL and much greater near the DL. Also, uncertainty estimated based on variability in LCS recovery is conservative because some sources of variability are not included, such as subsample variability and matrix analyte recovery. This SOP covers multiple soil matrices and the uncertainty among the various matrices is variable.

6. Interferences

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, LC vials/caps, disposable pipettes, and other apparatus that lead to discrete artifacts or elevated baselines in the selected ion current profiles. The presence and magnitude of method interferences are determined by analysis of solvent and laboratory blanks.

6.2 Matrix interferences may be caused by contaminants from the sample, sampling devices, or storage containers. The extent of matrix interferences will vary considerably from sample source to sample source depending on variations of the sample matrix. The analysis of matrix spikes is critical for determining the impact of matrix interferences.

6.3 *Warnings:*

6.3.1 All reagents and solvents should be of pesticide residue purity or higher to minimize interference problems, preferably LC/MS grade.

6.3.2 Contaminants have been found in improperly cleaned glassware and glass syringes. TPs stick to surfaces if the

TABLE 3 QC Acceptance Criteria and Uncertainty[A]

Parameter	Average Recovery, %	Standard Deviation of Percentage Recovery	Number of Replicates, n	Lower Control Limit (LCL), %	Upper Control Limit (UCL), %	Uncertainty (95 % Confidence Interval)
BPA	92.6	4.5	6	70	130	4.7
OP	88.4	6.5	6	60	130	6.9
NP	92.9	3.4	6	70	130	3.6
NP1EO	98.4	7.0	6	70	130	7.3
NP2EO	96.1	4.5	6	70	130	4.7
BPA-D_6 (surrogate)	91.1	3.2	8	70	130	2.7
Br-OP (surrogate)	87.9	4.7	8	70	130	3.9
n-NP (surrogate)	87.4	2.6	8	70	130	2.2
n-NP2EO (surrogate)	93.6	6.1	8	70	130	5.1

[A] Uncertainty calculation based upon 95 % confidence interval and a two-tailed Student *t* distribution.
Uncertainty = Student *t* Value [(standard deviation) / (number of LCS)^{½}].