



Designation: D7574 – 23

Standard Test Method for Determination of Bisphenol A in Environmental Waters by Liquid Chromatography/Tandem Mass Spectrometry¹

This standard is issued under the fixed designation D7574; 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 bisphenol A (BPA) extracted from water utilizing solid phase extraction (SPE), separated using liquid chromatography (LC) and detected with tandem mass spectrometry (MS/MS). BPA is qualitatively and quantitatively determined by this method. This test method adheres to multiple reaction monitoring (MRM) mass spectrometry.

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

1.3 The method detection limit (MDL) and reporting limit (RL) for BPA are listed in [Table 1](#).

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](#)

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.

[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 *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 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 Range

Analyte	MDL ^A (ng/L)	Reporting Range ^B (ng/L)
Bisphenol A	5	20–600

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

^B Lowest point of the reporting range, reporting limit, is calculated from the LV 1 concentration calibration standard in Table 4. Fig. 1 displays the signal/noise ratio at the reporting limit.

- 3.3.11 *ND*, *n*—non-detect
- 3.3.12 *P&A*, *n*—Precision and Accuracy
- 3.3.13 *PPB*, *n*—parts per billion
- 3.3.14 *PPT*, *n*—parts per trillion
- 3.3.15 *QA*, *adj*—Quality Assurance
- 3.3.16 *QC*, *adj*—Quality Control
- 3.3.17 *RL*, *n*—Reporting Limit
- 3.3.18 *RSD*, *n*—Relative Standard Deviation
- 3.3.19 *RT*, *n*—Retention Time
- 3.3.20 *SDS*, *n*—Safety Data Sheets
- 3.3.21 *SRM*, *n*—Single Reaction Monitoring
- 3.3.22 *SS*, *n*—Surrogate Standard
- 3.3.23 *TC*, *n*—Target Compound
- 3.3.24 μM , *n*—micromolar, 1×10^{-6} moles/L
- 3.3.25 *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 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 resulting methyl tert-butyl ether (MTBE) extract is solvent exchanged into methanol, concentrated to a volume of 0.2 mL, brought to a final volume of 1 mL with water and then analyzed by LC/MS/MS operated in the multiple reaction monitoring (MRM) mode.

4.3 The target compound, surrogate and internal standards are identified by retention time and two SRM transitions. The target analyte and surrogate are quantitated using the primary SRM transitions utilizing internal standard calibration. The final report issued for each sample lists the concentration of BPA and the bisphenol A (Ring-13C12) surrogate recovery.

5. Significance and Use

5.1 The first reported synthesis of BPA was by the reaction of phenol with acetone by Zincke.⁴ BPA has become an important high volume industrial chemical used in the manufacture of polycarbonate plastic 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

⁴ Zincke, T., 1905, "Mittheilungen aus dem chemischen Laboratorium der Universitat Marburg," *Justus Leibigs Annals Chemie*, Vol. 343, pages 75–79.

laminates for printed circuit boards, composites, paints, adhesives, dental sealants, protective coatings and many other products.⁵

5.2 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 and will biodegrade. BPA has been reported to have adverse effects in aquatic organisms and may be released into environmental waters directly at trace levels through landfill leachate and POTW effluents. This method has been investigated for use with surface water and secondary and tertiary POTW effluent samples therefore, it is applicable to these matrices only. It has not been investigated for use with salt water or solid sample matrices.

6. Interferences

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other apparatus producing discrete artifacts or elevated baselines. The use of plastic supplies and equipment must be avoided because they may contain BPA. 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 a detergent, rinsed in hot water followed by 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, then methanol. Detergents in plastic containers that contain BPA 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.

7. Apparatus

7.1 *LC/MS/MS System*:

7.1.1 *Liquid Chromatography System*—A complete LC system is needed in order to analyze samples. This should include a sample injection system, a solvent pumping system capable of mixing solvents, a sample compartment capable of maintaining required temperature and a temperature controlled column compartment. A system that is capable of performing at the flows, pressures, controlled temperatures, sample volumes and requirements of the standard may be used.

7.1.1.1 *Columns*—Column to separate instrument background (isolator): A short (2.1 mm × 50 mm) C8 or C18 column stable at higher pH up to 12 and an analytical column.⁶

⁵ Additional information about BPA is available at <http://www.bisphenol-a.org> (2008).

⁶ A Waters ACQUITY UPLC (a trademark of the Waters Corporation, Milford, MA) HSS T3, 1.8 μm , 2.1 mm × 50 mm column was used, if you are aware of an alternative column that meets the performance of the standard, 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.

7.1.1.2 *Tandem Mass Spectrometer (MS/MS) System*—A MS/MS system capable of MRM analysis. A system that is capable of performing at the requirements in this standard may be used.

7.2 *SPE Vacuum Manifold System*—A solid phase extraction vacuum manifold or similar may be utilized.

7.3 Organic solvent evaporation device.

8. Reagents and Materials

8.1 *Purity of Reagents*—High Performance Liquid Chromatography (HPLC) pesticide residue analysis and spectrophotometry grade chemicals must be used in all tests. Unless indicated otherwise, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.⁷ 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

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

8.3 *Gases*—Ultrapure nitrogen and argon.

8.4 Acetonitrile (CAS # 75-05-8).

8.5 Methanol (CAS # 67-56-1).

8.6 2-Propanol (CAS # 67-63-0).

8.7 Acetone (CAS # 67-64-1).

8.8 Methyl tert-butyl ether (MTBE, CAS # 1634-04-4).

8.9 Ammonium Hydroxide (CAS # 1336-21-6) (ACS reagent grade or better).

8.10 Concentrated HCl (CAS # 7647-01-0).

8.11 Bisphenol A (BPA, 2,2'-Bis(4-hydroxyphenyl)propane, CAS # 80-05-7).

8.12 Bisphenol A (Ring-13C12) represents ¹³C labeled bisphenol A where all ring carbon atoms are uniformly labeled ¹³C.

8.12.1 Bisphenol A (Ring-13C12) is used as a surrogate in this standard.

8.13 Bisphenol A (Propane-D6) represents deuterium labeled bisphenol A where the 2 methyl moieties contain all ²H.

8.13.1 Bisphenol A (Propane-D6) is used as an internal standard in this method.

8.14 *Solid Phase Extraction Cartridges*⁹—An SPE cartridge suitable for the extraction of BPA.

NOTE 1—If plastic cartridges are used, BPA may be found, therefore it is advisable that the cartridges be lot certified BPA-free. BPA may adhere to plastic cartridges which will cause lower recoveries. Glass cartridges have a much lower adhesive tendency to BPA and should not contain BPA in the packing or support materials, therefore glass cartridges should be used.

9. Hazards

9.1 Normal laboratory safety applies to this method. Analysts should wear safety glasses, gloves and lab coats when working with acids. Analysts should review the Safety Data Sheets (SDS) for all reagents used in this method.

10. Sample Collection, Preservation, and Storage

10.1 *Sampling*—Grab samples must be collected in amber glass bottles, minimum size of 250 mL. Rinsing of the bottle with 10 % methanol in water, water, and 10 % methanol/2 % NH₄OH in water is required in order to get quantitative transfer of the sample into the SPE cartridge and extraction process. BPA tends to adsorb to surfaces and rinsing will allow optimum recoveries. Conventional sampling practices should be followed. Refer to Guide D3856 and Practices D3694. Pre-cleaned bottles demonstrated to be free of interferences may be used. Automatic sampling equipment should be free from plastics and tubing that contains BPA and other potential sources of contamination or adhesion.

10.2 *Preservation*—Adjust sample to pH 2 with concentrated HCl at time of collection. Store samples between above freezing and 6 °C from the time of collection until extraction. Extract the sample within 7 days of collection and completely analyze within 14 days of extraction.

11. Preparation of LC/MS/MS

11.1 *LC Set Up for Liquid Chromatography BPA Isolator Column for Low Level BPA Analysis*—BPA may be a contaminant in the LC system due to the widespread use of plastic parts and tubing. Incorporating an isolator column into the LC system allows for the low level analysis of BPA and reduces the risk of high biased data. The LC conditions in this standard allow for the BPA in the system to elute 0.4 min later than BPA from the sample injection. The BPA concentration found in the LC system used was below the MDL of the standard but an isolator column must be incorporated to eliminate the risk of high bias. An isolator column was placed after the mixer of two solvent feeds and before the port of the multi-port valve which contains the injection loop. No plastics are used in the system at this point ensuring that the first eluted BPA peak is only from the BPA in the sample and not the LC system. This placement allows for the impurities in the LC, such as BPA, to be trapped by the isolator column and elute after the BPA from the sample.

⁷ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar 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 A source for the labeled BPA standards is Cambridge Isotope Laboratories, 50 Frontage Road, Andover, MA 01810-5413. 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 A Waters Oasis (a trademark of the Waters Corporation, Milford, MA) HLB 5cc (200 mg) LP Glass Cartridges were used, if you are aware of an alternative column that meets the performance of the standard, 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.

Consult with the instrument manufacturer for the proper placement of the isolator column for optimum results.

11.2 *LC Analytical Column*—C18 column or equivalent.

11.3 *LC Operating Conditions*—Injections of all calibration standards and samples are made at a 50 µL volume using a full loop injection. If a 50 µL volume loop is installed in the LC, a “full loop” mode is the preferred technique when performing fast, quantitative analyses. This mode should be used whenever accuracy and precision are the primary concerns. Specific instrument manufacturer specifications should be followed to achieve maximum performance. The first sample analyzed after the calibration curve is a blank to ensure there is no carry-over. The gradient conditions for the liquid chromatograph are shown in [Table 2](#).

11.4 *LC Auto Sampler Conditions*—Wash Solvents: Weak wash is 1.2 mL of 5 % methanol in water. Strong wash is 1 mL of 30 % acetonitrile/30 % methanol/30 % 2-propanol/10 % water. The strong wash solvent is needed to eliminate carry-over between injections. The weak wash is used to remove the strong wash solvent. Specific instrument manufacturer specifications should be followed in order to eliminate sample carry-over in the analysis of BPA. Temperatures: Column 40 °C, Sample compartment 15 °C. Seal Wash: 5 min.

11.5 *Mass Spectrometer Parameters*—The instrument utilized may require different settings. Variable parameters depending on analyte are shown in [Table 3](#).

The instrument is set in the Electrospray source setting.

- Capillary Voltage: 3.5 kV
- Cone: ESI Negative 40 Volts ([Table 3](#))
- Extractor: 3 Volts
- RF Lens: 0.3 Volts
- Source Temperature: 120 °C
- Desolvation Temperature: 400 °C
- Desolvation Gas Flow: 800 L/h
- Cone Gas Flow: 20 L/h
- Low Mass Resolution 1:14
- High Mass Resolution 1:14
- Ion Energy 1:1
- Entrance Energy: –1
- Collision Energy: Variable depending on analyte ([Table 3](#))
- Exit Energy: 0
- Low Mass Resolution 2:14
- High Mass Resolution 2:14
- Ion Energy 2:1
- Multiplier: 650
- Collision Cell Pirani Gauge: 7×10^{-3} Torr
- Analyser Penning Gauge: 3×10^{-5} Torr
- Inter-Channel Delay: 0.02 s
- Inter-Scan Delay: 0.02 s
- Repeats: 1
- Span: 0 Daltons
- Dwell: 0.05 s

11.5.1 In order to acquire the maximum number of data points per MRM channel with optimum sensitivity, the scan, delay and dwell times may be changed and optimized according to the instrument. The SRM chromatograms displayed in [Fig. 1](#) contain 17 data points across the peak at the reporting limit. Each peak requires at least 10 scans per peak for adequate quantitation. This standard contains only one target compound, one surrogate and one internal standard which are in one MRM experiment window. For details regarding retention times and SRM transitions cone and collision energies, refer to [Table 3](#).

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 described below must be followed when performing the test method.

12.2 *Calibration and Standardization*—To calibrate the instrument, analyze eight calibration standards containing the eight concentration levels of BPA and BPA (Ring-13C12) surrogate with a constant concentration of BPA (Propane-D6) Internal Standard prior to analysis as shown in [Table 4](#). A calibration stock standard solution is prepared from standard materials or purchased as certified solutions. Stock Standard Solution A (Level 8) containing BPA and BPA (Ring-13C12) is prepared at Level 8 concentration and aliquots of that solution are diluted to prepare Levels 1 through 7. Stock Internal Standard Solution B is made at a concentration of 7.5 ppm bisphenol A (Propane-D6) in methanol. The following steps will produce standards with the concentrations values shown in [Table 4](#). The analyst is responsible for recording initial component weights carefully when working with the pure materials, and correctly carrying the weights through the dilution calculations.

12.2.1 Prepare Stock Standard Solution A (Level 8) by adding to a 25 mL volumetric flask individual solutions of the following: 37.5 µL of 100 ppm BPA in methanol and 37.5 µL of 100 ppm BPA (Ring-13C12) in acetonitrile then dilute to 25 mL with 90 % water/10 % methanol to ensure the BPA remains in solution and does not adhere to the walls of the flask. The 100 ppm BPA stock solution is made in methanol to ensure solubility. The 100 ppm BPA (Ring-13C12) in acetonitrile is purchased. The preparation of the Level 8 standard can be accomplished using different volumes and concentrations of stock solutions as is accustomed in the individual laboratory.

TABLE 2 Gradient Conditions for Liquid Chromatography

Time (Minutes)	Flow (µL/Minute)	Percent Water/5 mmolar NH ₄ OH	Percent Methanol/5 mmolar NH ₄ OH
0	300	100	0
1	300	100	0
2	250	75	25
5	250	25	75
6	250	25	75
7	300	0	100
9	300	0	100
10	300	100	0
12	300	100	0

TABLE 3 Retention Times, SRM transitions, SRM Ratios and Analyte-Specific Mass Spectrometer Parameters

Analyte	Primary/Confirmatory	Retention time (min)	Cone Voltage (Volts)	Collision Energy (eV)	SRM Mass transition (Parent > Product)	Primary/Confirmatory SRM Area Ratio
Bisphenol A	Primary Confirmatory	5.9	-40 -40	19 25	227 > 211.9 227 > 132.8	2.97
Bisphenol A (Ring-13C12) Surrogate	Primary Confirmatory	5.9	-40 -40	19 25	239 > 224 239 > 138.8	3.02
Bisphenol A (Propane-D6) Internal Standard	Primary Confirmatory	5.9	-40 -40	19 25	233 > 214.9 233 > 137.7	3.31

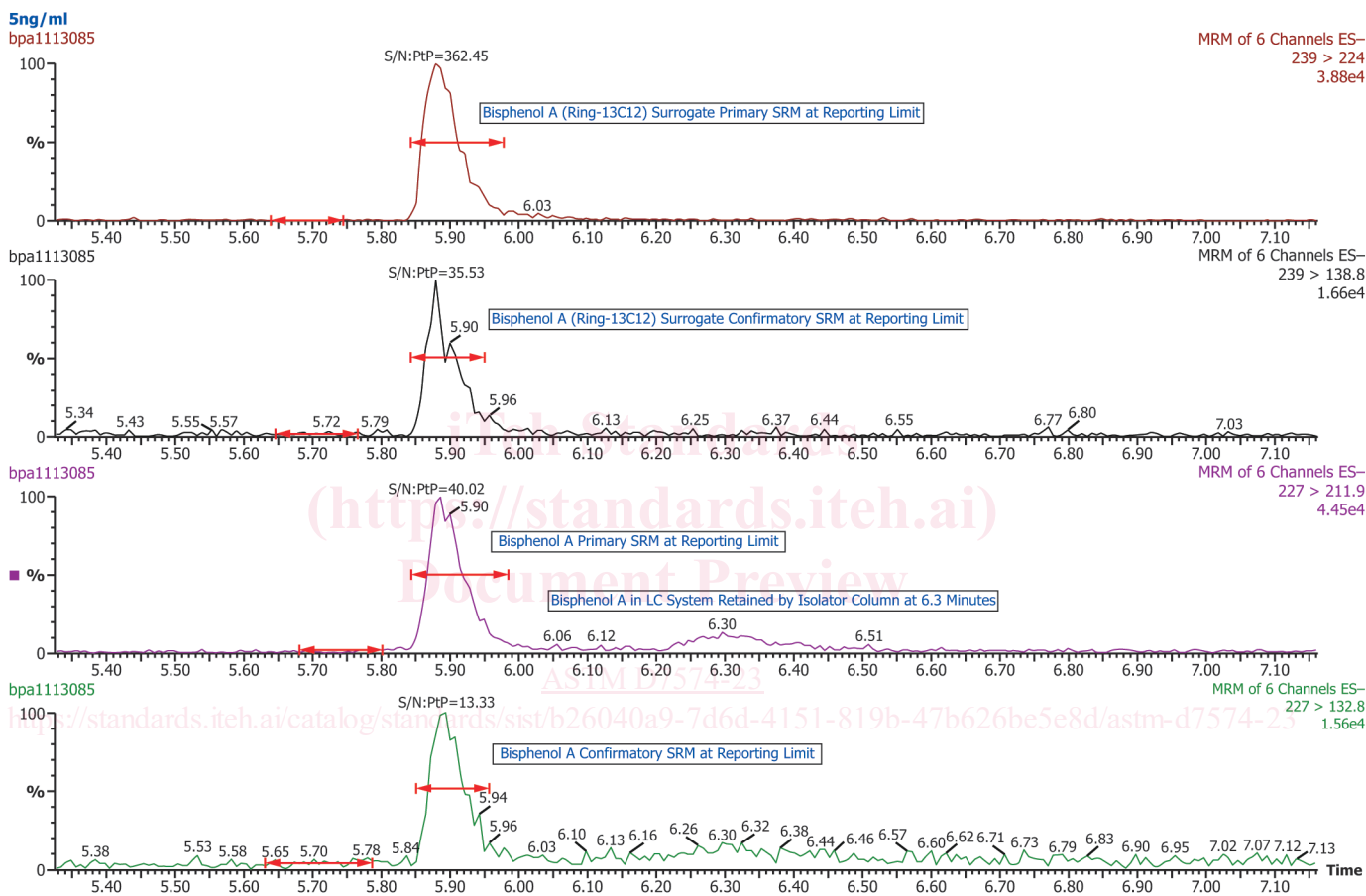


FIG. 1 Example SRM Chromatograms Signal/Noise at Reporting Limit

TABLE 4 Concentrations of Calibration Standards (ppb)

Analyte/ Surrogate/ Internal Standard	LV 1	LV 2	LV 3	LV 4	LV 5	LV 6	LV 7	LV 8
BPA	5	10	25	50	75	100	125	150
BPA (Ring-13C12)	5	10	25	50	75	100	125	150
Surrogate BPA (Propane-D6)	75	75	75	75	75	75	75	75
Internal Standard								

Depending on the stock concentrations prepared, the solubility at that concentration will have to be ensured.

12.2.2 Aliquots of Stock Standard Solution A and Stock Internal Standard Solution B are then diluted with 90 % water/10 % methanol to prepare the desired calibration levels in 2 mL amber LC vials. The calibration vials must be used within 24 h to ensure optimum results. Stock calibration standards are routinely replaced every six months if not previously discarded for QC criteria failure.

12.2.3 Inject each standard and obtain a chromatogram for each one. An internal standard calibration technique is used monitoring the primary and confirmatory SRM transition of each analyte. Calibration software is utilized to conduct the quantitation of the target analyte and surrogate using the primary SRM transition. The ratio of the primary/confirmatory SRM transition area counts are given in Table 3. These are given as informative and will vary depending on the individual

tuning conditions. The primary/confirmatory SRM transition area ratio must be within 30 % of the individual labs accepted primary/confirmatory SRM transition area ratio. The primary SRM transition of each analyte is used for quantitation and the confirmatory SRM transition for confirmation. This gives added confirmation by isolating the parent ion, fragmenting it into two product ion fragments, and relating it to the retention time in the calibration standard.

12.2.3.1 Many laboratories may not have tandem mass spectrometry (MS/MS) capability. A single quadrupole mass spectrometer (MS) or time-of-flight mass spectrometer (TOF-MS) may be used if it is capable of meeting or exceeding the performance criteria in the standard. A mass spectrometer operated in the selected ion monitoring (SIM) mode may be able to meet the method detection limit in this standard. However, the laboratory is responsible to generate the optimum MS conditions for the parent and confirmatory ions as well as their ion area ratio acceptance criteria which must meet or exceed the criteria in this standard.

12.2.4 The calibration software manual should be consulted to use the software correctly. The quantitation method is set as an internal standard calibration using the peak areas in ppt, ppb or ppm units as long as the analyst is consistent. Concentrations may be calculated using the data system software to generate linear regression or quadratic calibration curves. Forcing the calibration curve through the origin is not recom-

mended. Curves should be evaluated using relative error or relative standard error.¹⁰

12.2.5 An internal standard is used to account for experimental drift in the standard due to matrix interferences that result in ion enhancement or suppression. BPA (Propane-D6) internal standard is added to all calibration standards and sample extracts to obtain a concentration of 75 ppb. A calibration curve is generated using the Response of Analyte verses the known concentrations as shown in Fig. 2. The response of the analyte is calculated using Eq 1.

$$Response\ of\ Analyte = \frac{(Peak\ area\ of\ Analyte)}{\left(\frac{Peak\ Area\ of\ Internal\ Standard}{Concentration\ of\ Internal\ Standard}\right)} \quad (1)$$

12.2.6 Linear calibration may be used if the point of origin is excluded and a fit weighting of 1/X is used in order to give more emphasis to the lower concentrations. Each calibration point used to generate the curve must have a calculated percent deviation less than ±25 % from the generated curve.

12.2.7 Quadratic calibration may be used if the point of origin is excluded and a fit weighting of 1/X is used in order to

¹⁰ Management and Technical Requirements for Laboratories Performing Environmental Analysis; Module 4: Quality Systems for Chemical Testing; The NELAC Institute, 2017.

Compound name: BPA
 Coefficient of Determination: R² = 0.999725
 Calibration curve: -0.000461076 * x² + 1.09371 * x + -0.00350138
 Response type: Internal Std (Ref 5), Area * (IS Conc./IS Area)
 Curve type: 2nd Order, Origin: Exclude, Weighting: 1/x, Axis trans: None

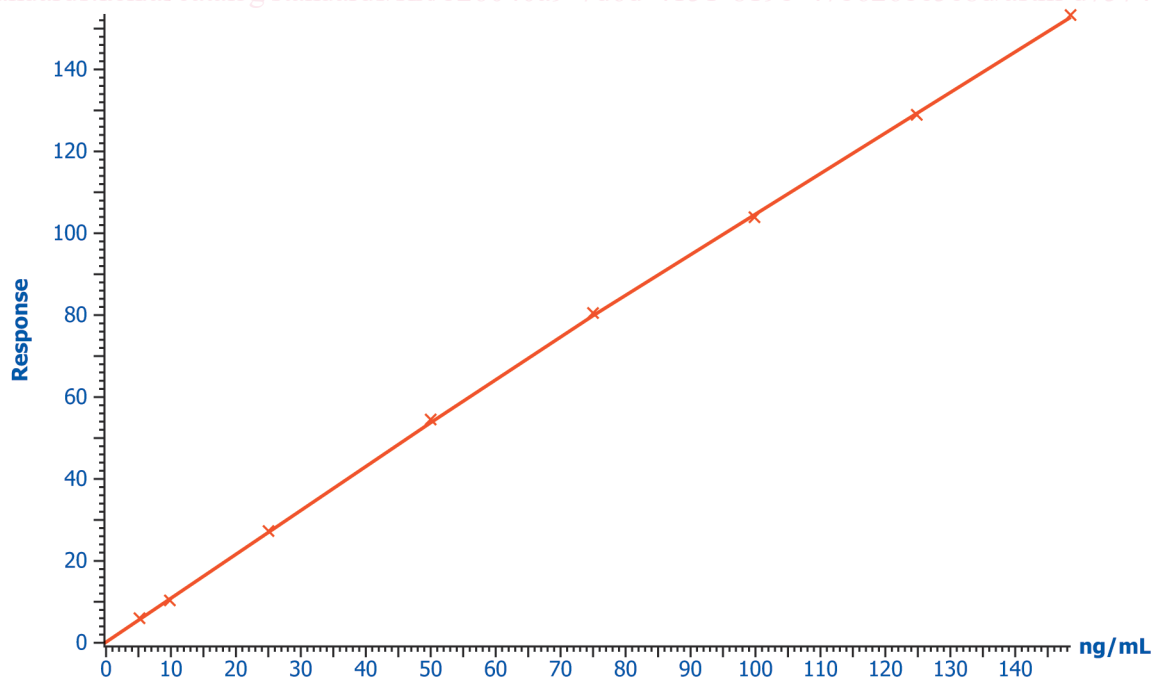


FIG. 2 Example Calibration Curve for BPA

give more emphasis to the lower concentrations. Each calibration point used to generate the curve must have a calculated percent deviation less than ±25 % from the generated curve.

12.2.8 The retention time window of the MRM transitions must be within 5 % of the retention time of the analyte in a midpoint calibration standard. If this is not the case, re-analyze the calibration curve to determine if there was a shift in retention time during the analysis and the sample needs to be re-injected. If the retention time is still incorrect in the sample, refer to the analyte as an unknown.

12.3 A mid-level calibration check is required at the end of each batch of 20 samples or less and must be within ±25 % of the calculated concentration. Based upon the 8-point calibration curve from 5 ppb to 150 ppb in Table 4, this mid-level check should be at 75 ppb. The same 75 ppb standard that was used to generate the calibration curve should be used as the calibration check. Instrument stability may be verified by comparing the midpoint of the calibration standard before and after the batch. If the mid-level calibration check does not meet the acceptance criteria, instrument maintenance must be performed such as cleaning the probe and sample cone(s). A new calibration curve will need to be generated as described in 12.2 before samples can be analyzed.

12.4 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., perform a precision and bias study to demonstrate laboratory capability.

12.4.1 Analyze at least four replicates of a sample solution containing BPA and bisphenol A (Ring-13C12) surrogate at a concentration near the midpoint of the calibration curve. The matrix and chemistry of the solution should be similar to the solution used in this test method. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

12.4.2 Calculate the mean (average) percent recovery and relative standard deviation (RSD) of the four values and compare to the acceptable ranges of quality control (QC) acceptance criteria for the initial demonstration of performance in Table 5.

12.4.3 This study should be repeated until the single operator precision and mean recovery are within the limits in Table 5. If a concentration other than the recommended concentration is used, refer to Test Method D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

12.5 Laboratory Control Sample (LCS):

12.5.1 To ensure that the test method is in control, analyze a LCS prepared with BPA at a concentration near the midpoint

of the calibration curve. The LCS is prepared following the analytical method and analyzed with each batch of 20 samples or less. Prepare a stock matrix spiking solution in methanol containing BPA at 1.0 ppm. Spike 75 µL of this stock matrix solution into 250 mL of water to yield a concentration of 300 ppt of BPA in the sample. The result obtained for the LCS must fall within the limits in Table 5.

12.5.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all samples in the batch must be re-analyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

12.6 Method Blank:

12.6.1 Analyze a reagent water blank with each batch of 20 or fewer samples. The concentration of BPA found in the blank must be below the detection limit or significantly below the confidence limits of the known concentration of the analyte in the associated test sample. If the concentration of BPA is found above this level, analysis of samples is halted until the contamination is eliminated and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

12.7 Matrix Spike (MS):

12.7.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch of 20 or fewer samples by spiking the sample with a known concentration of BPA and following the analytical method. Prepare a stock matrix spiking solution in methanol containing BPA at 1.0 ppm. Spike 75 µL of this stock matrix spiking solution into 250 mL of water to yield a concentration of 300 ppt for BPA in the sample.

12.7.2 If the spiked concentration plus the background concentration exceeds that of the Level 8 calibration standard, the sample must be diluted to a level near the midpoint of the calibration curve.

12.7.3 Calculate the percent recovery of the spike (P) using Eq 2:

$$P = 100 \frac{|A(V_s + V) - BV_s|}{CV} \quad (2)$$

where:

- A = concentration found in spiked sample,
- B = concentration found in unspiked sample,
- C = concentration of analyte in spiking solution,
- V_s = volume of sample used,
- V = volume of spiking solution added, and
- P = percent recovery.

TABLE 5 QC Acceptance Criteria

Analyte	Test Conc. (ng/L)	Initial Demonstration of Performance			Lab Control Sample		MS/MSD		
		Recovery (%)		Precision	Recovery (%)		Recovery (%)		Precision
		Lower Limit	Upper Limit	Maximum % RSD	Lower Limit	Upper Limit	Lower Limit	Upper Limit	Maximum % RSD
Bisphenol A	300	43	120	20	40	120	40	120	25
Bisphenol A (Ring-13C12) Surrogate	300	45	120	16	42	120	40	120	27