Designation: ~~D8024 – 16~~ D8024 – 23

Standard Test Method for Determination of (Tri-n-butyl)-n-tetradecylphosphonium chloride (TTPC) in Water by Multiple Reaction Monitoring Liquid Chromatography/Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation D8024; 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 (Tri-n-butyl)-n-tetradecylphosphonium chloride (TTPC) in water by dilution with acetone, filtration and analysis by liquid chromatography/tandem mass spectrometry. This test method is not amenable for the analysis of isomeric mixtures of Tributyl-tetradecylphosphonium chloride. TTPC is a biocide that strongly adsorbs to soils.[2] The water samples are prepared in a solution of 75 % acetone and 25 % water because TTPC has an affinity for surfaces and particles. The reporting range for this method is from ~~100–4000~~100 ng ~~ng/L./~~L to 4000 ng ~~/~~L. This analyte is qualitatively and quantitatively determined by this method. This test method adheres to multiple reaction monitoring (MRM) mass spectrometry.

1.2 A full collaborative study to meet the requirements of Practice D2777 has not been completed. This test method contains single-operator precision and bias based on single-operator data. Publication of standards that have not been fully validated is done to make the current technology accessible to users of standards, and to solicit additional input from the user community.

1.3 The Method Detection Limit[3] (MDL) and Reporting Range[4] for the target analyte are listed in Table 1.

1.3.1 The reporting limit in this test method is the minimum value below which data are documented as non-detects. Analyte detections between the method detection limit and the reporting limit are estimated concentrations and are not reported following this test method. The reporting limit is calculated from the concentration of the Level 1 calibration standard as shown in Table 4 for TTPC after taking into account a 2.5 mL water sample volume and a final diluted sample volume of 10 mL (75 % acetone/25 % water). The final solution volume is 10 mL because a 7.5 mL volume of acetone is added to each 2.5 mL water sample which is shaken and filtered.

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

1.5 *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] 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] More information on TTPC can be found at http://www.buruenergy.com/wp-content/uploads/BE-Environmental-Properties-of-Proposed-Biocide-BE-91.pdf (2014) and http://iaspub.epa.gov/sor_internet/registry/substreg/searchandretrieve/advancedsearch/externalSearch.do?p_type=CASNO&p=81741-28-8 (2014).

[3] The MDL is determined following the Code of Federal Regulations, 40 CFR Part 136, Appendix B, as a guide. A detailed process determining the MDL is explained in the reference and is beyond the scope of this test method to be explained here.

[4] Reporting range concentration is calculated from Table 4 concentrations assuming a 50 µL injection of the Level 1 calibration standard for TTPC, and the highest level calibration standard with a 10 mL final diluted sample volume starting with a 2.5 mL water sample. Volume variations will change the reporting limit and ranges.

TABLE 1 Method Detection Limit and Reporting Range

Analyte	MDL (ng/L)	Reporting Range (ng/L)
TTPC	13	100–4000

1.6 *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:*[5]

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
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E2554 Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques

2.2 *Other Standards:*

40 CFR Part 136, Appendix B Definition and Procedure for the Determination of the Method Detection Limit[6]
EPA Publication SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods[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 *reporting limit, RL, n*—the minimum concentration below which data are documented as non-detects.

3.2.2 *reporting limit check sample, RLCS, n*—a sample used to ensure that if the analyte was present at the reporting limit, it would be confidently identified.

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

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.

3.2.4.1 *Discussion*—

The IRM ~~shall~~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 *CRW, n*—Chicago River Water

3.3.3 *IC, n*—Initial Calibration

3.3.4 *LC, n*—Liquid Chromatography

[5] 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.

[6] Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, http://www.access.gpo.gov.

[7] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

TABLE 2 Gradient Conditions for Liquid Chromatography

Time (min)	Flow (mL/min)	Percent 95 % Water: 5 % Acetonitrile	Percent Acetonitrile	Percent 400 mM Ammonium Acetate (95 % Water: 5 % Acetonitrile)
0	0.3	95	0	5
1	0.3	95	0	5
4	0.4	0	95	5
11	0.4	0	95	5
12	0.4	95	0	5
15	0.4	95	0	5

TABLE 3 Retention Time, SRM Ions, and Analyte-Specific Mass Spectrometer Parameters

Chemical	Primary/ Confirmatory	SRM Transition	Cone (V)	Collision (eV)	Retention Time (minutes)	Primary/ Confirmatory SRM Area Ratio
TTPC	Primary (Quantitation)	399.5→229.3	40	45	8.1	NA
	First Confirmatory	399.5→75.9	40	46		0.92
	Second Confirmatory	399.5→343.5	40	10		3.02

TABLE 4 Concentrations of Calibration Standards (ng/L)

Concentrations (ng/L)	LV1	LV2	LV3	LV4	LV5	LV6	LV7	LV8
TTPC	25	50	100	200	400	600	800	1000

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

3.3.6 *MDL, n*—Method Detection Limit

3.3.7 *MeOH, n*—Methanol

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

3.3.9 *MRM, n*—Multiple Reaction Monitoring

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

3.3.11 *NA, adj*—Not Available

3.3.12 *ND, n*—non-detect

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

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 *RLCS, n*—Reporting Limit Check Sample

3.3.19 *RSD, n*—Relative Standard Deviation

3.3.20 *RT, n*—Retention Time

3.3.21 *SDS, n*—Safety Data Sheets

3.3.22 *SRM, n*—Single Reaction Monitoring

3.3.23 *SS, n*—Surrogate Standard

3.3.24 *TC, n*—Target Compound

3.3.25 *TTPBr, n*—(Tri-n-butyl)-n-tetradecylphosphonium bromide

3.3.26 *TTPC, n*—(Tri-n-butyl)-n-tetradecylphosphonium chloride

3.3.27 *VOA, n*—Volatile Organic Analysis

4. Summary of Test Method

4.1 The operating conditions presented in this test method have been successfully used in the determination of TTPC in water; however, this test method is intended to be performance based and alternative operating conditions can be used to perform this method provided data quality objectives are attained.

4.2 For TTPC analysis, samples are shipped to the lab on ice and analyzed within 14 days of collection. A sample (2.5 mL) is transferred to a VOA vial, a TTPC spike solution is added to Laboratory Control and Matrix Spike samples before the addition of acetone. An isotopically labeled TTPC surrogate would be added at this point. An isotopically labeled TTPBr-D29 surrogate is now available and should be incorporated into this method by the user if requested by the customer.[8] 7.5 mL of acetone is them added and the solution is mixed by hand or vortex for ~~1 minute.~~ 1 min. The samples are then filtered through a Nylon membrane syringe driven filter unit[9] and then analyzed by LC/MS/MS. All concentrations reported only to the reporting limit.

4.3 TTPC is identified by comparing the single reaction monitoring (SRM) transition and its confirmatory SRM transitions if correlated to the known standard SRM transition (Table 3) and quantitated utilizing an external calibration. The final report issued for each sample lists the concentration of TTPC, if detected, or RL, if not detected, in ng/L and surrogate recovery, if available.

5. Significance and Use

5.1 TTPC may be used in various industrial and commercial products for use as a biocide. Products containing TTPC have been approved for controlling algal, bacterial, and fungal slimes in industrial water systems.[2] TTPC should not be persistent in water

TABLE 5 Preparation of Calibration Standards

Solution	LV1	LV2	LV3	LV4	LV5	LV6	LV7	LV8
A[A]	25 µL	50 µL	100 µL	200 µL	400 µL	600 µL	800 µL	1000 µL
B[B]	975 µL	950 µL	900 µL	800 µL	600 µL	400 µL	200 µL	0 µL

[A] Solution A: Level 8 stock solution prepared according to Section 12 and at Table 4 concentrations.
[B] Solution B: 75 % Acetone, 25 % Water.

[8] A surrogate, TTPBr-D29, was custom synthesized by Cambridge Isotope Laboratories Inc., Andover, MA 01810 and was found to be acceptable. Any commercial source of TTPBr-D29 surrogate may be used, SRM transition 428.6 > 372.5 was used. If you are aware of an alternative source 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.

[9] A Whatman Puradisc (a trademark of Whatman International Limited of Maidstone, Kent) 25 NYL Disposable Filter unit (Diameter 25 mm, 0.2 µm Nylon membrane syringe driven filter unit has been found suitable for use for this method, any filter unit may be used that meets the performance of this method may be used. If you are aware of an alternative filter 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.

but may be deposited in sediments at concentrations of concern. Hence, there is a need for quick, easy and robust method to determine TTPC concentration at trace levels in water matrices for understanding the sources and concentration levels in affected areas.

5.2 This method has been used to determine TTPC in reagent water and a river water (Table 8).

NOTE 1—This test method has been used to characterize TTPC in real world water samples with success and similar recoveries as shown in Table 8.

6. Interferences

6.1 All glassware is washed in hot water with detergent and rinsed in hot water followed by distilled water. The glassware is then dried and heated in an oven at ~~250°C for 15 to 30 minutes.~~ 250 °C for 15 min to 30 min. All glassware is subsequently rinsed ~~and/or sonicated with acetone, n-propanol and/or acetonitrile.~~or sonicated, or both, with acetone, n-propanol, or acetonitrile, or combinations thereof.

6.2 TTPC should not be a common contaminant found in a laboratory, unless involved in the analysis or matrices that contain TTPC. TTPC has been found to continue to adhere to glassware and syringes after routine glassware washing. Rinsing glassware with acetone, ~~n-propanol and/or~~n-propanol, or acetonitrile, or combinations thereof, or even sonication, may be required to remove TTPC. All of the materials and supplies are routinely demonstrated to be free from interferences of TTPC by analyzing laboratory blanks under the same conditions as the samples. If found, measures should be taken to remove the contamination or data should be qualified, background subtraction of blank contamination is not allowed.

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

6.4 Matrix interferences may be caused by contaminants in the sample. The extent of matrix interferences can vary considerably depending on variations in the sample matrices.

6.5 Automatic pipettes with polypropylene tips were used to prepare the standards, spiking, and calibration solutions. The use of glass syringes for preparing standards, spiking, and calibration solutions generated erratic results; glass syringes should be avoided for these critical tasks. A thoroughly cleaned ~~10~~10 mL or 20 mL hypodermic glass syringe with a nylon filter was found to perform well to filter the 10 mL prepared sample. ~~20 mL~~ 20 mL Luer-Lock polypropylene syringes have also been shown to meet the performance of this test method; these are disposable and do not require cleaning before use. It seems when preparing small volumes of solutions, concentrations are affected by adhesion of TTPC to the syringe barrel or plunger.

TABLE 6 QC Acceptance Criteria

NOTE 1—Table 6 data is preliminary until a multi-lab validation study is completed.

Analyte	Spike Conc. ng/L	Initial Demonstration of Performance			Laboratory Control Sample	
		Recovery (%)		Precision	Recovery (%)	
		Lower Limit	Upper Limit	Maximum % RSD	Lower Control Limit (LCL) %	Upper Control Limit (UCL) %
TTPC	2000	70	130	30	70	130

TABLE 7 MS/MSD QC Acceptance Criteria

NOTE 1—Table 7 data is preliminary until a multi-lab validation study is completed.

Analyte	Spike Conc. ng/L	MS/MSD		Precision
		Recovery (%)		RPD (%)
		Lower Limit	Upper Limit	
TTPC	2000	70	130	30

TABLE 8 Single-Laboratory Recovery Data in Water

Sample	Reagent Water P&A Data (2000 ng/L spike)	CRW P&A Data (2000 ng/L spike)
	TTPC	TTPC
MB 1	<RL	<RL
MB 2	<RL	<RL
P&A 1	1861	1898
P&A 2	1891	1965
P&A 3	1882	1933
P&A 4	1894	1871
P&A 5	1975	1929
P&A 6	1975	1974
Average Recovery (ng/L)	1893	1928
% Average Recovery	94.6	96.4
Standard Deviation	42.8	39.1
RSD (%)	2.26	2.03

NOTE 2—The use of PTFE, PVDF and polypropylene filter units resulted in poor performance and low recoveries.

7. Apparatus

7.1 *LC/MS/MS System:*

7.1.1 *Liquid Chromatography ~~System~~System*—~~—~~A complete LC system is required 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 LC system that is capable of performing at the flows, pressures, controlled temperatures, sample volumes, and requirements of this test method ~~shall~~must be used.

7.1.2 *Analytical Column*[10]—A reverse phase C18 particle column was used to develop this test method. Any column that achieves adequate resolution may be used. The retention times and order of elution may change depending on the column used and need to be monitored.

7.2 *Tandem Mass Spectrometer ~~System~~System*—~~—~~A MS/MS system capable of multiple reaction monitoring (MRM) analysis or any system that is capable of meeting the requirements in this test method ~~shall~~must be used.

7.3 *Adjustable Volume Pipettes*—~~10, 20, 100, and 1000 µL and 5 and 10 mL.~~10 µL, 20 µL, 100 µL, 1000 µL, 5 mL, and 10 mL.

NOTE 3—Any pipette may be used providing the data generated meets the performance of this test method.

7.3.1 *Pipette Tips*—Polypropylene pipette tips free of release agents or low retention coating of various sizes.

7.4 *Class A Volumetric Glassware.*

7.5 *Filtration Device.*

[10] A Waters Acquity UPLC BEH C18, ~~2.1~~2.1 mm × 100 mm and 1.7 µm particle size ~~column, or equivalent, has been found suitable for use. It was used to develop this test method and generate the precision and bias~~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] ~~data presented in Section~~ which you may attend.~~16~~.

7.5.1 *Hypodermic Syringe*—A Luer-Lock tip glass or polypropylene syringe capable of holding a syringe driven filter unit.

7.5.2 A ~~10~~10 mL or 20 mL Lock Tip Syringe size is recommended since a 10 mL prepared sample size is used in this test method. If a smaller volume syringe is used, do not wash out the syringe or change filters while filtering the same sample if multiple refills of the syringe is required in order to filter the ~~10 mL~~ 10 mL prepared sample.

7.5.3 *Filter Unit*[11]—Nylon filter units were used to filter the samples.

7.6 *Vials*—2-mL autosampler vials (LC vials) with pre-slit PTFE/silicone septa or equivalent.

7.7 *VOA Vials*—40 mL.

7.8 *Sonicator.*

7.9 *Oven,* capable to achieve ~~250°C.~~250 °C.

8. Reagents and Materials

8.1 *Purity of Reagents*—High Performance Liquid Chromatography (HPLC) pesticide residue analysis and spectrophotometry grade chemicals ~~shall~~must be used in all tests. Unless indicated otherwise, it is intended that all reagents ~~shall~~must conform to the Committee on Analytical Reagents of the American Chemical Society.[12] Other reagent grades may be used provided they are first determined to be of sufficiently high purity to permit their use without affecting the accuracy of the measurements.

8.2 *Purity of Water*—Unless otherwise indicated, references to water ~~shall~~must be understood to mean reagent water conforming to Type 1 of Specification D1193. It ~~shall~~must be demonstrated that this water does not contain contaminants at concentrations sufficient to interfere with the analysis.

8.3 All prepared solutions are routinely replaced every year if not previously discarded for quality control failure.

8.4 *Gases*—Ultrapure nitrogen and argon.

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

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

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

8.8 Ammonium Acetate (CAS # 631-61-8).

8.9 2-Propanol (isopropyl alcohol, CAS # 67-63-0).

8.10 Ottawa Sand (CAS # 14808-60-7).

8.11 (Tri-n-butyl)-n-tetradecylphosphonium chloride (CAS # 81741-28-8).

8.12 (Tri-n-butyl)-n-tetradecylphosphonium bromide –D29 (TTPBr-D29, CAS # NA, optional surrogate).

[11] A Whatman Puradisc 25 NYL Disposable Filter unit (diameter 25 mm, 0.2 µm nylon membrane syringe driven filter unit) ~~has been found suitable for use for this method. Any filter unit may be used~~ was used. If you are aware of an alternative filter that meets the performance of ~~this method.~~ 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.

[12] ~~*Reagent Chemicals, American Chemical Society Specifications,*~~*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.