Designation: D8018 – 15

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

This standard is issued under the fixed designation D8018; 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 procedure covers the determination of (Tri-n-butyl)-n-tetradecylphosphonium chloride (TTPC) in a soil matrix by extraction with acetone, filtration, dilution with water, and analysis by liquid chromatography/tandem mass spectrometry. TTPC is a biocide that strongly adsorbs to soils.[2] The sample extracts 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 250 to 10 000 ng/kg. This analyte is qualitatively and quantitatively determine by this method. This method adheres to multiple reaction monitoring (MRM) mass spectrometry.

1.2 The Method Detection Limit (Note 1) (MDL) and Reporting Range (Note 2) for the target analyte are listed in Table 1.

NOTE 1—The MDL is determined following the Code of Federal Regulations, 40 CFR Part 136, Appendix B, as a guide utilizing solvent extraction of soil. Two-gram sample of Ottawa Sand was utilized. A detailed process determining the MDL is explained in the reference and is beyond the scope of this standard to be explained here.

NOTE 2—Reporting range concentration is calculated from Table 2 concentrations assuming a 50 µL injection of the Level 1 calibration standard for TTPC, and the highest level calibration standard with a 20 mL final extract volume of a 2 g soil sample. Volume variations will change the reporting limit and ranges.

1.2.1 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 2 for TTPC after taking into account a 2 g sample weight and a final extract volume of 20 mL in 75 % acetone/25 % water. The final extract volume is 20 mL because a 15 mL volume of acetone is added to each soil sample and only the liquid layer after extraction is filtered leaving the solid behind followed by the addition of 5 mL of water to the acetone extract.

1.3 *Units*—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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1193 Specification for Reagent Water

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D5681 Terminology for Waste and Waste Management

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 Documents:*[4]

EPA Publication SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods

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

3. Terminology

3.1 For determinations of terms used in this standard, refer to Terminology D5681.

[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] 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] 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.

[4] Available from National Technical Information Service (NTIS), 5301 Shawnee Rd., Alexandria, VA 22312, http://www.ntis.gov or at http://www.epa.gov/epawaste/hazard/testmethods/index.htm.

TABLE 1 Method Detection Limit and Reporting Range[A]

Analyte	MDL (ng/kg)	Reporting Range (ng/kg)
TTPC	32.7	250–10 000

[A]Acronyms are defined in 3.3.

3.2 *Definitions of Terms Specific to This Standard:*

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

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

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 *P&A*—Precision and Accuracy

3.3.13 *PPT, n*—parts-per-trillion

3.3.14 *QA, adj*—Quality Assurance

3.3.15 *QC, adj*—Quality Control

3.3.16 *RL, n*—Reporting Limit

3.3.17 *RLCS, n*—Reporting Limit Check Sample

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

3.3.25 *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 soil; 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. Mention of trade names or suppliers is not an endorsement of use, it is provided for informational purposes only. Any apparatus, supply, standard, or reagent may be used provided that it is shown to be acceptable to meet the performance criteria of the method.

4.2 For TTPC analysis, samples are shipped to the lab on ice and analyzed within 14 days of collection. A sample (~2 g) 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 could be added at this point, presently requires a custom synthesis and should be incorporated into this method by the user if requested by the customer.[5] Then add 15 mL of acetone and hand shake or vortex for one minute. The samples are allowed to settle, and are then filtered through a Nylon membrane syringe driven filter unit[6] leaving the solids behind, 5 mL of ASTM Type 1 water is added to the filtered extract and then analyzed by LC/MS/MS. All concentrations reported, only to the reporting limit, using this method are based upon a dry weight basis.

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/kg (Dry Weight Basis) and surrogate recovery, if available.

5. Significance and Use

5.1 This test method has been developed by the US EPA Region 5 Chicago Regional Laboratory (CRL).

5.2 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 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 various soil matrices for understanding the sources and concentration levels in affected soils and sediments.

5.3 This method has been used to determine TTPC in sand, a commercial top soil and four ASTM reference soils (Table 4).

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. All glassware is subsequently rinsed 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

[5] A custom synthesized surrogate, TTPC (D29), may be an inexpensive viable surrogate.

[6] 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 that meets the performance of this method may be used. The use of PTFE, PVDF, and polypropylene filter units resulted in poor performance.

TABLE 2 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

TABLE 3 Retention Times, 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	40		3.02

TABLE 4 Single-Laboratory Recovery Data in Six Soil Types

Sample	Ottawa Sand (2500 ng/kg spike)	ASTM Frederick Sand (2500 ng/kg spike)	ASTM Silt (2500 ng/kg spike)
MB 1	<RL	<RL	<RL
MB 2	<RL	<RL	<RL
P&A 1	2074.5	2121.4	1477.8
P&A 2	2244.6	2145.9	1482.3
P&A 3	2286.4	2171.3	1364.2
P&A 4	2077.8	2215.4	1543.9
P&A 5	2192.1	2038.5	1545.7
P&A 6	1953.1	2079.2	1462.1
Average Recovery (ng/kg)	2138.1	2128.6	1479.3
% Average Recovery	85.5	85.1	59.2
Standard Deviation	125.0	63.7	66.5
RSD (%)	5.8	3.0	4.5
Sample	**ASTM Lean Clay (2500 ng/kg spike)**	**ASTM Fat Clay (2500 ng/kg spike)**	**Top Soil (2500 ng/kg spike)**
MB 1	<RL	<RL	<RL
MB 2	<RL	<RL	<RL
P&A 1	394.6	790.2	1764.4
P&A 2	986.4	783.2	1750.1
P&A 3	386.4	772.4	1758.9
P&A 4	392.4	774.9	1771.6
P&A 5	435.3	791.7	1659.6
P&A 6	375.5	751.7	1778.3
Average Recover (ng/kg)	395.1	777.4	1747.2
% Average Recovery	15.8	31.1	69.9
Standard Deviation	20.8	14.8	44.0
RSD (%)	5.3	1.9	2.5

contain TTPC. TTPC has been found to continue to adhere to glassware and syringes after routine glassware washing. Rinsing glassware with acetone, n-propanol, or acetonitrile, or both, or even sonication, may be required to remove TTPC. All of the materials and supplies are routinely demonstrated to be free from interferences and 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 are used with this method. The use of glass syringes for standards preparation, spiking and calibrations generated erratic results and should be avoided. A thoroughly cleaned 20 mL hypodermic glass syringe with a nylon filter is used to filter the 20 mL sample extracts and has been shown to perform well when filtering these large volumes. Preparing small volumes of samples and standards, like 1 mL calibration standards, may be affected by adhesion of TTPC to the syringe barrel or plunger. The use of PTFE, PVDF, and polypropylene filter units resulted in poor performance and low recoveries.

NOTE 3—The use of polypropylene disposable syringes to filter samples and polypropylene LC vials with polyethylene caps have been shown to perform in the performance criteria of the method and may be used.

7. Apparatus

7.1 *LC/MS/MS System:*

7.1.1 *Liquid Chromatography System*[7]—A complete LC system is required in order to analyze samples, this should include a sample injection system, a solvent pumping system

[7] A Waters Acquity UPLC H-Class System, or equivalent, has been found suitable for use.

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 the standard shall be used.

7.1.2 *Analytical Column*[8]—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*[9]—A MS/MS system capable of multiple reaction monitoring (MRM) analysis or any system that is capable of meeting the requirements in this standard shall be used.

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

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:*

7.5.1 *Hypodermic Syringe*—A luer-lock tip glass syringe capable of holding a syringe driven filter unit.

7.5.2 A 20 mL Lock Tip Glass Syringe size is recommended since a 20 mL sample size is used in this test method.

7.5.3 *Filter Unit*[10]—Nylon filter units were used to filter the samples.

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

7.7 *VOA Vials*—40 mL.

8. Reagents and Materials

8.1 *Purity of Reagents*—High Performance Liquid Chromatography (HPLC) pesticide residue analysis and spectrophotometry grade chemicals shall be used in all tests. Unless indicated otherwise, it is intended that all reagents shall conform to the Committee on Analytical Reagents of the American Chemical Society.[11] 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 be understood to mean reagent water conforming to Type 1 of Specification D1193. It shall 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 Acetone (CAS # 67-64-1).

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

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

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

8.8 2-Propanol (isopropyl alcohol, CAS # 67-63-0).

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

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

9. Hazards

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

10. Sampling

10.1 *Sampling and Preservation*—Grab samples are collected in glass containers with polytetrafluoroethylene lined caps. As part of the overall quality assurance program for this test method, field blanks exposed to the same field conditions as samples are collected and analyzed according to this test method to assess the potential for field contamination. This test method is based on a 2 g sample size per analysis. If different sample sizes are used, spiking solution amounts may need to be modified. EPA publication SW-846 may be used as a sampling guide. Samples shall be shipped on ice with a trip blank. Once received the sample temperature is taken and should be less than 6°C. If the receiving temperature is greater than 6°C, the sample temperature is noted in the case narrative accompanying the data. Samples should be stored refrigerated between 0 and 6°C from the time of collection until analysis. The sample should be analyzed within 14 days of collection. No holding time study has been done on the various soil matrices tested in this test method. Holding time may vary depending on the matrix and individual laboratories should determine the holding time in their matrix.[12]

11. Preparation of LC/MS/MS

11.1 *LC Chromatograph Operating Conditions:*

11.1.1 Injections of all standards and samples are made at a 50 µL volume. Other injection volumes may be used to optimize conditions. Standards and sample extracts shall be in a 75:25 acetone:water solution. In the case of extreme concentration differences amongst samples, it is wise to analyze a blank after a concentrated sample and before a dilute sample to minimize carry-over of analytes from injection to injection. However, there should not be carry-over between samples. The LC utilized to develop this test method has a flow through LC

[8] A Waters Acquity UPLC BEH C18, 2.1 × 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 data presented in Section 16.

[9] A Waters Xevo TQ-S triple quadrupole mass spectrometer, or equivalent, has been found suitable for use.

[10] 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 that meets the performance of this method may be used. The use of PTFE, PVDF, and polypropylene filter units resulted in poor performance.

[11] Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, D.C. 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 Formulators, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[12] A guide to help and determine sample holding times can be found at http://www.epa.vom/esd/cmb/resaerch/bs_033cmb06.pdf (2014).