Designation: E2787 – 11 (Reapproved 2016)

Standard Test Method for Determination of Thiodiglycol in Soil Using Pressurized Fluid Extraction Followed by Single Reaction Monitoring Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation E2787; 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 thiodiglycol (TDG) in soil using pressurized fluid extraction (PFE). A commercially available PFE system[2] was used, followed by analysis using liquid chromatography (LC), and detected with tandem mass spectrometry (MS/MS). TDG is qualitatively and quantitatively determined by this method. This method adheres to single reaction monitoring (SRM) mass spectrometry.

1.2 The Method Detection Limit (MDL) and Reporting Range for TDG are listed in Table 1.

1.2.1 The MDL is determined following the Code of Federal Regulations, 40 CFR Part 136, Appendix B.

1.2.2 The reporting limit (RL) is calculated from the concentration of the Level 1 calibration standard as shown in Table 4. The RL for this method is 200 ppb. Reporting range concentrations are calculated from Table 4 concentrations assuming a 5 µL injection of the lowest level calibration standard, 5 g sample, and a 2 mL final extract volume.

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]

D653 Terminology Relating to Soil, Rock, and Contained Fluids

D1193 Specification for Reagent Water

D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents

D3740 Practice for Minimum Requirements for Agencies Engaged in Testing and/or Inspection of Soil and Rock as Used in Engineering Design and Construction

E2554 Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques

2.2 *Other Documents:*

EPA publication SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods[4]

40 CFR Part 136, Appendix B, The Code of Federal Regulations

3. Terminology

3.1 *Abbreviations:*

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

3.1.2 *ND*—non-detect

3.1.3 *SRM*—single reaction monitoring

3.1.4 *MRM*—multiple reaction monitoring

4. Summary of Test Method

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

[1] This test method is under the jurisdiction of ASTM Committee E54 on Homeland Security Applications and is the direct responsibility of Subcommittee E54.03 on Decontamination.

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[2] The PFE system that was used to develop this test method was Accelerated Solvent Extraction (ASE®) which is a patented technique by Dionex, Sunnyvale, CA 94088.

[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), U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA, 22161 or at http://www.epa.gov/epawaste/hazard/testmethods/index.htm

TABLE 1 Method Detection Limit and Reporting Range

Analyte	MDL (ppb)	Reporting Range (ppb)
Thiodiglycol	54	200–16 000

4.2 For TDG analysis, samples are shipped to the lab between 0 and 6°C. In the lab, the soils are spiked with 3,3'-thiodipropanol (TDP, surrogate) and extracted by PFE. The extract is filtered using a syringe driven filter unit, reduced in volume, reconstituted with water, and analyzed directly by LC/MS/MS within 7 days.

4.3 TDG and TDP are identified by retention time and one SRM transition. The target analyte and surrogate are quantitated using the SRM transitions utilizing an external calibration. The final report issued for each sample lists the concentration of TDG and the TDP recovery.

5. Significance and Use

5.1 TDG is a Schedule 2 compound under the Chemical Weapons Convention (CWC). Schedule 2 chemicals include those that are precursors to chemical weapons, chemical weapons agents or have a number of other commercial uses. They are used as ingredients to produce insecticides, herbicides, lubricants, and some pharmaceutical products. Schedule 2 chemicals can be found in applications unrelated to chemical weapons. TDG is both a mustard gas precursor and a degradant as well as an ingredient in water-based inks, ballpoint pen inks, dyes, and some pesticides.[5]

5.2 This method has been investigated for use with soil.

6. Interferences

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other apparatus producing discrete artifacts or elevated baselines. All of these materials are demonstrated to be free from interferences by analyzing laboratory reagent blanks under the same conditions as samples.

6.2 All glassware is washed in hot water with a 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 min. All glassware is subsequently cleaned with acetone, then methanol.

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 depending on variations of the sample matrix.

7. Apparatus

7.1 *LC/MS/MS System:*

7.1.1 *Liquid Chromatography (LC) System*[6]—A complete LC system is required in order to analyze samples. Any LC system that is capable of performing at the flows, pressures, controlled temperatures, sample volumes, and requirements of the standard may be used.

7.1.2 *Analytical Column*[7]—A reverse-phase analytical column with strong embedded basic ion-pairing groups 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.

7.1.3 *Tandem Mass Spectrometer (MS/MS) System*[8]—A MS/MS system capable of multiple reaction monitoring (MRM) analysis or any system that is capable of performing at the requirements in this standard may be used.

7.2 *Pressurized Fluid Extraction Device*[9]:

7.2.1 A PFE system was used for this test method with appropriately-sized extraction cells. Cells are available that will accommodate the 5–10 g sample sizes used in this test method. Cells should be made of stainless steel or other material capable of withstanding the pressure requirements (≥2000 psi) necessary for this procedure. Any pressurized fluid extraction device may be used that can meet the necessary requirements in this test method.

7.2.2 *Whatman Glass Fiber Filters*—19.8 mm, Dionex Corporation, Part # 047017 were used because they are specially designed for the PFE system used or equivalent.

7.3 A solvent blowdown device[10] with 24- and 50-vial capacity trays and a water bath maintained at 60°C for analyte concentration from solvent volumes up to 50 mL or similar device may be used.

7.4 A nitrogen evaporation device[11] equipped with a water bath that can be maintained at 50°C for final analyte concentration (<10 mL volume) or similar may be used.

7.5 *Filtration Device:*

7.5.1 *Hypodermic Syringe*—A luer-lock tip glass syringe capable of holding a syringe driven filter unit of PTFE 0.20 µm or similar may be used.[12]

7.5.1.1 A 25 or 50 mL luer-lock tip glass syringe size is recommended in this test method.

7.5.2 *Filter*—A filter unit of PTFE 0.20 µm or similar may be used.

[5] Additional information about CWC and thiodiglycol is available on the Internet at http://www.opcw.org (2009).

[6] A Waters Alliance® High Performance Liquid Chromatography (HPLC) System was used to develop this test method. Waters Corporation, Milford, MA 01757.

[7] SIELC–Primesep SB™ 5 µm, 100 Å particle, 150 mm × 2.1 mm particle size was used to develop this test method, any column that achieves adequate resolution may be used. SIELC Technologies, Prospect Heights, IL 60070.

[8] A Waters Quattro micro™ API mass spectrometer was used to develop this test method. Waters Corporation, Milford, MA 01757.

[9] A Dionex Accelerated Solvent Extraction (ASE® 200) system was used for this test method with appropriately-sized extraction cells. Dionex Corporation, Sunnyvale, CA 94088.

[10] A TurboVap LV was used in this test method from Caliper Life Sciences, Hopkinton, MA 01748.

[11] A N-Evap 24-port nitrogen evaporation device was used in this test method from Organomation Associates Inc., West Berlin, MA 01503.

[12] Millex® HV Syringe Driven Filter Unit PTFE 0.20 mm (Millipore Corporation, Catalog # SLLGC25NS) was shown to perform in this test method, any filter unit may be used if it can perform to the specifications in this test method.

7.5.2.1 *Discussion*—Any filter unit may be used that meets the requirements of the test method.

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.[13] 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 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 *2-Propanol* (CAS # 67-63-0).

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

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

8.8 *Ammonium Formate* (CAS # 540-69-2).

8.9 *Formic Acid* (64-18-6).

8.10 *Thiodiglycol* (CAS # 111-48-8).

8.11 *3,3'-Thiodipropanol* (CAS # 10595-09-2).

8.11.1 *Ottawa Sand Standard,* (CAS # 14808-60-7) or equivalent.

8.11.2 *Drying Agent,* Varian–Chem Tube–Hydromatrix®, 1kg (Part # 198003) was used because it was recommended by the PFE manufacturer or equivalent.

9. Hazards

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

10. Sampling

10.1 *Sampling*—Grab samples must be collected in precleaned amber glass bottles with Teflon® lined caps demonstrated to be free of interferences. This test method requires at least a 5 g sample size per analysis. A 100 g sample amount should be collected to allow for quality control samples and re-analysis. Conventional sampling practices should be followed.

10.2 *Preservation*—Store samples between 0 and 6°C from the time of collection until analysis. Analyze the sample within 7 days of collection.

11. Preparation of LC/MS/MS

11.1 *LC Chromatograph Operating Conditions*[6]:

11.1.1 Injection volumes of all calibration standards and samples are 5 µL and are composed of primarily water. The first sample analyzed after the calibration curve is a water blank to ensure there is no carry-over. The gradient conditions for the liquid chromatograph are shown in Table 2.

11.1.2 *Temperatures*—Column, 30°C; Sample compartment, 15°C.

11.1.3 *Seal Wash*—Solvent: 50% Acetonitrile/50% Water; Time: 5 min.

11.1.4 *Needle Wash*—Solvent: 50% Acetonitrile/50% Water; Normal Wash, approximately a 13-s wash time.

11.1.5 *Autosampler Purge*—Three loop volumes.

11.1.6 Specific instrument manufacturer wash and purge specifications should be followed in order to eliminate sample carry-over in the analysis.

11.2 *Mass Spectrometer Parameters*[8]:

11.2.1 To acquire the maximum number of data points per SRM channel while maintaining adequate sensitivity, the tune parameters may be optimized according to your instrument. Each peak requires at least 10 scans per peak for adequate quantitation. This standard contains one target compound and one surrogate which are in different SRM experiment windows in order to optimize the number of scans and sensitivity. Variable parameters regarding retention times, SRM transitions, and cone and collision energies are shown in Table 3. Mass spectrometer parameters used in the development of this method are listed in Table 3.

TABLE 2 Gradient Conditions for Liquid Chromatography

Time (min)	Flow (µL/min)	Percent CH_3CN	Percent Water	Percent 500 mM Ammonium Formate/2% Formic Acid
0	300	0	95	5
2	300	0	95	5
3	300	50	45	5
6	300	90	5	5
10	300	90	5	5
12	300	0	95	5
16	300	0	95	5

[13] *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.