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.

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[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.

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

Analyte	SRM Mass Transition (Parent > Product)	Retention Time (min)	Cone Voltage (Volts)	Collision Energy (eV)
Thiodiglycol	123.1 > 104.9	2.75	18	5
3,3'-Thiodipropanol	151.2 > 133.1	5.75	19	8

The instrument is set in the Electrospray (+) positive source setting.
Capillary Voltage: 3.5 kV
Cone: Variable depending on analyte (Table 3)
Extractor: 2 V
RF Lens: 0.2 V
Source Temperature: 120°C
Desolvation Temperature: 300°C
Desolvation Gas Flow: 500 L/h
Cone Gas Flow: 25 L/h
Low Mass Resolution 1: 14.5
High Mass Resolution 1: 14.5
Ion Energy 1: 0.5
Entrance Energy: –1
Collision Energy: Variable depending on analyte (Table 3)
Exit Energy: 2
Low Mass Resolution 2: 15
High Mass resolution 2: 15
Ion Energy 2: 0.5
Multiplier: 650
Gas Cell Pirani Gauge: 3.3 × 10^{-3} Torr
Inter-Channel Delay: 0.02 s
Inter-Scan Delay: 0.1 s
Repeats: 1
Span: 0 Daltons
Dwell: 0.1 s

12. Calibration and Standardization

12.1 The mass spectrometer must be calibrated per manufacturer specifications before analysis. In order to obtain valid and accurate analytical values within the confidence limits, the following procedures 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 TDG and TDP in water prior to analysis as shown in Table 4. A calibration stock standard solution is prepared from standard materials or purchased as certified solutions. Aliquots of Level 8 are then diluted with water to prepare the desired calibration levels in 2 mL amber glass 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 quality control failure. The analyst is responsible for recording initial component weights carefully when working with pure materials and correctly carrying the weights through the dilution calculations. Calibration standards are not filtered.

12.2.1 Inject each standard and obtain its chromatogram. An external calibration is used monitoring the SRM transition of each analyte. Calibration software is utilized to conduct the quantitation of the target analyte and surrogate. The SRM transition of each analyte is used for quantitation and confirmation. This gives confirmation by isolating the parent ion, fragmenting it to the product ion, and also relating it to the retention time in the calibration standard.

12.2.2 The calibration software manual should be consulted to use the software correctly. The quantitation method is set as an external calibration using the peak areas in 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. The calibration curves may be either linear or quadratic depending on your instrument. Forcing the calibration curve through the origin is not recommended. Each calibration point used to generate the curve must have a calculated percent deviation less than 30% from the generated curve.

12.2.3 Linear calibration may be used if the coefficient of determination, r^2, is >0.98 for the analyte. 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. If one of the calibration standards other than the high or low point causes the r^2 of the curve to be <0.98, this point must be re-injected or a new calibration curve must be regenerated. If the low or high (or both) point is excluded, minimally a five point curve is acceptable, but the reporting range must be modified to reflect this change.

12.2.4 Quadratic calibration may be used if the coefficient of determination, r^2, is >0.99 for the analyte. 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. If one of the calibration standards, other than the high or low, causes the curve to be <0.99, this point must be re-injected or a new calibration curve must be regenerated. If the low and/or high point is excluded, a six point curve is acceptable using a quadratic fit. An initial eight point curve over the calibration range is suggested in the event that the low or high point must be excluded to obtain a coefficient of determination >0.99. In this event, the reporting range must be modified to reflect this change.

12.2.5 The retention time window of the SRM 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.

12.2.6 A midpoint calibration check standard must be analyzed at the end of each batch of 20 samples or within 24 h after the initial calibration curve was generated. This end calibration check should be the same calibration standard that was used to generate the initial curve. The results from the end calibration check standard must have a percent deviation less than 30% from the calculated concentration for the target

TABLE 4 Concentrations of Calibration Standards (PPB)

Analyte/Surrogate	LV 1	LV 2	LV 3	LV 4	LV 5	LV 6	LV 7	LV 8
Thiodiglycol	500	1000	2000	4000	8000	16 000	32 000	40 000
3,3'-Thiodipropanol	500	1000	2000	4000	8000	16 000	32 000	40 000

analyte and surrogate. If the results are not within these criteria, the problem must be corrected and either all samples in the batch must be re-analyzed against a new calibration curve or the affected results must be qualified with an indication that they do not fall within the performance criteria of the test method. If the analyst inspects the vial containing the end calibration check standard and notices that the sample evaporated affecting the concentration, a new end calibration check standard may be made and analyzed. If this new end calibration check standard has a percent deviation less than 30% from the calculated concentration for the target analyte and surrogate, the results may be reported unqualified.

12.3 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 or new instrument, perform a precision and bias study to demonstrate laboratory capability.

12.3.1 Analyze at least four replicates of a sample containing TDG and TDP at a concentration between 4 and 10 ppm in Ottawa sand. This test method was tested at ~6.4 ppm. Each replicate must be taken through the complete analytical test method.

12.3.2 Calculate the mean (average) percent recovery and relative standard deviation (RSD) of the four values and compare to the acceptable ranges of the quality control (QC) acceptance criteria for the Initial Demonstration of Performance in Table 5.

12.3.3 This study should be repeated until the single operator precision and mean recovery are within the limits in Table 5.

12.3.4 The QC acceptance criteria for the Initial Demonstration of Performance in Table 5 were generated from a single-laboratory. The analyst must be aware that the performance data generated from single-laboratory data tend to be significantly tighter than those generated from multi-laboratory data. It is recommended that the laboratory generate its own in-house QC acceptance criteria which meet or exceed the criteria in this standard. References on how to generate QC acceptance criteria are Practice E2554 or Method 8000B in EPA publication SW-846 may be helpful.

12.4 *Surrogate Spiking Solution:*

12.4.1 A surrogate standard solution consisting of TDP is added to each 5 g soil sample. The TDP is added to each sample to achieve a concentration of 6.4 mg/kg (that is, 160 µL of a 200 ppm methanol solution containing TDP is added to a 5 g soil sample). The result obtained for the surrogate recovery must fall within the limits of Table 5. If the limits are not met, the affected results must be qualified with an indication that they do not fall within the performance criteria of the test method.

12.5 *Method Blank:*

12.5.1 Analyze a blank with each batch of 20 or fewer samples. The concentration of TDG found in the blank must be below the MDL. If the concentration of TDG 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.

12.6 *Laboratory Control Sample (LCS):*

12.6.1 To ensure that the test method is in control, analyze a LCS prepared with TDG at a concentration in the reporting range between 4 and 10 ppm. The LCS is prepared following the analytical method and analyzed with each batch of 20 samples or less. An Ottawa sand sample is spiked with TDG to achieve a concentration of 6.4 mg/kg (that is, 160 µL of a 200 ppm methanol solution containing TDG is added to a 5 g soil sample). The result obtained for the LCS must fall within the limits in Table 5.

12.6.2 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.

12.7 *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. This is accomplished by spiking the sample with a known concentration of TDG and following the analytical method. The matrix spike soil sample is spiked with TDG to achieve a concentration of 6.4 mg/kg (that is, 160 µL of a 200 ppm methanol solution containing TDG is added to a 5 g soil 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 1:

$$P = 100\,\frac{|\,A(V_s+V) - BV_s\,|}{CV} \qquad (1)$$

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

TABLE 5 Quality Control Acceptance Criteria

Analyte/Surrogate	Test Conc. (mg/kg)	Initial Demonstration of Performance			Lab Control Sample	
		Recovery (%)		Precision	Recovery (%)	
		Lower Limit	Upper Limit	Maximum % RSD	Lower Limit	Upper Limit
Thiodiglycol	6.4	30	130	46	30	130
3,3'-Thiodipropanol	6.4	30	130	39	30	130

P = percent recovery.

12.7.4 The percent recovery of the spike shall fall within the limits in Table 6. If the percent recovery is not within these limits, a matrix interference may be present in the selected sample. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

12.7.5 The matrix spike/matrix spike duplicate (MS/MSD) limits in Table 6 were generated by a single-laboratory in two matrices. The matrix variation between different soils may have a tendency to generate significantly wider control limits than those generated by a single laboratory in one surface soil matrix. It is recommended that the laboratory generate its own in-house QC acceptance criteria which meet or exceed the criteria in this standard.

12.7.5.1 The laboratory should generate its own in-house QC acceptance criteria after the analysis of 15–20 matrix spike samples of a particular soil matrix. References on how to generate QC acceptance criteria are Practice E2554 or Method 8000B in EPA publication SW-846 may be helpful.

12.8 *Duplicate:*

12.8.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch of 20 or fewer samples. If the sample contains the analyte at a level greater than 5 times the detection limit of the method, the sample and duplicate may be analyzed unspiked; otherwise, an MSD should be used.

12.8.2 Calculate the relative percent difference (RPD) between the duplicate values (or MS/MSD values) as shown in Eq 2. Compare to the RPD limit in Table 6.

$$RPD = \frac{|MSR - MSDR|}{(MSR + MSDR)/2} \times 100 \quad (2)$$

where:

RPD = relative percent difference,
MSR = matrix spike recovery, and
$MSDR$ = matrix spike duplicate recovery.

12.8.3 If the result exceeds the precision limit, 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.

13. Procedure

13.1 The soil samples are shipped chilled between 0 and 6°C in pre-cleaned amber glass jars with Teflon® lined caps and stored in the laboratory between 0 and 6°C. If the samples are above 6°C when received or during storage or not analyzed within 7 days of collection, the data are qualified estimated and noted in the case narrative that accompanies the data.

13.2 *Pressurized Fluid Extraction:*

13.2.1 Mix the soil or sediment sample thoroughly, especially composite samples. Note the overall appearance of the sample; for example, how much water or liquid phase is present and whether foreign objects such as sticks, leaves, rocks, etc., are present. It is important to consult the client on how the samples should be processed. Decant and discard any water layer if the client wants only the solid portion analyzed; alternatively, if the client requires the analysis of both phases, then pour the liquid layer into a separate container, measure and conduct the appropriate extraction procedure. Prior to weighing, discard foreign objects, unless instructed otherwise by the client.

13.2.2 Three cell sizes applicable to this test method are available for the PFE System: 11, 22 and 33 mL. The 33 mL cell equals the volume of the largest Soxhlet thimble commonly used for this test method. In general, when choosing a cell size, select the smallest cell that holds enough sample to produce accurate extraction results. The 11 mL cell holds approximately 10 g, the 22 mL cell holds approximately 20 g, and the 33 mL cell holds approximately 30 g. Take into account any drying agent needed, which increases sample volume. When preparing the sample, make sure that the drying agent and sample are thoroughly mixed.

13.2.3 Weigh out samples into crucibles or evaporating dishes depending on known contaminant levels as follows: 5 g for high level, 10 g for medium level, and 30 g for low level analysis, on a dry basis. Take into consideration any action levels or detection limits required by the client, as well as the sizes of the extraction cells that fit in the PFE and plus the water content of the samples which will determine the amount of diatomaceous earth required to dry them sufficiently. Be sure to include any relevant QA/QC samples.

13.2.4 Spike each soil sample with 160 µL of a 200 ppm methanol solution containing TDP.

13.2.5 For the matrix spike and LCS/LCSD, spike each sample with 160 µL of a 200 ppm methanol solution containing TDG.

13.2.6 Most matrices should be mixed with a drying agent[14] before being loaded into the cells. The drying agent recommended by the PFE manufacturer was used in this test method. It dries samples quickly, provides a cleaner transfer of the mixtures to the cell, extracts well and prevents clogging of the frit in the end cap of the extraction cell, which normally occurs when sodium sulfate is used to dry samples. If the sample appears dry, use 4 g sample to 1 g diatomaceous earth. If the sample appears wet, use 4 g sample to 2 g diatomaceous earth. If the sample is a liquid, use 5 g sample to 3 g diatomaceous earth. Mix the sample with diatomaceous earth thoroughly in a small mortar or evaporating dish. Add diatomaceous earth and stir the mixture until a sandy texture is observed.

TABLE 6 MS/MSD Quality Control Acceptance Criteria

Analyte/Surrogate	Test Conc. (mg/kg)	MS/MSD		
		Recovery (%)		Precision
		Lower Limit	Upper Limit	Maximum RPD (%)
Thiodiglycol	6.4	30	130	37
3,3'-Thiodipropanol	6.4	30	130	21

[14] The drying agent recommended by the PFE manufacturer used in this test method is Varians' Chem Tube Hydromatrix® which was used to develop this test method. Varian Inc., Palo Alto, CA 94304.

13.2.7 To prepare a 5 g sample, collect 22 mL PFE cells with appropriately sized caps. Hand-tighten the main body of the extraction cell with a cell cap and insert a disposable glass fiber filter at the bottom of the cap. Place the prepared sample into each cell.

13.2.8 Fill any void volume in the cell with inert material, such as diatomaceous earth or clean sand. Assemble each extraction cell by hand-tightening the cell caps on each end. Do not use a wrench or other tool to tighten the cap. If the extraction cells are packed too tightly, an over-pressurized condition can cause the system to shut down. Prior to using the cell caps, verify that the white O-rings are in place and in good condition. Check the polyether ether ketone (PEEK) seals inside the caps and replace if necessary.

13.2.9 Load the cells in numerical order and hang the cells vertically in the tray slots from their top caps. The bottom cap contains the glass fiber filter.

13.2.10 Load the rinse tubes into the rinse slots.

13.2.11 For each sample setup, load a 60 mL labeled collection vial into the corresponding vial tray position. The label or any markings must be between 34 and 78 mm from the top of the collection vial or the solvent sensor will return an error when trying to read the solvent level in the vial, and the PFE will move onto the next row of the sequence. Prepare a method on the PFE using the following conditions (These parameters are based on the PFE system to develop this test method):

Pressure: 1500 psi
Temperature: 100°C
Preheat Time: 5 min
Purge during pre-heat: Off
Heat Time: 5 min
Static Time: 5 min
Flush Volume: 40 %
Purge Time: 60 s
Static Cycles: 2
Solvent: Methanol

13.2.12 If the type of solvent or solvent mixture in any of the bottles has changed or the PFE system has not been used recently, the lines should be rinsed by pressing the "rinse" button on the control panel before use.

13.2.13 If the PFE system is run under method control, it will extract cells in numerical order. It will inject each extract into the corresponding receiving vial with the same number until all the cell slots have been loaded and extracted or until it cannot load two cells in a row. If it is run under schedule control, the PFE system will inject the extract(s) of each vial into the corresponding receiving vial(s) designated in the schedule.

13.2.14 The PFE system extract is then concentrated in the nitrogen evaporation device to a small volume (2–3 mL). After concentration in the nitrogen evaporation device, the sample extract is filtered using a syringe-driven filter unit PTFE with a 0.20 µm pore size to remove particulates in the sample. The sample is then transferred via pipette into 10 mL graduated concentrator tubes. Calibration standards are not filtered through the syringe-driven filter units since no particulates are present. Extracts are then placed on the nitrogen evaporation device at 50°C; the sides are rinsed with methanol and concentrated down to 0.4 mL. Final extracts are diluted to 2 mL final volume with HPLC-grade water. After use, empty the PFE cells and rinse or sonicate the end caps with water followed by acetone and methylene chloride. The syringes must be rinsed to full volume three times with methanol between all field samples, QC samples, blanks, and standards. Note that only cell bodies can be cleaned in a dishwater or high temperature cleaning unit (<400°C).

13.3 Once a passing calibration curve is generated, the analysis of samples may begin. An order of analysis may be method blank(s), laboratory control sample(s), sample(s), duplicate(s), and matrix spike sample(s) followed by an end calibration check standard.

14. Calculation or Interpretation of Results

14.1 For quantitative analysis of TDG and TDP, the SRM transitions are identified by comparison of retention times in the sample to those of the standards. External calibration curves are used to calculate the amount of TDG and surrogate. Calculate the concentration in mg/kg (ppm) for each analyte. TDG is reported if present at or above the reporting limit. If the concentration of the analyte is determined to be above the calibration range, the sample is diluted with reagent water to obtain a concentration near the midpoint of the calibration range and re-analyzed.

15. Report

15.1 Determine the results in units of mg/kg (ppm) in a soil sample. Calculate the concentration in the sample using the linear or quadratic calibration curve generated. All data that do not meet the specifications in the test method must be appropriately qualified.

16. Precision and Bias

16.1 The determination of precision and bias was conducted through the United States Environmental Protection Agency (US EPA) using a single-laboratory. A multi-laboratory validation is being planned. It is hoped that this test method will generate multi-laboratory participants within the next 5 years to enable a full validation study.

16.2 This test method was tested by the US EPA Chicago Regional Laboratory (CRL) on Ottawa Sand, Nebraska, and Georgia Soils. The characterization data for the soils are shown in Appendix X1. The samples were spiked with target compound and surrogate to obtain a ~6.4 ppm concentration of each as described in Section 12. Table 7 contains the recoveries for the TDP and Table 8 contains the recoveries for TDG.

17. Keywords

17.1 liquid chromatography; mass spectrometry; soil; thiodiglycol

TABLE 7 Single-Laboratory TDP Recovery Data

Sample ID	TDP Spike Volume (µL)	Spike Concentration (mg/L)	Soil Dry Mass (g)	Soil Concentration (mg/kg)	TDP Recovered (mg/kg)	TDP % Recovery
NE Method Blank	160	200	4.93	6.49	4.21	64.87
NE 1	160	200	4.94	6.48	4.42	68.21
NE 2	160	200	4.78	6.70	4.28	63.89
NE 3	160	200	3.92	8.17	5.56	68.06
NE 4	160	200	4.86	6.58	4.08	61.99
NE 5	160	200	4.86	6.58	4.78	72.69
Average % Recovery	–	–	–	–	–	66.62
Standard Deviation (SD)	–	–	–	–	–	3.83
% Relative SD						5.75
Sample ID	TDP Spike Volume (µL)	Spike Concentration (mg/L)	Soil Dry Mass (g)	Soil Concentration (mg/kg)	TDP Recovered (mg/kg)	TDP % Recovery
GA Method Blank	160	200	4.97	6.44	5.65	87.72
GA 1	160	200	4.88	6.56	4.73	72.05
GA 2	160	200	5.10	6.27	4.60	73.42
GA 3	160	200	5.00	6.40	4.15	64.78
GA 4	160	200	4.95	6.47	3.96	61.24
GA 5	160	200	4.91	6.52	4.20	64.41
Average % Recovery	–	–	–	–	–	70.60
Standard Deviation (SD)	–	–	–	–	–	9.62
% Relative SD						13.63
Sample ID	TDP Spike Volume (µL)	Spike Concentration (mg/L)	Soil Dry Mass (g)	Soil Concentration (mg/kg)	TDP Recovered (mg/kg)	TDP % Recovery
Sand Method Blank	160	200	5.11	6.26	4.47	71.32
Sand 1	160	200	4.92	6.50	3.27	50.32
Sand 2	160	200	5.00	6.40	3.80	59.32
Sand 3	160	200	4.99	6.41	4.89	76.22
Sand 4	160	200	4.91	6.52	4.28	65.67
Sand 5	160	200	5.09	6.29	4.04	64.33
Average % Recovery	–	–	–	–	–	64.53
Standard Deviation (SD)	–	–	–	–	–	9.09
% Relative SD						14.09

TABLE 8 Single-Laboratory TDG Recovery Data

Sample ID	TDG Spike Volume (µL)	Spike Concentration (mg/L)	Soil Dry Mass (g)	Soil Concentration (mg/kg)	TDG Recovered (mg/kg)	TDG % Recovery
NE Method Blank	0	–	4.93	0.00	ND	–
NE 1	160	200	4.94	6.48	3.95	61.04
NE 2	160	200	4.78	6.70	3.78	56.37
NE 3	160	200	3.92	8.17	4.98	60.94
NE 4	160	200	4.86	6.58	3.65	55.32
NE 5	160	200	4.86	6.58	4.08	61.94
Average % Recovery	–	–	–	–	–	59.12
Standard Deviation (SD)	–	–	–	–	–	3.04
% Relative SD						5.14
Sample ID	TDG Spike Volume (µL)	Spike Concentration (mg/L)	Soil Dry Mass (g)	Soil Concentration (mg/kg)	TDG Recovered (mg/kg)	TDG % Recovery
GA Method Blank	0	–	4.97	0.00	ND	–
GA 1	160	200	4.88	6.56	3.73	56.80
GA 2	160	200	5.10	6.27	3.78	60.38
GA 3	160	200	5.00	6.40	3.39	52.97
GA 4	160	200	4.95	6.47	2.88	44.58
GA 5	160	200	4.91	6.52	2.61	40.06
Average % Recovery	–	–	–	–	–	50.96
Standard Deviation (SD)	–	–	–	–	–	8.46
% Relative SD						16.60
Sample ID	TDG Spike Volume (µL)	Spike Concentration (mg/L)	Soil Dry Mass (g)	Soil Concentration (mg/kg)	TDG Recovered (mg/kg)	TDG % Recovery
Sand Method Blank	0	–	5.11	0.00	ND	–
Sand 1	160	200	4.92	6.50	2.73	42.03
Sand 2	160	200	5.00	6.40	3.11	48.57
Sand 3	160	200	4.99	6.41	4.35	67.88
Sand 4	160	200	4.91	6.52	3.65	56.06
Sand 5	160	200	5.09	6.29	3.47	55.16
Average % Recovery	–	–	–	–	–	53.94
Standard Deviation (SD)	–	–	–	–	–	9.63
% Relative SD						17.85

APPENDIX

(Nonmandatory Information)

X1. CHARACTERIZATION DATA FOR GA AND NE SOILS

TABLE X1.1

Properties	GA Soil	NE Soil
Sand	46%	6%
Silt	22%	60%
Clay	32%	34%
pH	5.0	5.6
Total Organic Carbon	0.2%	2.1%