Designation: E2838 – 21

Standard Test Method for Determination of Thiodiglycol on Wipes by Solvent Extraction Followed by Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation E2838; 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 details the determination of thiodiglycol (TDG), also known as 2,2'-thiobis-ethanol, on wipes with 3,3'-thiodipropanol (TDP) as the surrogate. This method is based upon solvent extraction of wipes by either sonication or a pressurized fluid extraction (PFE) technique as an alternative option. The extract is filtered, concentrated, and analyzed by liquid chromatography/tandem mass spectrometry (LC/MS/MS). TDG is qualitatively and quantitatively determined.

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

1.3 The method detection limit (MDL)[2] and reporting range[3] for TDG are listed in Table 1.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[4]

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

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[5]

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

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D5681.

3.2 *Abbreviations:*

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

3.2.2 *ND*—non-detect

3.2.3 *SRM*—single reaction monitoring

3.2.4 *MRM*—multiple reaction monitoring

3.2.5 *VOA*—volatile organic analysis

4. Summary of Test Method

4.1 For TDG wipe analysis, samples are shipped to the lab between 0 °C and 6 °C. The samples are to be extracted, concentrated, and analyzed directly by LC/MS/MS within seven days of collection. The handling, storage, preservation, and LC/MS/MS analysis are consistent between the two

[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] The MDL is determined following the Code of Federal Regulations, 40 CFR Part 136, Appendix B utilizing solvent extraction of wipes by sonication.

[3] Reporting range concentrations are calculated from Table 4 concentrations assuming a 10 µL injection of the lowest and highest level calibration standards with a 2 mL final extract volume. Volume variations will change the reporting limit and ranges. The reporting limit (RL), lowest concentration of the reporting range, is calculated from the concentration of the Level 1 calibration standard as shown in Table 4.

[4] 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.

[5] 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	CAS[A] Number	MDL (µg/wipe)	Reporting Range (µg/wipe)
Thiodiglycol	111-48-8	0.085	1–80
3,3'-Thiodipropanol (Surrogate)	10595-09-2	Not done for surrogates	1–80

[A] Chemical Abstract Service (CAS), a division of the American Chemical Society, 2540 Olentangy River Road, Columbus, OH, 43202, USA.

extraction procedures described in this test method. Only one extraction procedure is required, documenting which was performed.

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

5.1.1 Due to the rapid development of newer instrumentation and column chemistries, changes to the analysis described in this standard are allowed as long as better or equivalent performance data result. Any modifications shall be documented and performance data generated. The user of the data generated by this standard shall be made aware of these changes and given the performance data demonstrating better or equivalent performance.

5.2 TDG is a Schedule 2 compound under the Chemical Weapons Convention (CWC).[6] Schedule 2 chemicals include those that are precursors to chemical weapons, chemical weapons agents, or have a number of other non-military commercial uses. Schedule 2 chemicals can also be found in applications unrelated to chemical weapons. These chemicals are used as ingredients to produce insecticides, herbicides, lubricants, and some pharmaceutical products. TDG is a mustard gas precursor and a degradant as well as an ingredient in water-based inks, ballpoint pen inks, dyes, and some pesticides.

5.3 This method has been investigated for use on surface wipes. TDG is also a human metabolite resulting from sulfur mustard exposure but this method has not been investigated for such determinations.

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 shall be demonstrated to be free from interferences by analyzing laboratory reagent blanks under the same conditions as samples.

6.2 All reagents and solvents shall be of pesticide residue purity or higher to minimize interference problems.

6.3 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*[7]—An LC system is required in order to analyze samples. An 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 column that achieves adequate resolution shall be used. The retention times and order of elution may change depending on the column used and need to be monitored. A reverse-phase analytical column with strong embedded basic ion-pairing groups was used to develop this test method.

7.1.3 *Tandem Mass Spectrometer (MS/MS) System*[9]—An MS/MS system capable of multiple reaction monitoring (MRM) analysis or a system that is capable of performing at the requirements in this standard shall be used.

7.2 *Pressurized Fluid Extraction (PFE) Device*[10] (optional)—PFE devices with appropriately sized extraction cells are available that will accommodate the wipe sample sizes used in this test method. Cells shall be made of stainless steel or other material capable of withstanding the pressure requirements (≥2000 psi) necessary for this procedure. A pressurized fluid extraction device shall be used that can meet the necessary requirements in this test method.

7.3 *Glass Fiber Filters.*[11]

7.4 *Solvent Blowdown Device,* with 24- and 50-vial capacity trays and a water bath maintained at 50 to 60 °C for analyte concentration from solvent volumes up to 50 mL or similar device shall be used.[12]

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

[7] A Waters Alliance High Performance Liquid Chromatography (HPLC) System was used to develop this test method and generate the precision and bias data presented in Section 17. Any HPLC system that produces results that meet or exceed the performance criteria of this test method may be used.

[8] A SIELC- Primesep SB 5 µm, 100 Å particle, 150 by 2.1 mm column was used to develop this test method and generate the precision and bias data presented in Section 17. Any column that produces results that meet or exceed the performance criteria of this test method may be used.

[9] A Waters Quattro micro API mass spectrometer was used to develop this test method and generate the precision and bias data presented in Section 17. Any mass spectrometer that produces results that meet or exceed the performance criteria of this test method may be used.

[10] A Dionex Accelerated Solvent Extraction (ASE 200) system with appropriately sized extraction cells was used to develop this test method and generate the precision and bias data presented in Section 17. Any extraction system that produces results that meet or exceed the performance criteria of this test method may be used.

[11] Whatman Glass Fiber Filters 19.8 mm, Part No. 047017, specially designed for the PFE system[10] were used to develop this test method and generate the precision and bias data presented in Section 17. Any filter that produces results that meet or exceed the performance criteria of this test method may be used.

[12] A TurboVap LV by Caliper Life Sciences, Hopkinton, MA 01748 was used. Any evaporation system that produces results that meet or exceed the performance criteria of this test method may be used.

7.5 *Sonication Device,* capable of holding 40 mL vials.[13]

7.6 *Nitrogen Evaporation Device,* equipped with a water bath that can be maintained at 50 °C for final analyte concentration (<10 mL volume) or similar shall be used.[14]

7.7 *Wipes.*[15]

7.8 *Filter Paper.*[16]

7.9 *Kuderna-Danish (K-D) Vials,* 10 mL.

7.10 *Amber VOA Vials,* 40 mL for sonication, or 60 mL for PFE.

7.11 *Filtration Device:*

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

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

7.11.2 *Filter Units*[17]—A filter unit of polytetrafluoroethylene (PTFE) 0.20 µm was used for the sonication extraction and a polyvinylidene fluoride (PVDF) 0.22 µm was used for the PFE process. Either PTFE or PVDF filter units shall be used.

NOTE 1—Any filter unit brand that meets the requirements of the test method may be used.

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.[18] 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 ASTM Type I 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*—Nitrogen (purity ≥97 %) and argon (purity ≥99.999 %).

8.4 *Acetic Acid* (CH_3CO_2H, CAS No. 64-19-7).

8.5 *Acetone* (CH_3COCH_3, CAS No. 67-64-1).

8.6 *Acetonitrile* (CH_3CN, CAS No. 75-05-8).

8.7 *Ammonium Formate* (NH_4CO_2H, CAS No. 540-69-2).

8.8 *Formic Acid* (HCO_2H, CAS No. 64-18-6).

8.9 *Methanol* (CH_3OH, CAS No. 67-56-1).

8.10 *Thiodiglycol* ($S(CH_2CH_2OH)_2$, CAS No. 111-48-8).

8.11 *3,3'-Thiodipropanol* ($S(CH_2CH_2CH_2OH)_2$, CAS No. 10595-09-2).

8.12 *Drying Agent.*[19]

8.13 *Sand*—Reagent grade sand, such as Ottawa sand.

9. Hazards

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

10. Glassware Washing, Sampling, and Preservation

10.1 *Glassware Washing*—All glassware is washed in hot tap water with a detergent and rinsed in hot water conforming to ASTM Type I of Specification D1193. 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 and methanol, respectively.

10.2 *Sampling*—The wipe sample is folded and placed into a 40 mL pre-cleaned amber glass VOA vial with a PTFE-lined cap in the field. The wipe is shipped to the laboratory between 0 °C and 6 °C. The required surrogate and matrix spike solutions are added to the wipe in the VOA vial at the laboratory. Field blanks are needed to follow conventional sampling practices.

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

11. Preparation of LC/MS/MS

11.1 LC chromatograph operating conditions for the LC used to develop this test method:[7]

11.1.1 Injection volumes of all calibration standards and samples are 10 µL. The first sample analyzed after the calibration curve is a blank to ensure there is no carry-over. The gradient conditions for the liquid chromatograph are shown in Table 2.

[13] A Bransonic Model 5510 Sonicator by Branson Ultrasonics, Americas Headquarters, 41 Eagle Road, Danbury, CT 06810 was used. Any sonicator that produces results that meet or exceed the performance criteria of this test method may be used.

[14] An N-Evap 24-port nitrogen evaporation device by Organomation Associates Inc., West Berlin, MA 01503 was used. Any evaporation system that produces results that meet or exceed the performance criteria of this method may be used.

[15] Certi-Gauze pads, sterile, 3 by 3 in. (Part No. 52639), were used to develop this test method and generate the precision and bias data presented in Section 17. Any gauze pad that produces results that meet or exceed the performance criteria of this test method may be used.

[16] Whatman 42 ashless, 125 mm filter paper (Catalog No. 1442 125) was used to develop this test method and generate the precision and bias data presented in Section 17. Any filter paper that produces results that meet or exceed the performance criteria of this test method may be used.

[17] An IC Millex-LG Syringe-Driven Filter Unit PTFE 0.20 µm (Catalog No. SLLGC25NS) and Millex-GV Syringe-Driven Filter Unit PVDF 0.22 µm (Catalog No. SLGV033NS) were used to develop this test method and generate the precision and bias data presented in Section 17. Any filter that produces results that meet or exceed the performance criteria of this test method may be used.

[18] *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 *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.

[19] Varian – Chem Tube – Hydromatrix, 1 kg (Part No. 198003) was used to develop this test method and generate the precision and bias data presented in Section 17 by recommendation of the PFE manufacturer. Any drying agent that produces results that meet or exceed the performance criteria of this test method may be used.

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

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 shall be followed in order to eliminate sample carry-over in the analysis.

11.2 *Mass Spectrometer Parameters:*[9]

11.2.1 To acquire the maximum number of data points per SRM channel while maintaining adequate sensitivity, the tune parameters shall be optimized according to the instrument. Each peak requires at least ten 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 for the mass spectrometer used to develop this test method. Other mass spectrometer parameters used in the development of this method are listed below:

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

Analyte	SRM Mass Transition (m/z) (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 V
Entrance Energy: –1 V
Collision Energy: Variable depending on analyte (Table 3)
Exit Energy: 2 V
Low Mass Resolution 2: 14.5
High Mass Resolution 2: 14.5
Ion Energy 2: 0.5 V
Multiplier: 650 V
Gas Cell Pirani Gauge: 0.33 Pa
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 shall be calibrated per manufacturer specifications before analysis. In order to obtain valid and accurate analytical values within the confidence limits, the following procedures shall 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 shall 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 in 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. Confirmation occurs by isolating the parent ion, fragmenting it to the product ion, and relating it to the retention time in the calibration standard.

TABLE 4 Concentrations of Calibration Standards (µg/L)

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

12.2.2 The calibration software manual shall 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 shall 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 shall be re-injected or a new calibration curve shall be regenerated. If the low or high (or both) point is excluded, minimally a five-point curve is acceptable, but the reporting range shall 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 shall be re-injected or a new calibration curve shall be regenerated. If the low or high (or both) 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 shall be excluded to obtain a coefficient of determination >0.99. In this event, the reporting range shall be modified to reflect this change.

12.2.5 The retention time window of the SRM transitions shall 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 re-inject the sample. If the retention time is still incorrect, refer to the analyte as an unknown.

12.2.6 A midpoint calibration check standard shall 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 shall be the same calibration standard that was used to generate the initial curve. The results from the end calibration check standard shall have a percent deviation less than 30 % from the calculated concentration for the target analyte and surrogate. If the results are not within these criteria, the problem shall be corrected, and either all samples in the batch shall be re-analyzed against a new calibration curve or the affected results shall 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 shall 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 shall be reported unqualified if all other quality control parameters are acceptable.

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 and verify that all technicians are adequately trained and follow all relevant safety procedures. Refer to Practice D2777 as a guide.

12.3.1 Analyze at least four replicates of a wipe sample containing TDG and TDP between Levels 3 and 6 of the calibration range in the final extract concentration. Each replicate shall 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 ranges of the quality control (QC) acceptance criteria for the initial demonstration of performance in Table 5.

12.3.3 This study shall 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 are preliminary until a collaborative study is conducted. Single-lab data is shown in Section 17. The analyst shall be aware that the performance data generated from single-laboratory data tend to be significantly tighter than those generated from multi-laboratory data. The laboratory shall generate its own in-house QC acceptance criteria which meet or exceed the criteria in this standard.

TABLE 5 Quality Control Acceptance Criteria

Analyte/Surrogate	Test Conc. (µg/wipe)	Initial Demonstration of Performance			Lab Control Sample	
		Recovery (%)		Precision	Recovery (%)	
		Lower Limit	Upper Limit	Maximum % RSD	Lower Limit	Upper Limit
Thiodiglycol	16	30	130	40	30	130
3,3'-Thiodipropanol	16	30	130	40	30	130

References on how to generate QC acceptance criteria are found in Practice E2554 or Method 8000B in EPA publication SW-846.

12.4 *Surrogate Spiking Solution:*

12.4.1 Surrogate standard solution consisting of TDP is added to each sample in order to achieve a final concentration of 16 µg/wipe (that is, 80 µL of a 200 ppm methanol solution containing TDP is added to a wipe). TDP was chosen as a surrogate to reduce the cost of analysis. Carbon-13 labeled or deuterated TDG may be used as a surrogate.

12.5 *Method Blank:*

12.5.1 Analyze a wipe material blank with each batch of 20 or fewer samples. The blank is spiked with the surrogate spiking solution and taken through the entire sample preparation process. The concentration of TDG found in the blank shall be below the MDL. If the concentration of TDG is found above this level, sample analysis is halted until the contamination is eliminated, and a blank shows no contamination at or above this level or the results shall 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 an LCS prepared with TDG at a concentration of 16 µg/wipe. The LCS is prepared following the analytical method and analyzed with each batch of 20 samples or less. Each LCS wipe sample is spiked with TDG to achieve a final concentration of 16 µg/wipe (that is, 80 µL of a 200 ppm methanol solution containing TDG is added to a wipe). The result obtained for the LCS shall fall within the limits in Table 5.

12.6.2 If the result is not within these limits, sample analysis is halted until the problem is corrected, and either all samples in the batch shall be re-analyzed or the results shall 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 an 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 wipe sample is spiked with TDG to achieve a concentration of 16 µg/wipe (that is, 80 µL of a 200 ppm methanol solution containing TDG is added to a wipe).

12.7.2 If the spiked concentration plus the background concentration exceed that of the Level 8 calibration standard, the sample shall 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:

$$P = 100\,\frac{[A(V_s+V)] - BV_s}{CV} \tag{1}$$

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
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 shall be employed: the matrix interference shall be removed, all samples in the batch shall be analyzed by a test method not affected by the matrix interference, or the results shall 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 are from a single-lab study. The matrix variation between different wipes may tend to generate significantly wider control limits than those generated by a single laboratory in one surface wipe matrix. It is recommended that the laboratory generate an in-house QC acceptance criteria which meet or exceed the criteria in this standard.

12.7.5.1 The laboratory shall generate an in-house QC acceptance criteria after the analysis of 15 to 20 matrix spike samples of a particular wipe matrix. References on how to generate QC acceptance criteria are found in Practice E2554 or Method 8000B in EPA publication SW-846.

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 five times the detection limit of the method, the sample and duplicate may be analyzed unspiked; otherwise, an MSD shall 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 value to the RPD limit in Table 6.

$$RPD = \frac{[MSR - MSDR]}{(MSR+MSDR)\div 2} \times 100 \tag{2}$$

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 shall be re-analyzed or the results shall be qualified with an indication that they do not fall within the performance criteria of the test method.

13. Sonication Procedure

13.1 In the lab, spike all samples with TDP surrogate spiking solution and prepare laboratory control and matrix

TABLE 6 MS/MSD Quality Control Acceptance Criteria

Analyte/Surrogate	Test Conc. (µg/wipe)	MS/MSD		
		Recovery (%)		Precision
		Lower Limit	Upper Limit	Maximum RPD (%)
Thiodiglycol	16	30	130	40
3,3'-Thiodipropanol	16	30	130	40

spike samples as described in Section 12. Spike all samples in the same vials that were used for collection in the field to eliminate sample loss due to transfer.

13.2 Add 10 mL of 90 % MeOH/10 % water with 10 mM acetic acid to each sample VOA vial. The solvent shall fully immerse the wipe if folded properly.

13.3 Cap and shake vial, loosen cap on vial to eliminate pressure if necessary, and sonicate for 10 min.

NOTE 2—If vials are sealed during sonication process they may require periodic venting to reduce pressure and prevent accidental explosion.

13.4 Transfer the extraction solvent into a 25 mL lock-tip hypodermic syringe fitted with a PTFE filter unit as described in Section 7; transfer the filtered sample to a 10 mL K-D vial for evaporation.

13.5 Rinse the syringe/syringe-driven filter unit with methanol (3 mL), adding the rinse to the volume within the K-D vial.

13.6 Place K-D vial on nitrogen evaporator at 50 °C.

13.7 Extract the wipe again by adding 10 mL of methanol to the vial containing the wipe and sonicate for 10 min.

13.8 Concentrate the sample within the K-D vial to <2 mL using the nitrogen evaporator while the wipe is sonicating.

13.9 Filter the second extract using the same procedure as stated in 13.4, combining fractions in the K-D vial. Rinse the syringe/syringe-driven filter unit with methanol (3 mL) adding it to the sample volume within the K-D vial.

13.10 Concentrate sample within the K-D vial using the nitrogen evaporator device to 2 mL and transfer to a 2 mL LC sample vial for analysis.

14. Pressurized Fluid Extraction Procedure (PFE) (optional)

14.1 To prepare each sample, collect 22 mL PFE cells with appropriately sized caps. Hand-tighten the body of a cell body with a cell cap and insert a disposable glass fiber filter at the bottom of the cap. Place one folded wipe into each cell.

14.2 Spike each wipe with TDP surrogate as described in Section 12.

NOTE 3—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.

14.3 For the matrix spike and laboratory control samples, spike the wipe with spike solution containing TDG as described in Section 12.

14.4 Fill any void volume in the cell with inert material, such as hydromatrix or clean sand. Assemble each extraction cell by hand-tightening the caps on each end. Do not use a wrench or other tool to tighten the cap. If the extraction vessels are packed tightly, an over-pressurized condition can cause the system to shut down.

14.5 Load the cells in numerical order. Hang the cells vertically in the tray slots from the top caps; bottom cap shall contain the glass fiber filter.

14.6 Load rinse tubes into the rinse slots.

14.7 For each loaded sample, load a 60 mL labeled collection vial into the corresponding vial tray position. The label or any markings shall 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.

14.8 Extraction parameters for PFE system used to develop this test method are shown in Table 7.

NOTE 4—The parameters are different depending upon the wipe material used.

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

14.10 If the PFE is run under method control, it will extract cells in numerical order, injecting 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 will inject the extract(s) of each vial into the corresponding receiving vial(s) designated in the schedule.

14.11 The PFE extract is then concentrated in a nitrogen evaporation device to a small volume (8 to 10 mL). After concentration in the nitrogen evaporation device, the sample extract is decanted into a 10 mL K-D concentrator tube. If necessary, filter the extract using a Millex GV syringe-driven PVDF 0.22 µm pore size filter unit. Extracts are then placed on the nitrogen evaporation device at 50 °C, the sides are rinsed with methanol, and concentrated to 4 mL. If sample turnaround is less of a concern, the sample can be brought to a final volume of 2 mL, thereby improving the reporting limit.

NOTE 5—After use, empty the PFE cells and rinse or sonicate the end caps with water followed by acetone. Only the cell bodies, not the caps, can be cleaned in a dishwater or high temperature cleaning unit (less than 400 °C).

15. Calculation or Interpretation of Results

15.1 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 µg/wipe 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

TABLE 7 PFE Extraction Parameters

PFE Extraction Parameters	Whatman 42 Wipe	Gauze Pad
Pressure (Pa)	5.17×10^6 Pa	1.03×10^7 Pa
Temperature (°C)	50	100
Preheat Time (Minutes)	1	5
Purge During Pre-Heat	Off	Off
Heat Time (Minutes)	5	5
Static Time (Minutes)	1	5
Flush Volume (%)	60	40
Purge Time (Minutes)	1	1
Static Cycles	1	2
Solvent	10 mM Acetic Acid, 90:10 MeOH:H_2O	