Designation: D7598 – 16 (Reapproved 2017)

Standard Test Method for Determination of Thiodiglycol in Water by Single Reaction Monitoring Liquid Chromatography/Tandem Mass Spectrometry[1]

This standard is issued under the fixed designation D7598; 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 surface water by direct injection using liquid chromatography (LC) and detected with tandem mass spectrometry (MS/MS). TDG is qualitatively and quantitatively determined by this test method. This test method adheres to single reaction monitoring (SRM) mass spectrometry.

1.2 This test method has been developed by U.S. EPA Region 5 Chicago Regional Laboratory (CRL).

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 The detection verification level (DVL) and reporting range for TDG are listed in Table 1.

1.4.1 The DVL is required to be at a concentration at least 3 times below the reporting limit (RL) and have a signal/noise ratio greater than 3:1. Fig. 1 displays the signal/noise ratio at the DVL.

1.4.2 The RL is the concentration of the Level 1 calibration standard as shown in Table 2. The reporting limit for this test method is 100 µg/L.

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

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

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

D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water

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

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

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

2.2 *Other Documents:*

U.S. EPA publication SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods[3]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *detection verification level, DVL, n*—a concentration that has a signal/noise ratio greater than 3:1 and is at least three times below the reporting limit (RL).

3.2.2 *independent reference material, IRM, n*—a material of known purity and concentration obtained either from the National Institute of Standards and Technology (NIST) or other reputable supplier. The IRM shall be obtained from a different lot of material than is used for calibration.

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[2] 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.

[3] 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 Detection Verification Level and Reporting Range

Analyte	DVL (µg/L)	Reporting Range (µg/L)
Thiodiglycol	20	100–10 000

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, n*—Precision and Accuracy

3.3.13 *PPB, n*—parts per billion

3.3.14 *PPT, n*—parts per trillion

3.3.15 *QA, adj*—Quality Assurance

3.3.16 *QC, adj*—Quality Control

3.3.17 *RL, n*—Reporting Limit

3.3.18 *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 *µM, n*—micromolar, 1×10^{-6} moles/L

3.3.25 *VOA, n*—Volatile Organic Analysis

4. Summary of Test Methods

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

4.2 For thiodiglycol analysis, samples are shipped to the lab between 0°C and 6°C and analyzed within 7 days of collection. In the lab, the samples are spiked with surrogate, filtered using a syringe-driven filter unit and analyzed directly by LC/MS/MS.

4.3 Thiodiglycol and 3,3'-thiodipropanol (surrogate) 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 3,3'-thiodipropanol surrogate recovery.

5. Significance and Use

5.1 Thiodiglycol 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. Thiodiglycol is both a mustard gas precursor and degradant as well as an ingredient in water-based inks, ballpoint pen inks, dyes and some pesticides.[4]

5.2 This test method has been investigated for use with reagent and surface water.

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, 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 cleaned with acetone, then methanol.

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 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*—A complete LC system is needed in order to analyze samples.[5] This should include a sample injection system, a solvent pumping system capable of mixing solvents, a sample compartment capable of maintaining required temperature and a temperature controlled column compartment. A 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*[6]—Any column that achieves adequate resolution may be used. The retention times and order of elution may change depending on the column that is used and need to be monitored.

[4] Additional information about CWC and thiodiglycol is available from the Organization for the Prohibition of Chemical Weapons (OPCW), http://www.opcw.org.

[5] A Waters Alliance High Performance Liquid Chromatography (HPLC) System (a trademark of the Waters Corporation, Milford, MA), or equivalent, was found suitable for use. The multi-laboratory study included Agilent and Waters LC systems.

[6] A SIELC—A Primesep SB 5 µm, 100 Å particle, 150 mm × 2.1 mm, or equivalent, was found suitable for use.

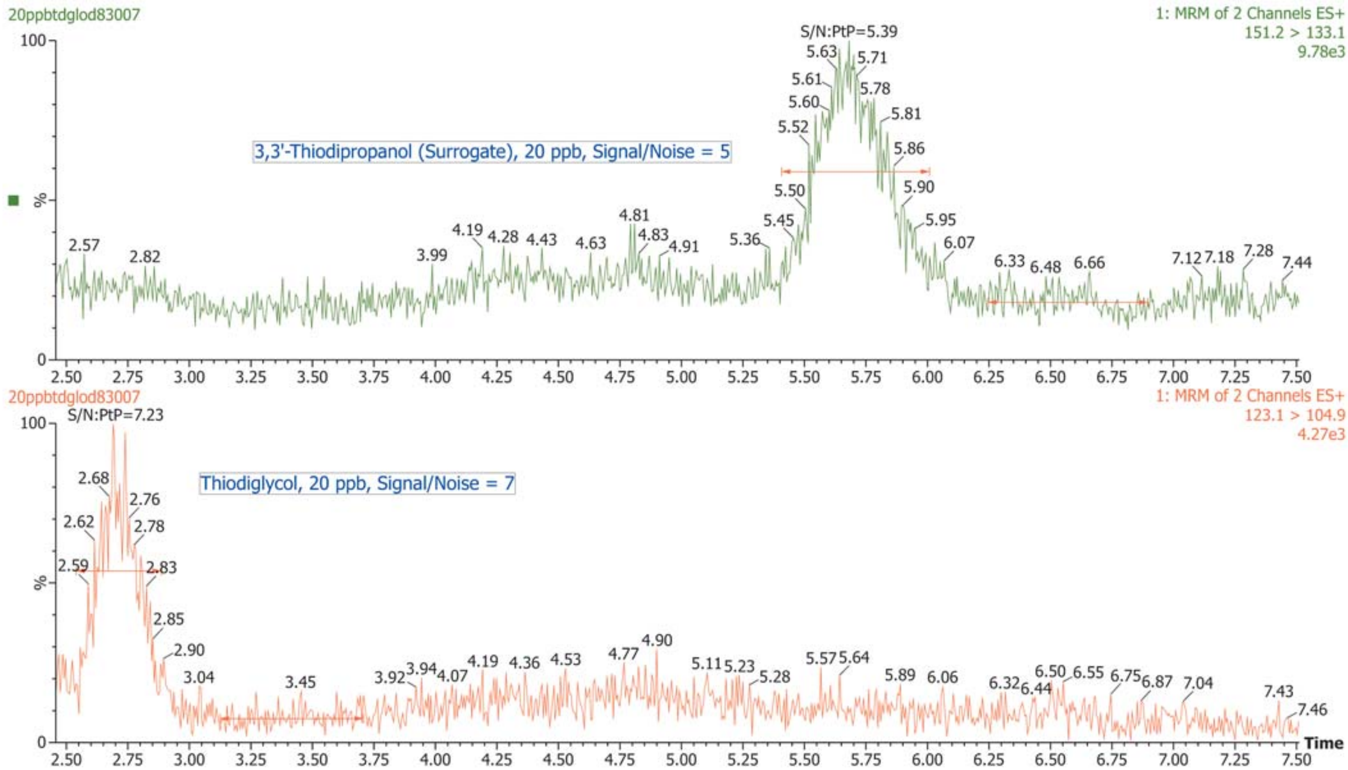

FIG. 1 Example SRM Chromatograms Signal/Noise at Detection Verification Level

TABLE 2 Concentrations of Calibration Standards (PPB)

Analyte/Surrogate	LV 1	LV 2	LV 3	LV 4	LV 5	LV 6	LV 7
Thiodiglycol	100	250	500	1 000	2 500	5 000	10 000
3,3'-Thiodipropanol	100	250	500	1 000	2 500	5 000	10 000

7.1.3 *Tandem Mass Spectrometer (MS/MS) System*—A MS/MS system capable of MRM analysis.[7] A system that is capable of performing at the requirements in this standard may be used.

7.2 *Filtration Device:*

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

7.2.1.1 A 25-mL lock tip glass syringe size is recommended since a 25-mL sample size is used in this test method.

7.2.2 *Filter Unit*[8]—A PVDF befilter units were used to filter the samples.

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.[9] Other reagent grades may be used provided they are first determined they are 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 Methanol (CAS # 67-56-1).

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

8.7 Ammonium formate (CAS # 540-69-2).

8.8 Formic acid (64-18-6).

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[7] A Waters Quattro micro API mass spectrometer (a trademark of the Waters Corporation, Milford, MA), or equivalent, was found suitable for use. The multi-laboratory study included Applied Biosystems and Waters mass spectrometers.

[8] A Millex HV Syringe Driven Filter Unit PVDF 0.45 µm (Millipore Corporation, Catalog # SLHV033NS; Millex is a trademark of Merck KGAA, Darmstadt, Germany) has been found suitable for use for this test method, any filter unit may be used that meets the performance of this test method may be used.

[9] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. 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 Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.9 Thiodiglycol (CAS # 111-48-8).

8.10 3,3'-Thiodipropanol (CAS # 10595-09-2).

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 Safety Data Sheets (SDS) for all reagents used in this test method.

10. Sampling

10.1 *Sampling*—Grab samples must be collected in ≥25-mL pre-cleaned amber glass bottles with Teflon-lined caps demonstrated to be free of interferences. This test method requires a 25-mL sample size per analysis. Conventional sampling practices should be followed. Refer to Guide D3856 and Practices D3694.

10.2 *Preservation*—Store samples between 0°C and 6°C from the time of collection until analysis. Analyze the sample within 1 day of collection.

11. Preparation of LC/MS/MS

11.1 *LC Chromatograph Operating Conditions:*[5]

11.1.1 Injection volumes of all calibration standards and samples are 50 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 3.

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

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

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

11.1.5 *Autosampler Purge*—Three loop volumes.

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

11.2 *Mass Spectrometer Parameters:*[7]

11.2.1 In order 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 only 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 4.

The instrument is set in the Electrospray (+) positive setting.
Capillary Voltage: 3.5 kV
Cone: Variable depending on analyte (Table 4)
Extractor: 2 Volts
RF Lens: 0.2 Volts
Source Temperature: 120°C
Desolvation Temperature: 300°C
Desolvation Gas Flow: 500 L/hr
Cone Gas Flow: 25 L/hr
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 4)
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 seconds
Inter-Scan Delay: 0.1 seconds
Repeats: 1
Span: 0 Daltons
Dwell: 0.1 Seconds

TABLE 3 Gradient Conditions for Liquid Chromatography

Time (min)	Flow (µL/min)	Percent CH_3CN	Percent Water	Percent 500 mmolar Ammonium Formate/2% Formic Acid
0	300	0	95	5
2.5	300	0	95	5
6	300	90	5	5
10	300	90	5	5
12	300	0	95	5
16	300	0	95	5

12. Calibration and Standardization

12.1 The mass spectrometer must be calibrated per manufacturer specifications before analysis. In order that analytical values obtained using this test method are valid and accurate within the confidence limits of the test method, the following procedures must be followed when performing the test method.

12.2 *Calibration and Standardization*—To calibrate the instrument, analyze seven calibration standards containing the seven concentration levels of TDG and 3,3'-thiodipropanol prior to analysis as shown in Table 2. A calibration stock standard solution is prepared from standard materials or purchased as certified solutions. Stock standard solution A (Level 7) containing TDG and 3,3'-thiodipropanol is prepared at Level 7 concentration and aliquots of that solution are diluted to prepare Levels 1 through 6. The following steps will produce standards with the concentration values shown in Table 2. The analyst is responsible for recording initial component weights carefully when working with pure materials and correctly carrying the weights through the dilution calculations.

12.2.1 Prepare stock standard solution A (Level 7) by adding to a 100-mL volumetric flask individual methanol solutions of the following: 250 µL of TDG and 3,3'-thiodipropanol each at 4 g/L, dilute to 100 mL with water. The preparation of the Level 7 standard can be accomplished using different volumes and concentrations of stock solutions as is accustomed in the individual laboratory. Depending on stock concentrations prepared, the solubility at that concentration will have to be ensured.

12.2.2 Aliquots of Solution A 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 hours to ensure optimum results. Stock calibration standards are routinely replaced every six months if not previously discarded for quality control failure. Calibration standards are not filtered.

TABLE 4 Retention Times, SRM Ions, 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

12.2.3 Inject each standard and obtain a chromatogram for each one. 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.

12.2.4 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. Forcing the calibration through the origin is not recommended.

12.2.5 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.

12.2.6 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 or high point is excluded, a six point curve is acceptable using a quadratic fit. An initial seven-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. Each calibration point used to generate the curve must have a calculated percent deviation less than 25 % from the generated curve.

12.2.7 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.

12.2.8 A midpoint calibration check standard must be analyzed at the end of each batch of 20 samples or within 24 hours 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 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 All samples are prepared using Class A glass volumetric glassware. The sample volume used throughout this test method is 25 mL. Every sample, the entire 25-mL volume, is filtered through the filtration device described in Section 7.2 only after all required spiking solutions are added and mixed throughout the sample.

12.3.1 A new filter unit is used for each sample. The syringe must be cleaned between each filtration. It is the analyst's responsibility to ensure that the syringe is clean. A possible way of cleaning the syringe between filtrations is first by rinsing with at least 5 syringe volumes of water, followed by at least 3 volumes of acetone, then 3 volumes of methanol and finally rinsed with water to remove any residual solvent.

12.4 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, new instrument, etc., perform a precision and bias study to demonstrate laboratory capability.

12.4.1 Analyze at least four replicates of a sample solution containing TDG and 3,3'-thiodipropanol at a concentration in the calibration range of Levels 3 to 5. The matrix and chemistry should be similar to the solution used in this test method. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

12.4.2 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.

12.4.3 This study should be repeated until the single operator precision and mean recovery are within the limits in Table 5. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

12.4.3.1 The QC acceptance criteria for the initial demonstration of performance in Table 5 were generated from a

TABLE 5 QC Acceptance Criteria

Analyte	Test Conc. (µg/L)	Initial Demonstration of Performance			Lab Control Sample	
		Recovery (%)		Precision	Recovery (%)	
		Lower Limit	Upper Limit	Maximum % RSD	Lower Limit	Upper Limit
Thiodiglycol	2500	83	134	12	81	137
3,3'-Thiodipropanol (Surrogate)	2500	73	132	12	72	133

multi-laboratory method validation involving seven laboratories. The descriptive statistics from this validation are shown in the Precision and Bias Section. The analyst must be aware that the performance data generated from multiple-laboratory data tend to be significantly wider than those generated from single-laboratory data. It is recommended that the laboratory generate their own in-house QC acceptance criteria which meets or exceeds the criteria in this standard. References on how to generate QC acceptance criteria are ASTM Standards Practices D2777, D5847, and E2554 or Method 8000B in U.S. EPA publication SW-846, which may be helpful.

12.5 *Surrogate Spiking Solution:*

12.5.1 A surrogate standard solution containing 3,3'-thiodipropanol is added to all samples. A stock surrogate spiking solution is prepared in methanol at 2500 ppm. Spiking 25 µL of this spiking solution into a 25 mL water sample results in a concentration of 2.5 ppm of the surrogate 3,3'-thiodipropanol in the 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.

12.6 *Method Blank:*

12.6.1 Analyze a reagent water blank with each batch of 20 or fewer samples. The concentration of TDG found in the blank must be below the DVL. 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.

12.7 *Laboratory Control Sample (LCS):*

12.7.1 To ensure that the test method is in control, analyze a LCS prepared with TDG at a concentration in the calibration range of Levels 3 to 5. The LCS is prepared following the analytical method and analyzed with each batch of 20 samples or less. Prepare a stock matrix spiking solution in methanol containing TDG at 2500 ppm. Spike 25 µL of this stock solution into 25 mL of water to yield a concentration of 2.5 ppm of TDG in the sample. The result obtained for the LCS must fall within the limits in Table 5.

12.7.2 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.

12.8 *Matrix Spike (MS):*

12.8.1 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 by spiking the sample with a known concentration of TDG and following the analytical method. Prepare a stock matrix spiking solution in methanol containing TDG at 2500 ppm. Spike 25 µL of this stock solution into 25 mL of water to yield a concentration of 2.5 ppm of TDG in the sample.

12.8.2 If the spiked concentration plus the background concentration exceeds that of the Level 7 calibration standard, the sample must be diluted to a level near the midpoint of the calibration curve.

12.8.3 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.

12.8.4 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.

12.8.5 The matrix spike/matrix spike duplicate (MS/MSD) limits in Table 6 were generated by seven laboratories across the country using surface waters collected near their facilities. The matrix variation between the seven different surface waters may have a tendency to generate significantly wider control limits than those generated by a single laboratory in one surface water matrix. It is recommended that the laboratory generate their own in-house QC acceptance criteria which meets or exceeds the criteria in this standard.

12.8.5.1 The laboratory should generate their own in-house QC acceptance criteria after the analysis of 15–20 matrix spike samples of a particular surface water matrix. References on how to generate QC acceptance criteria are ASTM standards Practices D5847, D2777, and E2554 or Method 8000B in U.S. EPA publication SW-846, which may be helpful.

TABLE 6 MS/MSD QC Acceptance Criteria

Analyte	Test Conc. (µg/L)	MS/MSD		
		Recovery (%)		Precision
		Lower Limit	Upper Limit	Maximum RPD (%)
Thiodiglycol	2500	44	140	20
3,3'-Thiodipropanol (Surrogate)	2500	58	132	17

12.9 *Duplicate:*

12.9.1 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.

12.9.2 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. Relative percent difference:

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

where:

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

The vertical bars in Eq 2 indicate the absolute value of the difference, hence, RPD is always expressed as a positive value.

12.9.3 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 water samples are shipped chilled between 0°C and 6°C in ≥25 mL pre-cleaned amber glass bottles with Teflon-lined caps and stored in the laboratory between 0°C and 6°C. The samples must be analyzed within 7 days of collection. If the samples are above 6°C when received or during storage, or not analyzed within 7 days of collection the data is qualified estimated and noted in the case narrative that accompanies the data.

13.2 In the laboratory, a 25-mL Class A glass volumetric flask is used to measure a 25-mL aliquot of the sample. Every sample is then spiked with the surrogate as described in Section 12.5. The laboratory control and matrix spike samples are then spiked with the target compound as described in Sections 12.7 and 12.8. The samples are then shaken in order to mix the spike solutions throughout the water sample. The sample, the entire 25-mL volume, is filtered through the filtration device described in Section 7.2. An aliquot of that filtered sample is placed into 2-mL amber glass LC vials for analysis.

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), 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 3,3'-thiodipropanol surrogate, 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/L (ppb) 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 mid-point of the calibration range and re-analyzed.

15. Report

15.1 Determine the results in units of µg/L (ppb) in a water sample. Calculate the concentration in the sample using the linear or quadratic calibration curve generated. All data that does not meet the specifications in the test method must be appropriately qualified.

16. Precision and Bias[10]

16.1 The determination of precision and bias was conducted through EPA and generated applicable data to determine the precision and bias as described in Practice D2777.

16.2 This test method was tested by U.S. EPA Region 5 Chicago Regional Laboratory (CRL) on reagent water. The samples were spiked with target compound and surrogate to obtain a 2500 ppb concentration of each as described in Section 12. Table 7 contains the recoveries and standard deviation (SD) for the surrogate and target compound.

16.3 This test method was tested by U.S. EPA Region 5 Chicago Regional Laboratory (CRL) on Chicago River water. The samples were spiked with target compound and surrogate to obtain a 2500 ppb concentration of each as described in Section 12. Table 8 contains the recoveries and standard deviation (SD) for the surrogate and target compound.

16.4 *Multi-Laboratory Validation*—This test method has been tested by seven laboratories using reagent water and their local surface waters. The incorporation of the testing laboratory's individual local surface water was chosen to validate the test method using various surface water matrices. The surface waters were from California, Colorado, Ohio, Maryland, Mississippi, Massachusetts and Virginia. The reagent and local surface waters were spiked across the reporting range in quadruplicate for reagent water and duplicate for surface water. The multi-laboratory data for reagent water is shown in Table 9 and for surface waters in Table 10. Results of this collaborative study may not be typical of the results for matrices other than those studied. Grubbs' outliers were removed.

[10] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1186. Contact ASTM Customer Service at service@astm.org.

TABLE 7 Single-Laboratory Recovery Data in Reagent Water

Precision and Accuracy Samples	Measured ppb from 2.50 ppm spikes	
	Thiodiglycol	3,3'-Thiodipropanol
1	2.77	2.85
2	2.83	2.83
3	2.84	2.89
4	2.93	2.92
5	2.95	2.91
Average Recovery	2.86	2.88
Average Percent Recovery	114.56 %	115.20 %
Standard Deviation (SD)	0.075	0.039
% Relative SD	2.61 %	1.34 %

TABLE 8 Single-Laboratory Recovery Data in Chicago River Water

Sample	Measured ppm from 2.50 ppm spikes	
	Thiodiglycol	3,3'-Thiodipropanol
Blank (Chicago River Water)	ND	2.85
1	2.60	3.20
2	2.66	3.23
3	2.62	3.20
4	2.63	3.22
5	2.78	3.22
Average Recovery	2.66	3.15
Average Percent Recovery	106.40 %	126.00 %
Standard Deviation (SD)	0.072	0.149
% Relative SD	2.69 %	4.73 %

TABLE 9 Multi-Laboratory Recovery Data in Reagent Water

Analyte	Spike Conc. (ppb)	# Results	# Labs	Bias			Precision			
				Mean Recovery (%)	Min Recovery (%)	Max Recovery (%)	Overall SD (%)	Pooled within-lab SD (%)	Overall RSD (%)	Pooled within-lab RSD (%)
3,3'-Thiodipropanol (Surrogate)	2500	112	7	108.64	84.60	134.00	12.40	7.91	11.41	7.18
Thiodiglycol	100	26	7	105.26	81.20	150.00	16.08	10.27	15.28	10.29
Thiodiglycol	250	28	7	111.03	91.00	148.00	13.83	7.40	12.46	6.32
Thiodiglycol	1000	4	1	88.78	86.90	89.80	1.32	1.32	1.49	1.49
Thiodiglycol	2500	28	7	102.36	82.68	135.00	12.98	6.62	12.68	6.06
Thiodiglycol	7500	24	6	106.13	73.57	143.00	18.83	10.47	17.75	9.70

TABLE 10 Multi-Laboratory Recovery Data in Surface Water

Analyte	Spike Conc. (ppb)	# Results	# Labs	Bias			Precision			
				Mean Recovery (%)	Min Recovery (%)	Max Recovery (%)	Overall SD (%)	Pooled within-lab SD (%)	Overall RSD (%)	Pooled within-lab RSD (%)
3,3'-Thiodipropanol (Surrogate)	2500	54	7	92.26	50.80	118.00	19.51	6.23	21.15	7.72
Thiodiglycol	100	14	7	86.43	37.00	110.80	22.94	13.34	26.54	15.69
Thiodiglycol	250	14	7	104.90	78.20	129.00	12.38	10.10	11.80	9.95
Thiodiglycol	2500	14	7	94.68	71.60	123.60	15.13	4.77	15.98	4.52
Thiodiglycol	7500	12	6	93.95	70.79	118.00	15.00	6.89	15.97	6.67

17. Quality Control

17.1 A crucial part of a test method is quality control. A laboratory should follow their in-house QA/QC procedures and should meet or exceed the criteria given in this test method. The quality-control criteria are given in the various test method sections. Section 10 contains the sampling and preservation requirements and Section 12 contains the majority of quality control requirements when following this test method. Section 12 includes requirements for calibration, precision and bias study to demonstrate laboratory capability, initial demonstration of performance, surrogate, method blank, reporting limit check, laboratory control, matrix spike and duplicate sample requirements. An IRM should be incorporated into the analysis periodically to verify that standard concentrations are comparable between sources. The IRM criteria should be based upon the laboratories QA/QC policies and the individual data quality objectives.

18. Keywords

18.1 liquid chromatography; mass spectrometry; thiodiglycol; water