



Designation: D7598 – 16 (Reapproved 2017)

Standard Test Method for Determination of Thiodiglycol in Water by Single Reaction Monitoring Liquid Chromatography/Tandem Mass Spectrometry¹

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 $\mu\text{g/L}$.

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.*

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. 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 Methods³

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.

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.

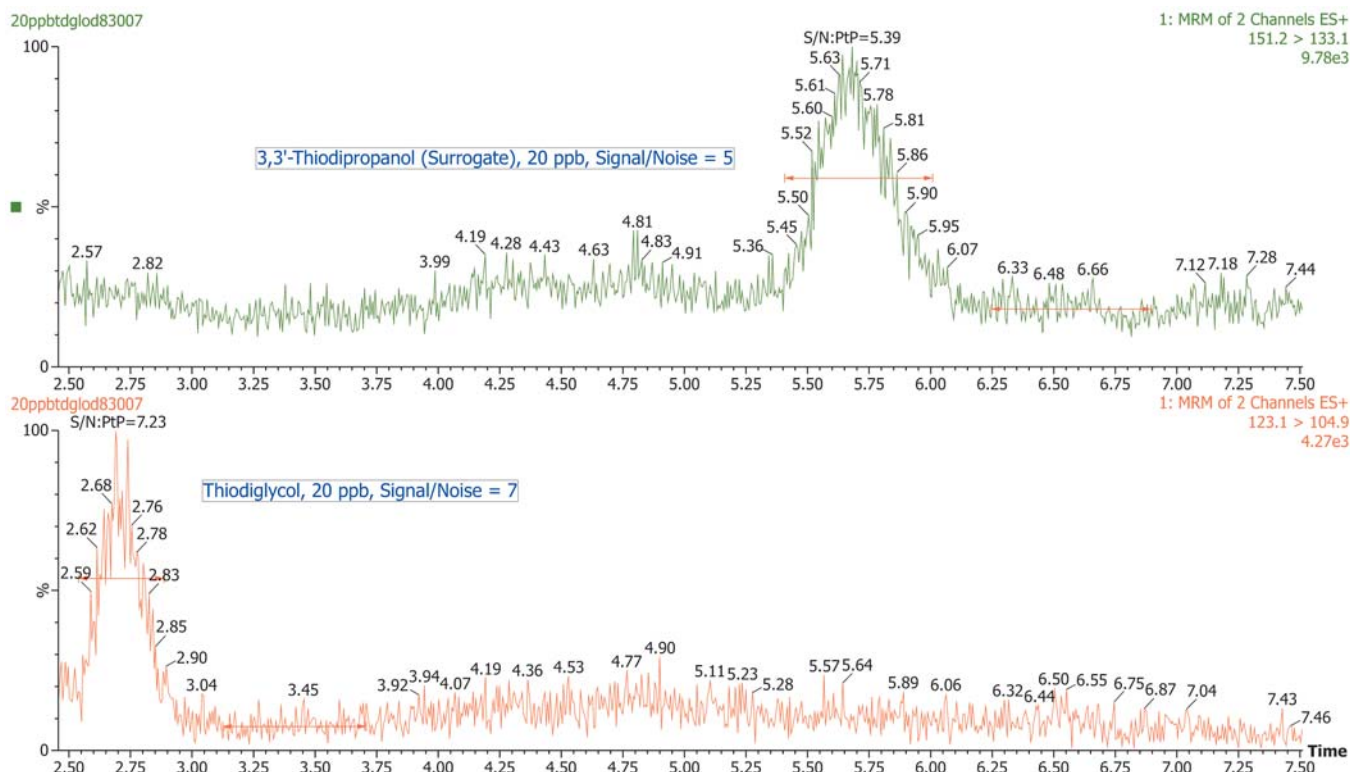


FIG. 1 Example SRM Chromatograms Signal/Noise at Detection Verification Level

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 bfilter 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).

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.