Designation: ~~D7731 – 11ε1~~ D7731 – 17

Standard Test Method for Determination of Dipropylene Glycol Monobutyl Ether and Ethylene Glycol Monobutyl Ether in Sea Water by Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation D7731; 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.

~~ε[1] NOTE—This test method was changed editorially in August 2011.~~

1. Scope

1.1 This ~~procedure~~ test method covers the determination of ~~Dipropylene Glycol Monobutyl Ether (DPGBE) and Ethylene Glycol Monobutyl Ether~~dipropylene glycol monobutyl ether (DPGBE) and ethylene glycol monobutyl ether (EGBE) in sea water by direct injection using liquid chromatography (LC) and detection with tandem mass spectrometry (MS/MS). These analytes are qualitatively and quantitatively determined by this test method. This test method adheres to selected reaction monitoring (SRM) mass spectrometry.

1.2 The ~~Detection Verification Level~~detection verification level (DVL) and ~~Reporting Range~~reporting range for DPGBE and EGBE are listed in Table 1.

1.2.1 The DVL is required to be at a concentration at least 3 times below the ~~Reporting Limit~~reporting limit (RL) and have a signal/noise ratio greater than 3:1. Fig. 1 and Fig. 2 display the signal/noise ratio of the single reaction monitoring (SRM) transition.

1.2.2 The reporting limit is the concentration of the Level 1 calibration standard as shown in Table 4 for DPGBE and EGBE, taking into account the ~~20%~~ 20 % sample preparation dilution factor.

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 *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~~ safety, health, and ~~health~~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:*[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

2.2 *Other Standards:*[3]

EPA ~~publication~~Publication SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods

3. Terminology

3.1 *Definitions:*

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

[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.

Current edition approved ~~May 1, 2011~~Dec. 15, 2017. Published ~~June 2011~~January 2018. Originally approved in 2011. Last previous edition approved in 2011 as D7731 – 11ε1. DOI: ~~10.1520/D7731-11E01.~~10.1520/D7731-17.

[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~~5301 Shawnee Rd., Alexandria, VA 22312, http://www.ntis.gov.

TABLE 1 Detection Verification Level (DVL) and Reporting Range

Analyte	DVL (µg/L)	Reporting Range (µg/L)
DPGBE	0.2	1–10
EGBE	25	125–1250

3.2 ~~*Definitions:*~~*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 3 times below the ~~Reporting Limit~~reporting limit (RL).

3.2.2 *reporting limit, RL, n*—the concentration of the lowest-level calibration standard used for quantification.

3.2.2.1 *Discussion*—

In this test method, a ~~20 mL~~ 20-mL sample aliquot is diluted to a ~~25 mL~~ 25-mL final volume after thoroughly rinsing the collection vial with acetonitrile for quantitative transfer. In this case, the lowest calibration level of 100 ppb for EGBE would allow for a reporting limit of 125 ppb to be achieved.

3.3 ~~*Symbols:*~~*Abbreviations:*

~~3.2.1 *ppb*—parts per billion, µg/L~~

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

~~3.2.2 *ppt*—parts per trillion, ng/L~~

3.3.2 *NA*—no addition

~~3.2.3 *mM*—millimolar, 1 x 10^{-3} moles/L~~

3.3.3 *ND*—non-detect

~~3.2.4 *NA*—no addition~~

3.3.4 *ppb*—parts per billion, µg/L

~~3.2.5 *ND*—non-detect~~

3.3.5 *ppt*—parts per trillion, ng/L

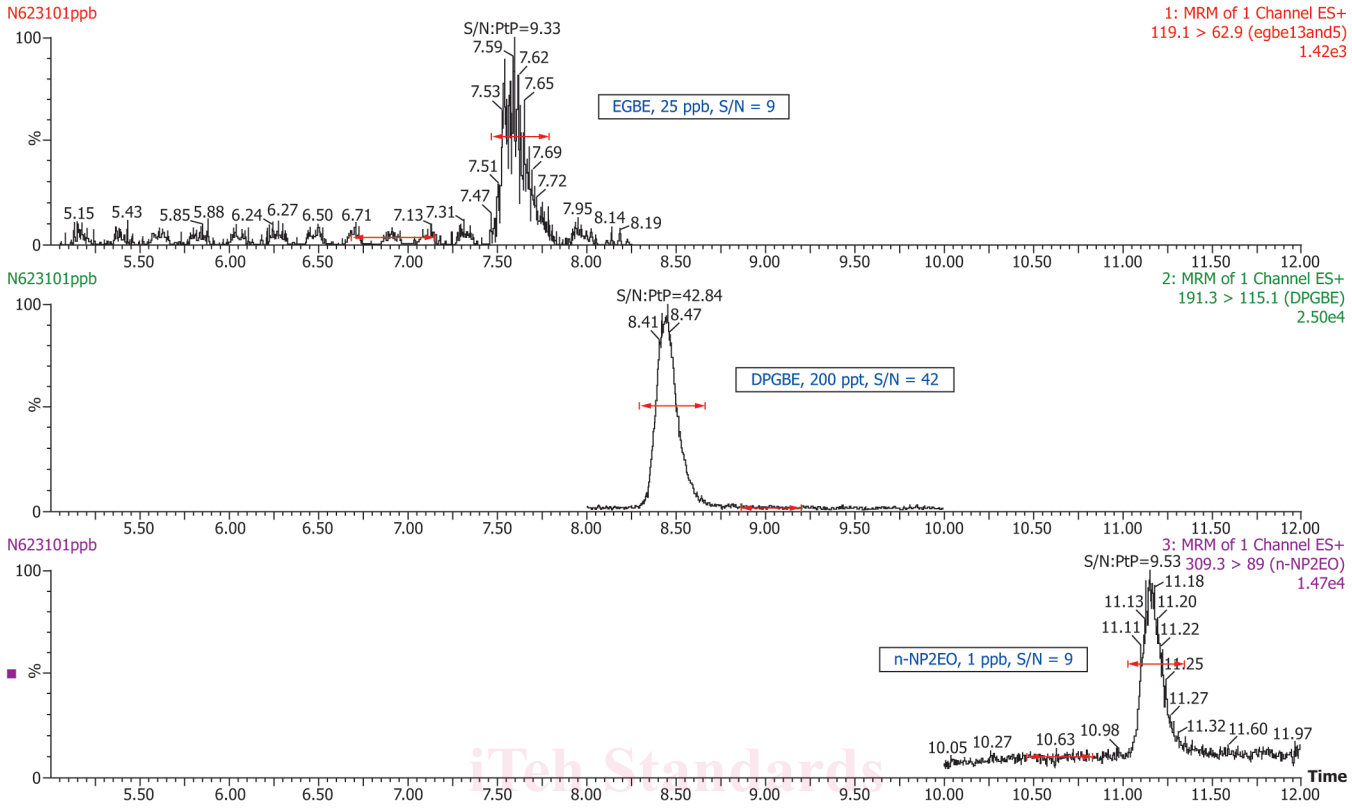

FIG. 1 Detection Verification Level Signal/Noise ~~Ratio.~~Ratio

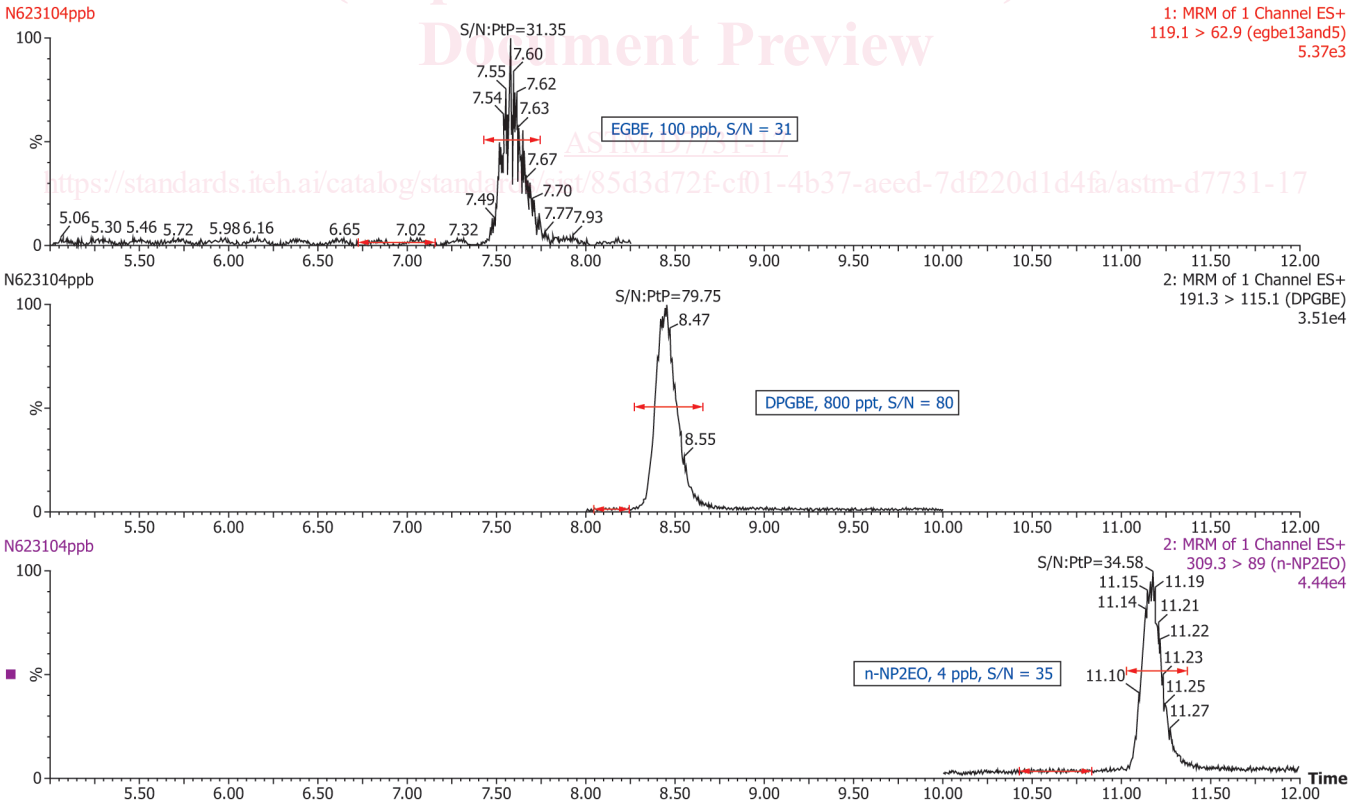

FIG. 2 Reporting Level (Calibration ~~standard)~~Standard) Signal/Noise ~~Ratio.~~Ratio

4. Summary of Test Method

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

4.2 For DPGBE and EGBE analysis, samples are shipped to the lab between 0°C and 6°C and analyzed within 5 days of collection. The DOW MSDS sheet on ~~DOWANOL* DPNB~~ DOWANOL*DPNB glycol ether (DPGBE) ~~Issue~~(Issue Date: ~~06/18/2010~~06/18/2010) lists that the material is readily biodegradable. The Organisation for Economic Co-Operation and Development (OECD) 302B Test lists ~~96%~~ 96 % biodegradation in 28 days.

4.3 In the lab, the entire collected ~~20 mL~~ 20-mL sample is spiked with surrogate and brought to a volume of 25 mL with acetonitrile. This prepared sample is then filtered using a syringe driven filter unit, and analyzed by LC/MS/MS. If visible oil is present, the prepared sample is allowed to settle resulting in an oil layer at the top of the ~~25 mL~~ 25-mL solution. A portion of the aqueous (bottom) layer is filtered, leaving the oil layer behind, through a syringe driven filter assembly and analyzed by LC/MS/MS.

4.4 DPGBE, EGBE, and surrogate are identified by retention time and one SRM transition. The target analytes and surrogate are quantitated using the SRM transitions utilizing an external calibration. The final report issued for each sample lists the concentration of DPGBE, EGBE, and the surrogate recovery.

5. Significance and Use

5.1 DPGBE and EGBE have a variety of residential and industrial applications such as cleaning formulations, surface coatings, inks, and cosmetics. These analytes may be released into the environment at levels that may be harmful to aquatic life.

5.2 This test method has been investigated for use with reagent and sea 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 detergent and rinsed in hot water followed by distilled water. Detergents containing DPGBE or EGBE must not be used. 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 followed by 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 in 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~~*LC/MS/MS System:*

7.1.1 *Liquid Chromatography System*—A complete LC system is needed in order to analyze samples.[4] Any 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*—~~Waters- XBridge™~~,Waters XBridge,[5] 2.1 ~~x~~× 150 mm, ~~3.5 µm~~ 3.5-µm particle size was used to develop this test method. Any column that achieves baseline resolution of these analytes may be used. Baseline resolution simplifies data analysis and can reduce the chance of ion suppression, leading to higher limits of detection. 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 System*—A MS/MS system capable of SRM analysis.[6] Any system that is capable of performing at the requirements in this procedure may be used.

7.2 *Filtration Device:*

7.2.1 *Hypodermic ~~syringe~~—Syringe*—A ~~Lock Tip Glass Syringe~~ lock-tip glass syringe capable of holding a ~~Millex®~~Millex HV Syringe Driven Filter Unit PVDF 0.22 µm,[7,8] or similar, may be used.

7.2.1.1 A ~~25 mL Lock Tip Glass Syringe~~ 25-mL lock-tip glass syringe size was used in this test method.

---

[4] A Waters Alliance High Performance Liquid Chromatography (HPLC) ~~System~~ System, a trademark of the Waters Corporation, Milford, MA, was used to develop this test method. All parameters in this test method are based on this system and may vary depending on your instrument.

[5] The Waters XBridge is a trademark of the Waters Corporation, Milford, MA.

[6] A Waters Quattro micro API tandem quadrupole mass ~~spectrometer~~ spectrometer, a trademark of the Waters Corporation, Milford, MA, was used to develop this test method. All parameters in this test method are based on this system and may vary depending on your instrument.

[7] The sole source of supply of the Millex HV Syringe Driven Filter Unit PVDF 0.45 µm known to the committee at this time is Millipore Corporation, Catalog # SLHV033NS. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[8] Millex is a trademark of Merck KGAA, Darmstadt, Germany.

7.2.2 *Filter*—~~Millex®~~Millex HV Syringe Driven Filter Unit PVDF 0.22 ~~µm (Millipore Corporation, Catalog #SLGV033NS) or similar~~µm, or similar, 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.[9] 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 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 Formic Acid (CAS # 64-18-6).

8.7 2–Propanol (CAS # 67-63-0).

8.8 *DPGBE*—Dipropylene Glycol Monobutyl Ether (CAS # 29911-28-2).

8.9 *EGBE*—Ethylene Glycol Monobutyl Ether ~~(CAS#~~ (CAS # 111-76-2).

8.10 *n-NP2EO*—~~normal- Nonylphenol Diethoxylate (CAS#~~ normal-Nonylphenol Diethoxylate (CAS # Not available).

8.11 EGBE-D_4 (2-butoxyethanol (1,1,2,2-D_4)) (Optional Surrogate, Unlabeled ~~CAS# 111-76- 2).~~CAS # 111-76-2).

9. Hazards

9.1 Normal laboratory safety applies to this test 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 test method.

10. Sampling

10.1 *Sampling and Preservation*—~~—~~Grab samples should be collected in ~~20 mL~~ 20-mL pre-cleaned glass vials with ~~Teflon® lined~~ TFE-fluorocarbon–lined septa caps demonstrated to be free of interferences. The vial should be filled to approximately 20 mL. This may be just below the neck of the vial, depending on the vial manufacturer. This test method is based on a ~~20 mL~~ 20-mL sample size per analysis. Each sample should be collected in duplicate and a quadruplicate sample must be included with each sample batch of 10 for MS/MSD quality control analyses. Store samples between 0°C and 6°C from sample collection to sample preparation. Analyze the sample within ~~5~~five days of collection.

[9] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, ~~D.C.~~DC. For ~~Suggestions~~suggestions on the testing of reagents not listed by the American Chemical Society, see ~~*Annual*~~*Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National ~~Formulators~~Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

11. Preparation of Apparatus

11.1 *Liquid Chromatograph Operating Conditions:*[4]

11.1.1 Injection volumes of all calibration standards and samples are made at ~~100 µL~~ 100-µL volume. 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. Divert the column flow away from the electrospray source from 0 to 5 minutes after injection. Flow diversion to waste may be done using the mass spectrometer divert valve. Divert tubing configurations vary from manual injection. Sea water samples contain nonvolatile salts, the first 5 minute elution is diverted in order to keep the mass spectrometer source clean.

11.2 *LC Conditions:*

11.2.1 *Needle Wash Solvent*—~~60% Acetonitrile/40% 2-propanol~~60 % Acetonitrile/40 % 2-propanol.

11.2.2 *Temperatures*—Column, 30°C; ~~Sample~~sample compartment, 15°C.

11.2.3 *Seal Wash*—~~60% Acetonitrile/40%~~ 60 % Acetonitrile/40 % 2-propanol.

11.3 *Mass Spectrometer Parameters:*[6]

11.3.1 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 procedure contains DPGBE, EGBE, and one surrogate which are in three SRM acquisition functions to optimize sensitivity. Variable parameters regarding retention times, SRM transitions, and cone and collision energies are shown in Table 3~~Table 3.~~. Mass spectrometer parameters used in the development of this test method are listed here:

~~Capillary Voltage: 3.5 kV~~
~~Cone: Variable depending on analyte (Table 3)~~
~~Extractor: 2 Volts~~
~~RF Lens: 0.2 Volts~~
~~Source Temperature: 120°C~~
~~Desolvation Temperature: 350°C~~
~~Desolvation Gas Flow: 800 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 3)~~
~~Exit Energy: 1~~
~~Low Mass Resolution 2: 14.5~~
~~High Mass resolution 2: 14.5~~
~~Ion Energy 2: 0.8~~
~~Multiplier: 650~~
~~Gas Cell Pirani Gauge: 7.0 x 10^{-3} Torr~~
~~Inter-Channel Delay: 0.1 seconds~~
~~Inter-Scan Delay: 0.1 seconds~~
~~Dwell: 0.1 seconds~~
~~Solvent Delay: 5 minutes~~

Capillary Voltage:	3.5 kV
Cone:	Variable depending on analyte (Table 3)
Extractor:	2 Volts
RF Lens:	0.2 Volts
Source Temperature:	120°C
Desolvation Temperature:	350°C
Desolvation Gas Flow:	800 L/hr
Cone Gas Flow:	25 L/hr
Low Mass Resolution 1:	14.5

TABLE 2 Gradient Conditions for Liquid Chromatography

Time (min)	Flow (mL/min)	Percent ~~95% Water/ 5%~~ 95 % Water/ 5 % CH_3CN	Percent CH_3CN	Percent ~~2%~~ 2 % Formic Acid ~~95% Water/ 5%~~ 95 % Water/ 5 % CH_3CN
0.0	0.30	95	0	5
2.0	0.30	95	0	5
5.0	0.30	0	95	5
14.0	0.30	0	95	5
15.0	0.30	95	0	5
18.0	0.30	95	0	5