Designation: 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.

1. Scope

1.1 This test method covers the determination of 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 (DVL) and 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 (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 % 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, 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:*[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 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.

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 3 times below the 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 sample aliquot is diluted to a 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 *Abbreviations:*

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

3.3.2 *NA*—no addition

3.3.3 *ND*—non-detect

3.3.4 *ppb*—parts per billion, µg/L

3.3.5 *ppt*—parts per trillion, ng/L

[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), 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

4. Summary of Test Method

4.1 This is a 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 glycol ether (DPGBE) (Issue Date: 06/18/2010) lists that the material is readily biodegradable. The Organisation for Economic Co-Operation and Development (OECD) 302B Test lists 96 % biodegradation in 28 days.

4.3 In the lab, the entire collected 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 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:*

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,[5] 2.1 × 150 mm, 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*—A lock-tip glass syringe capable of holding a 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 size was used in this test method.

7.2.2 *Filter*—Millex HV Syringe Driven Filter Unit PVDF 0.22 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

[4] A Waters Alliance High Performance Liquid Chromatography (HPLC) 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, 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.

[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 *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.

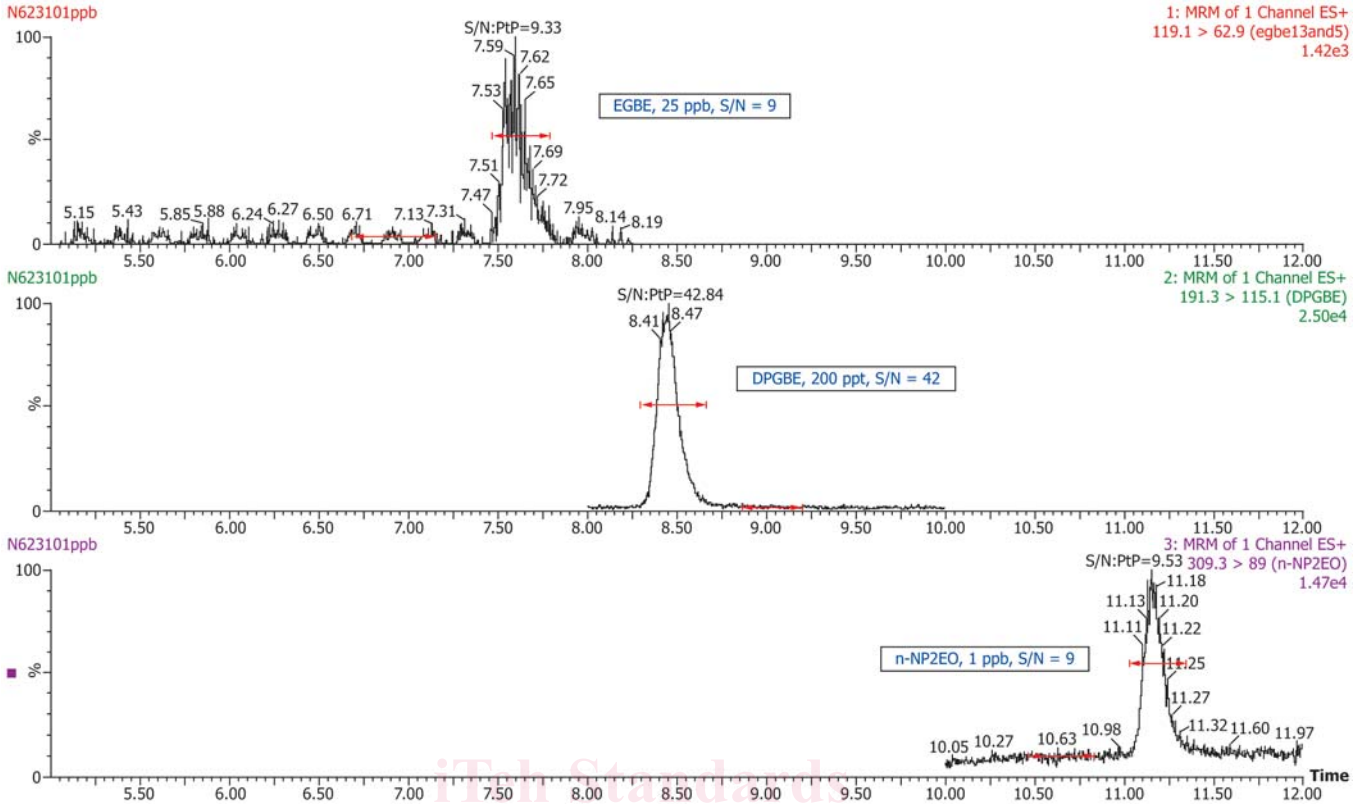

FIG. 1 Detection Verification Level Signal/Noise Ratio

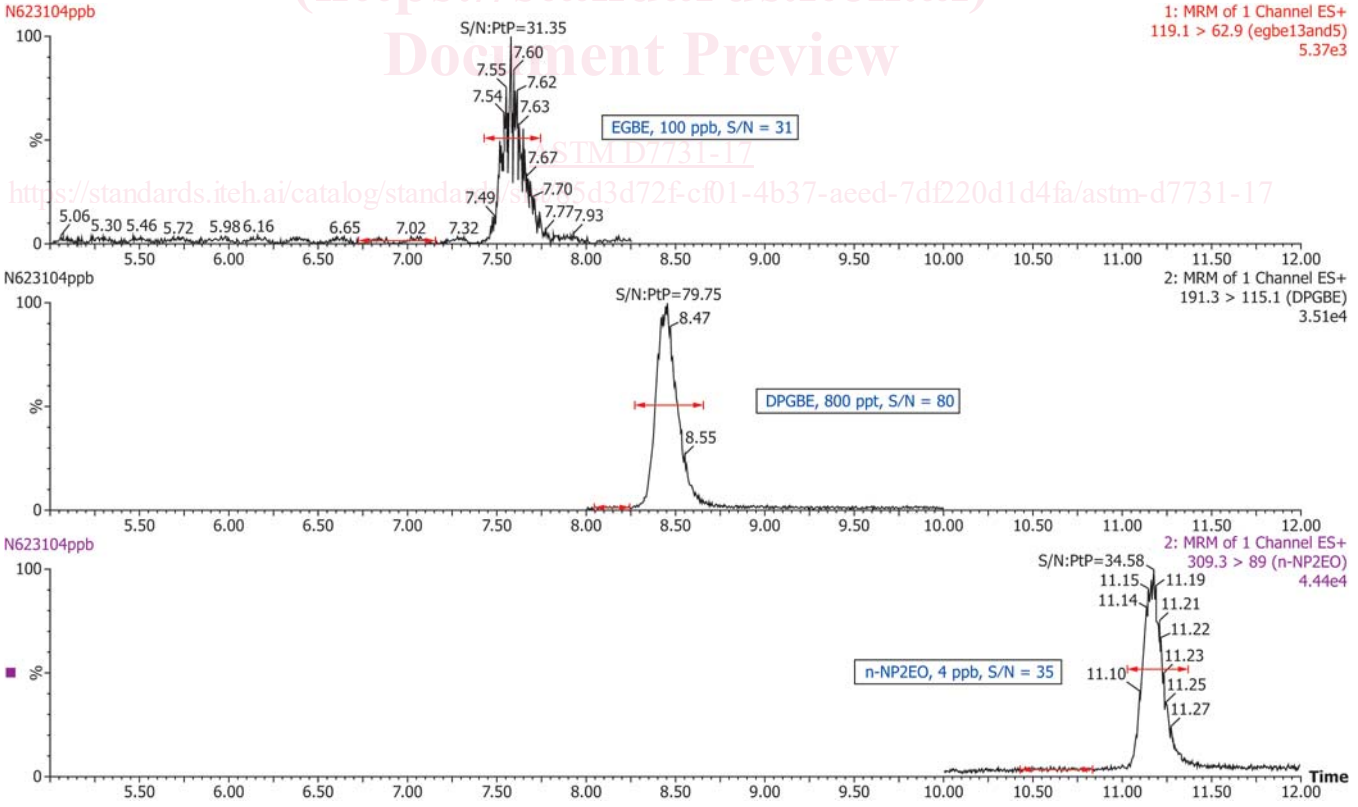

FIG. 2 Reporting Level (Calibration Standard) Signal/Noise Ratio

used provided they are first determined to be of sufficiently high purity to permit their use without affecting the accuracy of the measurements.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type 1 of Specification D1193. It must be demonstrated that this water does not contain contaminants at concentrations sufficient to interfere with the analysis.

8.3 *Gases*—Ultrapure nitrogen and argon.

8.4 Acetonitrile (CAS # 75-05-8).

8.5 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 # 111-76-2).

8.10 *n-NP2EO*—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).

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 pre-cleaned glass vials with 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 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 five days of collection.

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 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.

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

11.2.3 *Seal Wash*—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. 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:	7.0×10^{-3} Torr
Inter-Channel Delay:	0.1 seconds
Inter-Scan Delay:	0.1 seconds
Dwell:	0.1 seconds
Solvent Delay:	5 minutes

TABLE 2 Gradient Conditions for Liquid Chromatography

Time (min)	Flow (mL/min)	Percent 95 % Water/ 5 % CH_3CN	Percent CH_3CN	Percent 2 % Formic Acid 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

TABLE 3 Retention Times, SRM transitions, and Specific Mass Spectrometer Parameters

Analyte	Retention time (min)	Cone Voltage (Volts)	Collision Energy (eV)	SRM Mass Transition (Precursor > Product)
DPGBE	8.5	19	7	191.3 > 115.1
EGBE	7.6	13	5	119.1 > 62.9
n-NP2EO (Surrogate)	11.2	28	10	309.3 > 89.0
EGBE-D_4(Optional Surrogate)	7.6	13	5	123.0 > 66.8

12. Calibration and Standardization

12.1 The mass spectrometer must be calibrated in accordance with manufacturer specifications before analysis. In order to obtain accurate analytical values through using this test method within the confidence limits, the following procedures must be followed when performing this test method. Prepare all solutions in the lab using Class A volumetric glassware.

12.2 *Calibration and Standardization*—To calibrate the instrument, analyze six calibration standards and the DVL containing (nominal concentrations in Table 4) DPGBE, EGBE and *n*-NP2EO. A calibration solution is prepared from standard materials or they are purchased as certified solutions. Level 6 calibration solution containing the targets and surrogate is prepared and aliquots of that solution are diluted to prepare Levels 1 through 5 and the DVL. The following steps will produce standards with the concentration values shown in Table 4. The analyst is responsible for recording initial component weights correctly and calculating and preparing appropriate dilution calculations.

12.2.1 Prepare Level 6 calibration stock standard at 1000 ppb for EGBE, 8 ppb for DPGBE and 40 ppb for *n*-NP2EO in 80 % water/20 % acetonitrile. The EGBE and DPGBE concentrated stock solutions were prepared in methanol at approximately 2-g/L concentration and the *n*-NP2EO surrogate concentrated stock solution was prepared in acetonitrile at approximately 0.5 g/L. The preparation of the stock standard can be accomplished using different volumes and concentrations of stock solutions as is accustomed in the individual laboratory. Depending on the prepared stock concentrations, the solubility at that concentration will have to be ensured.

12.2.2 Aliquots of Level 6 calibration stock standard are then diluted with 80 % water/20 % acetonitrile to prepare the desired calibration levels in 2-mL amber glass autosampler vials. The calibration vials must be used within 24 hours to ensure optimum results. Stock calibration standards are routinely replaced every seven days if not previously discarded for quality control failure. Calibration standards are not filtered.

12.2.3 Inject each standard and obtain its chromatogram. An external calibration technique is used to monitor the SRM transitions of each analyte. Calibration software is utilized to conduct the quantitation of the target analytes and surrogates using the SRM transition. 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 units. Concentrations may be calculated using the data system software to generate linear regression or quadratic calibration curves. Forcing the calibration curve through the origin is not recommended.

12.2.4 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 point, or both, is excluded, minimally a five-point curve is acceptable but the reporting range must be modified to reflect this change.

12.2.5 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 causes the curve to be <0.99, this point must be re-injected or a new calibration curve must be regenerated. Minimally a six point curve is acceptable using a quadratic fit. Each calibration point used to generate the curve must have a calculated percent deviation less than 25 % from the generated curve.

12.2.6 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 re-inject the sample. If the retention time is still incorrect in the sample, refer to the analyte as an unknown.

12.2.7 A calibration midpoint 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 35 % from the calculated concentration for the target analytes and surrogates. 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

TABLE 4 Concentrations of Calibration Standards (PPB)

Analyte/Surrogate	DVL	LV1	LV2	LV3	LV4	LV5	LV6
DPGBE	0.20	0.80	1.6	2.4	3.2	4.0	8.0
EGBE	25	100	200	300	400	500	1000
n-NP2EO (Surrogate)	1.0	4.0	8.0	12	16	20	40

or the affected results must be qualified with an indication that they do not fall within the performance criteria of this test method. If the analyst inspects the vial containing the end calibration check standards and notices that the samples 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 35 % from the calculated concentration for the target analyte and surrogate, the results may be reported unqualified.

12.3 If a laboratory has not performed the test before or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

12.3.1 Analyze at least four replicates of a sample solution containing the targets and surrogate at a concentration in the calibration range of Levels 3 to 5. The Level 3 concentration of the six-point calibration curve was used to set the quality control (QC) acceptance criteria in this test method. 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 pre-treatment steps.

12.3.2 Calculate the mean (average) percent recovery and relative standard deviation (RSD) of the four values and compare to the acceptable ranges of the QC acceptance criteria for the initial demonstration of performance in Table 5.

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

12.3.3.1 The QC acceptance criteria for the initial demonstration of performance in Table 5 is preliminary until more data and multi-laboratory study is completed. Data generated from a single-laboratory validation from reagent and sea water matrices are shown in the precision and bias, Section 16. It is recommended that the laboratory generate their own in-house QC acceptance criteria which meet or exceed the criteria in this test method. A reference on how to generate QC acceptance criteria is in Method 8000B in EPA Publication SW-846.

12.4 *Surrogate Spiking Solution:*

12.4.1 A surrogate spiking methanol solution containing *n*-NP2EO is added to all samples. A stock surrogate spiking solution is prepared at 2.4 ppm. Spiking 100 µL of this spiking solution into a 20-mL water sample results in a concentration of 12 ppb of the surrogate 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 this test method.

12.4.1.1 *n*-NP2EO has been shown to be absorbed into the oil layer yielding a non-detect as a result. If oil is present in the sample, the recovery of the *n*-NP2EO surrogate may be very low or not detected at or above the reporting limit.

12.5 *Method Blank:*

12.5.1 Analyze a reagent water blank with each batch of 20 or fewer samples. The concentration of the DPGBE and EGBE found in the blank must be below the DVL. If the concentration of DPGBE or EGBE 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 this test method. If DPGBE or EGBE are found in a method blank at greater than the reporting limit the reporting limit must be raised to at least 2 times the concentration of the DPGBE and EGBE found in the blank. This may occur if samples are encountered that have a high concentration of DPGBE, a water blank between samples may be required to remove carry-over between samples.

12.6 *Laboratory Control Sample (LCS):*

12.6.1 To ensure that this test method is in control, analyze a LCS prepared with the target analytes 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 the DPGBE at 0.48 ppm and EGBE at 60 ppm. Spike 100 µL of this stock solution into 20 mL of water to yield a concentration of 2.4 ppb for the DPGBE and 300 ppb for EGBE in the sample. The LCS result must be within the limits in Table 5. Matrix spiking solutions are routinely replaced every seven days if not previously discarded for quality control failure.

12.6.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all samples in the batch must be re-analyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of this test method.

12.7 *Matrix Spike/Matrix Spike Duplicate (MS/MSD):*

12.7.1 To check for interferences in the specific matrix being tested, perform a MS/MSD on at least one sample from each batch of 10 or fewer samples by spiking the sample with a known concentration of DPGBE and EGBE and following the analytical method. Prepare a stock matrix spiking solution in methanol containing the DPGBE at 0.48 ppm and EGBE at 60 ppm. Spike 100 µL of this stock solution into 20 mL of water to yield a concentration of 2.4 ppb for the DPGBE and 300 ppb for EGBE in the sample. The result obtained for the MS/MSD must fall within the limits in Table 6. Matrix spiking

TABLE 5 Preliminary QC Acceptance Criteria

Analyte/Surrogate	Test Conc. (µg/L) in Reagent Water	Initial Demonstration of Performance			Lab Control Sample	
		Recovery (%)		Precision	Recovery (%)	
		Lower Limit	Upper Limit	Maximum % RSD	Lower Limit	Upper Limit
DPGBE	2.4	50	150	30	50	150
EGBE	300	50	150	30	50	150
n-NP2EO (Surrogate)	12	25	150	30	25	150