Designation: D7599 − 16 (Reapproved 2017)

Standard Test Method for Determination of Diethanolamine, Triethanolamine, *N*-Methyldiethanolamine and *N*-Ethyldiethanolamine in Water by Single Reaction Monitoring Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation D7599; 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 diethanolamine, triethanolamine, *N*-methyldiethanolamine and *N*-ethyldiethanolamine (referred to collectively as ethanolamines in this test method) in surface water by direct injection using liquid chromatography (LC) and detected with tandem mass spectrometry (MS/MS). These analytes are 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 the ethanolamines 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 ratios at the DVLs and at higher concentrations for *N*-methyldiethanolamine.

1.4.2 The reporting limit is the concentration of the Level 1 calibration standard as shown in Table 2 for diethanolamine, triethanolamine, and *N*-ethyldiethanolamine and Level 2 for *N*-methyldiethanolamine. The reporting limit for *N*-methyldiethanolamine is set at 50 µg/L due to poor sensitivity at a 5 µg/L concentration which did not meet the DVL criteria. The DVL for *N*-methyldiethanolamine is at 10 µg/L, which forces a raised reporting limit (chromatograms are shown in Fig. 1). However, the multi-laboratory validation required a spike of all target analytes at 25 µg/L. The mean recovery for *N*-methyldiethanolamine at this level was 88 % as shown in Table 3. If your instrument's sensitivity can meet the requirements in this test method, *N*-methyldiethanolamine may have a 25 µg/L reporting limit.

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

[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.

TABLE 1 Detection Verification Level and Reporting Range

Analyte	DVL (µg/L)	Reporting Range (µg/L)
Diethanolamine	5	25–500
Triethanolamine	5	25–500
N-Ethyldiethanolamine	5	25–500
N-Methyldiethanolamine	10	50–500

2.2 *Other Documents:*

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 3 times below the reporting limit (RL).

3.2.2 *ethanolamines, n*—in this test method, diethanolamine, triethanolamine, *N*-methyldiethanolamine and *N*-ethyldiethanolamine collectively.

3.2.3 *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.

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 ethanolamines 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 Diethanolamine, triethanolamine, *N*-methyldiethanolamine and *N*-ethyldiethanolamine and diethanolamine-D_8 (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 diethanolamine, triethanolamine, *N*-methyldiethanolamine and *N*-ethyldiethanolamine and the diethanolamine-D_8 surrogate recovery.

5. Significance and Use

5.1 *N*-Ethyldiethanolamine, *N*-methyldiethanolamine and triethanolamine are Schedule 3 compounds under the Chemical Weapons Convention (CWC). Schedule 3 chemicals include those that have been produced, stockpiled or used as a chemical weapon, poses otherwise a risk to the object and purpose of the CWC because they possess such lethal or incapacitating toxicity as well as other properties that might enable it to be used as a chemical weapon, poses otherwise a risk to the object and purpose of the CWC by virtue of it's importance in the production of one or more chemicals listed in Schedules 1 or 2, or it may be produced in large commercial quantities for purposes not prohibited under the CWC.[4] Ethanolamines have a broad spectrum of applications. They are used to produce adhesives, agricultural products, cement grinding aids, concrete additives, detergents, specialty cleaners, personal care products, gas treatments, metalwork, oil well chemicals, packaging and printing inks, photographic chemicals, rubber, textile finishing, urethane coatings, textile lubricants, polishes, pesticides, and pharmaceuticals. Ethanolamines are readily dissolved in water, biodegradable and the bio-concentration potential is low.[5]

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

[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.

[4] Additional information about CWC and ethanolamines are available from the Organisation for the Prohibition of Chemical Weapons, https://www.opcw.org.

[5] Additional information can be found on the Dow Chemical Company website at http://www.dow.com/amines/prod/index.htm.

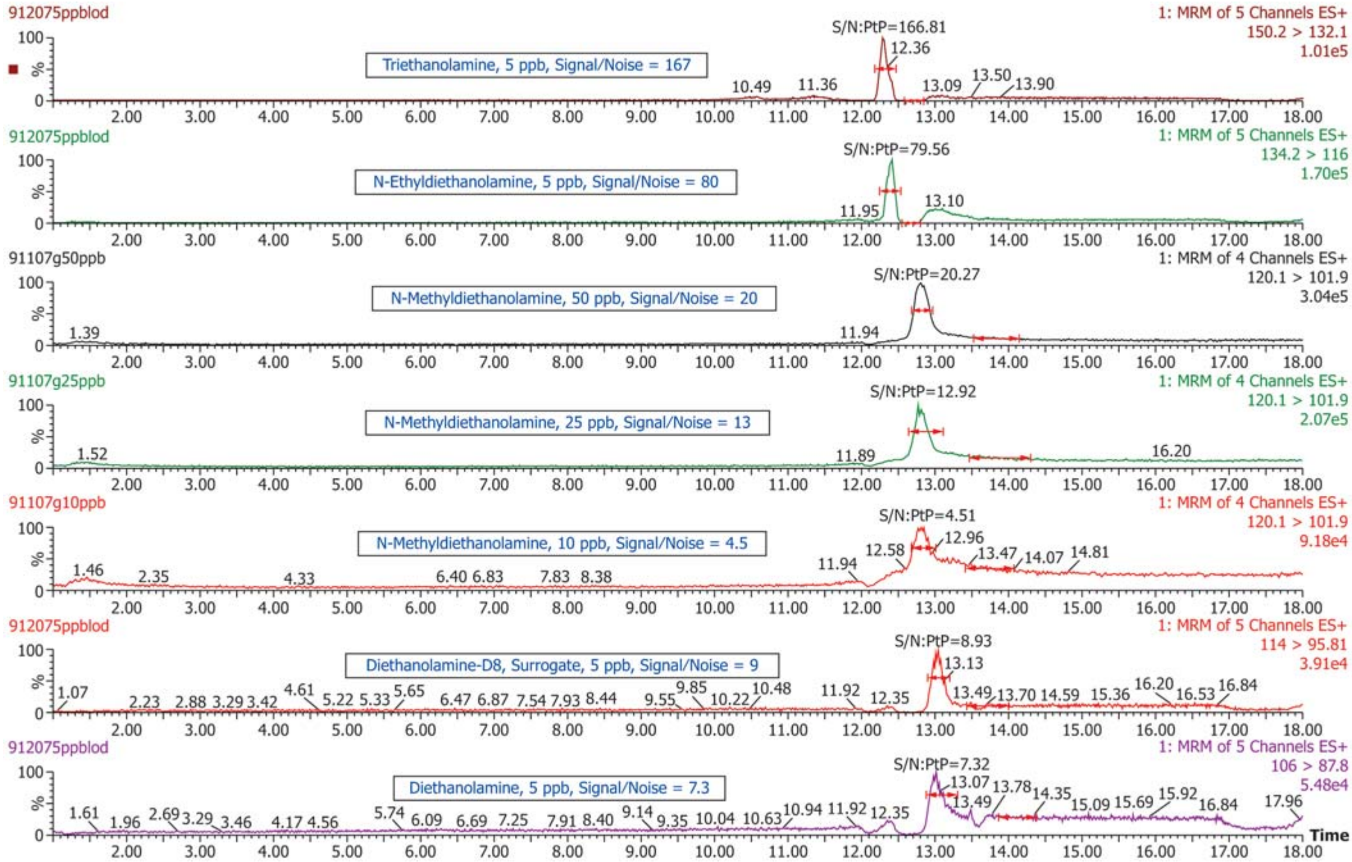

FIG. 1 Example SRM Chromatograms Signal/Noise Ratios

TABLE 2 Concentrations of Calibration Standards (PPB)

Analyte/Surrogate	LV 1	LV 2	LV 3	LV 4	LV 5	LV 6	LV 7
Diethanolamine	25	50	75	150	250	350	500
Triethanolamine	25	50	75	150	250	350	500
N-Ethyldiethanolamine	25	50	75	150	250	350	500
N-Methyldiethanolamine	25	50	75	150	250	350	500
Diethanolamine-D_8 (Surrogate)	25	50	75	150	250	350	500

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. Detergents containing ethanolamines must not be used to clean glassware. 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.[6] 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-Waters*[7]—A HILIC column was used to develop this test method. Any column that achieves

[6] 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.

[7] A Waters Atlantis (a trademark of the Waters Corporation, Milford, MA) HILIC Silica, 100 mm × 2.1 mm, 3 µm particle size, or equivalent, has been found suitable for use.

TABLE 3 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 (%)
Diethanolamine	25	24	6	96.34	51.00	156.96	31.31	10.96	32.50	9.49
Diethanolamine	50	24	6	101.41	54.00	154.80	29.54	7.97	29.13	7.91
Diethanolamine	200	24	6	101.57	61.00	138.00	20.98	10.50	20.66	10.85
Diethanolamine	425	24	6	102.06	70.00	138.82	17.98	5.90	17.61	5.70
Triethanolamine	25	24	6	87.70	35.96	157.20	27.00	25.18	30.79	27.48
Triethanolamine	50	24	6	94.95	67.00	121.66	16.39	9.57	17.26	9.66
Triethanolamine	200	22	6	105.00	79.50	132.00	14.06	11.81	13.39	11.52
Triethanolamine	425	24	6	96.94	40.00	144.94	27.56	4.41	28.43	5.76
N-Ethyldiethanolamine	25	24	6	90.61	31.00	132.00	39.42	7.47	43.51	10.42
N-Ethyldiethanolamine	50	23	6	111.88	49.00	146.00	28.71	7.19	25.66	7.56
N-Ethyldiethanolamine	200	24	6	106.20	60.00	134.00	23.09	11.96	21.74	12.23
N-Ethyldiethanolamine	425	24	6	99.67	51.00	130.00	23.07	4.68	23.15	6.01
N-Methyldiethanolamine	25	24	6	88.43	41.72	133.60	25.24	13.29	28.55	16.70
N-Methyldiethanolamine	50	24	6	102.28	56.00	153.80	25.85	8.73	25.27	8.22
N-Methyldiethanolamine	200	24	6	101.02	59.00	136.50	20.07	9.51	19.87	9.54
N-Methyldiethanolamine	425	24	6	94.75	63.00	115.76	15.02	3.34	15.85	3.72
Diethanolamine-D_8 (Surrogate)	200	96	6	103.02	60.00	151.95	21.13	9.40	20.51	9.25

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.

7.1.3 *Tandem Mass Spectrometer (MS/MS) System*—A MS/MS system capable of MRM analysis.[8] 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*[9]—PVDF filter 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.[10] 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 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 acetate (CAS # 631-61-8).

8.8 Diethanolamine (CAS # 111-42-2).

8.9 Triethanolamine (CAS # 102-71-6).

8.10 *N*-Ethyldiethanolamine (CAS # 139-87-7).

8.11 *N*-Methyldiethanolamine (CAS # 105-59-9).

8.12 Bis(2-hydroxyethyl)-D_8-amine; (Diethanolamine-D_8), where the ethylene moieties contain all ^2H (CAS # 103691-51-6).

8.12.1 Diethanolamine-D_8 is used as a surrogate in this standard.

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.

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

[9] 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.

[10] *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.

10.2 *Preservation*—Store samples between 0°C and 6°C from the time of collection until analysis. Analyze the sample within 7 days of collection.

11. Preparation of LC/MS/MS

11.1 *LC Chromatograph Operating Conditions:*[6]

11.1.1 Injection volumes of all calibration standards and samples are 25 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 4.

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 ethanolamines.

11.2 *Mass Spectrometer Parameters:*[8]

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 surrogate and four target compounds which are located in the same multiple reaction monitoring (MRM) experiment window. Variable parameters regarding retention times, SRM Transitions and cone and collision energies are shown in Table 5.

TABLE 4 Gradient Conditions for Liquid Chromatography

Time (min)	Flow (µL/min)	Percent CH_3CN	Percent Water	Percent 200 mmolar Ammonium Acetate
0	400	95	0	5
1	400	95	0	5
2	400	90	0	10
4	300	90	0	10
10	300	60	30	10
13	300	60	30	10
15	300	40	50	10
18	300	30	60	10
20	300	30	60	10
25	300	95	0	5
27	300	95	0	5

The instrument is set in the Electrospray (+) positive setting.
Capillary Voltage: 0.5 kV
Cone: Variable depending on analyte (Table 5)
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 5)
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

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 the ethanolamines and diethanolamine-D_8 surrogate 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 diethanolamine, triethanolamine, *N*-methyldiethanolamine and *N*-ethyldiethanolamine and diethanolamine-D_8 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: 50 µL of diethanolamine, triethanolamine, *N*-methyldiethanolamine, *N*-ethyldiethanolamine and diethanolamine-D_8 each at 1 g/L concentration, 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

TABLE 5 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)
Diethanolamine	106 > 87.8	13.0	25	11
Triethanolamine	150.2 > 132.1	12.3	25	14
N-Ethyldiethanolamine	134.2 > 116	12.4	25	13
N-Methyldiethanolamine	120.1 > 101.9	12.8	25	13
Diethanolamine-D_8 (Surrogate)	114 > 95.8	13.0	25	12

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.

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 analytes 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 diethanolamine, triethanolamine, *N*-methyldiethanolamine, *N*-ethyldiethanolamine and diethanolamine-D_8 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 6.

12.4.3 This study should be repeated until the single operator precision and mean recovery are within the limits in Table 6. 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 6 were generated from a multi-laboratory method validation involving six 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 Practice D2777, Practice D5847, Practice E2554, or Method 8000B in EPA publication SW-846, which may be helpful.

12.5 *Surrogate Spiking Solution:*

12.5.1 A surrogate standard solution containing diethanolamine-D_8 is added to all samples. A stock surrogate spiking solution is prepared in methanol at 200 ppm. Spiking 25-µL of this spiking solution into a 25 mL water sample results in a concentration of 200 ppb of the surrogate in the sample. The result obtained for the surrogate recovery must fall within the limits of Table 6. 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 the ethanolamines found in the blank must be below the DVL. If the concentrations of the ethanolamines are 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.

TABLE 6 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
Diethanolamine	200	52	151	19	51	152
Triethanolamine	200	83	127	21	75	135
N-Ethyldiethanolamine	200	53	160	21	51	161
N-Methyldiethanolamine	200	53	149	17	52	150
Diethanolamine-D_8 (Surrogate)	200	51	156	16	50	156

12.7 *Laboratory Control Sample (LCS):*

12.7.1 To ensure that the test method is in control, analyze a LCS prepared with diethanolamine, triethanolamine, *N*-methyldiethanolamine and *N*-ethyldiethanolamine 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 diethanolamine, triethanolamine, *N*-methyldiethanolamine and *N*-ethyldiethanolamine each at 200 ppm. Spike 25 µL of this stock solution into 25 mL of water to yield a concentration of 200 ppb of the ethanolamines in the sample. The result obtained for the LCS must fall within the limits in Table 6.

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 ethanolamines and following the analytical method. Prepare a stock matrix spiking solution in methanol containing diethanolamine, triethanolamine, *N*-methyldiethanolamine and *N*-ethyldiethanolamine at 200 ppm. Spike 25 µL of this stock solution into 25 mL of water to yield a concentration of 200 ppb of the ethanolamines 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:

$$P = 100 \frac{|A(V_s + V) - BVs|}{CV} \tag{1}$$

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 7. If the percent recovery is not within these

TABLE 7 MS/MSD QC Acceptance Criteria

Analyte	Test Conc. (µg/L)	MS/MSD		
		Recovery (%)		Precision
		Lower Limit	Upper Limit	Maximum RPD (%)
Diethanolamine	200	51	143	20
Triethanolamine	200	5	264	74
N-Ethyldiethanolamine	200	Detect	191	19
N-Methyldiethanolamine	200	Detect	161	16
Diethanolamine-D_8 (Surrogate)	200	74	135	25

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 7 were generated by six laboratories across the country using surface waters collected near their facilities. The matrix variation between the six 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 Practice D5847, Practice D2777, Practice E2554, or Method 8000B in EPA publication SW-846, which may be helpful.

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 7. Relative percent difference:

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

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 the ethanolamines and diethanolamine-D_8 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 amounts of diethanolamine, triethanolamine, *N*-methyldiethanolamine, *N*-ethyldiethanolamine and diethanolamine-D_8 surrogate. Calculate the concentration in µg/L (ppb) for each analyte. The individual ethanolamines may be 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[11]

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 compounds and surrogate to obtain a 200 ppb concentration of each as described in Section 12. Table 8 contains the recoveries and standard deviation (SD) for the surrogate and target compounds.

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 200 ppb concentration of each as described in Section 12. Table 9 contains the recoveries and standard deviation (SD) for the surrogate and target compounds.

16.4 *Multi-Laboratory Validation*—This test method has been tested by six laboratories using reagent water and their

[11] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1188. Contact ASTM Customer Service at service@astm.org.

TABLE 8 Single-Laboratory Recovery Data in Reagent Water

Precision and Accuracy Samples	Measured ppb from 200 ppb Spikes				
	Diethanolamine	Triethanolamine	*N*-Ethyldiethanolamine	*N*-Methyldiethanolamine	Diethanolamine-D_8 (Surrogate)
1	177.9	164.3	194.4	175.3	191.7
2	173.9	158.4	196.6	172.7	177.8
3	178.5	165.6	196.5	174.3	183.3
4	229.9	194.5	252.4	225.1	221.6
5	176.6	161.5	198.4	178.0	178.8
6	180.5	164.8	204.3	188.5	176.9
Average Recovery	186.2	168.2	207.1	185.7	188.4
Average Percent Recovery	93.1 %	84.1 %	103.6 %	92.8 %	94.2 %
Standard Deviation (SD)	21.51	13.16	22.45	20.13	17.18
% Relative SD	11.6 %	7.8 %	10.8 %	10.8 %	9.1 %

TABLE 9 Single-Laboratory Recovery Data in Chicago River Water

Precision and Accuracy Samples	Measured ppm from 200 ppm Spikes				
	Diethanolamine	Triethanolamine	*N*-Ethyldiethanolamine	*N*-Methyldiethanolamine	Diethanolamine-D_8 (Surrogate)
Blank 1 Chgo. River Water	ND	ND	ND	ND	405.9
Blank 2 Chgo. River Water	ND	ND	ND	ND	312.8
1	231.3	139.6	125.5	37.8	227.6
2	211.9	141.6	119.7	39.7	202.3
3	249.3	142.5	120.9	45.5	219.3
4	236.1	158.0	127.1	41.3	218.6
5	234.2	143.5	121.5	39.4	211.8
6	232.6	145.4	125.4	38.4	215.3
Average Recovery	232.6	145.1	123.4	40.4	251.7
Average Percent Recovery	116.3 %	72.6 %	61.7 %	20.2 %	125.9 %
Standard Deviation (SD)	12.03	6.61	3.02	2.79	71.31
% Relative SD	5.2 %	4.6 %	2.4 %	6.9 %	28.3 %

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, 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 3 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.

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

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 (%)
Diethanolamine	25	12	6	97.32	44.32	160.00	37.87	28.99	38.91	30.72
Diethanolamine	50	12	6	93.84	70.00	132.60	18.36	7.24	19.56	7.54
Diethanolamine	200	12	6	97.31	62.65	127.00	18.16	5.56	18.66	7.17
Diethanolamine	425	12	6	102.45	67.44	138.35	26.44	4.66	25.81	4.72
Triethanolamine	25	11	6	98.07	67.20	152.04	28.47	8.35	29.03	7.36
Triethanolamine	50	12	6	115.60	80.80	169.22	29.65	13.32	25.65	9.54
Triethanolamine	200	12	6	134.51	74.00	236.00	55.22	28.39	41.06	17.43
Triethanolamine	425	10	6	102.65	72.47	181.15	37.53	9.28	36.56	7.83
N-Ethyldiethanolamine	25	12	6	74.70	0.00	115.20	37.99	7.31	50.85	9.29
N-Ethyldiethanolamine	50	12	6	95.90	14.00	135.40	40.08	4.76	41.79	10.92
N-Ethyldiethanolamine	200	12	6	93.00	17.00	128.75	36.95	4.88	39.74	5.47
N-Ethyldiethanolamine	425	12	6	85.40	13.00	124.70	36.23	9.31	42.42	8.90
N-Methyldiethanolamine	25	12	6	62.82	0.00	123.00	46.16	5.49	73.49	27.55
N-Methyldiethanolamine	50	12	6	74.85	8.03	120.00	42.01	6.34	56.13	8.60
N-Methyldiethanolamine	200	12	6	76.46	25.15	113.50	31.96	3.36	41.79	3.90
N-Methyldiethanolamine	425	12	6	68.55	27.08	103.53	27.00	3.83	39.39	4.56
Diethanolamine-D_8 (Surrogate)	200	48	6	104.92	71.00	136.00	13.46	8.89	12.83	8.38

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 ethanolamines; liquid chromatography; mass spectrometry; water