

Application News

High Performance Liquid Chromatograph Mass Spectrometer LCMS™-8045

Determination of Ethanolamines in water as per ASTM D-7599 by LCMS-8045

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User Benefits

- ◆ Highly sensitive LC-MS/MS method for the determination of four ethanolamines in water with surrogate standard.
- ◆ Better chromatographic separation with lower concentration of buffer.

■ Introduction

Overview: Monoethanolamine is bifunctional, and it contains both a primary amine and a primary alcohol. Monoethanolamine is produced by reacting ethylene oxide with ammonia. Further, the reaction also produces ethanolamines such as diethanolamine and triethanolamine. Ethanolamines is a colorless, flammable, viscous liquid with an ammonia-like odor. Ethanolamines are generally used in various fields such as adsorbents for various acid gases, metal corrosion inhibitors, pesticide solvents, pharmaceuticals, cosmetics, and surfactants. However, because ethanolamines have the property of forming carcinogenic nitrosamines, the European Commission prohibits the use of diethanolamine in cosmetics to reduce environmental contamination. In the ASTM standard, an analysis method for ethanolamines, containing diethanolamine, triethanolamine, N-methyldiethanolamine and N-ethyldiethanolamine, has been announced due to concerns about environmental pollution. Figure 1 shows the structure of ethanolamines.

This method was developed to determine ethanolamines in surface water by direct injection using Shimadzu liquid chromatography mass spectrometer LCMS-8045. These analytes are qualitatively and quantitatively determined by this test method with high sensitivity. The method conforms to the ASTM-D7599, and diethanolamine-D8 was used for the analysis as surrogate to ensure high recovery rate for all the samples tested. All glassware were properly washed with hot water and solvent to ensure reduced interference.

■ Experimental

Preparation of standard stock solution: 50 ppm standard in methanol was diluted with water to prepare standard solution at 5 ppm containing diethanolamine, triethanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, and surrogate, respectively.

Preparation of surrogate standard stock solution: 50 ppm standard in methanol was diluted with water to prepare standard solution of 5 ppm diethanolamine-D8.

Standard calibration levels:- Calibration standard solutions were prepared containing 7 of 5 ppb, 25 ppb, 50 ppb, 100 ppb, 250 ppb, 500 ppb and 1000 ppb of ethanolamines and diethanolamine- D8 surrogate prior to the analysis from intermediate stock of 5 ppm. Each level of standard solution was injected repeatedly to create calibration curve.

Three levels of spike solutions were prepared by spiking 50 µL, 100 µL and 250 µL of stock solution of 5 ppm in 5 mL of blank water, which results into the 50 ppb, 100 ppb and 250 ppb recovery solutions. Filter the entire solution through PVDF 0.45 µm syringe filter. Transferred the filtrate in to the HPLC vial for the analysis on LCMS-8045 as shown in Figure 2.

A surrogate standard stock solution containing diethanolamine-D8 is added to all samples. To 5 mL of each sample, added 200 µL of 5 ppm stock solution. Samples were filtered through PVDF 0.45 µm syringe filter. Transferred the filtrate in to the HPLC vial for the analysis.

UHPLC and LC-MS instrument parameters are shown in Table 1 and Table 2, respectively.



Figure 2. Nexera™ HPLC with LCMS™-8045

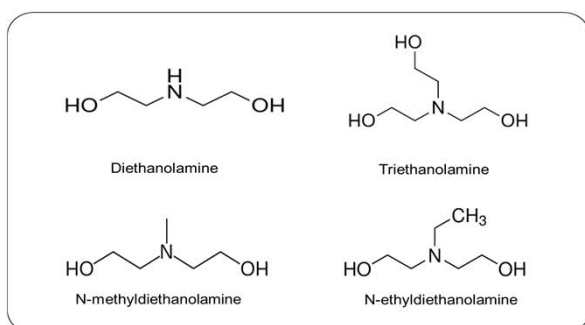


Figure 1. Structure of ethanolamines

Table 1. LC-MS instrument parameters

MS interface	Electro Spray Ionization (ESI)	
Nitrogen gas flow	Nebulizing gas- 3 L/min; Drying gas- 10 L/min	
MS temperatures	Desolvation line- 150°C; Heating block- 200°C	
MRM transitions (positive)	Triethanolamine	150.20>132.20
	N-Ethyldiethanolamine	134.20>116.30
	N-Methyldiethanolamine	120.20>102.25
	Diethanolamine	106.15>88.10
	Diethanolamine-D8 Surrogate	114.20>96.15

Table 2. UHPLC instrument parameters

Column	Shim-pack Velox™ HILIC (100 mm × 2.1 mm I.D., 2.7 µm; P/N 227-32025-03)
Mobile phase	A: Acetonitrile B: Water C: 20 mM Ammonium Acetate in water
Flow rate	0.4 mL/min
Elution mode	Gradient as per ASTM D-7599
Injection vol.	5 µL
Column temperature	35°C

Results

The calibration curve was prepared by plotting the results of measuring the ethanolamines mixed standard solution. The prepared recovery test solutions were injected, followed by the surrogate spiked samples in duplicates. According to the guideline of reference method, 5 ppb solution was considered as LOD. The established method is capable to achieve the much lower detection limit. However, due to the interference suppression, the detection level of some analytes was limited to 5 ppb. The calibration curves of all analytes showed good linearity in the range of 5 to 10 ppb with $r^2 > 0.99$. The recovery rate was measured at three points and confirmed that it passed the criteria of the ASTM method. The surrogate standard spiked in each sample solution produced acceptable results. The 5 ppb LOD solution chromatograms are shown in figure 3. Figure 4 shows the calibration chromatograms from 5-1000 ppb of ethanolamines. MRM was optimized for all ions to ensure the best response using a LabSolutions™ software.

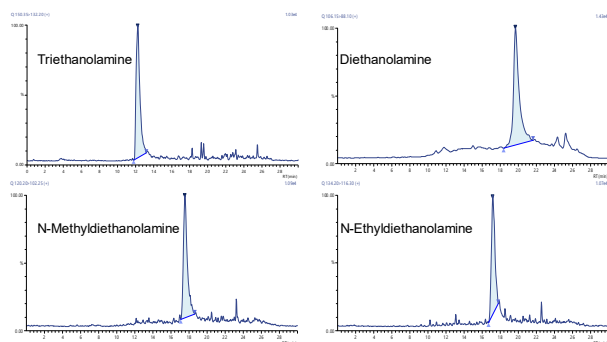


Figure 3. MRM chromatograms of 5 ppb standard

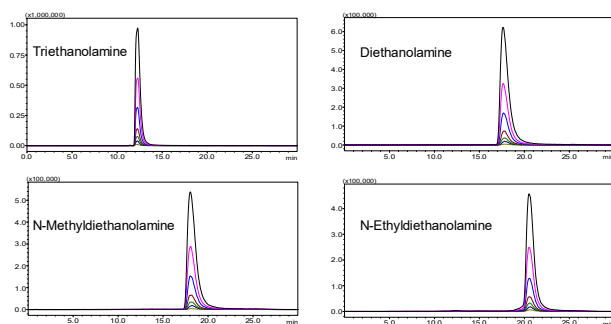


Figure 4. Overlaid MS chromatograms of ethanolamines for each standard.

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HILIC mode of separation was used for the analysis as described in ASTM-D7599. It was observed that the analyte response is largely affected by analysis temperature. Lower condition of source temperature provided better and reproducible results. LCMS-8045 is equipped with the heated ESI probe, however both heater and heating gas were turned off for better results. Since the water sample was used for direct analysis, some peak distortion was observed due to the difference in polarity between the sample solution and the mobile phase. The sample pretreatment co-injection function was used with acetonitrile as co-solvent to improve the peak shape of the analyte. Acetonitrile equal to sample injection volume was used before and after the sample aspiration. System suitability results, recovery test and surrogate spiked sample analysis shown in table 3, 4 and 5, respectively.

Table 3. Results of accuracy, regression and detection level

Analyte	% Accuracy	r^2	S/N at 5 ppb
Triethanolamine	101.1	0.993	438.4
N-Ethyldiethanolamine	102.2	0.999	137.9
N-Methyldiethanolamine	102.5	0.998	82.2
Diethanolamine	102.8	0.998	31.7
Diethanolamine-D8 Surrogate	102.1	0.999	320.4

Table 4. Results of sample recovery

Analyte	Observed concentration (ppb)		
	Level 1	Level 2	Level 3
	50 ppb	100 ppb	250 ppb
Triethanolamine	49.52	92.04	222.49
N-Ethyldiethanolamine	46.66	86.49	210.03
N-Methyldiethanolamine	47.85	88.67	217.12
Diethanolamine	62.24	104.99	228.55
Diethanolamine-D8 Surrogate	49.00	90.03	219.7

Table 5. Results of surrogate spiked samples

Analyte	Surrogate spiked samples (ppb)		
	Sample 1	Sample 2	Sample 3
Triethanolamine	BDL	BDL	BDL
N-Ethyldiethanolamine	ND	ND	ND
N-Methyldiethanolamine	ND	ND	ND
Diethanolamine	BDL	BDL	BDL
Diethanolamine-D8 Surrogate	175.26	178.32	171.38

Conclusion

Ultra-high sensitive LC-MS/MS method is developed for 4 ethanolamines by LCMS-8045 with surrogate spiked samples. LCMS-8045 has a capability for detecting ethanolamines as per the ASTM D-7599.

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