Highly sensitive method for determination of Ethanolamine in water as per ASTM D-7599 by LCMS-8045

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1. Introduction

Ethanolamine is an organic chemical compound with the formµLa $HOCH_2CH_2NH_2$ or C_2H_7NO. The molecule is bifunctional, containing both a primary amine and a primary alcohol. Ethanolamine is a colorless, viscous liquid with an odor reminiscent of ammonia. Diethanolamine, triethanolamine, N-methyldiethanolamine and N-ethyldiethanolamine are commonly used ethanolamine in different fields. Ethanolamine are present in many consumer products ranging from cosmetics, personal care products and household cleaning products. Ethanolamine have been linked to liver tumors.

Ethanolamine are found in soaps, shampoos, hair conditioners and dyes, lotions, shaving creams, paraffin and waxes, household cleaning products, pharmaceutical ointments, eyeliners, mascara, eye shadows, blush, make-up bases, foundations, fragrances, sunscreens[1]. The European Commission prohibits diethanolamine (DEA) in cosmetics, to reduce contamination from carcinogenic nitrosamines.

Ethanolamines have emulsification properties and are used in industrial applications such as chemical manufacturing and gas treating, as a plasticizing agent to help make plastic become pliable and soft, to remove carbon dioxide from ammonia gas in the production of synthetic ammonia, as a surfactant in agrochemicals, to help pesticides disperse into crops, which then helps repel insects from the crops, packaging and printing inks, photographic chemicals, rubber, textile finishing, urethane coatings, textile lubricants, polishes etc.

This highly sensitive method was developed to cover 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 Shimadzu LCMS-8045, a liquid chromatography mass spectrometry detector as per the ASTM-D7599. These analytes are qualitatively and quantitatively determined by this test method. The structures of ethanolamines are shown in figure 1. Diethnolamine-D_8(Surrogate) was used for the analysis to ensure perfect recovery for all the samples tested. All the glassware were washed properly with hot water and solvents to ensure to reduce the interference.

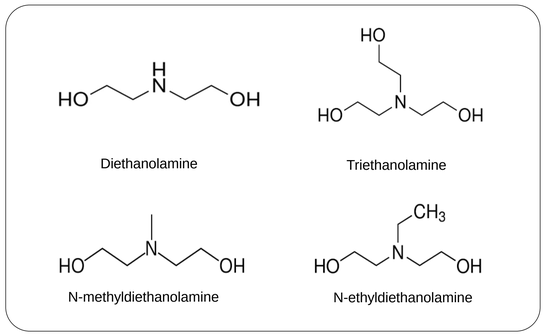

Figure 1. Structure of Ethanolamines

2. Materials and methods

2-1.Sample preparation

• Preparation of calibration standards, recovery and surrogate spiked sample

Calibration standard solutions were prepared containing 7 concentration levels of ethanolamines and diethanolamine- D8 surrogate prior to the analysis. The certified mix calibration standard stock in methanol was purchased and from that the intermediate stock of 5 ppm was prepared in water. From this standard stock solution, the seven level of calibration standard solution were prepared in water. The concentrations of the calibration solutions of 5 ppb, 25 ppb, 50 ppb, 100 ppb, 250 ppb, 500 ppb and 1000 ppb were prepared. The calibration curve was plotted with external standard method.

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.

A surrogate standard stock solution containing diethanolamine- D8 is added to all samples. A stock surrogate spiking solution of 5 ppm was prepared in water from the 50 ppm certified standard in methanol. 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.

MRM was optimsed for all the ions to ensure the best response of the LCMS/MS system using LabSolutions. HILIC mode of separation was used for the analysis as described by ASTM-D7599. It was observed that the analyte response is largely affected by analysis temperature. Lower source temperature condition gave better and reproducible results. LCMS-8045 is equipped with the heated ESI probe, however both heater and heating gas was turned off to get better results. Some peak distortion was observed due to polarity difference in sample solution and mobile phase since water samples were used directly for analysis. 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.

2-2. LC-MS/MS analysis

Figure 2. Nexera with LCMS-8045

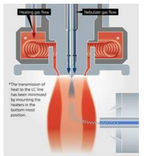

Figure 3. Heated ESI probe

LCMS-8045 triple quadrupole mass spectrometer by Shimadzu (shown in Figure 2), sets a new benchmark in triple quadrupole technology with an unsurpassed sensitivity (UF sensitivity), ultra fast scanning speed of 30,000 u/sec (UF scanning) and polarity switching speed of 5 msec (UF switching). This system ensures highest quality of data, with very high degree of reliability.

In order to improve ionization efficiency, the newly developed heated ESI probe (shown in Figure 3) combines high-temperature gas with the nebulizer spray, assisting in the desolvation of large droplets and enhancing ionization. This development allows high-sensitivity analysis of a wide range of target compounds with considerable reduction in background.

Table 1. Instrument parameters

MS Parameters (LCMS-8045)		
MS interface	Electro Spray Ionization (ESI)	
Nitrogen gas flow	Nebulizing gas- 3 L/min; Drying gas- 10 L/min	
MS temperatures	Desolvation line- 150 ^{0}C; Heating block- 200 ^{0}C;	
MRM transition (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
UHPLC condition		
Column	Shim-Pack Velox HILIC 2.7 µM (P/N 227-32025-03)	
Mobile phase	A: Acetonitrile B: Water C: 20mM Ammonium Acetate in water	
Flow rate	0.4 mL/min	
Elution mode	Gradient as per ASTM D7599	
Injection vol.	5 µL	
Column temperature	35 ^{0}C	

3. Results

Calibration curve was plotted for mix ethanolamine calibration standards. Injected the prepared recovery solutions followed by the surrogate spiked samples in duplicates. 5 ppb solution was considered as LOD solution as per the guidelines of reference method. The method established is capable of giving much lower detection limits. However, the interferences in few analytes limited the detection level to 5 ppb. Good linear response for all the analytes was observed from 5 ppb to 1000 ppb with r2 > 0.99. The 3-level recovery pass the criteria set by ASTM method. The surrogate standard spike in each sample solution produced acceptable results. The 5 ppb LOD solution chromatograms are shown in Figure 4. Figure 5 shows the calibration chromatograms from 5-100 ppb of ethanolamine. The recovery results and surrogate sample analysis and surrogate spike sample analysis results are given in table 2 and 3 respectively.

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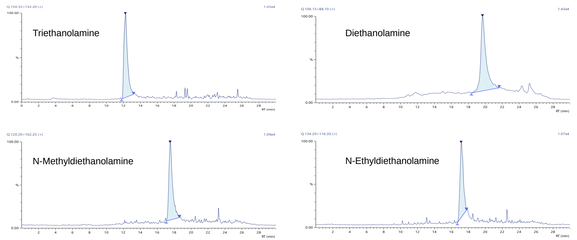

Figure 4. MRM chromatograms of 5 ppb standard

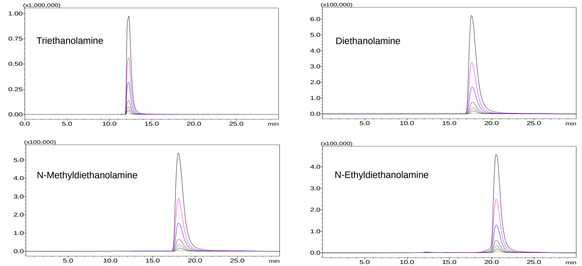

Figure 5. Linearity chromatograms of ethanolamines

Table 2. 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 3. Results of recovery and surrogate sample analysis

Analyte	% Recovery			Surrogate spiked samples		
	Level 1	Level 2	Level 3	Sample 1	Sample 2	Sample 3
	50 ppb	100 ppb	250 ppb			
Triethanolamine	49.52	92.04	222.49	BDL	BDL	BDL
N-Ethyldiethanolamine	46.66	86.49	210.03	ND	ND	ND
N-Methyldiethanolamine	47.85	88.67	217.12	ND	ND	ND
Diethanolamine	62.24	104.99	228.55	BDL	BDL	BDL
Diethanolamine D8 Surrogate	49.00	90.03	219.7	175.26	178.32	171.38

4. Conclusion

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

5. References

[1] ASTM D-7599:- Determination of Diethanolamine, Triethanolamine, N-Methyldiethanolamine and Ethyldiethanolamine in Water by Single Reaction Monitoring Liquid Chromatography/ Tandem Mass Spectrometry (LC/MS/MS)