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CO_2 Absorption Solvent Degradation Compound Identification Using Liquid Chromatography-Mass Spectrometry Quadrapole-Time of Flight (LCMSQTOF)

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Abstract

The degradation of the alkanolamine solvent used in the removal of acid gases from natural gas streams due to exposure to contaminants, thermal degradation and presence of oxygen or oxygen containing compounds will change the solvent properties, such as heat transfer coefficient, diffusion coefficient, and mass transfer coefficient of the solvent. Therefore, characterization and quantification of amine degradation product becomes one of the important analyses to determine alkanolamine solvent's health. In order to identify degradation products of alkanolamine solvent, analytical strategies by using mass spectrometry (MS) as detector have been studied extensively. In this work, due to the low concentration of the amine degradation product, a method was developed for identification of alkanolamine degradation products using LCMS-QTOF technique. A strategy for identification of trace degradation products has been identified. Six (6) alkanolamine degradation products had been identified by using LCMS-QTOF targeted analysis in the blended alkanolamine solvent used in natural gas processing plant. Another fifteen (15) molecular formulas having similarity in chemical structure to alkanolamine degradation products were identified using untargeted analysis strategy, as possible compounds related to degradation products. Using LCMS-QTOF via targeted and untargeted analysis strategy, without tedious column separation and reference standard, enables laboratory to provide a quick and indicative information for alkanolamine solvent's organic degradation compounds identification in CO_2 adsorption, within reasonable analysis time.

Keywords

CO_2 Absorption Solvent, Degradation Compound, Liquid

Chromatography-Mass Spectrometry Quadrupole-Time of Flight (LCMSQTOF)

1. Introduction

Removal of acid gases from natural gas streams using blended alkanolamine solvent has been widely used since decades ago [1]. In removing acid gases, many technology options are available but by far the most popular is the absorption by alkanolamine solvents. Several alkanolamine solvents have been proposed for acid gases removal. Among the common alkanolamines used are monoethanolamine (MEA), diethanolamine (DEA), di-isopropanolamine (DIPA) and methyldiethanolamine (MDEA) [2]. In a conventional acid gases removal plant, both absorption and desorption of acid gas are involved. The acid gas is absorbed by the alkanolamine solvent in the absorber. In the desorber, the acid gas is released by increasing the temperature of the column to break the chemical bonding of the akanolamine with the acid gases adsorbed [3].

Amine solvent can degrade due to exposure to contaminants, such as SO_x, NO_x, halogen compound, hydrocarbons, and other contaminants [4], which may be introduced from equipment components and maintenance activities. In addition, thermal degradation [4] [5] can happen during amine regeneration which is normally carried out around its boiling point. Presence of oxygen or oxygen containing compounds will also cause oxidative degradation [4] [5] especially under high temperature condition. These degradation processes can occur simultaneously and produce various degradation products that will eventually affect solvent properties, such as viscosity and surface tension. The change in solvent physical properties can potentially affect heat transfer coefficient, diffusion coefficient, and mass transfer coefficient in amine solvent. This may introduce operational problems, such as reduced solvent capacity, increased energy consumption, corrosion, fouling, and foaming. Foaming of amine is a common problem in natural gas processing plant which increases down time and reduces throughput [6]. It often occurs due to presence of amine degradation product, such as heat stable salts (HSS), though presence of corrosion inhibitors, hydrocarbon, and iron sulphide particles originating from corrosion [7] [8] are also the usual suspects. Therefore, characterization and quantification of amine degradation product becomes one of the important analyses to determine amine solvent's health for foaming prevention.

The type of alkanolamine degradation product and its relevant degradation reaction were mentioned and discussed in many literatures related to CO_2 adsorption. For example, degradation products from MDEA and Piperazine were compiled and tabulated in **Table 1**.

In order to identify degradation products of alkanolamine solvent, analytical strategies by using mass spectrometry (MS) as detector were mentioned in few literatures e.g. LC-MS, GC-MS and LCMS-QTOF [9] [15] [16] [17] [18]. For

Table 1. List of alkanolamine degradation compounds.

No	Compound	Mw g/mol	Formula	Type of Degradation	References
DP 1	Methanol	32.02621	CH_4O	MDEA Thermal degradation	[9]
DP 2	Ethylene Oxyde (EO)	44.02621	C_2H_4O	MDEA Thermal degradation	[9]
DP 3	Trimethylamine (TMA)	59.07350	C_3H_9N	MDEA Thermal degradation	[9]
DP 4	Ethylene Glycol (EG)	62.03678	$C_5H_{10}N_2O$	MDEA Thermal degradation	[9]
DP 5	N, N-dimethylethylamine (DMAE)	73.08915	$C_4H_{11}N$	MDEA Thermal degradation	[9]
DP 6	N-methylethanolamine (MAE)	75.06841	C_3H_9NO	MDEA Thermal degradation MDEA Oxidative degradation	[9] [9]
DP 7	N, N-(Dimethyl)ethanolamine (DMAE)	89.08406	$C_4H_{11}NO$	MDEA Thermal degradation MDEA Oxidative degradation	[9] [10]
DP 8	N-methylmorpholine (MM)	101.08406	$C_5H_{11}NO$	MDEA Thermal degradation	[9]
DP 9	Diethanolamine (DEA)	105.07898	$C_4H_{11}NO_2$	MDEA Thermal degradation MDEA Oxidative degradation	[9] [9]
DP 10	N, N-dimethylpiperazine (DMP)	114.1157	$C_6H_{14}N_2$	MDEA Thermal degradation PZ Thermal degradation	[9] [11]
DP 11	N-(2 hydroxyethyl) oxazolidin-2-one (HEOD)	131.1310	$C_5H_9O_3$	MDEA Thermal degradation	[9]
DP 12	N-(2 hydroxyethyl)-N-methylpiperazine (HMP)	144.12626	$C_7H_{16}N_2O$	MDEA Thermal degradation	[9]
DP 13	Triethanolamine (TEA)	149.10519	$C_6H_{15}NO_3$	MDEA Thermal degradation MDEA Oxidative degradation	[9] [10]
DP 14	N, N-bis (2 hydroxyethyl) piperazine (BHEP)	174.2440	$C_8H_{18}N_{202}$	MDEA Thermal degradation	[9]
DP 15	N, N, N-tris(2-hydroxyethyl) ethylenediamine (THEED)	192.14739	$C_8H_{20}N_2O_3$	MDEA Thermal degradation	[9]
DP 16	N-(2-(2-hydroxylethylmethylamino) ethyl]-N-methylpiperazine (HEMAEMP)	201.18411	$C_{10}H_{23}N_3O$	MDEA Thermal degradation	[12]
DP 17	N-methyl-N, N, N-tris(2-hydroxylethyl) ethylenediamine (MTHEED)	206.16304	$C_9H_{22}N_2O_3$	MDEA Thermal degradation	[12]
DP 18	N-[2-2-hydrocylethylmethylamino) ethyl]-N-(2-hydroxylethyl) piperazine (HEMAEHEP)	231.19468	$C_{11}H_{25}N_3O_2$	MDEA Thermal degradation	[12]
DP 19	N, N, N, N-tetrakis(2-hydroxylethyl) ethylenediamine (TEHEED)	236.17361	$C_{10}H_{24}N_2O_4$	MDEA Thermal degradation	[9]
DP 20	Methylamine	31.0422	CH_5N	MDEA Oxidative degradation	[13]
DP 21	Ethylene oxyde (EO)	44.02621	C_2H_4O	MDEA Oxidative degradation	[9]
DP 20	Dimethylamine	45.05785	C_2H_7N	MDEA Oxidative degradation	[13]
DP 21	Formic acid	46.00548	CH_2O_2	MDEA Oxidative degradation PZ Thermal degradation PZ Oxidative degradation	[14] [11] [11]
DP 22	Acetic acid	60.02113	CH_3COOH	MDEA Oxidative degradation PZ Thermal degradation PZ Oxidative degradation	[14] [11] [11]
DP 23	Glycolic acid	76.01604	$C_2H_4O_3$	MDEA Oxidative degradation PZ Thermal degradation PZ Oxidative degradation	[15] [11] [11]
DP 24	Oxalic acid	89.99531	$C_2H_2O_4$	MDEA Oxidative degradation PZ Thermal degradation PZ Oxidative degradation	[14] [11] [11]

Continued

DP 25	N-methylmorpholin-2-one	115.06333	$C_5H_9NO_2$	MDEA Oxidative degradation	[14]
DP 26	N-methylmorpholin-2,6-dione	129.04259	$C_5H_7NO_3$	MDEA Oxidative degradation	[14]
DP 27	2-[Methyl (2-hydroxyethyl) amino] acetic acid	133.07389	$C_5H_{11}NO_3$	MDEA Oxidative degradation	[15]
DP 28	N, N, N-trimethyl-N-(2-hydroxyethyl) ethylenediamine	146.14191	$C_7H_{18}N_2O$	MDEA Oxidative degradation	[10]
DP 29	N-(carboxymethyl) diethanolamine (bicine)	163.08446	$C_6H_{13}NO_4$	MDEA Oxidative degradation	[10]
DP 30	Ethyl enediamine (EDA)	60.06875	$C_2H_8N_2$	PZ Thermal degradation	[11]
DP 31	Imidazolidin-2-one (2-Imid)	86.04801	$C_3H_6N_2O$	PZ Thermal degradation	[11]
DP 32	N-methylpiperazine (MPZ)	100.10005	$C_5H_{12}N_2$	PZ Thermal degradation	[11]
DP 33	N-formylpiperazine (FPZ)	114.07931	$C_5H_{10}N_2O$	PZ Thermal degradation	[11]
DP 34	N-ethylpiperazine (EPZ)	114.1157	$C_6H_{14}N_2$	PZ Thermal degradation	[11]
DP 35	N-(2-hydroxyethyl)-N-methyl piperazine (HMP)	129.1266	$C_6H_{15}N_3$	PZ Thermal degradation	[11]
DP 36	N-(2-hydroxyethyl) piperazine (HEP)	130.11061	$C_6H_{14}N_2O$	PZ Thermal degradation	[11]
DP 37	Nitrous Acid	47.00073	HNO_2	PZ Oxidative degradation	[11]
DP 38	Nitric acid	62.99564	HNO_3	PZ Oxidative degradation	[11]
DP 39	Ethylenediamine (EDA)	60.06875	$C_2H_8N_2$	PZ Oxidative degradation	[11]
DP 40	Glycolic Acid	76.01604	$C_2H_4O_3$	PZ Oxidative degradation	[11]
DP 41	N-Formylpiperazine (FPZ)	114.07931	$C_5H_{10}N_2O$	PZ Oxidative degradation	[11]

trace concentration detection, LCMS-QTOF was commonly used due to its high sensitivity feature. In CO_2 absorption studies, many authors discussed the degradation products of alkanolamine, degradation path and solution to resolve issues caused by degradation products. But identification strategy on MS acquired data was seldom discussed in detail. Instead, a comprehensive identification strategy in characterization of trace degradation products using MS or MSMS had been extensively discussed in pharmaceutical or drug impurities/degradation products study [17] [19] [20] [21] [22], probably due to its stringent requirement for pharmaceutical product. Further, there is no standard strategy to derive unequivocal identification of trace degradation products qualitatively and it had been done in many different approaches. It is crucial to assure quality of the result finding to be reliable. In this work due to the low concentration of the alkanolamine degradation product, a method was developed for identification of alkanolamine degradation compounds using LCMS-QTOF technique. A strategy for identification of trace degradation products will be discussed.

2. Experimental

2.1. Alkanolamine Samples

Three types of alkanolamine solutions were used in this study. These include freshly prepared using purchased chemicals (Sample A1 and Sample A2), alkanolamine solutions taken from a natural gas processing plant used for 3 years without antifoam injection (Sample B), and alkanolamine solution taken from a natural gas processing plant operated for more than 20 years with regular antifoam injection (Sample C) as displayed in **Figure 1**. Sample B and C were subjected up to 120˚C and 90˚C during operation.

Sample A1 was prepared fresh with 30% methyl diethanolamine (MDEA) and Sample A2 was prepared with 7% piperazine, both diluted in ultrapure water. Both Sample A1 and A2 were used as baseline, for the identification of amine degradation products.

2.2. LCMS-QTOF Equipment

The analysis was performed employing Agilent 1290 Infinity II UHPLC coupled with Agilent 6545 Q-TOF MS system. The Q-TOF MS detector consisted of ion source Dual Jet Stream Electronic Ionization (AJS ESI) and QTOF mass spectrometer featured with ultralow thermal expansion alloy technology to minimize flight path alteration due to temperature fluctuation, minimal mass weight (MW) shifting by maintaining 1ppm mass accuracy with variation of 3˚C from calibration standard. The study was performed in ESI positive mode in the mass range of 45 to 1700 m/z. High purity nitrogen was used as nebulizer and auxiliary gas. Mass parameters were listed in **Table 2**. Gas temperature was optimized at 125˚C. At temperature above 125˚C, alkanolamine compounds was undetectable which possibly caused by amine degradation at ion source.

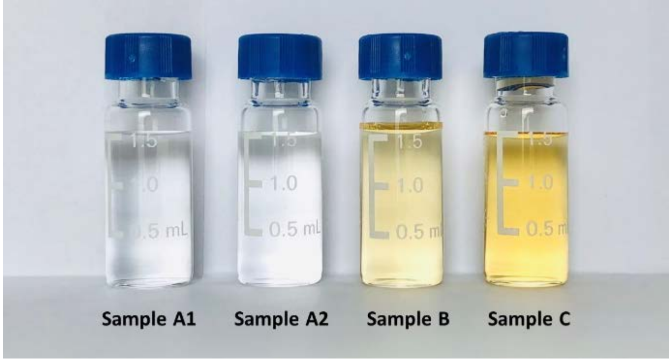


Figure 1. Appearance of sample A1, A2, B and C.

Table 2. Parameters of the QTOF methods in ESI +ve mode.

Section	Parameter	Set Point
Ion Source	Gas Temperature	125˚C
	Drying Gas	10 L/min
	Nebulizer	30 psi
	Sheath Gas Flow	11 L/min
	Capillary	3.25 µA
MS TOF	Fragmentor	180 V
	Skimmer	45 V

In this qualitative analysis, sample was introduced into QTOF detector through HPLC autosampler and union connector without analytical column assembly. Analytical column separation was not used in this method to prevent unknown contaminant source from the analytical column itself which might lead to misleading mass data analysis. The alkanolamine degradation sample was diluted at 1ppm w/w with 18.2 MΩ ultrapure deionized water and filtered with 0.22-micron PTFE syringe filter prior sample analysis. Total sample volume injection was set at 3 different injection volume of 1 uL, 10 uL and 15 uL respectively for each sample. Lower volume injection at 1uL was to obtain better mass spectra resolution and it was ideal for accurate mass identification. Higher volume injection at 10 uL and 15 uL was to further confirm if any trace degradation products presence and not traceable at lower volume injection of 1 uL. Eluent mixture was prepared with 0.1% formic acid in 18.2 MΩ ultrapure deionized water and methanol mixture (50:50 ratio), flow at 0.8 mL/min flow rate. Sample was eluted as single peak and detected at 5 mins. It was found that amine compounds tend to retain in the system and carried over to the next sample run. A flushing procedure was set by running with minimum 10 blank run after each sample run. It showed to be effective to remove the carried over amine compounds in the system.

2.3. Mass Data Analysis

Sample mass data generated from QTOF detector was processed by Agilent MassHunter Qualitative Analysis Workflows 10.0. The degradation compound identification strategy was conducted using targeted and untargeted analysis. Targeted analysis was conducted by screening the experimental accurate mass against a list of alkanolamine degradation compounds which was built as in-house mass library using Mass Hunter PCDL Manager. This in-house library database was constructed with a list of chemical name, molecular formula and theoretical accurate mass, consist of 41 alkanolamine degradation compounds related to MDEA and Piperazine degradation products, which were identified from number of literatures on amine degradation study (**Table 1**). The degradation compounds were identified based on highest match of mass, isotope abundance and isotope spacing between the experimental and theoretical accurate mass, with minimum 80% score as basis. Example is shown in **Figure 2**. Untargeted analysis was conducted using compound discovery workflow to perform broad compounds discovery covering molecular ion M+ species of M+, (M+H)+ and (M+Na)+. The experimental accurate mass detection was processed by Agilent MassHunter Qualitative Analysis Workflows 10.0 to generate a list of possible molecular formula. The most possible molecular formula was identified for each discovered compound, based on the highest match of mass, isotope abundance and isotope spacing between the experimental and theoretical accurate mass, minimum 80% score as basis. In the molecular formula generation, search criteria were set with 4 elements of Carbon, Hydrogen, Nitrogen, Oxygen with

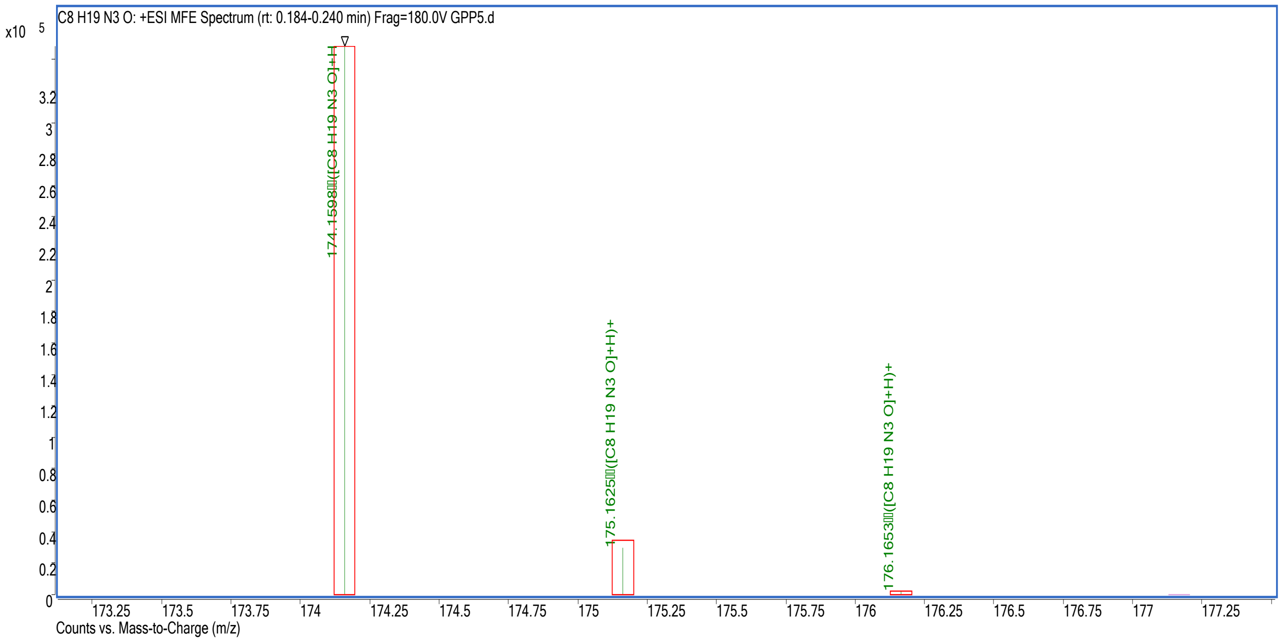


Figure 2. Example of a compound with detected accurate mass of 174.1598 m/z accompanied with its isotope at 175.1625 m/z and 176.1653 m/z. The experimental accurate mass was displayed as green peak, compared against the theoretical accurate mass indicated by the red boxes. This compound indicated good match with average score of 98.78%, derived from score (mass differences) 99.00%, score (isotope abundance) 97.39 and score (isotope spacing) 99.99%.

target range of 1 - 20, 0 - 50, 0 - 6, 0 - 8 respectively. The target range was set based on minimum basis of typical C, H, N, O elements with range of 0 - 10, 1 - 25, 0 - 3, 0 - 4 from the alkanolamine degradation products listed in Table 1, but with extended wider range about two times of typical range, to explore any larger molecular compounds probably derived from alkanolamine degradation. Compounds with carbon number above 20 were not targeted, to eliminate complex molecular structure that unlikely to happen. In order to relate the identified possible molecular formulas with alkanolamine degradation process, the possible molecular structures of each molecular formula were found using Chemspider, and chemical structures that could have derived from alkanolamine degradation products structure or its combination were shortlisted as possible degradation products. Those identified possible degradation products from untargeted analysis were considered as possible structures, but further confirmation was not covered in this study.

3. Results and Discussion

3.1. Chromatography

Sample was introduced into detector via auto-sampler without column separation, and entire sample eluted out at retention time 0.17 - 3.5 mins. The accurate mass identification was performed by focusing at this retention time. In total, four samples were analyzed which include sample A1, Sample A2, Sample B and Sample C (Figure 3).

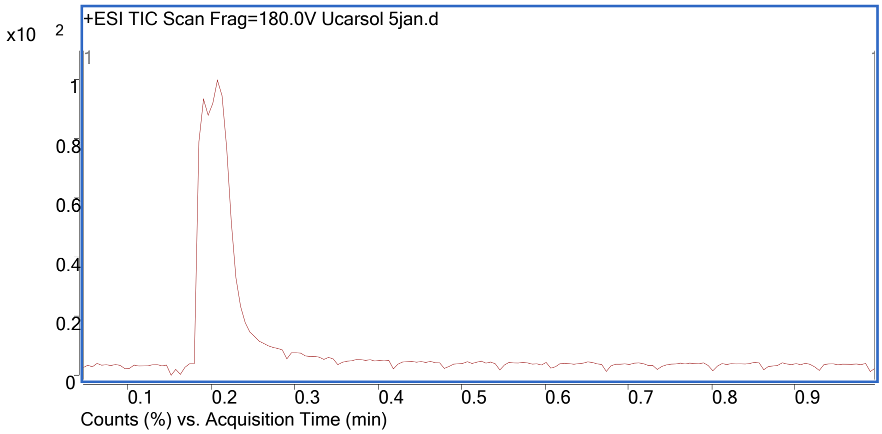


Figure 3. Chromatogram.

3.2. Sample A1—Freshly Prepared 30% Methyl Diethanolamine (MDEA)

In targeted analysis, two degradation products (DP) were found in sample A1 (freshly prepared MDEA), which were A1-DP1 and A1-DP2 with average score of 97.90% and 86.61%, representing degradation products of MM and TMA as shown in Table 3. The MM and TMA resulted from MDEA thermal degradation [9], most likely due to the effect of solvent storage. From the untargeted analysis result (Table 4), four compound masses were identified having molecular formula match with the CHNO elemental limit specified (C: 1 - 20, H: 0 - 80, N: 0 - 10, O: 0 - 10) and there was one potential chemical structure (Table 5) identified from Chemspider which display similar structure to morpholine and piperazine, potentially relate to alkanolamine degradation.

3.3. Sample A2—Freshly Prepared 7% Piperazine (Pz)

In targeted analysis, no alkanolamine degradation product was found in freshly prepared piperazine. From untargeted analysis (Table 6), one compound mass was identified having molecular formula match with the CHNO elemental limit specified (C: 1 - 20, H: 0 - 80, N: 0 - 10, O: 0 - 10) but no molecular structure found having similar structure to degradation product. It indicated fresh piperazine solvent did not contain any possible degradation product as it is stable during storage.

3.4. Sample B—Alkanolamine Solution Used in Natural Gas Processing Plant for 3 Years' Duration

Five (5) alkanolamine degradation products were found in sample B using targeted analysis with average mass score recorded as 82.41% - 97.52% (Table 7). The five (5) products were related to MDEA thermal degradation products [9]. In untargeted analysis result (Table 8), eleven (11) compound masses were identified from the broad compound discovery, with predicted molecular formula matched with CHNO element specified (C: 1 - 20, H: 0 - 50, N: 0 - 6, O: 0 - 8).

Table 3. Targeted analysis result for sample A1.

	Degradation compounds	Molecular Formula	Theoretical Mass	Experimental Mass	Mass Different (ppm)	Average Score	Species	Score (mass)	Score (Isotope Abundance)	Score (Isotope Spacing)
A1-DP1	N-methylmorpholine	$C_5H_{10}N_2O$	101.0841	101.0838	−2.81	97.90	(M+H)+	98.77	95.22	99.37
	MM						(M+Na)+	90.63	-	-
A1-DP2	Trimethylamine	C_3H_9N	59.0735	59.0738	4.83	86.61	(M+H)+	98.6	98.03	48.88
	TMA						(M+Na)+	55.37	-	-

Table 4. Untargeted analysis result for sample A1.

	Molecular Formula	Theoretical Mass	Experimental Mass	Mass Different (ppm)	Average Score	Species	Score (mass)	Score (Isotope Abundance)	Score (Isotope Spacing)	Number of compound found by molecular formula	Number of compound having structure correlate to degradation product
A1-CP1	$C_3H_9N_4O$	117.0782	117.0782	4.43	82.76	(M+H)+	96.28	99.09	36.12	0	0
A1-CP2	$C_{10}H_{15}N_4O_2$	223.1195	223.1195	0.07	86.70	(M+H)+	100	97.67	46.96	21	1
A1-CP3	$C_{14}H_{33}N_4O$	273.2658	273.2658	1.22	86.16	(M+H)+	99.11	94.73	49.98	0	0
A1-CP4	$C_{16}H_{33}N_4$	281.2704	281.2704	−0.47	86.37	(M+H)+	99.86	95.39	48.55	0	0

Table 5. Possible chemical structure resulted from alkanolamine degradation products (using untargeted analysis).

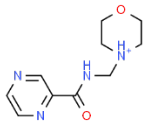
	Formula	Possible chemical structures
A1-CP2	$C_{10}H_{15}N_4O_2$	

Table 6. Untargeted analysis result for sample A2.

	Molecular Formula	Theoretical Mass	Experimental Mass	Mass Different (ppm)	Average Score	Species	Score (mass)	Score (Isotope Abundance)	Score (Isotope Spacing)	Number of compound found by molecular formula	Number of compound having structure correlate to degradation product
A2-CP1	$C_5H_{11}NO_2$	117.0783	117.0783	6.16	83.65	(M+H)+	92.93	97.95	47.93	0	0

The eleven predicted molecular formula recorded average mass score between 81.48% - 97.95%, indicating a good match. Based on the eleven predicted molecular formula, eighteen (18) potential chemical structure were identified from Chemspider database, consisted of chemical structure similar to MDEA, piperazine and alkanolamine degradation products of morpholine, methyl amine,

Table 7. Targeted analysis result for sample B.

	Degradation compounds	Molecular Formula	Theoretical Mass	Experimental Mass	Mass Different (ppm)	Average Score	Species	Score (mass)	Score (Isotope Abundance)	Score (Isotope Spacing)
B-DP1	N-Methylmorpholine (MM)	$C_5H_{11}NO$	101.08410	101.0837	−4.04	97.52	(M+H)+	97.51	97.43	97.67
B-DP2	N-Methyl N, N, N, Tris (2hydroxylethyl) ethylenediamine (MTHEED)	$C_9H_{22}N_2O_3$	206.16304	206.1619	−5.31	93.94	(M+H)+ (M+Na)+	89.12 89.22	97.78 98.84	48.82 97.47
B-DP3	Diethanolamine (DEA)	$C_4H_{11}NO_2$	105.07898	105.0788	−1.8	87.21	(M+H)+ (M+Na)+	98.66 99.65	99.29 96.24	49.8 45.9
B-DP4	Diisopropanolamine (DIPA)	$C_6H_{15}NO_2$	133.11028	133.1099	−3.15	86.44	(M+H)+ (M+Na)+	97.63 99.33	96.2 -	49.93 -
B-DP5	N, N, N, N-tetrakis (2-hydroxylethyl) ethylenediamine (TEHEED)	$C_{10}H_{24}N_2O_4$	236.17361	236.1726	−4.27	82.41	(M+H) + (M+Na)+	95.52 91.74	25.97 93.95	18.86 49.89

Table 8. Untargeted analysis result for sample B.

	Molecular Formula	Theoretical Mass	Experimental Mass	Mass Diff. (ppm)	Average Score	Species	Score Mass	Score Isotope Abundance	Score Isotope Spacing	Number of compound found by molecular formula	Number of compound having structure correlate to degradation product
B-CP1	$C_7H_{17}NO_3$	163.1208	163.1203	−3.34	97.95	(M+H)+	96.58	99.00	99.41	204	4
B-CP2	$C_{14}H_{24}NO_5$	286.1655	286.1665	3.81	92.78	(M+H)+	91.29	89.42	99.79	12	3
B-CP3	$C_{15}H_{22}N_2O$	246.1732	246.1739	2.85	90.24	(M+H)+	94.85 96.08 99.93	50.64 75.19 -	97.27 96.64 -	27,131	2
B-CP4	$C_7H_9O_4$	157.0501	157.0498	−1.49	87.23	(M+H)+	99.35	98.17	49.88	16	0
B-CP5	$C_4H_{11}NO_2$	105.0790	105.0787	−3.12	85.42	(M+H)+ (M+Na)+	98.41 98.86	95.77 -	47.03 -	1	0
B-CP6	$C_{16}H_{22}N_5O$	300.1824	300.1825	0.12	84.67	(M+H)+	99.99	88.25	49.74	23	2
B-CP7	$C_9H_{21}N_3O$	187.1685	187.1677	−4.05	83.91	(M+H)+	94.02	97.52	47.37	1634	4
B-CP8	$C_8H_{19}N_3O$	173.1528	173.1521	−4.26	83.14	(M+H)+	94.05	96.60	45.18	850	2
B-CP9	$C_8H_{16}N_2O$	156.1263	156.1258	−3.25	82.17	(M+H)+	96.95	84.48	49.83	5	0
B-CP10	$C_{15}H_{12}N_6O$	292.1073	292.1073	−0.02	81.91	(M+H)+ (M+Na)+	100.0 99.70	51.12 0	82.69 0	307	1
B-CP11	$C_9H_{21}N_4O$	201.1715	201.1720	2.31	81.48	(M+H)+	97.83	72.86	59.13	0	0

ethanolamine and ethylene diamine (Table 11), which potentially relates to alkanolamine degradation. The result of targeted and untargeted analysis confirmed that sample B had been exposed to thermal degradation and formed few organic degradation products in the natural gas processing plant operated for 3 years, compared to the freshly prepared Sample A1 and A2.

3.5. Sample C—Alkanolamine Solution Used in Natural Gas Processing Plant for 20 Years' Duration

Six (6) alkanolamine degradation products were found in sample C using targeted analysis with average mass score recorded as 82.31% - 99.64% (Table 9). Out of the six (6) products, five (5) products (C-DP1, C-DP2, C-DP3, C-DP5, C-DP6) were MDEA thermal degradation product and one (1) product (C-DP1) was related to piperazine thermal degradation [9]. In untargeted analysis result (Table 10), seventeen (17) compound masses were identified from the broad compound discovery indicating a good match with predicted molecular formula with the CHNO element specified (C: 1 - 20, H: 0 - 50, N: 0 - 6, O: 0 - 8). They had recorded average mass score between 80.66% - 98.78%. Based on these seventeen (17) predicted molecular formula, thirty-eight (38) potential chemical structure were identified from Chemspider database, consisted of chemical structure similar to MDEA, piperazine and alkanolamine degradation products of morpholine, methyl amine, ethanolamine and ethylene diamine (Table 11), which potentially related to alkanolamine degradation. The result of targeted and untargeted analysis indicated sample C had been exposed to more severe thermal degradation and formed more organic degradation products in the natural gas processing plant operated for 20 years, compared to sample A1, A2 and sample B.

3.6. Identification of Peaks and Compound Correlation with Chemical Reaction

All samples except A2 contained N-methyl morpholine (MM) which was a major

Table 9. Targeted analysis result for sample C.

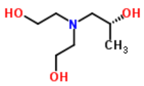
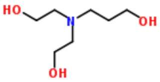
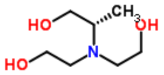
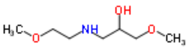
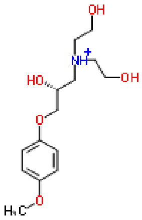
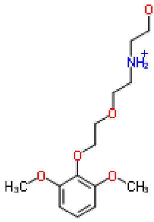
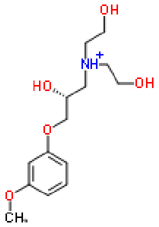
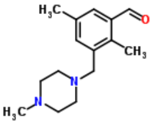
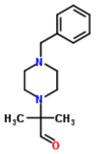
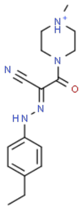
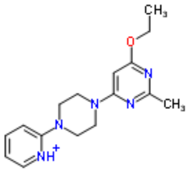
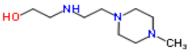
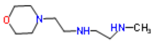
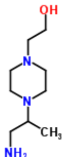
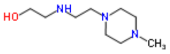
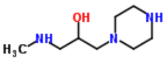
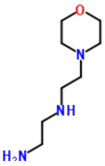
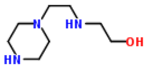
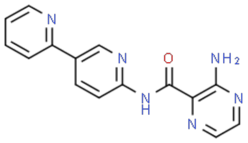
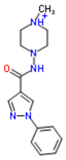
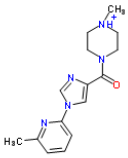
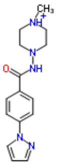
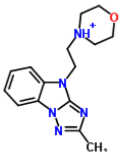
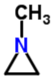
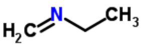
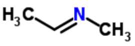
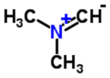
	Degradation compounds	Molecular Formula	Theoretical Mass	Experimental Mass	Mass Different (ppm)	Average Score	Species	Score (mass)	Score (Isotope Abundance)	Score (Isotope Spacing)
C-DP1	N, N'dimethylpiperazine (DMP)	$C_6H_{14}N_2$	114.1157	114.1154	−2.19	99.64	(M+H)+	99.36	99.82	99.99
C-DP2	N-methylmorpholine (MM)	$C_5H_{11}NO$	101.0841	101.0836	−6.22	98.05	(M+H)+ (M+Na)+	92.07 96.19	97.51 99.71	48.73 99.79
C-DP3	N-methyl, N, N, N, Tris (2hydroxylethyl) ethylenediamine (MTHEED)	$C_9H_{22}N_2O_3$	206.16304	206.1623	−3.55	94.75	(M+H)+ (M+Na)+	95.89 94.49	96.98 95.12	89.82 49.97
C-DP4	Diisopropanolamine (DIPA)	$C_6H_{15}NO_2$	133.11028	133.1099	−2.74	87.04	(M+H)+ (M+Na)+	98.27 97.62	99.26	49.92
C-DP5	Diethanolamine (DEA)	$C_4H_{11}NO_2$	105.07898	105.0788	−2.01	86.97	(M+H)+ (M+Na)+	98.75 99.94	98.21 93.35	49.91 49.87
C-DP6	N, N, N, N-tetrakis (2-hydroxylethyl) ethylenediamine (TEHEED)	$C_{10}H_{24}N_2O_4$	236.17361	236.1725	−4.65	82.31	(M+H)+ (M+Na)+	97.53 90.31	0 95.56	0 49.22

Table 10. Untargeted analysis result for sample C.

	Molecular Formula	Theoretical Mass	Experimental Mass	Mass Diff. (ppm)	Average Score	Species	Score Mass	Score Isotope Abundance	Score Isotope Spacing	Number of compound found by molecular formula	Number of compound having structure correlate to degradation product
C-CP1	$C_8H_{19}N_3O$	173.1528	173.1525	−1.73	98.78	(M+H)+	99.00	97.39	99.99	852	2
C-CP2	$C_9H_{21}N_3O$	187.1685	187.1680	−2.59	98.27	(M+H)+	97.51	99.07	98.82	1634	4
C-CP3	$C_7H_{17}NO_3$	163.1208	163.1203	−3.35	98.17	(M+H)+ (M+Na)+	96.56 91.21	99.34 99.93	99.98 99.38	204	4
C-CP4	$C_5H_{13}NO_2$	119.0946	119.0953	6.05	95.13	(M+H)+	92.99	97.26	96.85	2	0
C-CP5	$C_{15}H_{20}N_5O$	286.1668	286.1668	−0.03	90.00	(M+H)+	100	66.03	98.77	39	4
C-CP6	C_3H_7N	57.0578	57.0577	−2.97	87.39	(M+H)+ (M+Na)+	96.57 99.59	99.86 98.21	48.25 50.00	18	4
C-CP7	$C_6H_{12}N_2$	112.1001	112.0997	−3.05	86.85	(M+H)+	98.33	99.42	48.81	6	3
C-CP8	$C_7H_{17}N_3$	143.1422	143.1418	−3.20	86.30	(M+H)+	97.37	99.41	48.40	463	2
C-CP9	$C_4H_{11}NO_2$	105.0790	105.0787	−2.51	86.24	(M+H)+	98.97	95.52	49.64	1	0
C-CP10	$C_7H_{19}N_2O_4$	195.1345	195.1340	−2.57	86.05	(M+H)+	97.42	97.44	49.67	0	0
C-CP11	$C_{15}H_{22}N_2O$	246.1732	246.1738	2.26	85.6	(M+H)+ (M+Na)+ (M+K)+	95.57 97.51 84.69	47.29 54.21 41.81	99.82 99.44 48.18	27,131	2
C-CP12	$C_{16}H_{22}N_5O$	300.1824	300.1821	−1.2	84.94	(M+H)+	99.05	90.99	49.48	23	2
C-CP13	$C_{15}H_{20}N_4O_5$	336.1434	336.1438	1.33	83.72	(M+H)+	98.68	87.33	49.46	633	8
C-CP14	$C_{12}H_9N$	167.0735	167.0727	−5.07	82.46	(M+H)+	92.03	52.08	99.78	123	1
C-CP15	$C_{15}H_{24}N_5O$	290.1981	290.1981	0	81.85	(M+H)+ (M+Na)+	100 98.86	93.94 76.69	31.06 49.16	7	1
C-CP16	$C_{20}H_{31}N_6O_3$	403.2458	403.2455	−0.71	81.64	(M+H)+	99.55	79.09	48.87	11	1
C-CP17	$C_8H_{21}N_6$	201.1828	201.1818	−4.61	80.66	(M+H)+ (M+Na)+	91.61 98.77	94.84 0	41.77 0	0	0

temperature degradation product of MDEA as shown in Table 12 with highest abundance %. Sample B and Sample C contained more thermal degradation product of MDEA and PZ, which included MM, DEA, DIPA, and TEHEEE. DEA and DMP that came from CO_2 induced degradation of MDEA and PZ, while DIPA came from degradation of DEA [5]. Sample C contained additional two degradation products from MDEA which were MTHEED and DMP, probably due to the amine solutions had been used for more than 20 years. The presence of more degradation product in Sample B and Sample C could explain the severe foaming tendency of these amine solutions. Activated carbon filter should be installed to remove these organic degradation products to reduce foaming tendency. Alternatively, antifoam injection could be done.

Table 11. Possible chemical structures found in Chemspider, having structure similarity of alkanolamine degradation products (using untargeted analysis) for sample B and sample C.

	Formula	Presence		Possible chemical structures
1	$C_7H_{17}NO_3$	Sample B Sample C	B-CP1 C-CP3	   
2	$C_{14}H_{24}NO_5$	Sample B	B-CP2	  
3	$C_{15}H_{22}N_2O$	Sample B Sample C	B-CP3 C-CP11	 
4	$C_{16}H_{22}N_5O$	Sample B Sample C	B-CP6 C-CP12	 
5	$C_9H_{21}N_3O$	Sample B Sample C	B-CP7 C-CP2	   
6	$C_8H_{19}N_3O$	Sample B Sample C	B-CP8 C-CP1	   
7	$C_{15}H_{12}N_6O$	Sample B	B-CP10	
8	$C_{15}H_{20}N_5O$	Sample C	C-CP5	   
9	C_3H_7N	Sample C	C-CP6	   

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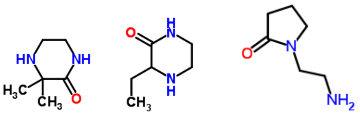
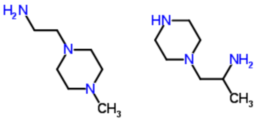
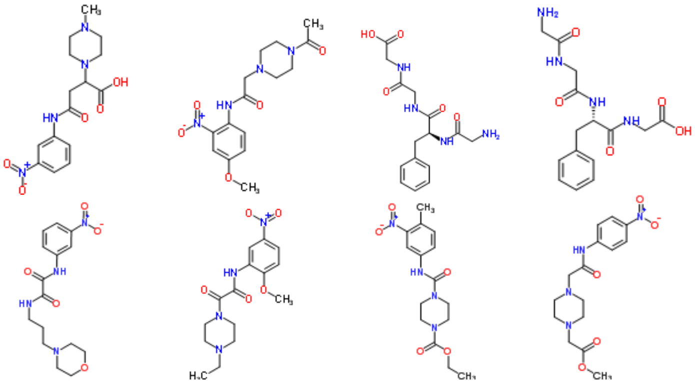
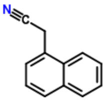
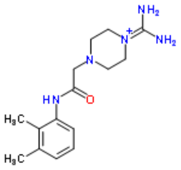
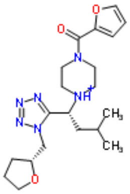
10	$C_6H_{12}N_2$	Sample C	C-CP7	
11	$C_7H_{17}N_3$	Sample C	C-CP8	
12	$C_{15}H_{20}N_4O_5$	Sample C	C-CP13	
13	$C_{12}H_9N$	Sample C	C-CP14	
14	$C_{15}H_{24}N_5O$	Sample C	C-CP15	
15	$C_{20}H_{31}N_6O_3$	Sample C	C-CP16	

Table 12. Comparison between Sample B and Sample C, in abundance % of alkanolamine products and its degradation products found via targeted analysis. It provided some qualitative indication on the reduction of MDEA and Pz alkanolamine product in sample C which had been recycled used in gas processing plant for more than 20 years compare to sample B which was 3 years.

		Sample A1	Sample A2	Sample B	Sample C
		Abundance %	Abundance %	Abundance %	Abundance %
Alkanolamine solvent					
Methyl Diethanol Amine (MDEA)	$C_3H_{12}NO_2$	90.2	ND[1]	72.9	47.2
Pipezine (Pz)	$C_4H_{10}N_2$	ND[1]	58.5	0.2	0.1
Alkanolamine degradation product (by targeted analysis)					
N-methylmorpholine (MM)	$C_5H_{11}NO$	8.9	ND[1]	5.3	3.3
N, N, N, N-tetrakis(2-hydroxylethyl) ethylenediamine (TEHEED)	$C_{10}H_{24}N_2O_4$	ND[1]	ND[1]	0.3	0.5

Continued

Diisopropanolamine (DIPA)	$C_6H_{15}NO_2$	ND[1]	ND[1]	0.2	0.2
Diethanolamine (DEA)	$C_4H_{11}NO_2$	ND[1]	ND[1]	0.1	0.1
N-methyl, N, N, N, Tris (2hydroxylethyl) ethylenediamine (MTHEED)	$C_9H_{22}N_2O_3$	ND[1]	ND[1]	ND[1]	0.1
N, N'dimethylpiperazine (DMP)	$C_6H_{14}N_2$	ND[1]	ND[1]	ND[1]	0.1
Other products mentioned in Table 1		ND[1]	ND[1]	ND[1]	ND[1]

Note 1: ND—Not Detected either the accurate mass score was below 80% or was not detected due to trace level below method detection limit.

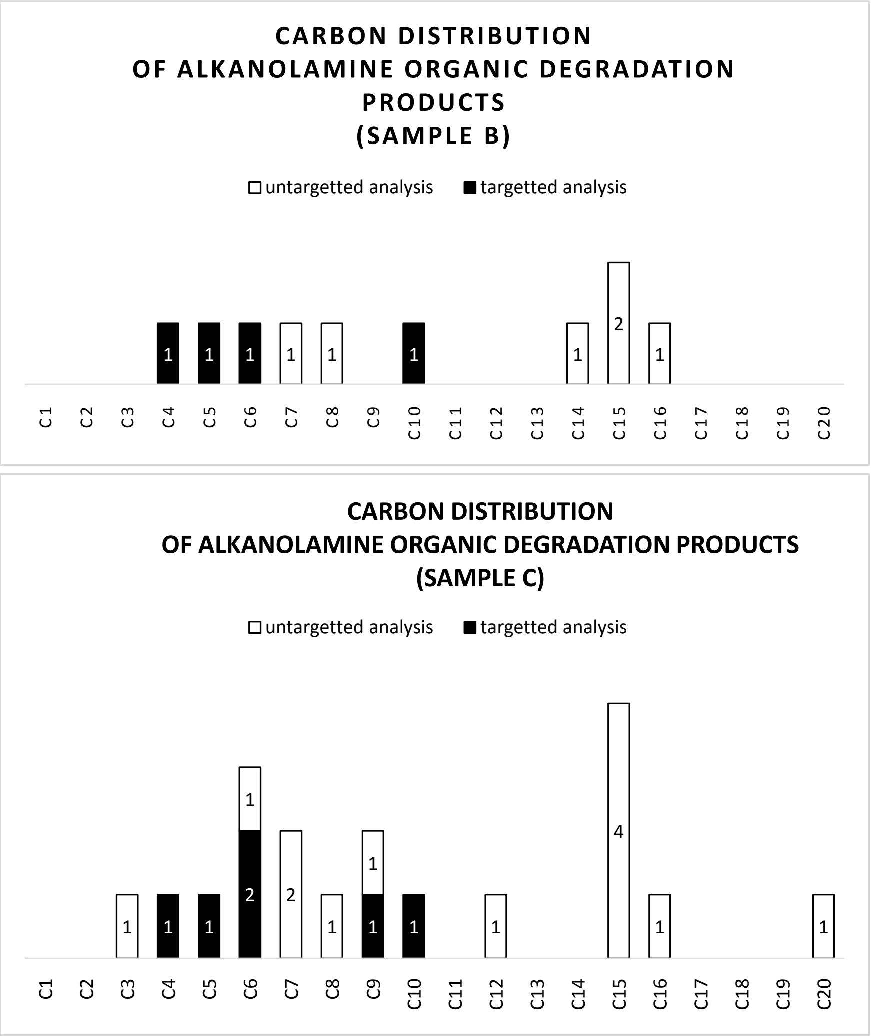


Figure 4. Carbon number distribution of alkanolamine organic degradation products in sample B and sample C.

Figure 4 showed the carbon number distribution of the potential degradation products found in sample B and sample C, to give overview of organic degradation products chain length distribution.

4. Conclusion

Six (6) alkanolamine degradation products have been identified by using

LCMS-QTOF targeted analysis in the blended alkanolamine solvent (MDEA and Pz) used in natural gas processing plant. Another fifteen (15) molecular formulas having similarity in chemical structure to alkanolamine degradation products were identified using untargeted analysis strategy, as possible compounds related to degradation product, but confirmation of its validation was not covered in this study. Using LCMS-QTOF via targeted and untargeted analysis strategy, without tedious column separation and reference standard, enables laboratory to provide a quick and indicative information for alkanolamine solvent's organic degradation compounds identification in CO_2 adsorption, within reasonable analysis time. In order to achieve higher accuracy, further extension of this LCMS-QTOF analysis using MSMS ion fragmentation would help to confirm the compound structure and investing in optimizing compound separation using analytical column will also improve the sensitivity of the method.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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