CO₂ Absorption Solvent Degradation Compound Identification Using Liquid Chromatography-Mass Spectrometry Quadrupole-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 CO₂ adsorption, within reasonable analysis time.

Keywords
CO₂ 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 alkanolamine 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 | CH₄O             | MDEA Thermal degradation  | [9]        |
| DP 2| Ethylene Oxide (EO)                   | 44.02621 | C₂H₄O            | MDEA Thermal degradation  | [9]        |
| DP 3| Trimethylamine (TMA)                  | 59.07350 | C₃H₇N            | MDEA Thermal degradation  | [9]        |
| DP 4| Ethylene Glycol (EG)                  | 62.03678 | C₃H₅N₂O          | MDEA Thermal degradation  | [9]        |
| DP 5| N, N-dimethyl ethylamine (DMAE)       | 73.08915 | C₄H₇N            | MDEA Thermal degradation  | [9]        |
| DP 6| N-methyethanolamine (MAE)             | 75.06841 | C₅H₁₀NO           | MDEA Thermal degradation  | [9]        |
| DP 7| N, N-(Dimethyl)ethanolamine (DMAE)    | 89.08406 | C₅H₁₀NO          | MDEA Thermal degradation  | [9]        |
| DP 8| N-methylmorpholine (MM)               | 101.08406 | C₅H₁₀NO       | MDEA Thermal degradation  | [9]        |
| DP 9| Diethanolamine (DEA)                  | 105.07898 | C₅H₁₀NO₂         | MDEA Thermal degradation  | [9]        |
| DP 10| N, N-dimethylpiperazine (DMP)        | 114.1157 | C₆H₁₂N₂           | MDEA Thermal degradation  | [9]        |
| DP 11| N-(2-hydroxyethyl) oxazolidin-2-one (HEOD) | 131.1310 | C₅H₁₀O          | MDEA Thermal degradation  | [9]        |
| DP 12| N-(2-hydroxyethyl)-N-methylpiperazine (HMP) | 144.12626 | C₆H₁₂N₂O      | MDEA Thermal degradation  | [9]        |
| DP 13| Triethanolamine (TEA)                 | 149.10519 | C₆H₁₀NO₂         | MDEA Thermal degradation  | [9]        |
| DP 14| N, N-bis (2 hydroxyethyl) piperazine (BH) | 174.2440 | C₆H₁₄N₂          | MDEA Thermal degradation  | [9]        |
| DP 15| N, N, N-tris(2-hydroxyethyl) ethylenediamine (THEED) | 192.14739 | C₇H₁₄N₂O₃ | MDEA Thermal degradation  | [9]        |
| DP 16| N-(2-(2-hydroxyethylmethylamino) ethyl]-N-methylpiperazine (HEMAEHEP) | 201.18411 | C₆H₁₄N₂O      | MDEA Thermal degradation  | [12]       |
| DP 17| N-methyl-N, N, N-tris(2-hydroxyethyl) ethylenediamine (MTHEED) | 206.16304 | C₆H₁₂N₂O₃     | MDEA Thermal degradation  | [12]       |
| DP 18| N-[2-(2-hydroxyethylmethylamino) ethyl]-N-(2-hydroxyethyl) piperazine (HEMAEHEP) | 231.19468 | C₇H₂₀N₂O₂     | MDEA Thermal degradation  | [12]       |
| DP 19| N, N, N-tetras(2-hydroxyethyl) ethylenediamine (TE) | 236.17361 | C₈H₁₆N₄O₄     | MDEA Thermal degradation  | [9]        |
| DP 20| Methylamine                           | 31.0422  | CH₃N             | MDEA Oxidative degradation | [13]       |
| DP 21| Ethylene oxide (EO)                  | 44.02621 | C₂H₄O            | MDEA Oxidative degradation | [9]        |
| DP 20| Dimethylamine                         | 45.05785 | C₂H₆N            | MDEA Oxidative degradation | [13]       |
| DP 21| Formic acid                           | 46.00548 | CH₂O₂            | MDEA Oxidative degradation | [14]       |
| DP 22| Acetic acid                           | 60.02113 | CH₃COOH          | MDEA Oxidative degradation | [14]       |
| DP 23| Glycolic acid                         | 76.01604 | C₃H₂O₃           | MDEA Oxidative degradation | [15]       |
| DP 25 | N-methylmorpholin-2-one | 115.06333 C₅H₉NO₂ | MDEA Oxidative degradation [14] |
| DP 26 | N-methylmorpholin-2,6-dione | 129.04259 C₅H₇NO₃ | MDEA Oxidative degradation [14] |
| DP 27 | 2-[Methyl (2-hydroxyethyl) amino] acetic acid | 133.07389 C₅H₇NO₃ | MDEA Oxidative degradation [15] |
| DP 28 | N, N, N-trimethyl-N-(2-hydroxyethyl) ethylenediamine | 146.1491 C₆H₁₄N₂O | MDEA Oxidative degradation [10] |
| DP 29 | N-(carboxymethyl) diethanolamine (bicine) | 163.08466 C₆H₁₁NO₄ | MDEA Oxidative degradation [10] |
| DP 30 | Ethylenediamine (EDA) | 60.06875 C₂H₈N₂ | PZ Thermal degradation [11] |
| DP 31 | Imidazolidin-2-one (2-Imid) | 86.04801 C₃H₆N₂O | PZ Thermal degradation [11] |
| DP 32 | N-methylpiperazine (MPZ) | 100.10005 C₆H₁₀N₂ | PZ Thermal degradation [11] |
| DP 33 | N-formylpiperazine (FPZ) | 114.07931 C₆H₁₀N₂O | PZ Thermal degradation [11] |
| DP 34 | N-ethylpiperazine (EPZ) | 114.1157 C₆H₁₁N₂ | PZ Thermal degradation [11] |
| DP 35 | N-(2-hydroxyethyl)-N-methyl piperazine (HMP) | 129.1266 C₆H₁₄N₃ | PZ Thermal degradation [11] |
| DP 36 | N-(2-hydroxyethyl) piperazine (HEP) | 130.11061 C₆H₁₂N₂O | PZ Thermal degradation [11] |
| DP 37 | Nitrous Acid | 47.00073 HNO₂ | PZ Oxidative degradation [11] |
| DP 38 | Nitric acid | 62.99564 HNO₃ | PZ Oxidative degradation [11] |
| DP 39 | Ethylenediamine (EDA) | 60.06875 C₂H₈N₂ | PZ Oxidative degradation [11] |
| DP 40 | Glycolic Acid | 76.01604 C₂H₄O₃ | PZ Oxidative degradation [11] |
| DP 41 | N-Formylpiperazine (FPZ) | 114.07931 C₆H₁₀N₂O | PZ Oxidative degradation [11] |

trace concentration detection, LCMS-QTOF was commonly used due to its high sensitivity feature. In CO₂ 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.](image)

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. 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).
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 | C₅H₁₀N₂O | 101.0841 | 101.0838 | -2.81 | 97.90 | (M+H)+ | 98.77 | 95.22 | 99.37 |
| MM                     |                   |                  |                   |                     |               |         |             |                          |                        |
| A1-DP2 Trimethylamine   | C₃H₉N | 59.0735 | 59.0738 | 4.83 | 86.61 | (M+H)+ | 98.6 | 98.03 | 48.88 |
| TMA                    |                   |                  |                   |                     |               |         |             |                          |                        |

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 C₅H₁₁NO₂ | 117.0782 | 117.0782 | 4.43 | 82.76 | (M+H)+ | 99.28 | 99.09 | 36.12 | 0 | 0 |
| A1-CP2 C₆H₁₁N₂O₂ | 223.1195 | 223.1195 | 0.07 | 86.70 | (M+H)+ | 100 | 97.67 | 46.96 | 21 | 1 |
| A1-CP3 C₁₀H₁₅N₄O | 273.2658 | 273.2658 | 1.22 | 86.16 | (M+H)+ | 99.11 | 94.73 | 49.98 | 0 | 0 |
| A1-CP4 C₁₆H₃₃N₄ | 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 C₆H₁₁N₂O₂ | ![Chemical structure](image) |

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 C₆H₁₁NO₂ | 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 Diff. (ppm) | Average Score | Species Score (mass) | Species Score (Isotope Abundance) | Species Score (Isotope Spacing) |
|-----------------------|-------------------|------------------|------------------|-----------------|---------------|----------------------|-----------------------------------|--------------------------------|
| B-DP1 N-Methylmorpholine (MM) | C₅H₁₁NO            | 101.08410        | 101.0837         | −0.04           | 97.52         | 97.51                | 97.43                             | 97.67                           |
| B-DP2 N-Methyl N, N, N, Tris (2-hydroxyethyl) ethylenediamine (MTHEED) | C₉H₂₂N₂O₃          | 206.16304        | 206.1619         | −5.31           | 93.94         | 89.12                | 97.78                             | 48.82                           |
| B-DP3 Diethanolamine (DEA) | C₆H₁₃NO₂            | 105.07989        | 105.0788         | −1.8            | 87.21         | 98.66                | 96.24                             | 45.9                            |
| B-DP4 Diisopropanolamine (DIPA) | C₆H₁₆NO₂            | 133.1099         | 133.1028         | −3.15           | 86.44         | 97.63                | 96.2                              | 49.93                           |
| B-DP5 N, N, N, N-tetrakis (2-hydroxyethyl) ethylenediamine (TEHEED) | C₁₀H₂₄N₂O₄          | 236.17361        | 236.1726         | −4.27           | 82.41         | 95.52                | 25.97                             | 18.86                           |

### Table 8. Untargeted analysis result for sample B.

| Molecular Formula | Theoretical Mass | Experimental Mass | Mass Diff. (ppm) | Average Score | Species | Score Mass | Score Isope Abundance | Score Isope Spacing | Number of compound found by molecular formula | Number of compound having structure correlate to degradation product |
|-------------------|------------------|------------------|-----------------|---------------|---------|-----------|-----------------------|---------------------|-----------------------------------------------|---------------------------------------------------------------|
| B-CP1 C₇H₁₇NO₃  | 163.1208         | 163.1203         | −3.34           | 97.95         | (M+H)+  | 96.58     | 99.00                 | 99.41               | 204                                           | 4                                                             |
| B-CP2 C₁₃H₂₃NO₅ | 286.1655         | 286.1665         | 3.81            | 92.78         | (M+H)+  | 91.29     | 89.42                 | 99.79               | 12                                            | 3                                                             |
| B-CP3 C₁₀H₁₇NO   | 246.1732         | 246.1739         | 2.85            | 90.24         | (M+H)+  | 96.08     | 75.19                 | 96.64               | 27,131                                        | 2                                                             |
| B-CP4 C₄H₉O₄    | 157.0501         | 157.0498         | −1.49           | 87.23         | (M+H)+  | 99.35     | 98.17                 | 49.88               | 16                                            | 0                                                             |
| B-CP5 C₁₁H₁₇NO₅ | 105.0790         | 105.0787         | −3.12           | 85.42         | (M+H)+  | 98.41     | 95.77                 | 47.03               | 1                                             | 0                                                             |
| B-CP6 C₁₀H₁₅NO   | 300.1824         | 300.1825         | 0.12            | 84.67         | (M+H)+  | 99.99     | 88.25                 | 49.74               | 23                                            | 2                                                             |
| B-CP7 C₁₃H₂₁NO₇ | 187.1685         | 187.1677         | −0.05           | 83.91         | (M+H)+  | 94.02     | 97.52                 | 47.37               | 1634                                          | 4                                                             |
| B-CP8 C₁₄H₂₃NO₉ | 173.1528         | 173.1521         | −4.26           | 83.14         | (M+H)+  | 94.05     | 96.60                 | 45.18               | 850                                           | 2                                                             |
| B-CP9 C₁₅H₂₄NO₁₀ | 156.1263         | 156.1258         | −3.25           | 82.17         | (M+H)+  | 96.95     | 84.48                 | 49.83               | 5                                             | 0                                                             |
| B-CP10 C₁₀H₁₇NO₃ | 292.1073         | 292.1073         | −0.02           | 81.91         | (M+H)+  | 100.0     | 51.12                 | 82.69               | 307                                           | 1                                                             |
| B-CP11 C₈H₁₇NO   | 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 alkanoamine 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) | C₂₉H₄₂N₂ | 114.1157 | 114.1154 | −2.19 | 99.64 | (M+H)+ | 99.36 | 99.82 | 99.99 |
| C-DP2                 | N-methylmorpholine (MM) | C₁₃H₂₁NO | 101.0841 | 101.0836 | −6.22 | 98.05 | (M+H)+ | 92.07 | 97.51 | 48.73 |
| C-DP3                 | N-methyl, N, N, N, Tris (2hydroxyethyl) ethylenediamine (MTHEED) | C₁₅H₃₀N₂O₃ | 206.16304 | 206.1623 | −3.55 | 94.75 | (M+H)+ | 95.89 | 96.98 | 89.82 |
| C-DP4                 | Diisopropanolamine (DIPA) | C₁₂H₂₀NO₂ | 133.11028 | 133.1099 | −2.74 | 87.04 | (M+H)+ | 98.27 | 97.62 | 49.92 |
| C-DP5                 | Diethanolamine (DEA) | C₆H₁₂NO₂ | 105.07898 | 105.0788 | −2.01 | 86.97 | (M+H)+ | 98.75 | 98.21 | 49.91 |
| C-DP6                 | N, N, N-N-tetrakis (2-hydroxyethyl) ethylenediamine (TEHEED) | C₂₀H₃₄N₂O₄ | 236.17361 | 236.1725 | −4.65 | 82.31 | (M+H)+ | 97.53 | 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 C₈H₁₉N₃O   | 173.1528         | 173.1525         | −1.73           | 98.78         | (M+H)+  | 99.00      | 97.39                   | 99.99            | 852                                           | 2                                                             |
| C-CP2 C₈H₁₉N₃O   | 187.1685         | 187.1680         | −2.59           | 98.27         | (M+H)+  | 97.51      | 99.07                   | 98.82            | 1634                                          | 4                                                             |
| C-CP3 C₆H₁₈NO₃   | 163.1208         | 163.1203         | −3.35           | 98.17         | (M+H)+  | 96.56      | 99.34                   | 99.98            | 204                                           | 4                                                             |
| C-CP4 C₆H₃NO₂    | 119.0946         | 119.0953         | 0.05            | 95.13         | (M+H)+  | 92.99      | 97.26                   | 96.85            | 2                                              | 0                                                             |
| C-CP5 C₇H₁₇NO₃   | 286.1668         | 286.1668         | −0.03           | 90.00         | (M+H)+  | 100        | 66.03                   | 98.77            | 39                                            | 4                                                             |
| C-CP6 C₇H₁₉N₂    | 57.0578          | 57.0577          | −2.97           | 87.39         | (M+H)+  | 96.57      | 99.86                   | 48.25            | 18                                            | 4                                                             |
| C-CP7 C₇H₁₉N₂    | 112.1001         | 112.0997         | −1.02           | 86.85         | (M+H)+  | 98.33      | 99.42                   | 48.81            | 6                                             | 3                                                             |
| C-CP8 C₇H₂₁N₄O   | 143.1422         | 143.1418         | −0.32           | 86.30         | (M+H)+  | 97.37      | 99.41                   | 48.40            | 463                                           | 2                                                             |
| C-CP9 C₈H₁₈NO₃   | 105.0790         | 105.0787         | −2.51           | 86.24         | (M+H)+  | 98.97      | 95.52                   | 49.64            | 1                                             | 0                                                             |
| C-CP10 C₉H₁₇N₃O₄ | 195.1345         | 195.1340         | −2.57           | 86.05         | (M+H)+  | 97.42      | 97.44                   | 49.67            | 0                                             | 0                                                             |
| C-CP11 C₈H₁₉N₃O   | 246.1732         | 246.1738         | 2.26            | 85.60         | (M+H)+  | 95.57      | 47.29                   | 99.82            | 27131                                         | 2                                                             |
| C-CP12 C₉H₂₁N₄O   | 300.1824         | 300.1821         | −1.2            | 84.94         | (M+H)+  | 99.05      | 90.99                   | 49.48            | 23                                            | 2                                                             |
| C-CP13 C₉H₂₁N₄O   | 336.1434         | 336.1438         | 1.33            | 83.72         | (M+H)+  | 98.68      | 87.33                   | 49.46            | 633                                           | 8                                                             |
| C-CP14 C₈H₁₉N₂    | 167.0735         | 167.0727         | −5.07           | 82.46         | (M+H)+  | 92.03      | 52.08                   | 99.78            | 123                                           | 1                                                             |
| C-CP15 C₉H₂₁N₄O   | 290.1981         | 290.1981         | 0.00            | 81.85         | (M+H)+  | 100        | 93.94                   | 31.06            | 7                                             | 1                                                             |
| C-CP16 C₉H₂₁N₄O   | 403.2458         | 403.2455         | −0.71           | 81.64         | (M+H)+  | 99.55      | 79.09                   | 48.87            | 11                                            | 1                                                             |
| C-CP17 C₉H₂₃N₈    | 201.1828         | 201.1818         | −4.61           | 80.66         | (M+H)+  | 91.61      | 94.84                   | 41.77            | 0                                             | 0                                                             |

The 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 CO₂ 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 |
|--------------|----------------|------------------------------|
| C₇H₁₇NO₃    | Sample B      | B-CP1                        |
|              | Sample C      | C-CP3                        |
| C₉H₁₉N₃O    | Sample B      | B-CP8                        |
|              | Sample C      | C-CP1                        |
| C₁₅H₂₂N₂O   | Sample B      | B-CP7                        |
|              | Sample C      | C-CP2                        |
| C₁₄H₂₄NO₅  | Sample B      | B-CP2                        |
|              | Sample C      | B-CP3                        |
| C₁₅H₂₂N₅O   | Sample B      | B-CP6                        |
|              | Sample C      | C-CP12                       |
| C₁₆H₂₂N₅O   | Sample B      | B-CP10                       |
| C₈H₁₇N₃O    | Sample C      | C-CP5                        |
| C₉H₂₁N₃O    | Sample B      | B-CP10                       |
|              | Sample C      | C-CP2                        |
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 | Alkanolamine solvent | Alkanolamine solvent | Alkanolamine solvent |
| Methyl Diethanol Amine (MDEA) | C$_{3}$H$_{12}$NO$_{2}$ | 90.2 | ND$^1$ | 72.9 | 47.2 |
| Pipezine (Pz) | C$_{4}$H$_{10}$N$_{2}$ | ND$^1$ | 58.5 | 0.2 | 0.1 |
| Alkanolamine degradation product (by targeted analysis) | Alkanolamine degradation product (by targeted analysis) | Alkanolamine degradation product (by targeted analysis) | Alkanolamine degradation product (by targeted analysis) |
| N-methylmorpholine (MM) | C$_{5}$H$_{11}$NO | 8.9 | ND$^1$ | 5.3 | 3.3 |
| N, N, N-tetrakis(2-hydroxyethyl) ethylenediamine (TEHEED) | C$_{6}$H$_{12}$N$_{2}$O$_{4}$ | ND$^1$ | ND$^1$ | 0.3 | 0.5 |
Continued

| Alkanolamine                          | Molecular Formula | ND ¹     | ND ²     | 0.2 | 0.2 |
|---------------------------------------|-------------------|----------|----------|-----|-----|
| Diisopropanolamine (DIPA)             | C₆H₁₅NO₂           | ND ¹     | ND ²     | 0.2 | 0.2 |
| Diethanolamine (DEA)                  | C₄H₁₁NO₂           | ND ¹     | ND ²     | 0.1 | 0.1 |
| N-methyl, N, N, N, Tris (2hydroxyethyl) ethylenediamine (MTHED) | C₆H₁₄N₂O₂ | ND ¹     | ND ²     | ND ³ | 0.1 |
| N, N’dimethylpiperazine (DMP)         | C₆H₁₄N₂            | ND ¹     | ND ²     | ND ³ | 0.1 |
| Other products mentioned in Table 1   |                   | ND ¹     | ND ²     | ND ³ | 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 CO₂ 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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