Comparison of Total Inorganic Carbon (TIC) Analysis with Titration Method Analysis in Determining Carbon Dioxide (CO₂) Content of Amine Solvent

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Abstract: Total Inorganic Carbon (TIC) is an analysis method to determine carbon content in a sample. In this paper, applicability of TIC method to determine carbon dioxide (CO₂) content in amine solvent is explored in detail. Both commercial and self-blended amine solutions, consisting of MDEA and PZ, were used in this study and bubbled with CO₂. TIC method was calibrated for both mid-level mode and high level mode. Difference in results were found when comparing TIC against the standard titration method; this is largely due to error in titration method during the methanol pH adjustment step. TIC method is considered to be better in terms of limit of detection, limit of quantification, recovery percentage, and susceptibility to error.

1. Introduction

In the present scenario, anthropogenic global warming is acknowledged as one of the environmental issues. Fossil fuels are considered as the leading source of energy consumed in the world where electricity, heat generation and transportation depend heavily on fossil fuel and this is responsible for two-third of the worldwide CO₂ emission [2]. As stated by C. Nwaoha et al. (2009), among various technologies for capturing CO₂, CO₂ capture by chemical absorption through the use of amine-based solvent is acknowledged as the most proven and commercially available technology [3]. Conventional industrial methods to reduce acid gas employ gas absorption device, such as scrubber and spray tower, but these current method have several disadvantages such as difficulty of obtaining accurate estimation of the gas-liquid mass transfer area. As an alternative to the current technologies, non-dispersive gas-liquid contact via a micro porous membrane is approached. According to Mansourizadeh and Ismail (2009), fluids can contact on opposite side of the membrane and gas-liquid interface is formed if suitable membrane configuration such as hollow fibre is used [1].

To select a suitable liquid absorbent, some criteria have to be taken into consideration, and one of the main criteria is its reactivity. Highly reactive solvent can lead to higher absorption rate and reduction of liquid mass transfer resistance [1]. Amine solvent which contains aqueous MDEA and PZ is the focus in this paper. The absorption of CO₂ by amine-based solvent can analogously be represented by an acid-base reaction, where the amine solvent acts as the base while CO₂ is the acid, to form salt like amine carbamate (AmineCOO⁻) and bicarbonate (HCO₃⁻) [3]. According to Xu Zhang, the reaction of CO₂ and PZ can be regarded as the rapid pseudo-first-order reaction in parallel with that of CO₂ with MDEA [4]. Below is the several reaction steps that can occur through absorption process [2, 3]:

\[ 2H₂O \rightleftharpoons H₂O⁺ + OH⁻ \]  
\[ CO₂ + 2H₂O \rightleftharpoons H₂O⁺ + HCO₃⁻ \]  
\[ HCO₃⁻ + H₂O \rightleftharpoons H₂O⁺ + CO₃²⁻ \]  
\[ MDEAH⁺ + H₂O \rightleftharpoons MDEA + H₂O⁺ \]  
\[ MDEA + CO₂ + H₂O \rightleftharpoons MDEAH⁺ + HCO₃⁻ \]  
\[ PZH₂⁺ + H₂O \rightleftharpoons PZH⁺ + H₃O⁺ \]
Analytical methods used in determining CO2 content and CO2 loading in this paper are titration and TIC. Amine content is determined by titrating solvent with hydrochloric acid (HCl) while for the CO2 content and loading, potassium hydroxide (KOH) is used. From the data of amine content and CO2 content, the CO2 loading of the solvent can be determined. TIC analytical method determines the content of CO2 in the sample by acidifying it with phosphoric acid (H3PO4) in the reaction chamber of the analyser in order to convert inorganic carbon compounds (carbonate and bicarbonate) into CO2 which is then measured by solid state non-dispersive (SSNDR) detector. Comparing with titration method, TIC method produces less chemical waste and consumes less chemicals, making its operating cost cheaper. Besides that, its throughput is much higher than titration method through auto sampler which can free up the technicians’ time for other tasks and analyses. The objective of this study is to compare titration analysis method with TIC analysis method in detail.

2. Methodology

2.1. Total Inorganic Carbon (TIC) Calibration

TIC calibration was done by using 1000 ppm sodium carbonate (Na2CO3) solution (stock solution) which was bought from Sigma-Aldrich. 8 standard solutions were prepared by diluting 1000 ppm Na2CO3 solution with distilled water to 0 ppm (distilled water), 1 ppm, 5 ppm, 10 ppm, 50 ppm, 100 ppm and 500 ppm and 1000 ppm in 50 mL volumetric flask. The volume of 1000 ppm Na2CO3 solution to be diluted was calculated by using the following equation:

\[ V_{stock} = \frac{m_{standard} \times V_{standard}}{m_{stock}} \]  

The prepared standards were then transferred into the vial bottles until the volume of the standards were about three-quarter of the bottles. TIC method was set to two different modes; high level mode and mid-level mode. Standard of 0 ppm, 1 ppm, 10 ppm, 50 ppm and 100 ppm were used for mid-level mode calibration. Meanwhile, standard of 0 ppm, 10 ppm, 100 ppm, 500 ppm and 1000 ppm were used for high level mode calibration. 1.3 M H3PO4 acid was used as the reagent to perform the analysis in OI Analytical Aurora 1030C TOC Analyser (Aurora) with the sample volume of 2 mL and 0.5 mL for high level and mid-level mode respectively. Sample injection was done by the auto sampler and the same sample volume was used during calibration procedure.

2.2. Sample Preparation

Amine solvent was prepared by blending MDEA (purity > 98%), PZ (purity > 99%) and distilled water in a 1 L bottle. The mass of each component was measured using electronic balance (FR-300 MK II). The solvent was prepared with 5 different concentration of amine (30wt%, 35wt%, 40wt%, 45wt% and 50wt %) with mass ratio between PZ and MDEA was 0.183. The blended amine solvent was bubbled with CO2 gas with different time intervals (0s, 2s, 4s, 6s, 8s, 10s, 60s, 120s, 240s, 360s and 480s) at atmospheric pressure. Commercial amine solvent that had been used in membrane contactor test rig was regenerated by using rotary evaporator at the temperature of 105°C for different time intervals (0 min, 15 min, 30 min, 45 min and 60 min).

2.3. Reagent Preparation

Three reagents were prepared for titration analysis and TIC analysis. HCl acid and KOH were used in titration while H3PO4 acid was used for TIC reagent.

2.3.1 KOH Preparation and Standardization

66 g of KOH pellet was weighed using electronic balance (FR-300 MK II). Distilled water was added in to completely dissolve the pellet. The KOH solution was then diluted in a 2 L volumetric flask.
of potassium hydrogen phthalate (KHP) was dissolved in about 40 mL of distilled water. About 6 drops of phenolphthalein were added into the KHP solution. The KHP solution was then titrated with the prepared KOH solution until the colour just turned to pink. The following equation was used to calculate the normality of the KOH solution:

\[
N_{\text{KOH}} = \frac{W_{\text{KHP}}}{204.22} \times \frac{1000}{V_{\text{KOH}}} \quad (13)
\]

2.3.2 HCl Preparation and Standardization

84 mL of concentrated HCl (37%) was diluted in 2 L volumetric flask with distilled water. The diluted HCl then was titrated with 25 mL of KOH (6 drops of phenolphthalein was added) until the colour turned to colourless. The following equation is the HCl normality calculation:

\[
N_{\text{HCl}} = \frac{V_{\text{KOH}} \times N_{\text{KOH}}}{V_{\text{HCl}}} \quad (14)
\]

2.3.3 H3PO4 Preparation and Standardization

69 mL of H3PO4 was diluted with distilled water in a 1 L volumetric flask. The diluted H3PO4 then was titrated with 25 mL of KOH (6 drops of phenolphthalein was added) until the colour turned to colourless. The following equation is the HCl normality calculation:

\[
N_{\text{H3PO4}} = \frac{1}{3} \times \frac{V_{\text{KOH}} \times N_{\text{KOH}}}{V_{\text{H3PO4}}} \quad (15)
\]

2.4. Titration

2.4.1 Amine Content Determination

4.5 g of sample (amine solvent) was diluted to 100 mL volume in a beaker with distilled water. The mixture then was stirred at 400 rpm by using magnetic stirrer (WiseStir). The mixture was titrated with the standardized HCl acid until the pH dropped to 4.5 (measured by pH meter probe). The following equation was used to calculate amine content in the sample:

\[
\text{Amine content, wt\%} = \frac{V_{\text{HCl}} \times N_{\text{HCl}} \times A}{W_{\text{sample}}} \quad (16)
\]

\[
A = \frac{r(MW_{\text{MDEA}} - MW_{\text{PZ}}) + MW_{\text{PZ}}}{10(2-r)} \quad (17)
\]

Where \(r\) is the mole fraction of MDEA in a mixture of MDEA and PZ only.

2.4.2 CO2 Content and CO2 Loading Determination

120 mL of methanol (CH₃OH) was titrated with the standardized KOH until its pH rose up to 11.2. 20 g of the sample was then added and stirred at 400 rpm with magnetic stirrer while titrating it with the KOH until its pH rose up to 11.2. The equations below were used to calculate CO2 content and CO2 loading of the sample: (Note: Regenerated amine is the 300 mL of lean solution that was refluxed for 24 hours by using electromantle)

\[
\text{CO2 content, wt\%} = \left( \frac{V_{\text{KOH}}}{W_{\text{sample}}} - \frac{V_{\text{KOH, regenerated amine}}}{W_{\text{regenerated amine}}} \right) \times N_{\text{KOH}} \times 4.4 \quad (18)
\]

\[
\text{CO2 loading, mol/mol} = \frac{\text{CO2 content, wt\%} \times B}{\text{Amine content, wt\%}} \quad (19)
\]

\[
B = \frac{MW_{\text{amine}}}{MW_{\text{CO2}}(1+y)} \quad (20)
\]

Where \(y\) is the mole fraction of PZ in a mixture of MDEA and PZ only.

2.5. Total Inorganic Carbon (TIC) Sample Preparation and Determination

1 mL of the sample was diluted 100 times in a 100 mL volumetric flask. The diluted sample was transferred into two TIC vials until three-quarter full. The two TIC vials were then analysed with two different modes of TIC respectively; high mode and mid-level mode, as shown in Table 1 below.
Table 1. Parameter setting for different modes of TIC

| Mode        | Sample Volume, mL | Acid Volume, mL | Reaction Time, min | System Pressure, psi |
|-------------|-------------------|-----------------|--------------------|----------------------|
| High level  | 0.2               | 2.0             | 3.0                | 25                   |
| Mid-level   | 2.0               | 0.5             | 2.5                | 20                   |

3. Result and Discussion

3.1 Titration

As CO₂ is dissolved in the solvent, CO₂ initially reacts with H₂O to produce carbonic acid (H₂CO₃), which subsequently dissociates to HCO₃⁻[6]. Referring to Equation (1), the presence of H₃O⁺ would reduce the pH value of the sample. In determining the CO₂ content through titration, OH⁻ is needed to neutralize H₃O⁺ and according to Chung et al. (2010), OH⁻ is also needed to convert free dissolved CO₂ into non-volatile ionic species [7]. Meanwhile, to determine the amine content in solvent, the pH of the solvent needs to be reduced by adding acid in order to protonate the amine. According to S.A. Freeman, acid is used to protonate PZ by adding two protons to the molecule, forming diprotonated PZ molecule (PZH₂²⁺) [5]. Stated by Jessica Narku-Tetteh et al. (2017), the protonation of amine in aqueous solution was performed by titrating the amine with HCl until methyl orange endpoint was achieved with the measurement of pH after every addition of 0.5 mL of HCl [8]. The following equations describe the chemistry behind titration method:

Amine content determination

\[ \text{MDEA} + H_3O^+ \rightleftharpoons \text{MDEAH}^+ + H_2O \]  

\[ \text{PZ} + 2H_3O^+ \rightleftharpoons \text{PZH}_2^{2+} + H_2O \]  

CO₂ content determination

\[ OH^- + H_3O^+ \rightleftharpoons H_2O \]  

\[ OH^- + CO_2 \rightleftharpoons HCO_3^- \]

Amine content was obtained by titrating it until its pH value dropped to 4.5 (specified in method for commercial amine solvent), but it turned out that equivalence point for the blended amine was less than 4.5. Similar observation for equivalence point was made when the commercial amine solvent was titrated. If titration is stopped at pH 4.5 as specified in the method, it will result in a bias in amine content determination. The accuracy in determining the amine content is important since it directly affects the result for CO₂ loading of the solvent, as shown in Equation (18). Therefore, it is suggested that the solvent needs to be titrated to the equivalence point in amine content titration.

Referring to Figure 1 and Figure 2, the pH value at the equivalence point of the blended solvent are approximately 3.4 and 3.2, respectively (determined from the graph). Meanwhile, the pH value at the equivalence point of the commercial amine solvent is 3.2, regardless of the concentration of CO₂ in the solvent.

Figure 1. Equivalence point determination graph of 50 wt. % for the blended amine solvent.

Figure 2. Equivalence point determination graph of 30 wt. % for the blended amine solvent.
In determination of CO₂ content, pH of methanol was first adjusted to 11.2 using KOH before addition of sample. This was found as a source of error because it was difficult to adjust the pH of methanol to 11.2 exactly. Table 2 shows a few examples of titration where the pH of methanol ranges from 11.24 to 11.40, instead of 11.2. These has resulted in error as the titration end-point is set at pH 11.2. The results will be more accurate if the titrations are allowed to proceed until the pH of methanol after KOH adjustment.

| Sample               | pH of methanol after KOH adjustment | CO₂ content, wt% | Titration to pH of methanol | Titration to pH of 11.2 |
|----------------------|-------------------------------------|------------------|-----------------------------|-------------------------|
| 30wt% amine          | 11.24                               | 0.48             | 0.48                        |
| 30wt% amine          | 11.30                               | 0.50             | 0.48                        |
| 30wt% amine          | 11.30                               | 0.50             | 0.48                        |
| 30wt% amine          | 11.35                               | 0.46             | 0.45                        |
| 30wt% amine          | 11.30                               | 0.53             | 0.52                        |
| Commercial           | 11.30                               | 0.72             | 0.71                        |
| Amine Solvent        | 11.40                               | 0.74             | 0.72                        |

T-test result: \( T_{stat}(4.317) > T_{critical}(2.447) \)

As shown in Table 3, Limit of Detection (LOD) and Limit of Quantification (LOQ) were established from amine solvent (30wt%) with low concentration of CO₂. LOD is defined as three times the standard deviation meanwhile LOQ is ten times the standard deviation.

| Titration to pH of 11.2 | 0.05 wt% | 0.07 wt% | 0.05 wt% | 0.03 wt% | 0.04 wt% | 0.02 wt% |
|-------------------------|----------|----------|----------|----------|----------|----------|
| Average                 | 0.04 wt% |
| Standard Deviation      | 0.02 wt% |
| Limit of Detection (LOD)| 0.05 wt% |
| Limit of Quantification (LOQ) | 0.18 wt% |

### 3.2 Total Inorganic Carbon (TIC)

In TIC, CO₂ content is determined by acidifying the sample in order to convert aqueous CO₂, carbamate and bicarbonate species into gaseous CO₂ [5]. CO₂ then will be carried in a nitrogen gas stream to be analysed by the detector.

\[
H_3O^+ + HCO_3^- \rightleftharpoons CO_2 + 2H_2O
\]  
(25)
As being stated in the methodology part, the equipment needs to be calibrated with Na$_2$CO$_3$ standard. The area under the curve, formed from the signal detected by the SSNDIR, is matched with the respective standard concentration. Table 4 show the calibration data for the high level and mid-level mode respectively by using Na$_2$CO$_3$ solutions as standards. Figure 5 show the calibration curve, plotted from the calibration data in Table 4. Linearity of both calibration curves are good as the $R^2$ (coefficient of correlation) values are both higher than 0.999.

### Table 4. Calibration data for high level and mid-level mode

| Carbon Concentration, ppm | Average (Avg) Area Under The Curve | Carbon Concentration, ppm | Average (Avg) Area Under The Curve |
|---------------------------|-------------------------------------|---------------------------|-------------------------------------|
| 0.000                     | 164                                 | 0.000                     | 2270                                |
| 10.000                    | 12230                                | 1.000                     | 12343                                |
| 100.000                   | 110741                               | 10.000                    | 103617                               |
| 500.000                   | 538201                               | 50.000                    | 455942                               |
| 1000.000                  | 1041923                              | 100.000                   | 905914                               |

![Figure 5. Calibration curve for TIC high level and mid-level mode.](image)

The sample volume injected into the chamber are 0.2 mL and 2 mL for high level and mid-level mode respectively. The difference in the sample volume injected in the chamber affect the amount of CO$_2$ released, as bigger sample volume will release higher amount of CO$_2$. This is illustrated in Table 4 where the average area for mid-level mode is higher than high level mode for 0 ppm, 10 ppm and 100 ppm. Limit of detection (LOD) and limit of quantification (LOQ) were established from blank analysis, as shown in Table 5 below. LOD is expressed as three standard deviations of the blank and LOQ is ten standard deviations of the blank. The LOD and LOQ values for both high level mode and mid-level mode are sufficiently low, well below the sample range of 2ppm to 350ppm (carbon content).

### Table 5. Measurement of blank by TIC at high and mid-level mode

| Carbon Concentration | High Level | Mid-level |
|----------------------|------------|-----------|
| -4.39 ppm            | 1.08 ppm   |
| -4.29 ppm            | 1.19 ppm   |
| -4.28 ppm            | 1.23 ppm   |
| -4.29 ppm            | 1.25 ppm   |
| -4.27 ppm            | 1.22 ppm   |
| Average              | -4.30 ppm (-0.00158 wt%) | 1.20 ppm (0.00044 wt%) |
| Standard Deviation   | 0.05 ppm (0.00002 wt%) | 0.06 ppm (0.00002 wt%) |
| Limit of Detection (LOD) | 0.14 ppm (0.00005 wt%) | 0.18 ppm (0.00007 wt%) |
| Limit of Quantification (LOQ) | 0.46 ppm (0.00017 wt%) | 0.60 ppm (0.00022 wt%) |

The original intention of having mid-level mode is to lower down the LOQ. Results from Table 5 shows that similar LOQ can be achieved with high level mode. Therefore, mid-level mode is not required. Besides, Table 6 shows that there is no significant difference in results between high level mode and mid-level mode.
Table 6. Comparison between high level mode and mid-level mode of 45 wt% self-blended amine

| CO2 Bubbling Time, s | CO2 content, wt% | CO2 loading, mol/mol |
|----------------------|------------------|----------------------|
|                      | High Level Mode | Mid-level Mode       |
|                      | CO2 loading, mol/mol |
| 2                    | 0.4305           | 0.8873               | 0.0205 | 0.0422 |
| 4                    | 0.5125           | 0.5041               | 0.0244 | 0.0240 |
| 6                    | 0.6617           | 0.6949               | 0.0315 | 0.0331 |
| 8                    | 0.8551           | 0.9166               | 0.0409 | 0.0438 |
| 10                   | 0.9380           | 0.9972               | 0.0445 | 0.0473 |

T-test result: \(T_{stat}(1.417) < T_{critical}(2.776)\) \(T_{stat}(1.413) < T_{critical}(2.776)\)

3.3 Comparison of Titration and Total Inorganic Carbon (TIC) Analysis

The data for the blended amine solvent is tabulated in Table 7, where comparison is made between TIC method at high level mode and titration method. It is observed that the difference between titration results and TIC results for most samples are above 5%. The significant difference in the results is very much likely due to the fact that titration method is subjected to error in methanol pH adjustment step. Due to this reason, TIC method is considered more accurate in comparison to titration method.

| Initial Amine Conc., wt.% | CO2 Bubbling Time, s | Amine, wt.% | CO2 wt.% | CO2 loading, mol/mol |
|---------------------------|----------------------|-------------|----------|----------------------|
|                           |                      |             | Titration | TIC                  |
|                           |                      |             | Titration | TIC                  |
| 30.00                     | 10                   | 29.48       | 1.1472   | 1.2091               | 0.0827 | 0.0872 |
|                           | 60                   | 28.50       | 3.4670   | 4.5247               | 0.2587 | 0.3376 |
|                           | 120                  | 28.27       | 4.1244   | 5.0523               | 0.3103 | 0.3801 |
|                           | 240                  | 27.71       | 5.4347   | 7.3498               | 0.4170 | 0.5640 |
|                           | 360                  | 27.68       | 6.5159   | 7.7182               | 0.5005 | 0.5929 |
|                           | 480                  | 27.56       | 6.1995   | 8.4774               | 0.4784 | 0.6542 |
|                           | 60                   | 38.59       | 3.7499   | 3.8051               | 0.2066 | 0.2097 |
|                           | 120                  | 37.96       | 5.4783   | 5.8692               | 0.3068 | 0.3287 |
|                           | 240                  | 37.28       | 7.3431   | 8.3391               | 0.4188 | 0.4756 |
|                           | 360                  | 36.98       | 8.4903   | 8.8870               | 0.4882 | 0.5110 |
|                           | 480                  | 36.89       | 8.3952   | 8.3295               | 0.4838 | 0.4801 |
| 40.00                     | 10                   | 29.48       | 1.1472   | 1.2091               | 0.0827 | 0.0872 |
|                           | 60                   | 28.50       | 3.4670   | 4.5247               | 0.2587 | 0.3376 |
|                           | 120                  | 28.27       | 4.1244   | 5.0523               | 0.3103 | 0.3801 |
|                           | 240                  | 27.71       | 5.4347   | 7.3498               | 0.4170 | 0.5640 |
|                           | 360                  | 27.68       | 6.5159   | 7.7182               | 0.5005 | 0.5929 |
|                           | 480                  | 27.56       | 6.1995   | 8.4774               | 0.4784 | 0.6542 |
|                           | 60                   | 38.59       | 3.7499   | 3.8051               | 0.2066 | 0.2097 |
|                           | 120                  | 37.96       | 5.4783   | 5.8692               | 0.3068 | 0.3287 |
|                           | 240                  | 37.28       | 7.3431   | 8.3391               | 0.4188 | 0.4756 |
|                           | 360                  | 36.98       | 8.4903   | 8.8870               | 0.4882 | 0.5110 |
|                           | 480                  | 36.89       | 8.3952   | 8.3295               | 0.4838 | 0.4801 |
| 45.00                     | 10                   | 29.48       | 1.1472   | 1.2091               | 0.0827 | 0.0872 |
|                           | 60                   | 28.50       | 3.4670   | 4.5247               | 0.2587 | 0.3376 |
|                           | 120                  | 28.27       | 4.1244   | 5.0523               | 0.3103 | 0.3801 |
|                           | 240                  | 27.71       | 5.4347   | 7.3498               | 0.4170 | 0.5640 |
|                           | 360                  | 27.68       | 6.5159   | 7.7182               | 0.5005 | 0.5929 |
|                           | 480                  | 27.56       | 6.1995   | 8.4774               | 0.4784 | 0.6542 |
|                           | 60                   | 38.59       | 3.7499   | 3.8051               | 0.2066 | 0.2097 |
|                           | 120                  | 37.96       | 5.4783   | 5.8692               | 0.3068 | 0.3287 |
|                           | 240                  | 37.28       | 7.3431   | 8.3391               | 0.4188 | 0.4756 |
|                           | 360                  | 36.98       | 8.4903   | 8.8870               | 0.4882 | 0.5110 |
|                           | 480                  | 36.89       | 8.3952   | 8.3295               | 0.4838 | 0.4801 |
| 50.00                     | 10                   | 29.48       | 1.1472   | 1.2091               | 0.0827 | 0.0872 |
|                           | 60                   | 28.50       | 3.4670   | 4.5247               | 0.2587 | 0.3376 |
|                           | 120                  | 28.27       | 4.1244   | 5.0523               | 0.3103 | 0.3801 |
|                           | 240                  | 27.71       | 5.4347   | 7.3498               | 0.4170 | 0.5640 |
|                           | 360                  | 27.68       | 6.5159   | 7.7182               | 0.5005 | 0.5929 |
|                           | 480                  | 27.56       | 6.1995   | 8.4774               | 0.4784 | 0.6542 |

T-test result: \(T_{stat}(3.699) > T_{critical}(2.042)\) \(T_{stat}(3.252) > T_{critical}(2.024)\)
Table 8. Data comparison for the commercial amine solvent

| Sample | Amine / wt.% | CO₂ / wt.% | CO₂ loading / mol/mol |
|--------|--------------|------------|-----------------------|
|        |              | Titration  | TIC                   | Titration  | TIC                   |
| A      | 47.54        | 0.7010     | 0.7928                | 0.0305     | 0.0345                |
| B      | 47.47        | 0.6797     | 0.7786                | 0.0296     | 0.0339                |
| C      | 47.34        | 0.6518     | 0.7891                | 0.0285     | 0.0345                |
| D      | 38.74        | 3.6101     | 3.7103                | 0.1927     | 0.1980                |
| E      | 40.96        | 4.4251     | 5.0123                | 0.2234     | 0.2530                |
| F      | 37.60        | 3.5278     | 4.0307                | 0.1940     | 0.2217                |
| G      | 41.41        | 3.9014     | 3.9253                | 0.1948     | 0.1960                |

T-test result: T_{stat} (2.583) > T_{critical} (2.447)

The data for the commercial amine solvent is tabulated in Table 8. Similar observation can be made, where there is a significant difference between TIC results and titration results.

4. Conclusion

Solvent analysis is very important to monitor the performance of solvent based acid gas removal technology. In this work, the applicability of TIC method to determine CO₂ content and CO₂ loading in amine solutions was studied. There is no need to use mid-level mode when analysing sample with low CO₂ content, as there is no significant difference between high level mode and mid-level mode in terms of LOD, LOQ, and results. In titration method, the error during the methanol pH adjustment step contributed to the difference in results with TIC method. TIC analysis is chosen as the preferred method due to lower LOD, lower LOQ, and less susceptible to error. In addition, TIC method does not involve volatile organic solvent which reduces cost and makes the analysis more environmental friendly. Besides, titration is less accurate compared to TIC. TIC is also seen to produce less chemical waste. Due to that, TIC analysis method is studied as a substitute to titration method, where TIC is seen as more convenient and requires less cost.

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