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Description of an Experimental Method to Measure the CO_2 Loading in Monoethanomine Solutions using $BaCO_3$ Titration Technique

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Abstract:

One of the main criteria for the selection of a suitable solvent is the CO_2 solubility capacity or CO_2 loading. The objective of this work is to provide students and early-career scientists a detailed description of a titration-based experiment to measure the CO_2 loading using simple and inexpensive volumetric and gravimetric lab apparatus. The performance of the method is corroborated by comparing the experimental uncertainty obtained during the determination of the CO_2 concentration in test samples (in an absorption unit at lab scale) with reference values obtained by mass balance based on a certified gas analyser. The results indicate that CO_2 loading values between the experimental method and the reference range from ±3 to 13%, which is in good agreement with other similar methods.

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1. INTRODUCTION

There are several methods available for measuring CO_2 loading in aqueous amine solutions; these are classified as indirect and direct techniques. Indirect techniques involve mass balances from the thermodynamic system from measurements of CO_2 in the gas phase and the overall CO_2 fed to the system, the difference between these amounts is equal to CO_2 in the liquid phase. Typical techniques employed for measuring CO_2 in the gas phase [1] are the following: Fourier transform infrared (FTIR) carbon dioxide sensors, gas chromatography (GC) and, proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS). Meanwhile, the direct techniques involve the CO_2 experimental measurement in the liquid phase, some of the analytical techniques used for this purpose are: attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy [2, 3], conductivity [4, 5], high-performance liquid chromatography (HPLC) [6] and titrimetric analysis [7].

Table **1** shows, qualitatively, the time-labour intensity, equipment and O&M cost, and CO_2 detection level of the most common analytical techniques used for measuring CO_2, in both liquid and gas phases. Among them, HPLC is the most common analytic technique used in a variety of industrial and scientific applications (e.g. pharmaceutical, environmental, forensics, chemicals) because of its versatility, the huge number of components able to detect and, high detection limit. This can reach a detection limit range as low as parts per trillion [8].

Another technique with high accuracy is mass spectroscopy (MS), with detection levels in the range of parts per billion [9]. Due to their high precision, it is very common to find HPLC equipment coupled with MS, not only for measuring CO_2, even for other chemical compounds [10]. Furthermore, these techniques have a minimum time-labour intensity and can provide high precision results in few minutes. However, HPLC-MS equipment is very expensive comparing with other analytical techniques because of their high capital cost. Also, their operation is not easy, requires qualified personnel. Thus, these techniques could not be the first option if there is not a budget or just want to make a few tests without very high accuracy.

Another technique that is very useful for high CO_2 detection levels is Gas Chromatography (GC), depending on the detector used for, this technique can provide CO_2 detection limits in the range of subpart per million [11, 12]. Nevertheless, the main disadvantages are GC equipment is expensive and is not be able to operate remotely, so the CO_2 source and GC equipment must be located close to each other.

One of the main techniques used for CO_2 monitoring in the gas sample is the CO_2 sensors by FTIR. This is because is very easy to operate, able to operate online (or directly from CO_2 source), provides results in just a few seconds, and is not costly in comparison with other analytical methods (e.g. HPLC, MS, GC, or ATR-FTIR spectroscopy). Nevertheless, its main drawback is the relatively low detection level (hundreds of ppm) [13, 14].

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) is also an easy method for CO_2 measuring in a liquid sample, this technique is very useful for the determination of unknown chemical species as on function of their molecular structure and wavenumber in the infrared spectrum. This technique is medium capital and O&M cost has a low time-labour intensity and provides results quickly, just a few seconds. However, it does not have the high levels of CO_2 detection that HPLC, GC or, MS techniques have.

On the other hand, the titration-based method consists of determining the number of moles of reagent (titrant), required to react quantitatively with the substance being determined. The main advantage of this analytical technique is the low capital cost and O&M cost. This is an ideal technique when is desired just a few tests or a non-capital budget is available. Nevertheless, the main disadvantages of this technique are the relatively high time-demanding and its very low accurate CO_2 detection level. For better results, accurate weighing of substrates and highly graduated apparatus are the keys. Another drawback is that fact is a manual off-line liquid analysis, so liquid samples should be taken, stored and, labelled for later analysis in the laboratory.

Among all the techniques measurement of CO_2 loading in aqueous amine solutions, the titration method with barium carbonate ($BaCO_3$) is one of the most employed due to its low capital cost. Although this has been used by many authors [15-18], there is still no work in the scientific literature with open access that explains in enough detail the experimental procedure for easy replication and reproducibility. Therefore, the originality of this work remains in the fact that it aims to provide a simple and detailed description of the experimental method for the measurement of CO_2

Table 1: Time-Labour Intensity, Equipment and Operation & Maintenance (O&M) Costs, and CO_2 Detection Level of the Most Common Analytical Techniques used for Measuring CO_2

Analytical method for CO_2 measuring	Phase of the sample	Time-labour intensity	Equipment cost	O&M cost	CO_2 detection level
Infrared CO_2 sensor (FTIR)	Gas	L	L	L	H
Mass spectroscopy (MS)	Gas	L	H	H	H
Gas Chromatography (GC) with flame ionisation detection (FID)	Gas	L	H	H	H
High-Performance Liquid Chromatography (HPLC)	Liquid	L	H	H	H
ATR-FTIR spectroscopy	Liquid	L	H	H	L
pH titration-based method	Liquid	H	L	L	L

L = low, H = high.

loading by titration with $BaCO_3$ that serves as a reference for new researchers in the area, non-chemical profiles, students or any other technical professional interested in the subject.

2. EXPERIMENTAL SECTION

2.1. Solutions of MEA Loaded with CO_2

Initially, a set of calibrations solutions were prepared using MEA, CO_2 and, deionized water. The set contained MEA concentration of 25wt% with different CO_2 loadings in the range from 0.1 - 0.5 mol CO_2/mol MEA. This range value was estimated according to vapor-liquid equilibrium values of CO_2-MEA-H_2O system at low CO_2 partial pressures ($P_{CO_2} < 100$ kPa) and at low temperature range ($T < 40°C$) [19, 20]. Then, the solutions were prepared gravimetrically using an analytical balance (OHAUS, model Explorer EX324) and then were loaded with CO_2 by carefully bubbling CO_2 (through a glass bubbler) into the solution until the desired amount of CO_2. During the experiment, the solutions were blended (using a magnetic stirrer) and cooled at 3 °C for accelerating the CO_2 absorption process.

2.2. Procedure for Measuring CO_2 Loading

The CO_2 concentration in the liquid phase was determined by taking 4 g. of solvent loaded with CO_2 and spilled in a 100 mL volumetric flask. According to Reaction 1, the CO_2-loaded solution is composed of two ionic species: bicarbonate (HCO_3^-) and MEA's basic cation ($C_2H_7NOH^+$). In order to convert the CO_2 dissolved (in form of bicarbonate) to a soluble stable salt, 6 mL of a 1 M NaOH solution was added (Reaction 2). After that, 50 mL of a 0.1 M $BaCl_2$ solution was added and blended to precipitate the $NaHCO_3$ to $BaCO_3$ (Reaction 3). The precipitation process takes near 4 hours to finish. This process could be accelerated in an isothermal bath circulator at 5 °C since Reaction 3 is favored at low temperatures.

$$C_2H_7NO + CO_2 + H_2O \leftrightarrow C_2H_7NOH^+ + HCO_3^- \quad (1)$$

$$C_2H_7NOH^+ + HCO_3^- + NaOH \leftrightarrow NaHCO_3 + C_2H_7NO + H_2O \quad (2)$$

$$NaHCO_3 + C_2H_7NO + H_2O + BaCl_2 \leftrightarrow NaCl + BaCO_3 + HCl + C_2H_7NO + H_2O \quad (3)$$

Then, the precipitate was filtered using the experimental apparatus shown in Figure **1**. It consists of a vacuum flask which is attached to a Büchner funnel via a black elastomer adapter. The hose barb of the flask is connected via a hose to a vacuum pump. Also, a glass microfiber filter was put inside of the Büchner funnel for recovery of the $BaCO_3$ precipitated (inset of Figure **1**). The precipitate was washed with deionized water several times until a solvent filtered reaches a pH value near between 9.6 and 9.8. Then, the clean $BaCO_3$ precipitate, which has a white appearance, was recovered from the filter and was transferred into a 250 mL round-bottomed flask along with 100 mL of deionized water. After that, the clean $BaCO_3$ precipitate was titrated with a 0.1 M HCl solution. Depend on the amount of acidic solution spent, is the CO_2 captured by the amine, such as shown in Reaction 4:

$$BaCO_3 + 2HCl \leftrightarrow BaCl_2 + CO_2 + H_2O \quad (4)$$

Figure **2** shows the lab instruments employed for titration of $BaCO_3$ for determining the CO_2 concentration in an aqueous MEA solution. It consists of a burette, which is held using a double burette clamp attached to a lab support stand; a lab magnetic stirring

Figure 1: Experimental apparatus used to filter the $BaCO_3$ precipitate from the ionic solution: 1) vacuum flask; 2) Büchner funnel with elastomer adapter; 3) hose; 4) vacuum pump and 5) glass microfiber filter.

heater, on which the flask is placed; a glass vacuum adapter is placed on the top of the flask and it is connected to a vacuum pump. Additionally, a pH meter (Hach, model HQ40d) was used to detect the endpoint of the neutralization reaction of $BaCO_3$ (a pH indicator also could be used).

Initially, in order to accelerate the CO_2 desorption by incrementing the superficial area, small glass balls (Θ= 4 mm) were employed for milling the carbonate lump by shaking the flask manually. Then, a few milliliters of the HCl solution was added to the flask carefully, it was closed with the glass vacuum adapter, then, heated at ~50 °C and afterward shaken again for accelerating CO_2 desorption. After that, the valve of the glass vacuum adapter was opened for extracting the CO_2 desorbed using the vacuum pump. This experimental sequence of shaking-extracting is completed when there are no bubbles in the solution anymore. Once the total amount of CO_2 is extracted, the solution is cooled at 20 °C and its pH is measured. It keeps adding acid to the system and repeating the previous experimental procedure until a pH range between 4.2-4.4 is reached. Depending on the amount of HCl solution spent, is the CO_2 captured by the MEA, such as shown as follows:

$$M_{CO_2} = 5\times10^{-4}(V_{HCl})(C_{HCl})(MW_{CO_2}) \qquad (5)$$

Where:

M_{CO_2} = Mass of CO_2 [g]

V_{HCl} = Volume of HCl solution spent [mL]

C_{HCl} = Molar concentration of HCl solution [mol/L]

MW_{CO_2} = CO_2 molecular weight [g/mol]

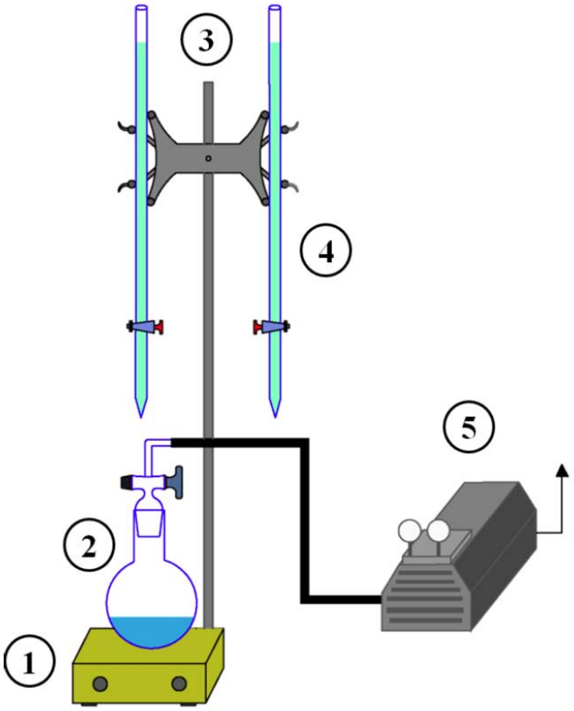

Figure 2: Lab instruments employed for titration of $BaCO_3$: 1) lab magnetic stirring heater; 2) flask connected to a glass vacuum adapter; 3) double burette clamp attached to a lab support stand; 4) burette and 5) vacuum pump.

3. METHOD VALIDATION

The experimental method is validated against a reference system to determine its accuracy and uncertainty. The reference data is obtained by the indirect method, performing experiments in a lab-scale absorption unit. The lab-scale absorption unit is showed in Figure **3**, this includes an absorption column (T-101) made of borosilicate glass Duran 3.3, with an internal diameter of 4” and height of 1.70 m; the packing used was 5/8” polypropylene pall ring; the total height of the packing is 1.20 m. Additionally, there are two atmospheric tanks: one for holding a CO_2-free MEA solution (TK-101) and another for the reception of CO_2 rich solution (TK-104); a pump with volumetric flow rate control for feeding of the MEA to the column (P-101); for the gas conditioning there are: a pressurized tank contained CO_2 (TK-102), an air compressor (TK-103) and volumetric flow measurement instruments (gas mixer, “M”, and rotameters). A 25 wt% MEA aqueous solution at 25 °C was used varying the solvent volumetric flow rate from 54 to 468 mL/min.

Meanwhile, for the feed gas stream, a mixture of air and CO_2 was used. Table **2** shows the feed condition of the gas (*Stream 3*).

Table 2: Feed Conditions of the Gas Stream

Flow rate (L/h)	4448
Absolute pressure (atm)	1.1
Temperature (°C)	26.1
Relative humidity (% HR)	45
Composition (v/v%)	
N_2	73.9
O_2	19.6
CO_2	5.0
H_2O	1.5

Initially, the gas was fed from the bottom of the column and its CO_2 concentration and relative humidity were measured at the outlet on the top of the column (*Stream 4*) using an analyzer gas (Testo 350 Portable Emission Analyzer) and humidity-temperature meter (Vaisala M170), respectively. Once the composition of the *Stream 4* was stabilized, the MEA solution was fed to the column from the top (*Stream 1*), it was fed for about 10 minutes until the concentration gas at the outlet was constant. Then, samples of the liquid phase in triplicate were taken from the bottom of the column (*Stream 2*) and its CO_2 loading was determined by the experimental method described above. The steps mentioned were repeated for each solvent flow rate change employed. Additionally, mass balances were performed to collect the reference data. It is pertinent to mention that, for calculating mass balances, it was assumed that there is no solubility of oxygen in the solvent and there is no evaporation of the amine, water only.

The results for the validation method are presented in Table **3**. As it can be seen, at a higher solvent flow rate (Q_{solv}), lower CO_2 concentrations in the liquid phase were obtained, as could be expected. This is because only the amount of amine is varied and, the CO_2 concentration of feed gas and the amine in the solvent are constants, so this behavior is then due to a dilution effect.

In addition, from Figure **4** it can be observed that deviation percentage between the CO_2 concentration obtained by experimental method ($w_{CO_2,meth}$) and the reference ($w_{CO_2,ref}$) is higher at a lower solvent flow rate (Q_{solv}). This is because the samples obtained at lower Q_{solv} have a higher amount of CO_2 dissolved in the amine, which requires a longer time for Reaction 2 to reach equilibrium. In other words, not enough time is being given for the total amount of HCO_3^- contained in the samples to transform into $NaHCO_3$. Therefore, the person interested in applying this method must make a trade-off between the time involved in this process and the desired uncertainty value.

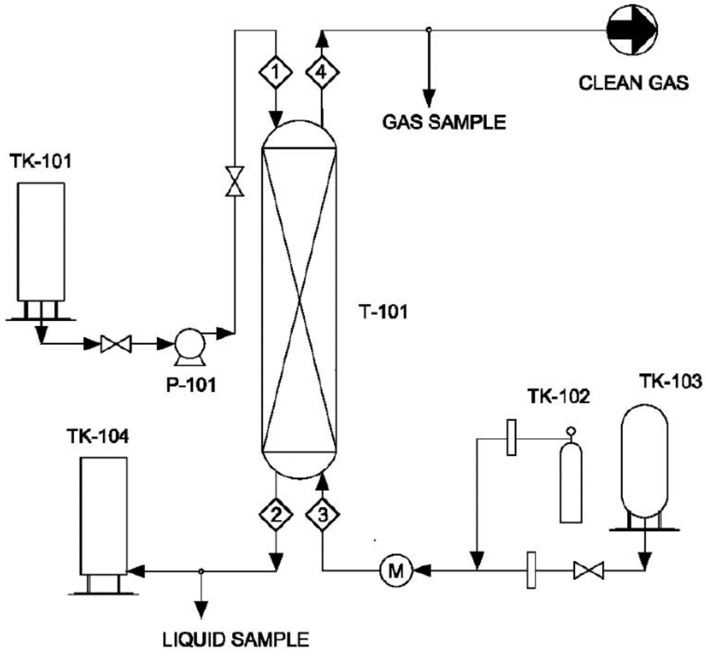

Figure 3: Schematic flow diagram of CO_2 capture lab unit.

Table 3: Data Obtained from the Validation Test (Reference) and the Method Used

Q_{solv} (mL/min)	y_{CO_2} (v/v%)	$w_{CO_2,ref}$ (mass fraction)	$w_{CO_2,meth}$ (mass fraction)	Deviation (%)
54	3.37	0.0493	0.0429	-13
128	2.36	0.0321	0.0305	-5
299	1.9	0.0162	0.0166	5
468	1.48	0.0117	0.0119	3

From the results, it can observe that the uncertainty between the experimental method developed and the reference values is ±3-13%; which is in good agreement with similar titration-based methods [15, 16]. This range of error could be attributed mainly to the lack of time to reach the chemical equilibrium of reactions, uncertainty in solvent weighing, losses of $BaCO_3$ precipitate during filtering and, visual errors in the burette reading during the titration.

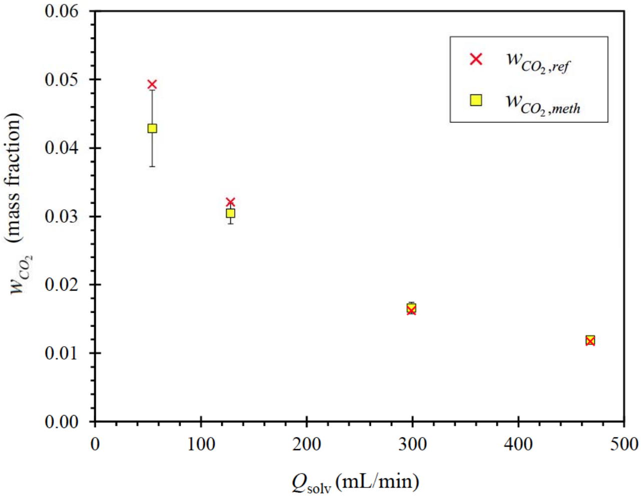

Figure 4: Comparison between CO_2 concentration in the liquid phase obtained by method and reference as funtion of Q_{solv}.

Finally, the experimental method described in this work is an alternative to students or technicians be able to measure CO_2 measuring in liquid sample using inexpensive and common apparatus in most of the laboratories. The main disadvantages are the poor CO_2 detection level and very high time-labor intensity in comparison to other analytical techniques. Although the method developed is not practical enough for the high time demanding, it is a reliable and inexpensive alternative for measuring CO_2 solubility in amine-based solutions.

4. CONCLUSIONS

A detailed titration-based method for measuring CO_2 loading in aqueous MEA solutions was presented. The method was validated against a reference system (a certified gas analyzer) to determine its accuracy and uncertainty. The results show that uncertainty between the titration-based method and the reference is ±3-13%; which is in good agreement with similar experiments. It is a reliable and inexpensive alternative for testing CO_2 solubility in amine aqueous solutions.

Although the method described in this work is not practical enough, it is very educational and illustrative to describe the process step by step, especially for students, non-chemical profiles and beginning scientists to measure the CO_2 load using common and inexpensive devices that are easy to find in most laboratories.

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DECLARATION OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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