



Absorption of Carbon Dioxide into Potassium Hydroxide: Preliminary Study for its Application into Liquid Scintillation Counting Procedure

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Abstract

This preliminary study presents a theoretical and experimental investigation on the absorption of CO₂ into KOH solution. The study provides variation of KOH concentrations at 1, 2, 3, 4, and 5 N. The value of pH was observed for each increment of sample volume. The absorbed CO₂ was measured by applying titration. The amounts of CO₂ resulted from every provided KOH concentration were respectively 0.0075, 0.0075, 0.0232, 0.0305, and 0.0395 mol. The results reveal an increase in absorbed CO₂ with each increment of KOH concentration. The absorption efficiency values of each KOH concentration were 0.3750, 0.4000, 0.3861, 0.3813, and 0.3950 mol total CO₂/mol KOH, respectively. The difference values of experimental and theoretical absorbed CO₂ may be caused by the formation of other compounds.

Keywords: Carbon dioxide, Potassium Hydroxide, Absorption

1. Introduction

Radiocarbon dating promotes the age approximation of both carbonate and organic samples by measuring the ¹⁴C activity [1]. It is broadly applied in numerous disciplines: archeology, quaternary and climate change studies, oceanography (past and present), environmental studies, compound-specific radiocarbon analysis (CSRA), biomedical, forensic, and related art history [2]. Its wide application evinces the importance of radiocarbon dating, so that further study of the development of this method is very important.

There are three recognized-analytical protocols to perform a laboratory test of carbon dating, namely accelerator mass spectrometry (AMS), liquid scintillation counting (LSC)-benzene, and LSC-CO₂.

These three protocols have been applied in any carbon-based product investigation. They are basically run by combusting the contents of the organic compounds and trapping the emitted carbon dioxide gases into the volatile CO₂ collector solution. AMS is the best and most widely used in large laboratories, yet its use is expensive. Other methods such as LSC can be considered cheaper to use but still reliable for accuracy [3].

Analysis with LSC has two common sample preparation methods: benzene synthesis and CO₂ absorption. These sample preparation methods basically convert the solid sample and reproduce CO₂ gas that is further captured by the absorber. The absorber solution has effectively contained the sample is mixed with a suitable cocktail for further

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analysis [4].

Benzene synthesis method converts volatile CO₂ into benzene by several intermediate steps (production of LiC and C₂H₂). In contrast, CO₂ absorption method directly absorbs CO₂ using an amine absorbent to form carbamates [5] as an intermediate compound. The intermediate product is immediately absorbed by hydroxide compounds (KOH, NaOH) to configurate carbonates as the end product for further analysis [6,7]. The CO₂ absorption method excels at its easy-to-use, safe, efficient, and cheaper [7]. These advantages are essential for CO₂ absorption as the preparation method prior to LSC.

Hydroxide and carbonate systems have been employed for CO₂ absorption since the early 20th century in different industrial processes. Although both applications still exist in specialized practices, they have suffered from decreased use for industrial gas filtration as alkanolamine presented as a promising alternative. Hydroxide and carbonate have received attention in the last two decades, specifically their combined use for CO₂ absorption. This combined system is believed to have an advantage over using amines, especially in terms of degradation in environment [8].

Absorber for volatile CO₂ plays a vital role since it determines the CO₂ quantity before performing LSC. Several studies have investigated several potential absorbers, namely kalium hydroxide (KOH), sodium hydroxide (NaOH), monoethanolamide (MEA), diethanolamine (DEA), triethanolamine (TEA), and ammonium hydroxide (NH₄OH) to coral samples. DEA presented the highest absorption capacity compared to other absorbers, yet KOH provided the highest counting efficiency value when analyzed with LSC Hidex 300 SL [6,7,9]. This is obviously interesting to consider KOH as an absorber in the LSC protocol.

KOH has been widely utilized in several industrial and environmental sectors, especially because of its vital role in absorbing emission gases [10, 11]. It indicates KOH's promising potential as a CO₂ gas capturing agent in the LSC procedure. However, studies that accommodate the potential for KOH for this procedure are scarce. Thus, this preliminary study will assess the KOH performance before implementing LSC procedure in further studies. This work investigates the performance of KOH as CO₂ absorber with various concentrations of 1, 2, 3, 4, and 5 N.

2. Materials and Methods

2.1. Materials

KOH ($\geq 85,0$ % purity; Merck ® Germany) was prepared and applied without any purification. Other chemicals namely HCl (37 % purity; Merck ® Germany), AgNO₃ (99.8 %; Merck ® Germany), and carrier gas N₂ (>99.999%) were also prepared. Distilled water degassed by boiling and cooled to ambient temperature under vacuum was prepared for alkaline solution.

2.2. Apparatus

A series of tools prior demonstrated by the cryogenic trap system of [4] was employed to isolate and absorb CO₂. The system was conducted under standard temperature (25°C). The experimental apparatus was composed of a three-necks 1000 mL flask equipped with an inlet for HCl storage, nitrogen cylinder, and 5 cryogenic traps (100-mL). Every channel was equipped with a control valve, while a flowmeter was installed on nitrogen cylinder. The system utilized certain agents to guarantee only CO₂ (generated by sample) and N₂ (carrier gas) would stream through KOH absorber solution. The first-two vials contained AgNO₃ as HCl vapor absorber, then the next-two vials applied silica gel as moisture absorber. (Fig. 1).

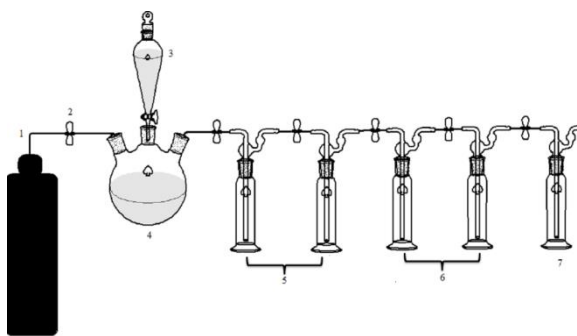


Figure 1. Design tool for the CO₂ absorption method. 1). Nitrogen Cylinder and Flow Meter, 2). Control Valve, 3).

HCl 10 %, 4). Three necks 1,000 mL flask, 5). Acid absorber, 6). Water Absorber, 7). CO₂ gas Absorber [4,12]

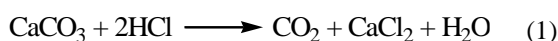
2.3. Procedure

2.3.1. Preparation of KOH solutions with various concentrations

KOH was weighted onto certain weights of every desired concentration (1 N = 2.8 g; 2 N = 5.6 g; 3 N = 8.4 g; 4 N = 11.2 g, and 5 N = 14 g). The prepared bucks of KOH were then respectively dissolved with 50 mL distilled water in a volumetric flask.

2.3.2. Carbon dioxide absorption

Samples containing CaCO₃ were weighed with a mass variation of 5-50 g and were put into a three-necks 250 mL flask. The samples were then added with 10% HCl (via a series of tools in Figure 1). CaCO₃ in the sample reacted with HCl to generate CO₂ gas, CaCl₂, and water vapor. N₂ gas (carrier), transporting CO₂ gas from the reaction of sample and HCl, streamed through acid absorber (AgNO₃), water absorber (silica gel), and the tube containing CO₂ absorber (KOH) [4, 12, 13]. The pH was recorded at the end of the absorption process. Here is the reaction occurred in the system [12]:



2.3.3. HCl-titration for Absorber KOH

As much as 5 mL of each sample was transferred into 50 mL Erlenmeyer. Samples then were added with 1-2 drops MO indicator and were administered with HCl 5 M titration until orange-to-pink color shift appeared [6].

2.3.4. Data Analysis

The data were analyzed statistically with three replicate to obtain the mean and standard deviation.

3. Results and Discussions

3.1. Weight of CO₂ absorbed

The weight of absorbed CO₂ for each KOH concentration is presented in Figure 2. KOH 1 N solution provides optimum CO₂ absorption at 5 g sample. Meanwhile, KOH 2 N and 3 N solutions experience optimum absorption of CO₂ at 10 g sample. For KOH 4 N and 5 N solutions, optimum CO₂ absorption occurs at 20 g sample. After the optimum sample addition achieved, all treatments experienced a very small increase in CO₂ concentration when adding the sample weights simultaneously up to 50 g. Overall, it confirms an increase in CO₂ absorbed by the KOH concentration increment. Absorbed CO₂ weight of KOH 5 N coincides with KOH 4 N for every samples weight yet excludes their application for 50 g samples. An acidimetric titration is further performed to investigate mol of absorbed CO₂ [14].

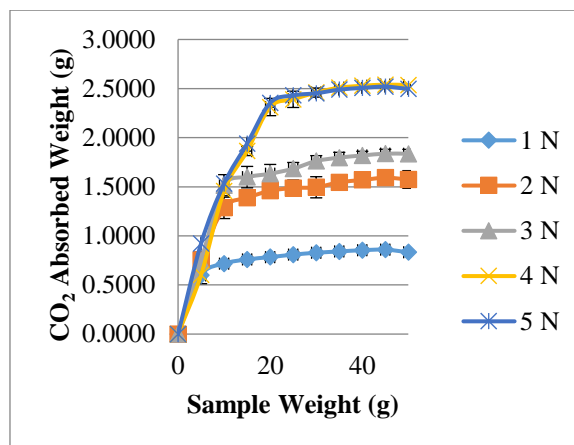


Figure 2. Samples v. CO₂ absorbed weights relationship for every KOH concentration

3.2. Total Carbon

Table 1 compares relationship between concentration of KOH solution (N), titration (mL), mol of CO₂, and weight of C (g) for every KOH concentration. KOH 4 N and 5 N solutions have alike weight after the end of administration (Fig. 2), but titration to each sample results higher actual mol of CO₂ absorbed by KOH 5 N than 4 N. Data conversion from absorbed CO₂ mol to weight C (g) also supports an increase in value as the KOH concentration increases.

Table 1. Volume of titration, number of mol CO₂, and weight of C for every KOH concentration

KOH concentration (N)	Volume of titration (mL)	mol CO ₂	Weight of C (g)
1	0.7500	0.0075	0.0900
2	1.6000	0.0160	0.1920
3	2.3167	0.0232	0.2784
4	3.0500	0.0305	0.3660
5	3.9500	0.0395	0.4740

3.3. pH-sample weight relationship

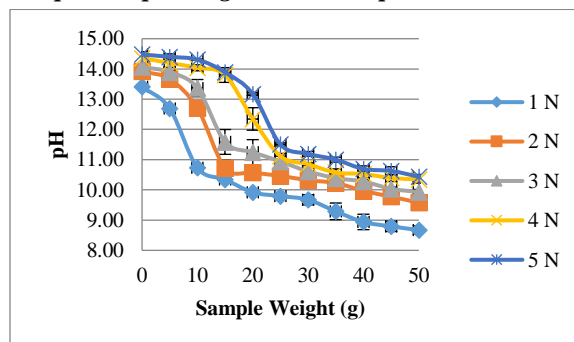


Figure 3. pH v. sample weight relation for every KOH concentration

Figure 3 provides relationship between sample weight and sample pH, showing a tendency to decrease pH along with decreasing KOH concentration (pH has a linear relationship with KOH concentration).

Figure 3 shows that there is a pH value above 14, based on the formula below [15, 16]:

$$pK_w = pH + pOH$$

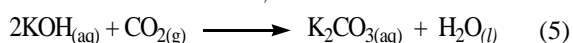
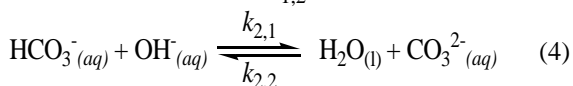
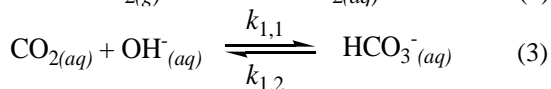
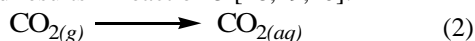
$$pH = pK_w - pOH$$

$$pOH = -\text{Log} [\text{OH}^-]$$

The logarithmic pH scale of the equation allows a pH value below 0 or above 14 due to the existence of strong acids and strong bases. pH 14 for a strong base the hydroxide ion concentration is one molar. pH value above 14 occurs because the hydroxide ion concentration exceeds one molar. A strong base for example a saturated NaOH solution has a pH of ≈ 15.0 [15,16,17].

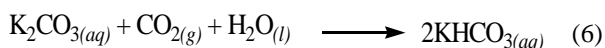
The system has the following reaction mechanism:

-Step 1: when absorption starts, reactions (2) and (3) begin concurrent. A large amount of OH^- reacts to give CO_3^{2-} (reaction 4) and the pH is decreased in this part. The highest amount of CO_2 is absorbed at this stage and results in reaction 5 [18,19,20]:



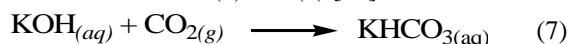
The K_2CO_3 produced exists as K^+ and CO_3^{2-} which dissociate in the absorber or absorbent.

-Step 2: since CO_2 is continuously introduced into the KOH solution during the reaction, CO_2 is simultaneously absorbed and affects to OH^- depletion and CO_3^{2-} accumulation through reaction (3) and forward reaction (4). However, concentration of CO_3^{2-} still adds up and triggers domination of the reverse reaction (4), then accelerates forward reaction (3). Hence, reaction (6) is activated. While a small amount of H^+ is released from HCO_3^- , which impose pH at this stage [19].



-Step 3: diminutive OH^- concentration occurs while chemical absorption almost done. Therefore, CO_2 is considered to have been physically absorbed at its equilibrium value in water at a certain partial pressure. KOH is a limiting reactant, the entire

absorption reaction of CO_2 and KOH in aqueous solution can be summarized as reaction (7), which stands for reactions (5) and (6) [19]:



3.4. CO₂ Absorption Efficiency

Table 2. CO₂ Absorption Efficiency in KOH solutions

KOH concentration (N)	CO ₂ Absorption Efficiency*
1	0.3750
2	0.4000
3	0.3861
4	0.3813
5	0.3950

* expressed as total mol CO₂/mol KOH solution

Table 2 presents absorption efficiency of CO₂ for every KOH concentration. The absorption efficiency is expressed as the mol CO₂ absorbed per mol KOH solution. The absorption efficiency of CO₂ seems not experiencing increase with the increase in KOH concentration.

3.5. Comparison of Experimental and Theoretical of CO₂ absorbed

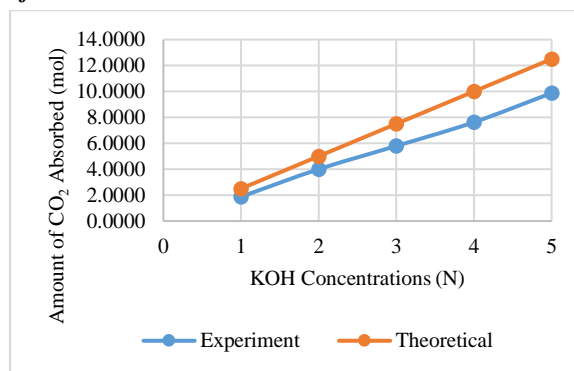


Figure 4. Comparison of Experimental and Theoretical of CO₂ absorbed in each KOH solution

The number of mol CO₂ absorbed at each KOH concentration is presented in Figure 4. There is a difference in mol absorbed CO₂ resulted between experimental results and theoretical. [19] and [21] also experienced the similar case in the test with NaOH, obtained other compounds namely Trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), while the KOH test obtained $\text{K}_2\text{CO}_3 \cdot \text{KHCO}_3 \cdot 1.5\text{H}_2\text{O}$. This might come from the formation of other compounds in a small concentration (minor compound) which causes an insufficient amount of CO₂ absorbed.

After CO₂ absorption, estimation of absorbed CO₂ amount is performed. Gravimetric measurement (Figure 2) indicates alike post-absorption weights of both KOH 4 N and 5 N. In contrast, different mol quantities of absorbed CO₂ on both KOH 4 N and 5

N is observed (Table 1), indicating the difference in accuracy with gravimetric.

This work still applied conventional titration method because of its high precision. However, this classical method demands highly on reagent and sometimes yields unfavorable output. Several sophisticated methods have been developed and applied to automate titration. For example, titration can be carried out in a continuous flow mode based on a controlled flow ratio and a detector [22]. This method will be beneficial for quantifying carbon in CO₂-absorbed solution.

4. Conclusions

Total carbon of every KOH concentration (1, 2, 3, 4, and 5 N respectively) are 0.0900, 0.1920, 0.2784, 0.3660, and 0.4740 g. Total carbon indicates analogue increase with KOH concentration. Absorption efficiency of every KOH concentration (1, 2, 3, 4, and 5 N respectively) are 0.3750, 0.4000, 0.3861, 0.3813, and 0.3950. KOH 5 N demonstrates the highest performance, indicated by both its total absorbed carbon and efficiency. Difference between the amount of CO₂ absorbed by KOH experimentally and in theory is observed, might be caused by the other compounds being formed.

5. Conflicts of interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

6. Acknowledgments

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