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Contributed Paper

## Development of a Simple Jam-jar Apparatus for Direct Analysis of Solid and Liquid Samples

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### ABSTRACT

This work describes a method based on vaporization techniques, for direct determination of calcium carbonate in fortified calcium tablets and for determination of total carbonate content in water. A discarded jam jar was adapted to be used as a closed reaction chamber. A piece of cylindrical glass was fitted at the bottom to form a base for the sample vial. In the experiment, a vial containing a carbonated sample was placed inside the jar, surrounded by a pH indicator solution (acceptor solution). The samples containing the carbonate were transformed from these solid or liquid states by acidification to a carbon dioxide gaseous phase inside the jar. The diffused carbon dioxide was then trapped into the indicator acceptor (Cresol red). The change of the absorbance of cresol red, based on alteration of solution pH, was detected at wavelength 440 nm. The system showed good linearity between absorbance and carbonate concentration allowing direct measurement of carbonate in both solid and liquid samples. The results show that the developed system is both performs well and is cost-effective for quality control in industry and in environmental measurement.

**Keywords:** jam jar, carbonate, vaporization

### 1. INTRODUCTION

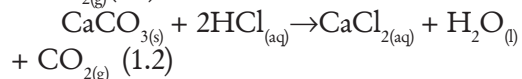
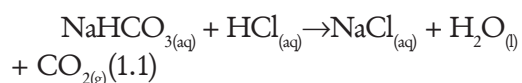
Carbonate compounds such as calcium carbonate ( $\text{CaCO}_3$ ) are important compounds that are widely used in several manufacturing sectors, including the pharmaceutical [1] and cement industries [2]. In pharmaceutical products,  $\text{CaCO}_3$  is commonly used medicinally as a calcium supplement or as an antacid. Calcium intake should be sufficient

to maintain constant concentrations of calcium in blood, muscle and intercellular fluids [3], but excessive consumption can be hazardous. However, calcium dietary supplements are sometimes required for treatment of calcium deficiency, especially in children, pregnant and lactating women, postmenopausal women and the elderly

[4-5]. To control the calcium content of the supplement,  $\text{CaCO}_3$ , the major compound, should be measured before distribution in the pharmaceutical market.

In the environmental field, carbonates play an important role in water pollution which is one of the most problematic environmental issues. Dissolved carbonate levels are key parameters reflecting water quality in terms of alkalinity and water hardness. Moreover, measurement of total carbonate in aqueous solution is equivalent to measurement of dissolved  $\text{CO}_2$ . Dissolved  $\text{CO}_2$  is in equilibrium with atmospheric  $\text{CO}_2$ , which is now being closely monitored due to concerns about climate change [6]. In industrial settings, water hardness must be constantly monitored to avoid costly breakdowns in boilers, cooling towers, and other equipment that comes in contact with water. Therefore, carbonate content in water must also be controlled.

Most methods for analysis of calcium carbonate ( $\text{CaCO}_3$ ) or hydrogen carbonate ( $\text{HCO}_3^-$ ) in solid and liquid samples are based on generation of  $\text{CO}_{2(g)}$  from either  $\text{CO}_3^{2-}$  (aq) or  $\text{CaCO}_{3(s)}$  as shown in reaction (1.1) and (1.2).



In the literatures, there are a limited number of methods available for determination of carbonate in solid samples. Most of them are based on analysis of  $\text{CaCO}_3$  in soil [7-12] and a few publications report on analysis of  $\text{CaCO}_3$  in cement [2, 13] and calcium supplements [1].

In contrast, there are several methods for determination of carbonate in water

samples. Titration is employed as the recommended method from the Association of Analytical Communities (AOAC) for determination of total alkalinity [14-15]. However, the titration method suffers from inadequate sensitivity and sample turbidity. Therefore, analysis of carbonate in aqueous samples can be carried out by using more sensitive techniques such as the infrared spectrometric method (IR) [16-17] and the ion chromatographic method [18-19]. These instruments, however, are expensive to purchase, operate and maintain.

For on-line analysis of carbonate compounds via volatilization, membrane-based techniques [7, 20-27] as well as membranless techniques [1-2, 28-30] has been popular coupled with flow injection. Carbonates and its related forms are acidified on-line to produce  $\text{CO}_2$  gas. In the membrane-based method,  $\text{CO}_2$  then diffuses across a hydrophobic semi-permeable membrane while in the membranless method,  $\text{CO}_2$  diffuses through the air gap into an acceptor solution. Then, detection occurs in the  $\text{CO}_2$ -absorbed acceptor. Detection of  $\text{CO}_2$  in the acceptor stream can be carried out using various techniques such as photometric detection of acid-base indicators [20-21, 23], traditional conductometric detection [23] and contactless conductivity detection [24-25].

This work attempts have been applied a jam jar as a simple scientific device for direct analysis of carbonate contents in both solid and liquid samples. Cresol red indicator acceptor, which is normally used for carbonate analysis, [6, 20, 23] was also employed in this work for absorption of the generated  $\text{CO}_2$ . The cresol red acceptor was subsequently transferred to a detection cell and was monitored by spectrophotometric detection.

## 2. MATERIALS AND METHODS

### 2.1 Design of the Jam-jar Apparatus

Figure 1 presents a schematic diagram of the jar apparatus. A jar was slightly modified to be a reaction cell consisting of four parts.

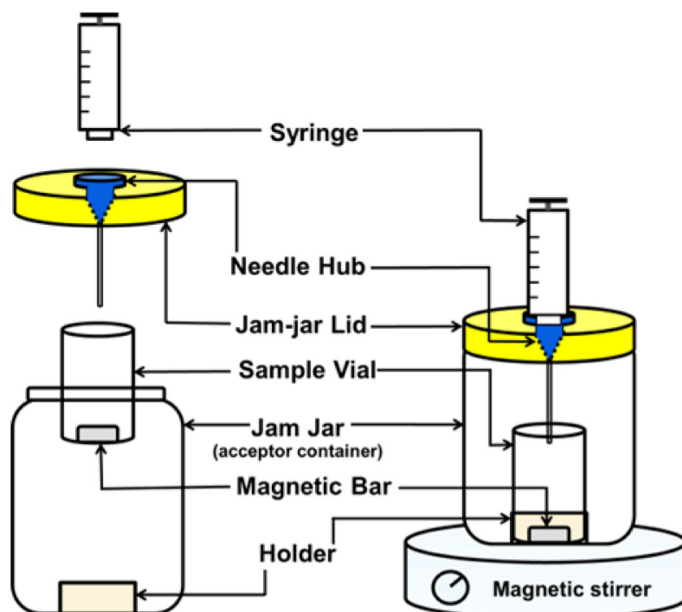
The first part was the jar (85 mm height, 45 mm i.d.) that was used as the acceptor container.

The second part was a small glass vial to be used as a sample holder (20 mm height, 30 mm i.d.). The bottom of the holder was

glued and placed in the center of the jar to fix the position of the sample.

The third part was a sample / standard vial (38 mm height, 28 mm i.d.) with a magnetic bar. The liquid sample was transferred into the sample vial by using a 3-mL plastic syringe as well as solid sample was directly weighed into the vial.

The last part was a plastic lid. A hole was drilled into the center of the lid and a needle hub was glued to fit in the hole for insertion of a syringe for acid injection.



**Figure 1.** Schematic diagram of a home-made jar apparatus for vaporization.

In order to develop a carbonate kit in the future, disposable plastic syringes were used instead of micropipette to quantify volume of solutions. Two 5-mL plastic syringes (Nipro, Thailand) were employed throughout the work. One was for loading the cresol red acceptor into the jar and another one was for acid injection into the sample vial. A small size of 3-mL plastic syringe (Nipro, Thailand) was used to transfer an aliquot of 2.0 mL of carbonate standard solutions and liquid samples into the vial. A magnetic stirrer (Model IKA colorsquid,

Germany) was employed for providing better and faster homogenization between the acid and carbonate.

### 2.2 Chemicals and Reagents

All chemicals used in this work were of analytical reagent (AR) grade. Deionized-distilled water was used for preparation of standard and reagent solutions.

In optimization, it is more convenient to use solutions of sodium hydrogen carbonate for analysis of solid [1] and liquid samples. For the optimization studies, a stock carbonate

solution (40 mmole  $\text{CO}_3^{2-}$ ) was prepared by dissolving 3.36 g of sodium hydrogen carbonate (Unilab, Philippines) in water and this solution was made up to the mark with water in a 50-mL volumetric flask. Appropriate dilution of this solution was employed for calibration of the analysis of calcium supplement and the analysis of water sample. In addition, crystals of calcium carbonate (Analar, England) were used directly as standards in some calibration work.

Cresol red (Merck, Germany) employed in the acceptor solution was prepared according to previous literatures [1, 20]. Acid used to solubilize both carbonate standard and sample was 1 M HCl (LobaChemie, India).

### 2.3 Sample Preparation

Four brands of calcium supplements (tablet form) were used. Samples were ground in a mortar. In quantitative analysis, ground samples were accurately weighed into the glass donor vials. The weight of solid sample employed in an analysis was 7 mg for tablets with 1000 or 1500 mg  $\text{CaCO}_3$  / tablet, and 27 mg for tablets with 625 mg  $\text{CaCO}_3$  / tablet. The samples were analyzed as described in the procedure.

Aquatic samples were analyzed without sample preparation. Each liquid sample (2 mL) was directly transferred into the glass donor vials with a magnetic bar.

### 2.4 General Procedure

As shown in figure 1, 5.0 mL of cresol red solution was firstly loaded into the jar as the acceptor container by using the 5-mL syringe. The standard carbonate or sample was accurately transferred into the small vial with a magnetic bar, and then this vial was situated on the sample holder inside the jar. The plastic lid was then closed tightly and 1 mL of acid

(1 M) was subsequently injected into the sample vial via the needle hub by using another syringe. The syringe was fixed in the needle hub during analysis. Carbonate in the sample/standard was suddenly converted into  $\text{CO}_{2(g)}$  and the liberated  $\text{CO}_2$  diffused from the vial into the headspace above it. Some of the  $\text{CO}_2$  gas was scrubbed into the cresol red acceptor for a fixed time. After that the lid was opened and the sample vial was immediately removed from the jar. The cresol red solution was subsequently transferred to a 10-mm cuvette. The color change of cresol red, which corresponded to the generated  $\text{CO}_2$ , was monitored by a Shimadzu spectrophotometer (Model UV-265FW, Japan) at 440 nm. Absorbance readings were used for the calibration plot and sample quantitation. All these steps were repeated for the next sample.

## 3. RESULTS AND DISCUSSION

### 3.1 Concentration of Indicator Acceptor

In this work, the color change of the cresol red (from purple to yellow), based on alteration of solution pH, was monitored at wavelength 440 nm for quantification of carbonate in the sample. Concentrations of cresol red in the range of 0.001 to 0.008% (w/v) were investigated. A higher concentration of cresol red produces a darker color, solution as shown in Figure 2.



**Figure 2.** A photograph of various concentrations of cresol red solution (pH 9.0) from 0.001 to 0.008 % (w/v) (left to right).

From the experiment, concentration of cresol red at 0.008% (w/v) resulted in poor linearity, therefore this concentration was omitted.

**Table 1.** The effect of concentration of indicator acceptor on sensitivity.

[Indicator] (% (w/v))	Linear equation (0.04 - 0.16 mmoleCO <sub>3</sub> <sup>2-</sup> )	r <sup>2</sup>
0.001	y = (1.429±0.005)x - (0.035±0.005)	0.998
0.002	y = (2.496±0.148)x - (0.075±0.016)	0.993
0.004	y = (5.730±0.155)x - (0.165±0.017)	0.998
0.008	y = (7.608±0.725)x - (0.195±0.079)	0.982

According to the results in Table 1, all concentrations except concentration of 0.008% (w/v) seem to be valid for adoption as acceptor solutions due to their linear calibrations. Although sensitivity is not a crucial problem for analysis of carbonate in solid calcium supplement samples, a highly sensitive method is preferred to accommodate samples containing low carbonate contents such as water sample. 0.004% (w/v) cresol red was selected as the acceptor solution as it provided the most sensitive condition.

### 3.2 Optimization of Solid Analysis

#### 3.2.1 Influence of Trapping Time and Volume of Acid on CO<sub>2</sub> Diffusion

Trapping time in this work is defined as the interval between HCl being injected into the sample under the closed system and the lid being removed.

For samples containing high carbonate content such as fortified calcium tablets, the sensitivity is not crucial; however the trapping-time interval was studied in order to balance between absorbance signal and throughput. The period of trapping time was optimized using 0.24 mmole CO<sub>3</sub><sup>2-</sup> of standard solution (corresponding to 24 mg CaCO<sub>3</sub>) with 3-mL of acid volume. According to the results in Table 2, the absorbance moderately increased with increasing trapping time. As expected, decreasing the trapping time resulted in faster sample throughput (data not shown). Unfortunately, the shortest interval time, which means maximizing sample throughput, gave the poorest precision (19.64 %RSD) owing to submerged bubbles sticking on the wall of the vial as well as on the magnetic bar. Occurrence of these bubbles containing CO<sub>2(g)</sub>, caused irreproducible signals.

**Table 2.** Effect of trapping time and volume of acid reagent.

Volume of 1 M HCl (mL)	Trapping time (s)	Absorbance ± SD	%RSD(n = 5)
3	30	0.331 ± 0.065	19.64
	60	0.515 ± 0.072	13.98
	90	0.709 ± 0.029	4.09
1	30	0.481 ± 0.013	2.70
	60	0.762 ± 0.009	1.18
	90	0.838 ± 0.010	1.19

In order to achieve a system with high sample throughput and good precision, decreased acid volume was further tested from 3 mL to 1 mL. As shown in Table 2., results indicated that the absorbance not only gradually increased as the volume of acid decreased at the same trapping time but also dramatically improved precision for those interval times (< 3%RSD). The smaller in depth the dispensed acid (inside the sample vial) the better the sensitivity. Decreasing the volume of acid reagent (decreasing depth) led to enhanced release of  $\text{CO}_{2(g)}$  from the sample vial for reaction with cresol red in the acceptor container (jar) [1].

Therefore, for solid analysis in this work, 30 s of trapping time with 1 mL of acid reagent was chosen as the optimum condition because this condition gave adequate absorbance readings and fast throughput of samples ( $120 \text{ samples h}^{-1}$ ).

### 3.2.2 Effect of Mole of the Acid Reagent

The mole of HCl required was studied using 0.8 M, 300  $\mu\text{L}$  of standard  $\text{NaHCO}_3$  solution corresponding to 0.24 mmole  $\text{CO}_3^{2-}$ . The amount of HCl was varied from 0.02 to 1 mmole. Any amount of acid above 0.2 mmole HCl was adequate (Figure 3).

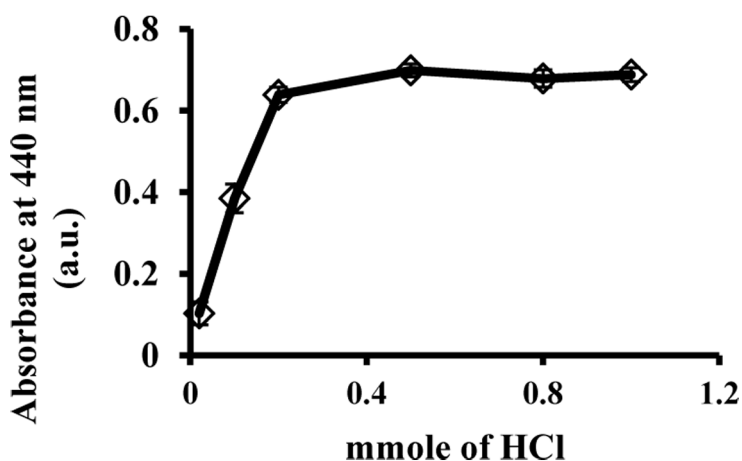


Figure 3. Effect of HCl.

However, to ensure excess acid to compensate for other possible neutralization processes of sample metrics, 1 mmole HCl was selected as the optimum.

## 3.3 Optimization of Liquid Analysis

### 3.3.1 Trapping Time and Aquatic Sample Volume

Natural water normally contains low levels of carbonate [6]. Therefore, sensitivity is the first priority. There were two possible ways to enhance sensitivity of this developed

system: elongation of trapping time and utilization of high volumes of sample. The trapping time was first studied by use of 1 mM  $\text{CO}_3^{2-}$  2 mL as test sample. We found that the increase of trapping time allowed  $\text{CO}_2$  to be trapped more and more during vaporization, resulting in sensitivity enhancement (data not shown). However, long trapping times, speed of analysis diminished. A trapping time of 180 s was selected to obtain sufficient absorbance reading as shown in Table 3.

**Table 3.** Effect of sample volume on absorbance and precision for trapping time 180 s.

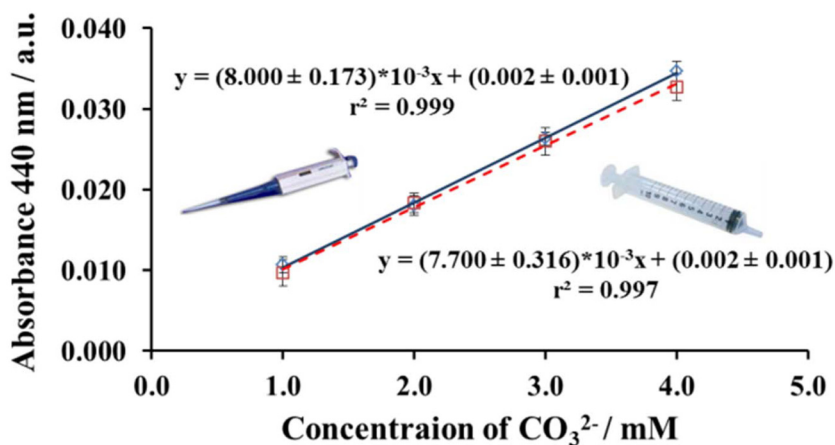
Sample volume (mL)	Absorbance $\pm$ SD	%RSD(n = 5)
2.00	0.013 $\pm$ 0.001	7.69
3.00	0.022 $\pm$ 0.003	13.64
5.00	0.035 $\pm$ 0.006	17.14

Another way to gain sensitivity was by increasing the sample volume. Sample volumes from 2.00 to 5.00 mL were examined. Results in Table 3 showed that absorbance gradually increased as the sample volume was increased from 2.00 to 5.00 mL. However, the precision become suddenly poorer because the depth level of the mixture in the sample vial hindered the diffusion of  $\text{CO}_{2(g)}$  (the same observation as in optimization of solid analysis).

Therefore, the volume of sample and acid solution required per analysis should not be greater than 3 mL. In this work, 2 mL of sample volume with 180s of trapping time was chosen with acceptable precision.

### 3.4 Precision Assessment of the Plastic Syringe for Control Volume of Solution

In order to develop this jam-jar system to be a carbonate test-kit in the future, simple and low-cost apparatuses are required. Thus, a cost-effective plastic syringe was studied to use for control volume of liquid sample and standard solutions instead of micropipette. Calibration curves of standard carbonate solution from both syringe and micropipette were compared (Figure 4). Results show good linearity of calibration curves and show no significant difference in the sensitivity (slope of equation) between plastic syringe and micropipette. This proves that the plastic syringe with the optimal condition could be able to control volume in sufficient precision for this analysis.

**Figure 4.** The possibility study for use of disposable syringe for limiting volume.

### 3.5 The Recommended Condition of the Jam-jar System

In order to summarize the recommended condition for determination of carbonate by the home-made jar apparatus in Figure 1, Table 4 was constructed.

### 3.6 Analytical Performance

Under the recommended conditions and operations, the final analytical performance of the developed method was examined (Table 5).

**Table 4.** Studied and selected parameters for optimization conditions for determination of carbonate in solid and liquid samples by jam-jar apparatus.

Parameters	Solid		Liquid	
	Studied	Selected	Studied	Selected
[indicator](%w/v)	0.001 to 0.008	0.004	-	0.004
Trapping time (s)	30 to 120	30	30 to 180	180
Sample amount	-	7 to 27 mg	2 to 5 mL	2 mL
Volume of 1 M HCl(mL)	1 and 3	1	-	1

**Table 5.** Analytical performance of the jam-jar system for determination of carbonate.

Performance	Value	
	Solid sample	Liquid sample
Linear working range	0.04-0.16 mmole CO <sub>3</sub> <sup>2-</sup> (4.0-16.0 mgCaCO <sub>3</sub> )	1-4 and 4-8 mM CO <sub>3</sub> <sup>2-</sup> (100-400 and 400-800 mgCaCO <sub>3</sub> /L)
Throughput (sample h <sup>-1</sup> )	120	20
Reproducibility (%RSD), n = 10	3.53(0.08 mmole CO <sub>3</sub> <sup>2-</sup> )	3.40(3.0 mM CO <sub>3</sub> <sup>2-</sup> )
Detection limit (3S/N)	0.036 mmole CO <sub>3</sub> <sup>2-</sup> (3.6 mgCaCO <sub>3</sub> )	1 mM CO <sub>3</sub> <sup>2-</sup> (100 mgCaCO <sub>3</sub> /L)
%recovery	96-102 <sup>(a)</sup>	96-104 <sup>(b)</sup>

(a) Carbonate contents in solid sample ranged from 0.060 to 0.078 mmole CO<sub>3</sub><sup>2-</sup> Standard carbonate added ranged from 0.060 to 0.058 mmole CO<sub>3</sub><sup>2-</sup> Carbonate found ranged from 0.120 to 0.134 mmole CO<sub>3</sub><sup>2-</sup>

(b) Carbonate contents in liquid samples ranged from 1.17 to 1.57 mM CO<sub>3</sub><sup>2-</sup> Standard carbonate added ranged from 1.17 to 1.26 mM CO<sub>3</sub><sup>2-</sup> Carbonate found ranged from 2.34 to 2.79 mM CO<sub>3</sub><sup>2-</sup>

Vaporization of the analyte to form CO<sub>2</sub> vapor before detection allowed use of external calibration, which is very convenient. Linear calibrations for both solid and liquid samples ( $r^2 > 0.99$ ) were obtained. With external calibration,

recovery ranged from 96 to 104% for water samples. The recovery from 96 to 102% of solid samples was carried out by adding exact amounts of standard CaCO<sub>3</sub> powder into sample vials together with samples of calcium supplements. Results also provided



satisfying reproducibility (RSD) of less than 5%. The developed jam-jar system gave rapid analysis of calcium carbonate in solid supplements ( $120 \text{ samples h}^{-1}$ ) and gave an acceptable through put of total carbonate contents in natural water ( $20 \text{ samples h}^{-1}$ ).

### 3.7 Application to Samples and Validations

In order to investigate the analytical applicability of the proposed method, the method was applied to the determination of calcium carbonate in calcium supplement

tablets (Figure 5) and the determination of total carbonate contents in natural water (Figure 6).

AOAC titration techniques [14] were employed for comparison to the proposed method. Paired  $t$ -test at 95% confidence [31] shows no significant different between the carbonate contents given by the developed method and those given by the standard methods (for solid:  $t_{\text{stat}} = 0.09$ ,  $t_{\text{critical}} = 2.20$  for liquid:  $t_{\text{stat}} = 1.58$ ,  $t_{\text{critical}} = 2.08$ ). This shows that the developed methods are accurate and reliable

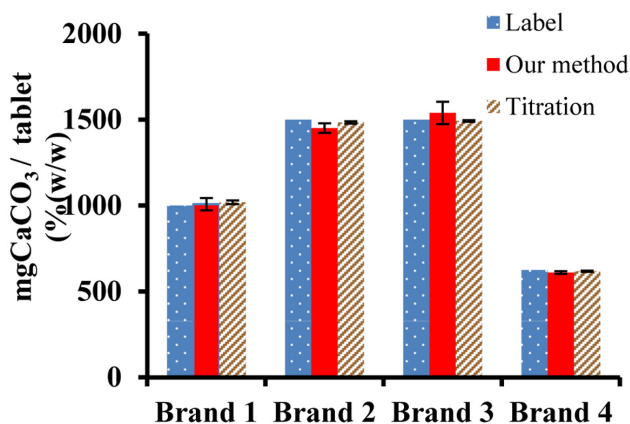


Figure 5. The CaCO<sub>3</sub> contents in calcium supplement tablets ( $n = 3$ ), determined by the developed jam-jar apparatus compared with labeled value and standard titration methods.

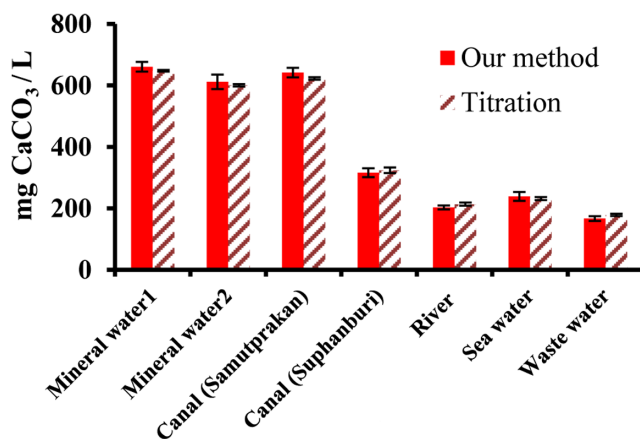


Figure 6. The total carbonate contents in water samples ( $n = 3$ ), given by our method and compared with the standard titration method.

#### 4. CONCLUSION

In this work, a discarded jam jar was adapted to be a valuable scientific tool for analytical techniques by using the basic principle of vaporization. The proposed system with two developed methods has been successfully applied for determination of calcium carbonate in fortified supplement tablets and for determination of carbonate contents in natural water. The home-made jar apparatus is cheap and easy to use, yet showed high accuracy and good precision.

#### AUTHORS DISCLOSURE STATEMENT

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