

An analytical approach for alkalinity measurement with a small volume of natural water by chemical equilibrium formula and geochemical modeling

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Key Points:

- We tested a method for an alkalinity measurement (as bicarbonate) using a small volume of water samples by spectrophotometry.
- Experimental processes to correct the bicarbonate concentration by the effect of the atmospheric CO₂ in a laboratory can be omitted.
- The sample volume was necessary only 0.1 mL (or 0.3 mL), which is applicable to broad fields.

Abstract

Spectrophotometry using a small sample volume has been developed to measure the alkalinity (or bicarbonate). However, the experimental and calculation processes are complicated, and the atmospheric CO₂ has to consider in preparing standard solutions. This study aims to quantify the dissolution of the atmospheric CO₂ when using spectrophotometry. Also, the effect on the standard solution in titrating that uses to make calibration curve are calculated to understand the effects of the different CO₂ concentrations in a laboratory. The difference between the bicarbonate concentrations and the calculated ones based on the updated chemical equilibrium formula was from 0.038 to 5.4×10^{-6} mg/L. The maximum difference was found at pH 5.0 in the 10 mg/L HCO₃⁻ standard solutions. The bicarbonate concentration without the atmospheric CO₂ reaction (C1) and with the atmospheric CO₂ reaction (C2) was calculated by the PHREEQC. The difference between C1 and C2 ranged from 0.01 to 0.02 mg/L, but the calculated bicarbonate concentrations between the HCl titration and the PHREEQC output were certainly different, which ranged from 3.1 to 11.5

mg/L at the pH 4.3 endpoint. In contrast, at the pH 4.8 endpoint, the difference was significantly decreased from 0.8 to 1.3 mg/L. The effect of the increasing atmospheric CO₂ by human breathing in a laboratory is only 0.05 mg/L in the standard solutions when titrating. From the results of this study, the experimental and calculation processes to correct the bicarbonate concentration by the effect of the atmospheric CO₂ in a laboratory may be omitted if natural waters are targeted.

Keywords: Alkalinity, Atmospheric CO₂, Natural water, Geochemical modeling, Spectrophotometry

1. Introduction

In natural waters, the pH, redox potential (E_h), and alkalinity affect the chemical reactions of dissolution and precipitation of minerals, the behavior of heavy metals, adsorption/desorption, and microbial reactions. Simultaneously, these reactions result in pH, E_h , and alkalinity (Stumm & Morgan, 1996). The alkalinity, therefore, is a crucial factor with the pH and E_h to understand the hydrogeochemical properties of the natural waters (Kim, 2018). The concentration of ions in the natural waters that neutralize the hydrogen ion is known as alkalinity, which is usually imparted by bicarbonate, carbonate, and hydroxide components (Muralikrishna & Manickam, 2017). In many aqueous systems, the alkalinity is controlled by carbonate chemistry, and most commonly is attributable to bicarbonate and less frequently to carbonate (Rounds, 2006). As the pH of most natural waters falls between 6.0 and 8.5, a region in which the equilibrium between bicarbonate and carbonate is strongly in favor of bicarbonate. In most cases, the alkalinity is approximately equal to the bicarbonate concentration (Schroeder, 2013). In other words, the bicarbonate concentration can be regarded as alkalinity in natural water.

For measuring the alkalinity (as HCO₃⁻), a lot of titration methods have been provided; for instance, the pH-titration-curve-inflection-point (PTC-IP) method, which finds the alkalinity endpoint from the inflection point of the pH titration curve, are revealed to be most accurate (Rounds, 2006; Kim, 2018). Gran titration, also, is likely to be appropriate for accurate estimation of the alkalinity using changes in the potential (Millero, Zhang, Lee, & Campbell, 1993; Kim 2018; Suga, Sakai, Toyofuku, & Ohkouchi, 2013). Traditional titration methods such as the pH indicator method and pre-selected pH method, are still commonly being used. According to APHA, AWWA, & WEF (2012), the pH endpoints are suggested by the different concentrations of the dissolved inorganic carbon (DIC): the endpoints of pH are 4.9, 4.6, and 4.3 at about 30, 150, and 500 mg/L of DIC, respectively.

In contrast, spectrophotometry has been also carried out to measure the alkalinity in seawater using bromocresol green (BCG; Breland & Byrne, 1993), a titration system (Millero et al. 1993), and bromophenol blue (Nand & Ellwood, 2018). In natural water such as river water, groundwater, and hot spring water, spectrophotometry using hydrochloric acid and BCG with a small volume

of water samples has been developed (Mishima, Ohsawa, Yamada, & Kitaoka, 2009). When using BCG, the alkalinity (mainly bicarbonate) can be detected using an absorbance ratio on two wavelengths (445 nm and 616 nm) measured by a spectrophotometer. The spectrophotometry using a small volume of water samples is more versatile than the titration method because the volume for the titration is necessary at least 50 mL. In other words, the titration method is inapplicable if sufficient water quantity is not obtained in fields or experiments. The difficulty with spectrophotometry is that it has to take into account the atmospheric CO_2 concentration since the dissolution of the CO_2 affects the DIC in pure water (Jo, Chae, Koh, Yu, & Choi, 2009; Kim, Hamm, Kim, & Kim, 2018). To avoid that, nitrogen purging was provided (Brelend & Byrne, 1993; Yao & Byrne, 1998), but special equipment preparation is required, and experimental operations are complicated (Mishima et al., 2009).

A simplified experimental method was established to correct the amount of CO_2 dissolved in the standard solution using experiments and chemical equilibrium formulas (Mishima et al., 2009). The method is applicable to the determination of bicarbonate in a broad field of water samples in geology and petrology, including dripping water in caves, extracted pore water samples, and batch test samples after high-pressure/temperature tests. Knowing the bicarbonate concentration enables us to determine the reliability of major ion analyses by measuring a cation-anion balance. In the previous study (Mishima et al., 2009), the spectrophotometry was compared to the pre-selected pH titration method using pH 4.3 for the endpoint and 0.1 mol HCl solution, which was tested by hot spring water and drip water samples. They reported no significant difference (5% significance level) between the two methods. However, since it is inaccurate for water with low bicarbonate concentration (<10 mg/L), they proposed spectrophotometric measurements for natural water samples with high bicarbonate concentration (above 50 mg/L). They also carefully stated that the pre-selected pH titration method may be incorrect below 10 mg/L HCO_3^- solutions. However, the reason has been still unknown, and the dissolution rate of the atmospheric CO_2 was not quantified. These issues obstruct the use of the simplified experimental method.

Equilibrium-based geochemical modeling is a method for predicting the identity and extent of chemical reactions in geological processes (Palandri & Kharaka, 2004). A geochemical modeling program PHREEQC (Parkhurst & Appelo, 1999) is one of the most widely used software (e.g., Zhang, Lu, Zhang, Tu, & Zhu, 2020), which refers to thermodynamic databases such as phreeqc.dat, wateq4f.dat, llnl.dat, and so on. It has capabilities for speciation and saturation-index calculations, batch-reaction, and one-dimensional transport calculations with reversible and irreversible reactions, which include aqueous, mineral, gas, and solid-solution (Parkhurst & Appelo, 2013). This study aims to simulate the effect of the atmospheric CO_2 on the standard solution in titrating and tests the effects of the different CO_2 concentrations in a laboratory. Thus, the PHREEQC modeling was adopted. In addition, the study finds a reason why waters containing a low bicarbonate concentration (< 10 mg/L) are inaccurate

through PHREEQC modeling. In relation to the effect of the atmospheric CO₂ in preparing the standard solution for spectrophotometry, the present study developed the updated chemical equilibrium formulas and used them to quantify the dissolution of the atmospheric CO₂. Our final goal is to simplify the complex experimental procedure so that alkalinity can be measured with a spectrophotometer even with small sample volumes. As the first step, this study provides the analytical and geochemical modeling results.

2. Methods

2.1 Review of the spectrophotometry

2.1.1 Experiment procedure

The simplified experimental method using a spectrophotometer was expressed to help understand the chemical equilibrium formulas and the PHREEQC modeling (Figure 1).

- a) Standard solution: prepare a 1000 mg/L HCO₃⁻ standard solution using sodium bicarbonate (NaHCO₃), which may need approximately 1.423 g. The concentration of HCO₃⁻ in the standard solutions is determined by titration using 0.1 mol HCl solution before the experiment.
- b) Dilution of the standard solution: dilute using the standard solution made in a) and pure water, and make 100, 200, 300, 400, and 500 mg/L HCO₃⁻ standard solution. Put 10 mL of five standard solutions into the polyethylene terephthalate (PET) test tubes.
- c) Weigh out 10 mL of 0.1 mmol/L hydrochloric acid solution and 0.38 mL of 0.04 w/v% bromocresol green (BCG) solution and put them in six PET test tubes.
- d) Inject 0.1 mL of the five standard solutions and one pure water (for blank) into the six PET test tubes, respectively.
- e) Measure the absorbance ratio at 445 and 616 nm wavelengths of each standard solution and pure water.
- f) Prepare the calibration curve.

2.1.2 Calibration curve

The bromocresol green used in the analysis is a weak acid so the relationship between non-dissociated molecules (C_H) and dissociated ions (C_I), and pH is expressed by Henderson-Hasselbalch equation

$$pH = pK_a + \log\left(\frac{C_I}{C_H}\right) \quad (1)$$

where pK_a is the dissociation constant of the bromocresol green. When the temperature is constant, the C_I/C_H ratio is determined by pH (Mishima et al., 2009).

The non-dissociated molecules and dissociated ions of the bromocresol green have completely different absorption spectra. In acidic conditions, the absorption of non-dissociated molecules is dominant, while in alkaline conditions, the absorption of dissociated ions is predominant. The maximum absorption wavelength of non-dissociated molecules is 445 nm (A_1) and that of dissociated ions is 616 nm (A_2). The ratio of absorbance (A_2/A_1) at each wavelength is related to the concentration ratio of dissociated ions to non-dissociated molecules (C_I/C_H) by Lambert-Beer's law

$$\frac{A_2}{A_1} = \frac{(\varepsilon_{21} + \varepsilon_{22} \frac{C_I}{C_H})L}{(\varepsilon_{11} + \varepsilon_{12} \frac{C_I}{C_H})L} \quad (2)$$

where ε_{11} and ε_{12} are absorption coefficients of non-dissociated molecules and dissociated ions at 445 nm, respectively. ε_{21} and ε_{22} are absorption coefficients of non-dissociated molecules and dissociated ions at 616 nm, respectively. L stands for the optical path length. Substituting equation (2) into equation (1) leads to equation (3).

$$pH = pK_a + \log \left(\frac{\frac{A_2}{A_1} - \frac{\varepsilon_{21}}{\varepsilon_{11}}}{\frac{\varepsilon_{22}}{\varepsilon_{11}} - \frac{\varepsilon_{12}}{\varepsilon_{11}} \frac{A_2}{A_1}} \right) \quad (3)$$

When an HCO_3^- solution of a certain concentration (X) is added to an acid solution that is a known concentration, HCO_3^- consumes H^+ from the acid solution, so the excess H^+ remains (i.e., H-X). When the bromocresol green is added to this reaction system, H-X corresponds to the pH in equation (3).

$$pH = -\log(\text{H-X}) \quad (4)$$

Equation (3) can be rearranged for HCO_3^- concentration (i.e., X) using equation (4) as shown in equation (5).

$$[X] = [H^+] - K_a \left(\frac{\frac{\varepsilon_{22}}{\varepsilon_{11}} - \frac{\varepsilon_{12}}{\varepsilon_{11}} \frac{A_{616}}{A_{445}}}{\frac{A_{616}}{A_{445}} - \frac{\varepsilon_{21}}{\varepsilon_{11}}} \right) \quad (5)$$

The ratio of absorbance (A_{616}/A_{445}) in the standard solutions can be detected by the spectrophotometer and the absorption coefficients can be determined by a curve fitting method using the concentration of the standard solution experimented by the titration method. The H^+ in equation (5) can be calculated as follow

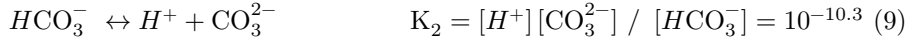
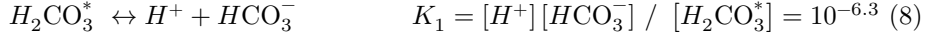
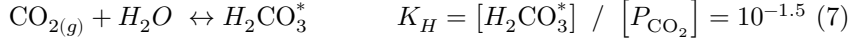
$$[H^+] = \frac{y}{V}h - \frac{V-y}{V}10^{-pH} \quad (6)$$

Therein, V expresses the volume of the volumetric flask (mL), h is the 0.1 N Hydrochloric acid indicated concentration (i.e., $0.1 \times \text{Factor}$), y stands for the volume of the 0.1 N Hydrochloric acid used in the dilution, and pH explains pH of the pure water used for the dilution.

2.2 Chemical equilibrium formula

An issue of the simplified experimental method using a spectrophotometer is the dissolution of the atmospheric CO_2 in pure water in preparing the standard solution (Mishima et al., 2009).

Equilibria in the carbonic acid system with approximate equilibrium constants at 25°C are expressed as (Appelo & Postma, 2005)



where $\text{H}_2\text{CO}_3^* = \text{CO}_{2(aq)} + \text{H}_2\text{CO}_3$. Actually $\text{CO}_{2(aq)}$ is about 600 times higher than H_2CO_3 at 25°C, but to facilitate calculations the two species are summed up as H_2CO_3^* (Appelo & Postma, 2005). Assuming that the carbonate concentration is negligible in the standard solution (**a**) because the pH of the pure water and the standard solutions falls between 5.5 and 8.5, equation (9) does not need to be taken into account. Thus, DIC can be expressed as

$$\text{DIC} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] \quad (10)$$

In the pure water before adding sodium bicarbonate, H_2CO_3^* and HCO_3^- are formed by dissolving CO_2 in the laboratory. For providing the chemical equilibrium formulas based on equations (8) and (10), the H_2CO_3^* and HCO_3^- concentrations are set to be a and d (mol/L), respectively. Also, in pure water, there is H^+ produced when H_2CO_3^* dissociates into HCO_3^- (equation (7)). Let the $[\text{H}^+]$ be b (mol/L). In addition, the HCO_3^- concentration in the standard solution is set to be c (mol/L). When sodium bicarbonate adds into the pure water, HCO_3^- in the pure water reacts to the H^+ and an equilibrium shift occurs ($\text{H}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3^*$). The HCO_3^- concentration to be consumed in this process defines as Y (mol/L) in this study. Therefore, equation (8) can be redefined as (Mishima et al. 2009)

$$K_1 = \frac{[b-Y][c+d-Y]}{[a+Y]} \quad (11)$$

The solution to transforming equation (11) into a second-order equation for Y is

$$Y = \frac{1}{2} \left[(b + c + d + K_1) \pm \sqrt{(b + c + d + K_1)^2 - 4(bc + bd - aK_1)} \right] \quad (12)$$

$$a = \frac{10-x}{10} \frac{(10^{-\text{pH}})^2}{K_1} \quad (13)$$

$$b = \frac{10-x}{10} 10^{-\text{pH}} \quad (14)$$

$$c = \frac{x}{10} [\text{HCO}_3^-]_{\text{std}} \quad (15)$$

$$d = \frac{10-x}{10} 10^{-[\text{HCO}_3^-]} \quad (16)$$

$$K_1 = 10^{-(1.1 \times 10^{-4} T^2 - 0.012 T \times 6.58)} \quad (17)$$

where $[\text{HCO}_3^-]_{\text{std}}$ represents the HCO_3^- concentration of the standard solution made by a) procedure (i.e., 1000 mg/L of HCO_3^-). x expresses the amount of the standard solutions (i.e., 1000 mg/L of HCO_3^- equals 10 mL). The pH and T are the pH and temperature of the pure water used for preparing the

standard solutions, respectively. It is assumed that the $[HCO_3^-]$ is equivalent to $[H^+]$ because the pH of the pure water indicates approx. 5.6 in a laboratory. equations (12) to (16) are updated for calculating the correct Y concentration in this study.

For the correct HCO_3^- , the following determines the concentration of the standard solutions:

$$[HCO_3^-] = [c + d - Y] \quad (18)$$

This study quantifies a dissolution concentration of the atmospheric CO_2 in pure water in preparing the standard solution (i.e., $[c] - [c + d - Y]$).

2.3 PHREEQC modeling

The speciation, gas-phase, and reaction tools in PHREEQC were adopted to understand the difference in the bicarbonate concentrations in the standard solutions in titrating, which needs for preparing the calibration curve. The modeling was conducted in two ways: one is the reaction without CO_2 (C1); another is with CO_2 (C2). It means that the $[d - Y]$ is found using the geochemical model in detecting the HCO_3^- concentrations on the titration. This study determined the amounts of $NaHCO_3$ adding to the pure water (1L) as follows: 7.12, 14.23, 35.58, 71.15, 142.30, 284.60, 426.90, 569.20, 711.50 mg, which corresponds to approximately 5, 10, 25, 50, 100, 200, 300, 400, and 500 mg/L HCO_3^- , respectively. In the case of C2, -3.5 of pCO_2 at 25°C and 1 atm were used for adopting the reaction between the pure water and the atmospheric CO_2 . In C1, the sodium bicarbonate just reacts to the pure water. We used the “REACTION” function in the PHREEQC to react the pure water and $NaHCO_3$, and the “GAS_PHASE” function was used to react the atmospheric CO_2 and the pure water for C2. The “phreeqc.dat” file was selected as the thermodynamic database in the study.

The bicarbonate concentration of 9 standard solutions (about 5.0 to 500.0 mg/L) was calculated using the PHREEQC modeling. Hydrochloric acid (HCl) was used as the acid solution. The endpoints of pH were selected by 4.3 and 4.8. The difference in the bicarbonate concentrations between C1 and C2 is estimated using two ways: one is to refer to the PHREEQC output files; another is to calculate the consumed HCl moles reaching pH 4.3 and 4.8. For example, a PHREEQC input file is shown in Figure 2, in which the pH endpoint was set to 4.8, and the sodium bicarbonate was 0.00847 mol, corresponding to about 500 mg/L HCO_3^- .

2.4 Change in the CO_2 concentration in a laboratory

The CO_2 concentration in a laboratory where the experiment performs can vary depending on human breath. Change in the CO_2 concentration in a laboratory affects the dissolution rate and pH of the standard solutions. Thus, this study measured changes in the CO_2 concentration in a laboratory (4.6 m × 6.2 m × 3.3 m) under two ventilators operating. The CO_2 concentration was measured

using CUSTOM CO2-M1 (CUSTOM Corp.). The results are shown in Table 1. The CO_2 concentration was 435 mg/L in the laboratory, which increased to 568 mg/L when one person worked for one hour. When two people were in the laboratory, the CO_2 concentration was further raised to 833 mg/L. Therefore, the authors handled the pH as a variable in calculating equations (13) and (14). The range of the pH was selected from 5.0 to 6.0.

3. Results

3.1 Dissolution rate of atmospheric CO_2 into pure water

In preparing the standard solution, the chemical equilibrium formula was used to quantify the dissolution rate of the atmospheric CO_2 in pure water. The parameters used for the calculation are represented in Table 2. The bicarbonate concentrations were set to 10, 25, 50, 100, 200, 300, 400, and 500 mg/L (i.e., $[c]$). The calculated concentrations of the corrected HCO_3^- (i.e., $[c+d-Y]$) and the difference (i.e., $[c] - [c+d-Y]$) with pH 5.0, 5.3, 5.6, and 6.0 are expressed in Table 3. The concentrations of the corrected HCO_3^- were higher than those of HCO_3^- because of the dissolution of the atmospheric CO_2 , but their difference was tiny. The difference decreases as the pH increases, which shows that pH has an inverse relationship with pCO_2 (e.g., Yang et al., 2020). The difference also falls as the concentrations of the corrected HCO_3^- rise, which is caused by the bicarbonate buffer system (equations (7) and (8); Wolf-Gladrow, Zeebe, Klaas, Körtzinger, & Dickson, 2007). The maximum difference (0.038 mg/L) was calculated when pH was 5.0, and the bicarbonate concentration was 10 mg/L. This result reflects that the inaccuracy for waters containing a low bicarbonate concentration (< 10 mg/L) as mentioned by Mishima et al. (2009) is increased. However, it is hard to conceive of this small difference affecting the inaccuracy. There may be other reasons to cause the inaccuracy between the titration method and the spectrophotometry. The dissolution rate of atmospheric CO_2 into pure water depends on its concentration. According to Table 2, assuming that atmospheric CO_2 concentration is 833 mg/L, pH can be calculated as 5.4 by PHREEQC. The difference is still small (Table 2). Considering the results of this tiny difference ($[c] - [c+d-Y]$), they are negligible unless an accuracy of 0.01 mg/L is required. Consequently, this study suggests that the atmospheric CO_2 correction can be omitted in using spectrophotometry.

3.2 Bicarbonate concentration in the standard solutions in titrating

The bicarbonate concentration without the atmospheric CO_2 reaction (C1) and with the atmospheric CO_2 reaction (C2) was presented in Table 4. The bicarbonate concentration was calculated by referring to the PHREEQC output file and by calculating consumed HCl using the pH 4.3 endpoint, which is modeled to reproduce the titration experiment (Figure 2). In this model, pCO_2 was set to -3.5 for C2. It is noted that the pH in Table 4 expresses the standard solutions. The moles of sodium bicarbonate were determined referring to the bicarbonate concentrations of the PHREEQC output for C1. Those were 5.04, 10.10, 25.29, 50.57, 101.04, 201.84, 302.40, 402.77, and 502.90 mg/L. In the

results of the PHREEQC output, the bicarbonate concentrations for C2 were higher than those of C1, and the pH for C2 was lower than that of C1. It indicates that the atmospheric CO_2 affects the bicarbonate concentrations in the standard solutions following equations (7) and (8). Figure 3 shows the bicarbonate concentrations for C1 and C2 with the difference between C1 and C2 (i.e., C2 minus C1). The difference rapidly increased from 0.11 to 0.73 mg/L on 5 to 200 mg/L of the standard solutions, and it remained flat at 0.73 mg/L from 200 to 500 mg/L of the standard solutions. Figure 4 depicts the carbonate (H_2CO_3^*) concentrations in the standard solutions for C1 and C2, and the difference. The carbonate concentrations showed 10 to 100 times lower than the bicarbonate concentrations. The carbonate concentration for C2 is higher than that of C1, and the difference above 200 mg/L of the standard solutions showed fewer changes than that of lower concentration ($< 200 \text{ mg/L HCO}_3^-$). It can be caused by the pH difference between the standard solutions of C1 and C2 (Table 4) because the abundance of the carbonate is increased as the pH of the solution decreases (Ishida, Kawai, Ichiba, & Sato, 2010; Yamamoto, 1983).

In contrast, less difference (-0.01 or $-0.02 \text{ mg/L HCO}_3^-$; C2 minus C1) was found between C1 and C2 based on the results of bicarbonate concentration calculated by the consumed HCl (Table 4). It reflects that the titration volumes of HCl until pH 4.3 are close to the same between C1 and C2. In practice, the bicarbonate concentrations are usually obtained by the experimental HCl titration. Thus, the maximum error caused by atmospheric CO_2 can be considered as 0.02 mg/L independent of the concentrations of the standard solutions, which would be negligible because it could not affect the ion balance in natural waters. However, the bicarbonate concentrations between the HCl titration and the PHREEQC output were certainly different (Table 4). The difference for C2 ranges from 3.1 to $11.5 \text{ mg/L HCO}_3^-$. (Figure 5a). This difference can be explained if a large amount of the HCl was dropped in the standard solutions. Thus, the endpoint of pH was changed to 4.8, and PHREEQC recalculated the consumed HCl. Table 5 shows the calculated bicarbonate concentrations for C1 and C2 at pH 4.8, and the difference in the bicarbonate concentrations between the HCl titration at pH 4.8 and the PHREEQC output for C2 is depicted in Figure. 5b. The difference was significantly decreased from 0.8 to -1.3 mg/L .

As shown in Table 1, if two people are in the laboratory, the CO_2 concentration is increased to 833 mg/L . Therefore, the bicarbonate concentration was recalculated using -3.0 of pCO_2 with the end point of pH 4.8 to confirm the effect of the atmospheric CO_2 on the titration. The calculation was conducted on the C2 modeling. The pH of the standard solutions ranged from 6.67 to 8.14 (Table 6), and it decreased from 0.1 to 0.5 compared with the results when -3.5 of pCO_2 was used (Table 3), which resulted from the dissolution of the atmospheric CO_2 increase. Although the bicarbonate concentration of the standard solutions calculated by the consumed HCl was decreased, the difference was small as 0.05 mg/L (Table 6). In other words, the effect of human breathing in a laboratory is only $0.05 \text{ mg/L HCO}_3^-$ in the standard solutions.

4. Discussion

From the chemical equilibrium formula, the effect of the atmospheric CO_2 on using the spectrophotometric method has resulted in a small difference between the HCO_3^- and the corrected HCO_3^- concentrations (i.e., $[c] - [c+d-Y]$), which led to that the effect is negligible unless an accuracy of 0.01 mg/L is required. Similarly, the small difference between C1 and C2 (0.01 or 0.02 mg/L HCO_3^-) calculated by the consumed HCl was found in the titration method regardless of changes in the atmospheric CO_2 concentration in a laboratory. According to APHA et al. (2012), the endpoint of pH in titrating depends on the DIC concentration in natural waters. However, the result of the present study provides that pH 4.8 is preferred as the endpoint for the “standard solutions”. Consequently, based on Figure. 5, it could conclude that inaccuracy for waters containing a low concentration of HCO_3^- (< 10 mg/L) using the spectrophotometry (Mishima et al. 2009) was caused by the titration error using pH 4.3.

A comparison between the calculated bicarbonate concentration this study provided and the measured one is necessary to verify the reliability of the calculated values. The endpoints of the pH were chosen to be 4.3 and 4.8, and then the consumed HCl was calculated for the calculation. The measured bicarbonate concentration of the dripping water samples in the Inazumi limestone cave, Japan was compared to the calculated one using the PHREEQC. The bicarbonate was measured by the spectrophotometric method (details are in Mishima et al. 2009 with pH and main anion-cation). In addition, for the comparison of the lower levels of the bicarbonate concentration, the calculation was conducted using the measured bicarbonate concentrations for groundwater, river water, and hot spring water samples in Japan referring to Katazakai & Zhang (2021), Ikawa, Shimada, Tokunaga, & Gotou (2007), and Yang (2021), respectively. The measured bicarbonate concentrations ranged from 4.8 mg/L and 50.7 mg/L (Table 7). For the groundwater, river water, and hot spring water samples, the bicarbonate concentrations were measured by the titration method until pH 4.8. The calculated bicarbonate concentrations at pH 4.3 in the dripping water were close to the measured one, whereas the other calculated samples were well reproduced at pH 4.8 (Table 7). The difference ranged from 0.1 to 1.5 mg/L. It reflects that the method this study used for the calculation of the bicarbonate concentration using PHREEQC is appropriate. However, the calculated value at the Jyogasaki was 5.6 mg/L with a difference of 0.8 mg/L. Similarly, although the difference of the standard solutions was small (Figure 5b), the difference was 0.82 mg/L on the 5 mg/L standard solution. The error reaches 16 % around the 5 mg/L of the bicarbonate. It is derived from the titration method, which may affect the inaccuracy of a low concentration of HCO_3^- (< 10 mg/L) using the spectrophotometry because it uses the calibration curve based on the titration method. Considering the results of Figure 5, setting the endpoint of the pH to be 5.0 or 5.1 is one of the alternative methods for the lower levels, but the experimental evaluation is strongly recommended.

5. Conclusion

The present study updated the chemical equilibrium formulas and used them to quantify the dissolution of the atmospheric CO_2 when using spectrophotometry. Also, it simulated the effect of the atmospheric CO_2 on the standard solution in titrating and tested the effects of the different CO_2 concentrations in a laboratory. In addition, the study finds a reason why waters containing a low concentration of HCO_3^- ($< 10 \text{ mg/L}$) are inaccurate using the PHREEQC modeling.

The difference between the bicarbonate concentrations of 10, 25, 50, 100, 200, 300, 400, and 500 mg/L (i.e., $[c]$) and the calculated bicarbonate concentrations based on the updated chemical equilibrium formula (i.e., $[c+d-Y]$) was from 0.038 to $5.4 \times 10^{-6} \text{ mg/L}$. The maximum difference was found at pH 5.0 in the 10 mg/L standard solutions. Assuming that atmospheric CO_2 concentration is 833 mg/L because of human breathing, the pH can be calculated as 5.4. The difference is still small. Considering the results of this tiny difference ($[c] - [c+d-Y]$), they are negligible unless an accuracy of 0.01 mg/L HCO_3^- is required.

The bicarbonate concentration without the atmospheric CO_2 reaction (C1) and with the atmospheric CO_2 reaction (C2) was calculated by the PHREEQC. The difference between C1 and C2 ranged from 0.01 to 0.02 mg/L, but the calculated bicarbonate concentrations between the HCl titration and the PHREEQC output were certainly different. The difference at the end point of the pH 4.3 ranged from 3.1 to 11.5 mg/L and increased as the bicarbonate concentration of the standard solutions increased. However, at the endpoint of the pH 4.8, the difference was significantly decreased from 0.8 to 1.3 mg/L. The effect of the increasing atmospheric CO_2 by human breathing in a laboratory is only 0.05 mg/L in the standard solutions when titrating.

As the reason for inaccuracy on the lower bicarbonate concentration solutions in using the spectrophotometry, it could consider that the large volume of the HCl solution was titrated to the standard solutions and the natural water samples when the calibration curve was made. From the results of this study, the experimental and calculation processes to correct the bicarbonate concentration by the effect of the atmospheric CO_2 in a laboratory (i.e., the procedures in relation to equations (12) to (18)) may be omitted if the groundwater, river water, hot spring water, and pore water after reacting at high pressure and temperature are targeted.

Conflict of interest statement

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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- Table 1** CO₂ concentration, temperature, and the number of people who were in a laboratory. The size of the laboratory is 4.6 m × 6.2 m × 3.3 m.

Time	CO ₂	Temperature	Person
	(mg/L)	(°C)	
14:11	435	20.8	1
15:11	568	21.3	1
16:04	825	21.8	2
17:10	833	21.8	2
17:30	789	21.8	1

Table 2 Input parameters used for calculating the dissolution of the atmospheric CO₂ to the standard solution using the chemical equilibrium formula. a and d explain the H₂CO₃^{*} and HCO₃⁻ concentrations, respectively. b is the H⁺ concentration in the pure water, c indicates the HCO₃⁻ concentration in the standard solution, Y is the HCO₃⁻ concentration to be consumed by reacting the H⁺ in the pure water, [HCO₃⁻std] represents the HCO₃⁻ concentration of the standard solution made by **a**) procedure, x expresses the amount of the standard solutions (i.e., 500 mg/L of HCO₃⁻ equals 5 mL), and the pH and T are the pH and temperature of the pure water, respectively.

Parameter	Value
a (mol/L)	1.126×10 ⁻⁵
b (mol/L)	2.009×10 ⁻⁶
c (mol/L)	1.638×10 ⁻³
d (mol/L)	2.009×10 ⁻⁶
K ₁	4.479×10 ⁻⁷
pH	5.0, 5.3, 5.6, 6.0
[HCO ₃ ⁻ std] (mg/L)	
T (°C)	25
x (mL)	0.10, 0.25, 0.5, 1, 2, 3, 4, 5

	pH=5.0	pH=5.3	pH=5.6	pH=6.0	pH=5.0	pH=5.3	pH=5.6	pH=6.0
HCO ₃ ⁻ Corrected Difference								
[c] HCO ₃ ⁻ ([c]-								
(mg/L) [c+d- [c+d-								
Y] Y])								
(mg/L) (mg/L)								
					×10 ⁻²	×10 ⁻²	×10 ⁻³	×10 ⁻⁴
					×10 ⁻²	×10 ⁻³	×10 ⁻³	×10 ⁻⁴
					×10 ⁻³	×10 ⁻³	×10 ⁻⁴	×10 ⁻⁴
					×10 ⁻³	×10 ⁻⁴	×10 ⁻⁴	×10 ⁻⁵
					×10 ⁻³	×10 ⁻⁴	×10 ⁻⁴	×10 ⁻⁵
					×10 ⁻⁴	×10 ⁻⁴	×10 ⁻⁵	×10 ⁻⁵
					×10 ⁻⁴	×10 ⁻⁴	×10 ⁻⁵	×10 ⁻⁶

pH=5.0	pH=5.3	pH=5.6	pH=6.0	pH=5.0	pH=5.3	pH=5.6	pH=6.0
				$\times 10^{-4}$	$\times 10^{-4}$	$\times 10^{-5}$	$\times 10^{-6}$

Table 3 The HCO_3^- concentration [c] and the corrected HCO_3^- concentration [c+d-Y] of the standard solutions with their differences (i.e., [c]-[c+d-Y]) when the pH is 5.0, 5.3, 5.6, and 6.0.

Table 4 The concentration of HCO_3^- , pH, consumed HCl on without the atmospheric CO_2 reaction (C1) and with the atmospheric CO_2 reaction (C2). The concentration of HCO_3^- was calculated by referring the PHREEQC output file and by calculating consumed HCl using the 4.3 pH end point. The moles of sodium bicarbonate were determined referring to the concentration of HCO_3^- of the PHREEQC output for C1. SS stands for standard solution.

NaHCO ₃ (mol)	PHREEQC output of Bicarbonate concentration		Titration of HCl (pH 4.3)	
	C1	C2	C1	C2
	pH of SS	HCO_3^- (mg/L)	pH of SS	
847.02×10^{-7}	8.06	5.04	7.16	
1694.05×10^{-7}	8.15	10.10	7.45	
4235.12×10^{-7}	8.23	25.29	7.79	
8470.24×10^{-7}	8.26	50.57	8.00	
16940.48×10^{-7}	8.27	101.04	8.13	
33880.95×10^{-7}	8.26	201.84	8.19	
50821.43×10^{-7}	8.25	302.40	8.21	
67761.90×10^{-7}	8.24	402.77	8.21	
84702.38×10^{-7}	8.23	502.90	8.20	

Table 5 The consumed HCl and the concentration of HCO_3^- on without the atmospheric CO_2 reaction (C1) and with the atmospheric CO_2 reaction (C2). The concentration of HCO_3^- was calculated by calculating consumed HCl using the 4.8 pH end point.

HCO ₃ for C2 (mg/L)	End point: pH 4.8			
	C1	C2		
	Consumed	HCO_3^-	Consumed	HCO_3^-
	HCl (mol)	(mg/L)	HCl (mol)	(mg/L)
	$\times 10^{-5}$		$\times 10^{-5}$	
	$\times 10^{-5}$		$\times 10^{-5}$	
	$\times 10^{-5}$		$\times 10^{-5}$	
	$\times 10^{-5}$		$\times 10^{-5}$	
	$\times 10^{-5}$		$\times 10^{-5}$	
	$\times 10^{-5}$		$\times 10^{-5}$	
	$\times 10^{-5}$		$\times 10^{-5}$	

$\times 10^{-5}$	$\times 10^{-5}$
$\times 10^{-5}$	$\times 10^{-5}$

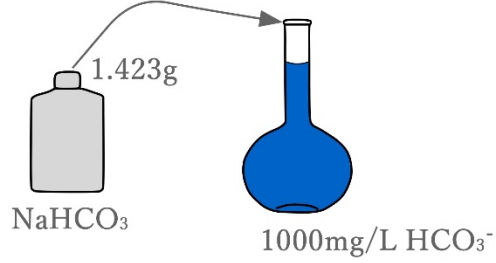
Table 6 The consumed HCl and the concentration of HCO_3^- on with the atmospheric CO_2 reaction (C2) recalculated by -3.0 of pCO_2 . The concentration of HCO_3^- was calculated by calculating consumed HCl using the pH 4.8 end point.

HCO_3^- (mg/L)	End point: pH 4.8		
	C2		
	pH of standard solution	Consumed HCl (mol)	HCO_3^- (mg/L)
5.16	6.67	9.73×10^{-5}	5.93
10.29	6.96	17.97×10^{-5}	10.96
25.63	7.35	42.67×10^{-5}	26.04
51.06	7.63	83.83×10^{-5}	51.15
101.65	7.87	166.10×10^{-5}	101.35
202.58	8.04	330.53×10^{-5}	201.68
303.13	8.1	494.83×10^{-5}	301.93
403.50	8.13	659.04×10^{-5}	402.12
503.63	8.14	823.19×10^{-5}	502.28

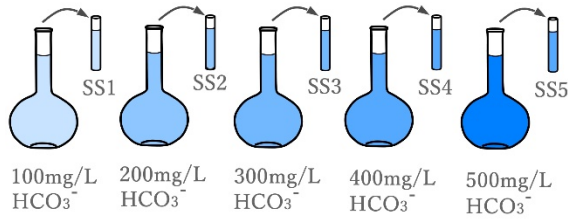
Table 7 Calculated and measured bicarbonate concentrations. The dripping water samples in the Inazumi limestone cave, Japan was referred to Mishima et al. (2009). The groundwater, river water, and hot spring water samples in Japan were referred to Katazakai and Zhang (2021), Ikawa et al. (2007), and Yang (2021).

Sample	Calculated HCO_3^- (mg/L)		Type of water and reference
	at pH 4.3	at pH 4.8	
SUI1	255.2	247.6	254.4
SUI2	250.2	242.7	249.3
SUI4	225.0	218.1	223.9
SIN2	190.0	183.8	188.5
SIN4	199.8	193.4	198.4
FSGD	48.1	44.9	45.4
FSGDS-G1	48.0	44.8	45.3
FSGDS-G2	53.4	50.1	50.7
River	37.3	34.3	34.5
Jyougannji	7.9	5.6	4.8
Sannou	19.5	17.0	16.5
No11	15.8	12.5	12.2
No32	14.1	11.1	10.4
No41	15.9	12.1	12.2

a) Standard solution (SS)



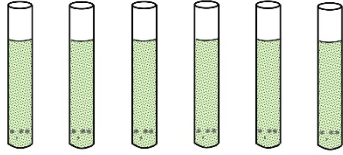
b) Dilution using a) solution



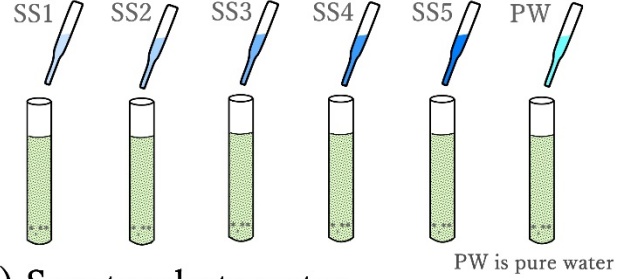
c) six HCl+BCG solutions

* 10mL of 0.1mmol HCl

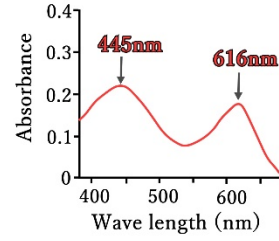
** 0.38mL of 0.04 w/v% Bromocresol green (BCG)



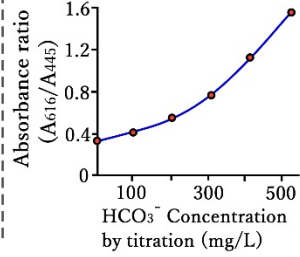
d) Injection SS into HCl+BCG (0.1mL)



e) Spectrophotometer



f) Calibration curve



$$X = H - K_a \left(\frac{\frac{\epsilon_{22} - \epsilon_{12} A_{616}}{\epsilon_{11} - \epsilon_{11} A_{445}}}{\frac{A_{616}}{A_{445}} - \frac{\epsilon_{21}}{\epsilon_{11}}} \right)$$

refer to Eqs.(2) and (5) in the manuscript for parameters

Figure 1 Experimental procedure for the spectrophotometry to detect HCO₃⁻.

SOLUTION 1 (C1)		Pure water	SOLUTION 2 (C2)	
temp	25		temp	25
pH	7		pH	7
pe	4		pe	4
redox	pe		redox	pe
units	mol/kgw		units	mol/kgw
density	1		density	1
-water	1 # kg		-water	1 # kg
REACTION 1		Standard Solution	REACTION 2	
NaHCO3	0.00847		NaHCO3	0.00847
HCO3 ⁻ by PHRREQC output			HCO3 ⁻ by PHRREQC output	
SAVE solution 1		HCl titration	SAVE solution 2	
Use solution 1 (C1 titration)			Use solution 2 (C2 titration)	
Reaction 11			Reaction 21	
HCl 0.0082331 # moles			HCl 0.0082328 # moles	
HCO3 ⁻ by consumed HCl			HCO3 ⁻ by consumed HCl	
END			END	

Figure 2 A PHREEQC input file for C1 (without CO₂ reaction) and C2 (with CO₂ reaction). In the input file, the pH endpoint was set to 4.8 and the sodium bicarbonate was 0.00847 mol which corresponds to the about 500 mg/L HCO₃⁻. The purple and red characters indicate the calculated bicarbonate concentration.

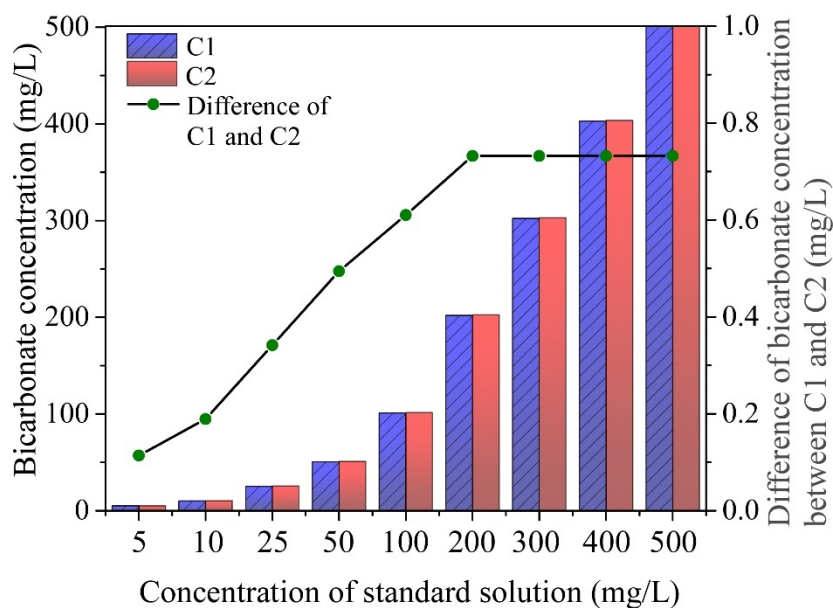


Figure 3 The bicarbonate (HCO_3^-) concentrations for C1 (without the CO_2 reaction) and C2 (with CO_2 reaction) with the difference between C1 and C2 (i.e., C2 minus C1).

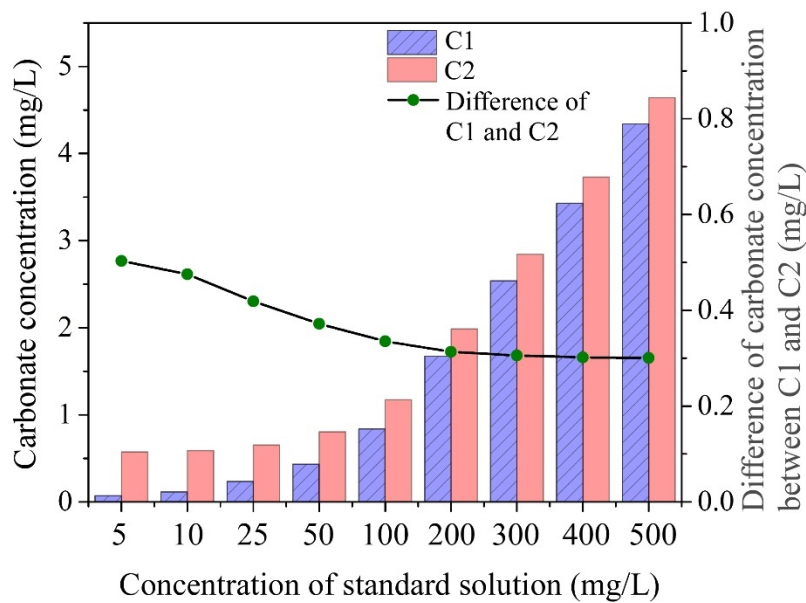


Figure 4 The carbonate (H_2CO_3^*) concentrations in the standard solutions for C1 and C2, and the difference.

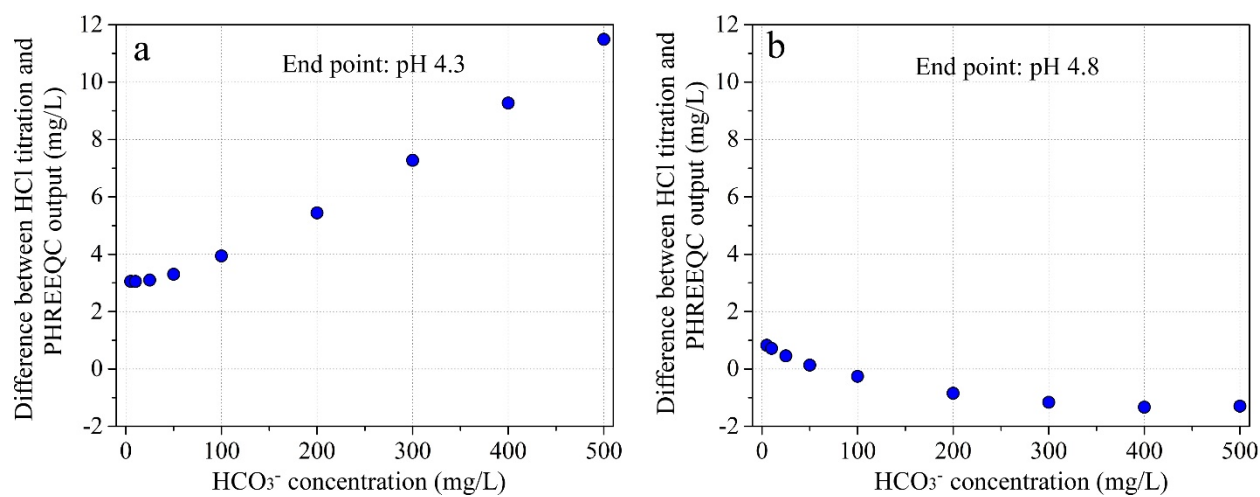


Figure 5 The bicarbonate concentrations between the HCl titration and the PHREEQC output at (a) pH 4.3 and (b) pH 4.8.