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Revised Analytical Methods for the Determination of Carbonic Species in Rain, Ground and Geothermal Waters

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ABSTRACT

The concentration of carbonic species (H_2CO_3, HCO_3^- and CO_3^{2-}) in natural waters is determined by the volumetric acid-base titration. In the case of low concentration carbonic water (e.g. rainwater), the Gran titration method is used. The application and limitations of the Gran titration method are discussed. The Gran titration method is based on locating the linear tendency of Gran functions F_1 to F_6. However, it is impossible to find the linear tendency of functions F_2, F_3, F_5 and F_6. Thus, in the case of rainwater, the Gran titration method is modified using only F_1 and F_4.

The titration methods for ground and geothermal waters are revised. The pH of the equivalence points, H_2CO_3EP, $NaHCO_3$EP, and Na_2CO_3EP depends on the total dissolved carbonic concentration C_T in a solution. Therefore, the location of the equivalence points through the corresponding points of inflexion is suggested. The procedure for groundwater containing only carbonic alkalinity is called here as Method 1.

The titration procedure for geothermal waters, Method 2, used by geochemists is conceptually incorrect. It is shown theoretically that there is an error of 14.59, 14.00, 17.84 and 19.92 % in the determination of carbonic species of pure Na_2CO_3 solutions C_T=0.05, 0.03, 0.01 and 0.005 m, respectively. The backward titration from H_2CO_3EP to the original pH after CO_2 removal, as had been practiced earlier in geothermal industry in order to estimate the contribution of silicic and boric alkalinities to the total alkalinity, is incorrect because the amount of standard base (NaOH) added is equivalent to silicic and boric alkalinities plus some OH^- alkalinity. In a Na_2CO_3 solution the added NaOH is equivalent to OH^- alkalinity only. The backward titration is only needed from the forward titration end point to the H_2CO_3EP in order to correct the total alkalinity for the excess of standard acid (HCl) added during the forward titration. In the case of a Na_2CO_3 solution, the H_2CO_3EP, after removal of CO_2 during the forward titration, is at pH=7, but not at pH=4.5 (3.8) as has been considered in literature. The revised procedure for the determination of carbonic species concentration is presented and illustrated for natural waters.

1. INTRODUCTION

Carbon dioxide (CO_2) plays a fundamental role in governing the geological and environmental processes on the Earth. The distribution of carbonic species (H_2CO_3, HCO_3^- and CO_3^{2-}) in natural waters permits the examination of the CO_2 exchange between atmosphere and waters, the evaluation of the buffering mechanisms and the definition of their acid-base neutralizing capacity, etc. In geothermal systems, the concentration of *CO_2* controls the fluid *pH* and pressure in the reservoir. Similarly, to understand the incrustation of calcite in the geothermal reservoir and production wells during exploitation demands a deep knowledge of CO_2 chemistry at high temperature and pressure. However, the first step in a geochemical modeling of natural processes is to create good quality analytical data.

Verma and Santoyo (2002) performed a statistical analysis of the IAEA interlaboratory calibration data. The overall error in the analytical data for geothermal waters was ±13% and there was no appreciable improvement in the analytical quality in the successive interlaboratory calibrations, which is probably due to the existence of systematic errors in the measurements from some laboratories. They also found some serious problems with sampling and analytical procedures for SiO_2 and HCO_3^-. The distribution of standards at least for SiO_2 and HCO_3^- together with samples is recommended for future interlaboratory programs, which is a common practice in the interlaboratory calibration for isotopic composition of water samples (Parr and Clements 1991). Recently, Verma (2004a) reported the preliminary results on the inconsistency in the titration method used for the determination of H_2CO_3, HCO_3^- and CO_3^{2-} in geothermal waters.

The volumetric acid-base titration is the only reliable method for the determination of carbonic species concentration in natural waters. From an analytical point of view there exist four principle types of natural water: *1.) rainwater containing low concentration of dissolved species and low alkalinity, 2.) ground and surface water which contains mainly carbonic alkalinity, 3.) geothermal water which has carbonic and other alkalinities,* and *4.) petroleum waters which have high concentration of salts and no contact with the present atmospheric CO_2.*

This paper presents the analytical procedures for measuring carbonic species concentration in the first three types of water. The CO_2 chemistry is discussed in brief to illustrate the theoretical aspects of the analytical methods. The application of the methods is elucidated in the case of natural water samples collected in the Los Humeros geothermal field.

2. CO_2 CHEMISTRY

The fundamental concepts on the CO_2 chemistry are well documented in the textbooks on aquatic chemistry (e.g. Stumm and Morgan 1981). Verma (2004b) summarized the mathematics associated with the CO_2-H_2O chemistry in one phase (liquid) or two phases (liquid and vapor) closed and open systems. Here we present the basic aspects of CO_2 chemistry related to the acid-base titration procedures for the determination of bicarbonate and carbonate in different types of water.

In the case of a biprotic acid like H_2CO_3 there are three equivalence points H_2CO_3EP, $NaHCO_3$EP, and Na_2CO_3EP associated with the dissolution of H_2CO_3 (CO_2), $NaHCO_3$, and Na_2CO_3, respectively. Since radicals do not deposit in a free state, the salt of the carbonic species is used here for the representation. Figure 1a shows the variation of the position of the equivalence points with the total dissolved carbonic concentration $C_T=10^{+1}$, 10^{-1}, 10^{-3} and 10^{-5} m in a liquid phase closed system. The following equations among the molar concentration of aqueous species should be satisfied at the respective equivalence points

$$[H^+]=[OH^-]+[HCO_3^-]+2[CO_3^{2-}] \tag{1a}$$

$$[H^+]+[H_2CO_3]=[OH^-]+[CO_3^{2-}] \tag{1b}$$

$$[H^+]+2[H_2CO_3]+[HCO_3^-]=[OH^-] \tag{1c}$$

The position of H_2CO_3EP is at pH=2.65, 3.65, 4.65 and 5.70 for $C_T=10^{+1}$, 10^{-1}, 10^{-3} and 10^{-5} m, respectively. Similarly, the Na_2CO_3EP is located at pH=12.61, 11.60, 10.53 and 9.98. It is clear that the positions of H_2CO_3EP Na_2CO_3EP tend to pH=7 when C_T tends to zero. However, the position of $NaHCO_3EP$ is at pH=8.23, 8.23, 8.23 and 7.64 for $C_T=10^{+1}$, 10^{-1}, 10^{-3} and 10^{-5} m, respectively. Its pH remains constant and then decreases for lower concentration. It can be explained through the equation 1(b) which is approximated to $[H_2CO_3] = [CO_3^{2-}]$ for higher C_T ($>10^{-3.76}$ m); whereas for C_T between $10^{-3.76}$ and 10^{-7} m, it is $[H_2CO_3] = [OH^-]$. Once C_T is lower then 10^{-7}m the equation reduces to $[H^+] = [OH^-]$. It means that the pH of the $NaHCO_3EP$ will be 7 for $C_T<=10^{-7}$ m. Thus, in summary, in a carbonic system, the pH of all the equivalence points tends to 7 when C_T tends to zero.

Figure 1b shows the acid-base titration curves (relationship between pH and added acid-base to the solution) in terms of pH and fraction of titrated equivalent carbonic acid concentration for initial concentration of $C_T=10^{+1}$, 10^{-1}, 10^{-3} and 10^{-5} m. There are two terms to be remembered during a titration: *equivalence point* and *end point*. We are interested in knowing the equivalence points through defining the end points for a particular titration. Sometimes, there may be vast difference between the location of an end point and the respective equivalence point (Verma, 2002). The end points for $NaHCO_3EP$ and H_2CO_3EP are considered at pH=8.25 and 4.5 (or 3.8), respectively in most of analytical procedure manuals (e.g. Giggenbach and Goguel 1989). The fixed pH end points for a titration were considered when dyes were used to locate the end points. Now, we can obtain the whole titration curve with the help of a pH-meter. So, there is no need to consider the fixed pH end points. It can be observed in Figure 1 that the H_2CO_3EP is at pH=2.65, 3.65, 4.65 and 5.70 for $C_T=10^{+1}$, 10^{-1}, 10^{-3} and 10^{-5} m, respectively. Thus, we have to titrate a sample to a pH value depending on the concentration of carbonic species C_T,. However, the C_T value for our samples is unknown beforehand.

The equivalence points are close to the corresponding point of inflexion in the titration curve. Therefore we have to plot the whole titration curve and find out the points of inflection to locate the corresponding equivalence points. The location of any equivalence point is sufficient, if the initial pH value is correctly measured. As we will see later, the measurement of pH is not very accurate for low concentration samples like rainwater. Therefore, it is always better to locate at least two equivalence points.

Verma (2004b) discussed that there is a higher error in the values with a common glass electrode for pH>10. The Na_2CO_3EP is near to pH=10 for $C_T>10^{-3}$m, so there will be a higher analytical error in its location. Therefore, our titration methods are, generally, based on the location of H_2CO_3EP and $NaHCO_3EP$ except for very low C_T.

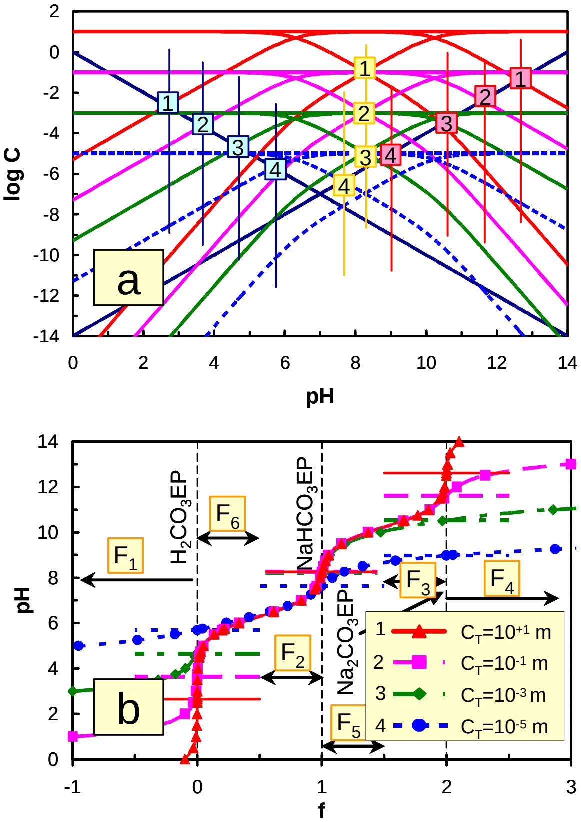


Figure 1: Carbonic system: (a) Chemical speciation as a function of pH at 25°C and 1 bar for $C_T=10^{+1}$, 10^{-1}, 10^{-3} and 10^{-5} m. All the carbonic species for a concentration are shown with the same color (e.g. red for $C_T=10^{+1}$ m). The location of each equivalence point H_2CO_3EP, $NaHCO_3$ and Na_2CO_3EP is numbered 1 to 4 for $C_T=10^{+1}$, 10^{-1}, 10^{-3} and 10^{-5} m, respectively and are shown with a square and vertical line of different colors (e.g. H_2CO_3EP with blue). (b) Titration curves for a carbonic system $C_T=10^{+1}$, 10^{-1}, 10^{-3} and 10^{-5} m. The parameter f represents the equivalent fraction of titrated carbonic acid (Stumm and Morgan 1981). F_1 to F_6 are Gran Function and the region of their validation are shown by arrows.

There is one more point to be emphasized on the appearance of the equivalence points (Figure 1b). The Na_2CO_3EP is not clear in the curves corresponding to $C_T=10^{-3}$ and 10^{-5} m. Similarly, there is no point of inflexion corresponding to the H_2CO_3EP in the curve for $C_T=10^{-5}$ m. Gran (1952) developed a titration procedure for such types of water, when there are no two points of inflexion in an acid-base titration curve. The application and limitations with the Gran titration procedure will be discussed here.

There is another limitation of acid-base titration for measuring bicarbonate and carbonate in the waters which contain other weak acid-bases like silicic and boric acid-base such as geothermal waters. We solve partially this limitation in the revised method for the determination of carbonic species concentration on the basis on initial pH and alkalinity alk with respect to H_2CO_3EP.

3. ANALYTICAL PROCEDURE FOR H_2CO_3, HCO_3^- AND CO_3^{2-} DETERMINATION

The basic CO_2 chemistry aspects discussed in the previous section will be used to improve the titration procedure for the determination of bicarbonate and carbonate in different types of water. We present the theoretical and experimental aspects of revised analytical method for measuring H_2CO_3, HCO_3^- and CO_3^{2-} in geothermal waters together with its limitations.

3.1 Rainwater

Verma et al. (1999) suggested the determination of both pH and alkalinity with respect to H_2CO_3EP in order to characterize and quantify the acidity in rainwater. Acidity in rainwater is thought to be due mostly to sulfuric and nitric acids which are formed with the oxidation of industrial or natural emissions of SO_2 (+H_2S) and NO_x. The dissolution of CO_2 also decreases the pH of rainwater, but it does not account for rainwater acidity.

In the case of carbonic systems the acid neutralizing capacity is termed alkalinity, while the base neutralizing capacity is termed acidity (Stumm and Morgan 1981). The terms alkalinity and acidity refer to how much strong acid or strong base a system is capable of neutralizing, respectively. Both of these terms are defined for certain pertinent equivalence points (EPs) for the system. Acidity is the negative of alkalinity for the same reference EP point. There are three equivalence points called the H_2CO_3EP, $NaHCO_3$EP and Na_2CO_3EP. Therefore, alkalinities alk, alk1 and alk2 are defined with respect to H_2CO_3EP, $NaHCO_3$EP and Na_2CO_3EP respectively as following

$$\text{alk} = [OH^-] - [H^+] + [HCO_3^-] + 2[CO_3^{2-}] \qquad (2a)$$

$$\text{alk1} = [OH^-] - [H^+] - [H_2CO_3] + [CO_3^{2-}] \qquad (2b)$$

$$\text{alk2} = [OH^-] - [H^+] - 2[H_2CO_3] - [HCO_3^-] \qquad (2c)$$

The addition (or removal) of H_2CO_3 (CO_2), $NaHCO_3$ or Na_2CO_3 does not change alk, alk1 or alk2, respectively; whereas the pH of the solution decreases (or increases). Because the rainwater has a very low amount of dissolved carbonic species, the alkalinity in rainwater is measured with the Gran titration method.

Gran (1952) derived 6 functions for a biprotic acid, based on the titration curve behavior of each side of the three equivalence points. Figure 1b shows the validation region for the Gran functions F_1 to F_6.

$$\begin{aligned}
F_1 &\equiv (V_0 + V_a + V_T)10^{-pH} \cong (V_S - V_T)\cdot N_{NaOH}\\
F_2 &\equiv (V_T - V_S)10^{-pH} \cong (V_M - V_T)\cdot K_1\\
F_3 &\equiv (V_T - V_M)10^{-pH} \cong (V_W - V_T)\cdot K_2\\
F_4 &\equiv (V_0 + V_a + V_T)10^{pH} \cong (V_T - V_W)\cdot {}^{N_{NaOH}}\!/_{K_W}\\
F_5 &\equiv (V_W - V_T)10^{pH} \cong (V_T - V_M)/K_1\\
F_6 &\equiv (V_M - V_T)10^{pH} \cong (V_T - V_S)/K_2
\end{aligned} \qquad (3)$$

Where V_0 is initial volume of the sample, V_a is amount of acid (HCl) added initially to the sample; V_S, V_M and V_W are the volume of base (NaOH) needed to reach to H_2CO_3EP, $NaHCO_3$EP and Na_2CO_3EP respectively; V_T is volume of NaOH added in steps noting pH; K_1 and K_2 are the first and second dissociation constants of carbonic acid; K_W is the dissociation constant of water and N_{NaOH} is the normality of standard base NaOH.

Theoretically, it is possible to obtain a linear plot of F_1 to F_6 as a function of V_T, but it is difficult experimentally to get a sufficient number of points in their validation regions for F_2, F_3, F_5 and F_6 (Verma et al 2002). Therefore, we proposed the use of F_1 and F_4 in order to determine the sample alkalinity alk and total dissolved carbonic concentration C_T.

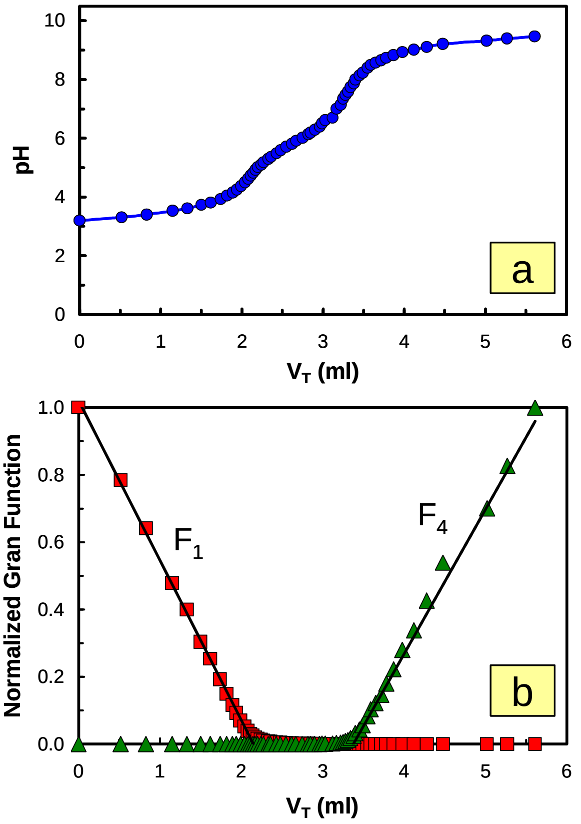


Figure 2: (a) Acid-base titration curve for a rainwater sample collected in the Los Humeros Geothermal field, Mexico. (b). Plot of Gran functions F_1 and F_4 for the titration curve given in Figure (a). The linear tendencies are used to calculate volumes V_S and V_W, which are the intersection of the linear tendencies on the V_T axis.

Table 1: Analytical results of the determination of carbonic species concentration, using Gran titration, in a rainwater sample.

Parameter	Value
pH initial	5.48
V_0(ml)	50
H_2SO_4 (N)	0.00973
V_a (ml)	1.85
V_S from F_1 (ml)	2.15
V_W from F_4 (ml)	3.37
Alk (eq/l)	-1.62E-05
C_T (m)	1.07E-04
pH Calculated	4.72
H_2CO_3 (m)	1.04E-04
HCO_3^- (m)	2.75E-06
CO_3^{2-} (m)	8.74E-12

$$\text{alk} = -\frac{V_S N_{NaOH} - V_a N_{H_2SO_4}}{V_0}$$
$$C_T = \frac{V_W - V_S}{2V_0} \tag{4}$$

Where N_{H2SO4} is the normality of acid (H_2SO_4) added initially to the sample.

The concepts of Gran titration procedure are illustrated through a rainwater sample. We added 1.85 ml of standard H_2SO_4 0.00973 N to 50 ml of the sample in order to get the pH near 3. Then the volume of standard NaOH 0.00875 N was added in step until the titrand pH was near 9.5, noting the pH and volume of added base. Figure 2a shows the titration curve. Using equations 3 the values of F_1 and F_4 were calculated and plotted in Figure 2b.

The linear tendency of the functions provides the following: V_S=2.15 ml and V_W=3.37 ml. Substituting the values of V_S and V_W and the concentration of standard acid and base in equations 4, we calculated the values of alk and C_T. The analytical data are given in Table 1.

The concentration of individual carbonic species is calculated using the following equations

$$\begin{aligned} H_2CO_3 &= C_T \cdot \alpha_0 \\ HCO_3^- &= C_T \cdot \alpha_1 \\ CO_3^{2-} &= C_T \cdot \alpha_2 \end{aligned} \tag{5}$$

Where α_0, α_1 and α_2 represent the fractions of the respective species formed by losing zero, one and two protons, respectively and α's are the only functions of pH at a given temperature (Stumm and Morgan 1981).

Verma et al. (1999) discussed the problem of measuring pH of rainwater. The pH of the rainwater is also calculated with the measured values of alkalinity alk and total dissolved carbonic concentration C_T. In this case, the difference between the measured and calculated values of pH is approximately 1. However, we found the difference of much higher than 1 in many cases. We are working to quantify the analytical error associated in measuring alk and C_T through the Gran titration method. This will be helpful for estimation of uncertainty of the calculated values of pH and carbonic species concentrations.

3.2 Groundwater

The analytical procedure (Method 1) for the determination of bicarbonate and carbonate in ground and surface waters has been well established by chemists and hydrologists since the beginning of the last century (Verma 2004b). Here the method 1 is modified by considering the end points as the points of inflexion corresponding to H_2CO_3EP and $NaHCO_3$EP in the whole titration curve, but the method is conceptually the same as presented by Verma (2004b). Its application will be discussed together with the titration method for geothermal waters.

3.3 Geothermal Water

The geothermal waters contain significantly high concentration of other alkalinities like boric and silicic together with carbonic alkalinity. Therefore, the first titration procedure (Method 1) is modified by geochemists for geothermal waters (Giggenbach and Goguel 1989). We will call it as Method 2. Figure 3 shows the Method 2 in a flow diagram (PNOC 2001).

To understand the limitations of this method let us analyze theoretically the acid-base titration for the given concentration Na_2CO_3 solutions as samples. Figure 4 shows titration curves for C_T=0.05, 0.03, 0.01 and =0.005 m with NaOH 0.1 N and HCl 0.1 N. By adding acid (HCl), the titration is considered forward, while it is backward by the addition of the base (NaOH). The volume of NaOH added to the solution (titrand) is expressed here as the total volume of HCl added minus the equivalent volume of NaOH currently added. For example, let the total volume of HCl added to the titrand for forward titration be 25 ml and the volume of NaOH added during the backward titration at an instant be 1 ml. Then the volume of equivalent HCl is calculated and subtracted from the total HCl added during the forward titration. The volume for the backward titration at the instant is 24 ml ($=V_a - N_{NaOH}/N_{HCl} \times V_b = 25 - 0.1/0.1 \times 1 = 24$ ml). This helps for a better graphical representation of titration curves.

Table 2 gives the values of carbonic species calculated from both methods: 1 and 2. Actually, Method 1 is based on the acid-base titration of a carbonic system; therefore, it provides theoretically consistent values. Since Method 2 is a modification of Method 1 for geothermal waters, it should also work for water samples containing only carbonic species and must provide similar results to that of Method 1.

A pure Na_2CO_3 solution has only carbonate. The Method 2 provides the values of CO_3^{2-} as 42.76, 25.80, 8.22 and 4.00 mil m for the samples containing theoretically CO_3^{2-} as 50.00, 30.00, 10.00 and 5.00 mil m, respectively. According to Method 2, there is HCO_3^- in the samples (Tables 2). However, there is no HCO_3^- in the samples. There is an error of 14.49, 14.00, 17.84 and 19.92% in the determination of CO_3^{2-} in respective samples.

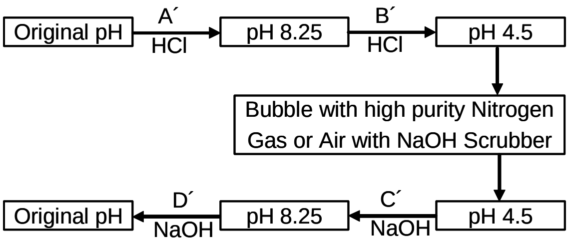
Let us evaluate the reasons for getting inappropriate values through the procedure (Method 2) given in Figure 3, used by the geothermal community. According to Method 2, A' is the amount of acid added to convert CO_3^{2-} to HCO_3^- and B' is the amount of acid added to convert HCO_3^- to H_2CO_3 (Figure 3). Why is it needed to titrate back to original pH after removing all the CO_2 from the titrand? In other words, what is physical-chemical significance of C' and D'? The amount of NaOH added in the backward titration is the value of C´+D´.

The parameters C' and D' for the back titration are considered in literature as equivalent to the alkalinities associated with weak acid-base other than the carbonic alkalinity present in the solution (Giggenbach and Goguel 1989, Arnorsson 2000, PNOC 2001 and others). Actually, there is no other weak acid-base in a Na_2CO_3 solution. It means if we titrate back from pH 4.5 to the original pH, we add OH^- alkalinity to the titrand. Thus considering this OH^- alkalinity to the non-carbonic alkalinity (silicic, boric and others) initially present in the sample (a Na_2CO_3 solution does not have any other non-carbonic alkalinity) is incorrect and produces analytical errors.

When there is no CO_2 and any other weak acid-base in the titrand, all the equivalence points should be at pH=7. It means that there is only need to titrate backward with NaOH to pH=7 in order to get the amount of excess acid added during the forward titration.

Thus, Method 2 used earlier by geochemists to determine HCO_3^- and CO_3^{2-} in geothermal waters is conceptually incorrect and will not be discussed further.

For samples with pH > 8.25



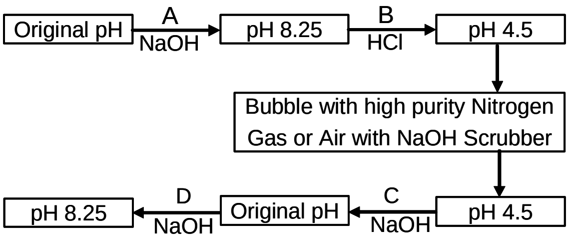
Calculations:

$$HCO_3^-\,(ppm) = \frac{\{(B' - A')\cdot N_{HCl} - (C' - D')\cdot N_{NaOH}\}\cdot 61017}{V_0}$$

$$CO_3^{2-}\,(ppm) = \frac{\{A'\cdot N_{HCl} - D'\cdot N_{NaOH}\}\cdot 60000}{V_0}$$

$$C_T\,(ppm) = \frac{\{B'\cdot N_{HCl} - C'\cdot N_{NaOH}\}\cdot 44010}{V_0}$$

For samples with pH < 8.25



Calculations:

$$HCO_3^-\,(ppm) = \frac{\{B\cdot N_{HCl} - (A + C)\cdot N_{NaOH}\}\cdot 61017}{V_0}$$

$$C_T\,(ppm) = \frac{\{B\cdot N_{HCl} - (C + D)\cdot N_{NaOH}\}\cdot 44010}{V_0}$$

Figure 3: A summary of titration procedure (Method 2), used in literature by geochemists, for the determination of HCO_3^- and CO_3^{2-} in geothermal waters (modified after PNOC, 2001). A, B, C and D and their primes are volume of HCl or NaOH added to the titrand as shown the flow diagrams.

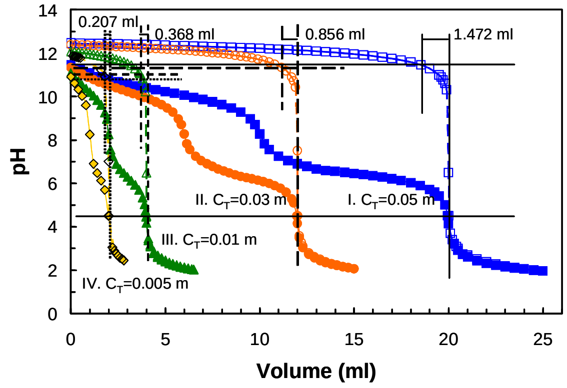


Figure 4: Theoretical titration curves for concentration C_T=0.05, 0.03, 0.01 and 0.005 m. The forward titration curves with HCl 0.01 N are represented by solid curves with filled symbols, while the backward titration curves with NaOH 0.01 N are represented by dashed curves and corresponding unfilled symbols.

Table 2: Theoretical calculation of carbonic species concentration in given concentration solution of Na_2CO_3 using Method 1 and Method 2. The calculations were performed using up to 4 decimal places, but the values are reported only up to 2 decimal places due to the limitation of space.

Parameter	Sample			
	I	II	III	IV
V_0 (ml)	20.00	20.00	20.00	20.00
C_T (m)	0.050	0.030	0.010	0.005
N_{HCl} (N)	0.1	0.1	0.1	0.1
N_{NaOH} (N)	0.1	0.1	0.1	0.1
Vol. HCl for $NaHCO_3$EP (ml)	10.00	6.00	2.00	1.00
pH H_2CO_3EP	4.15	4.15	4.19	4-32
Vol. HCl for pH=4.5 (ml)	19.95	11.96	3.98	1.99
CO_2 Liberation	yes	yes	no	no
Vol NaOH to reach pH from 4.5 to initial pH	1.47	0.86	0.37	0.21
Method 1				
H_2CO_3 (mil m)	0.00	0.00	0.00	0.00
HCO_3^- (mil m)	0.00	0.00	0.00	0.00
CO_3^{2-} (mil m)	50.00	30.00	10.00	5.00
C_T (mil m)	50.00	30.00	10.00	5.00
Method 2				
A´ (ml)	10.01	6.00	2.00	1.00
B´ (ml)	9.94	5.95	1.98	0.99
C´ (ml)	0.02	0.01	0.01	0.01
D´ (ml)	1.46	0.84	0.36	0.20
HCO_3^- (mil m)	6.87	3.91	1.61	0.91
CO_3^{2-} (mil m)	42.76	25.80	8.22	4.00
C_T (mil m)	49.63	29.71	9.83	4.92
Error (%)				
Method 1	0.00	0.00	0.00	0.00
Method 2	14.49	14.00	17.84	19.92

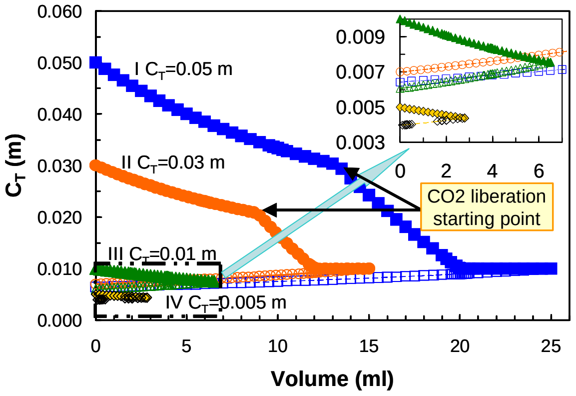


Figure 5: Variation of the total dissolved carbonic concentration during the titration. The liberation of CO_2 during forward titration exists only in the cases of C_T=0.05 and 0.01 m.

Figure 5 shows the variation of C_T with the added volume of HCl during the forward titration and of NaOH during the backward titration, presented by the filled symbol curve for the forward titration and unfilled symbol for the backward titration. C_T decreases due to dilution on adding standards, acid (HCl) and base (NaOH), but the amount of undissociated carbonic acid increases with the addition of HCl.

The initial CO_2 partial pressure of the solution ($p_{CO2(solu)}$) is lower than the atmospheric partial pressure of CO_2 ($p_{CO2(atmos)} = 10^{-3.5}$ atm). So, there may be, theoretically, some inflow of CO_2 in the solution from the atmosphere. It is assumed here that there is insufficient time to get the atmospheric CO_2 into the solution when $p_{CO2(solu)} < p_{CO2(atmos)}$; but when $p_{CO2(solu)} > p_{CO2(atmos)}$, the solution liberates CO_2 to the atmosphere until an equilibrium between the solution and atmospheric CO_2 is reached. It can be observed in Figure 5 that there is a liberation of CO_2 only for C_T=0.05 and =0.03 m. Verma (2004b) presented an extensive study on the liberation of CO_2 during the acid-base titration. He also discussed its effect on the location of $NaHCO_3$EP. A fast titration reduces the liberation of CO_2 to a negligible quantity.

3.3.1 Revised Analytical Procedure

The titration procedure, Method 1, for the determination HCO_3^- and CO_3^{2-} is only applicable for waters containing carbonic alkalinity, while Method 2 is theoretically incorrect. It is unfeasible to determine analytically the contribution of carbonic alkalinity to the alkalinities alk and alk1 in a sample which also contains other alkalinities like silicic and boric. Verma (2004a) observed such difficulties and revealed a revised titration procedure for natural waters containing boric and silicic alkalinities together with carbonic alkalinity like geothermal waters.

It consists of the determination of total alkalinity (alk) with respect to H_2CO_3EP. In the presence of boric and silicic species, alk is expressed as

$$\begin{aligned}\text{alk} &= [OH^-] - [H^+] + [HCO_3^-] + 2[CO_3^{2-}] + \\ &\quad [B(OH)_4^-] + [H_3SiO_4^-] \\ &= [OH^-] - [H^+] + C_T(\alpha_1 + 2\alpha_2) + \\ &\quad C_{TB}(\alpha_{1B}) + C_{TSi}(\alpha_{1Si})\end{aligned} \qquad (6)$$

where square brackets [ ] represent the molal concentration of the species. C_T, C_{TB} and C_{TSi} are the total concentration of carbonic, boric and silicic acids, respectively. Knowing the initial pH, silica (C_{TSi}), boron (C_{TB}) and total alkalinity (alk), the concentration of total dissolved CO_2 (C_T) is calculated through the above equation. With the values of C_T and initial pH, we calculate the concentration of individual carbonic species through equation 5.

This approach should not be used for waters which have initial pH higher than 10, since the measurement of pH through an electrode is not very accurate for water at pH>10. The interference of Na^+ is considerably high for pH>10. An error of ±0.1 in pH produces considerable error in the concentration of carbonate and bicarbonate at pH>10. So, the use of this approach is not recommended for the case of the titration of Na_2CO_3 solution. Natural waters mostly have pH values lower than 10. So, this procedure can be used without producing any significant errors except for rainwater.

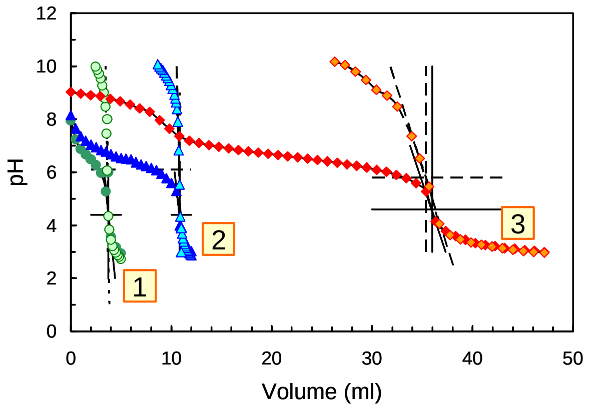


Figure 6: Titration curve for 25 ml of samples 1 and 2 and 20 ml of sample 3. The forward titration was performed with HCl 0.0237 N whereas the backward titration with NaOH 0.0199 N.

Table 3: Chemical analysis of three water samples from a spring, domestic well and lake. The data are reported up to 2 decimal places, but the calculations were conducted using at least 4 decimal places.

	Sample		
Parameter	1	2	3
Type	Spring	Domestic well	Lake
pH Field	8.0	8.2	9.0
pH Lab	7.97	8.12	9.00
Vol. Sample (ml)	25	25	20
Forward			
pH H_2CO_3EP	4.4	4.4	4.6
Vol. H_2CO_3EP	3.75	10.83	35.35
Backward			
pH H_2CO_3EP	6.1	6.1	5.8
Vol. H_2CO_3EP	3.65	10.80	35.94
Aver. Vol HCl (ml)	3.70	10.82	35.65
Alk (meq/l)	3.51	10.25	42.24
Alk Boric (meq/l)	0.0	0.01	0.62
Alk Silicic (meq/l)	0.02	0.03	0.03
Alk Carbonic (meq/l)	3.49	10.21	41.60
CT(mil m)	3.54	10.28	39.48
H_2CO_3 (ppm)	5	9	5
HCO_3^- (ppm)	210	613	2270
CO_3^{2-} (ppm)	1	5	131
Literature Data			
B(ppm)	0	2	18
SiO_2 (ppm)	82	99	12
HCO_3^- (ppm)	230	200	1872
CO_3^{2-} (ppm)			301
Alk Total (meq/l)	4.13	13.3	41.8

3.3.2 Example

The natural waters contain other alkalinities like boric, silicic, etc. together with carbonic alkalinity; therefore, the analytical method described in the previous subsection is appropriate for such types of water. We collected three water samples from: 1.) spring, 2.) domestic well and 3.) lake. In the case of natural water samples, it is not possible to evaluate the quality of analyzed data, since their true values of concentration are unknown. However, we present a comparison study for the carbonic species concentration determined in this study with that reported in the literature.

Figure 6 shows the titration curves for 25 ml of samples 1 and 2 and 20 ml of sample 3 with the HCl 0.0237 N and NaOH 0.0199 N solutions. It requires averages of 3.70, 10.82 and 35.65 ml of HCl to reach the H_2CO_3EP for the samples. Thus, the alkalinity (alk) is 3.51, 10.25 and 42.24, respectively.

Substituting the value of alkalinity (alk), concentrations of boron (C_{TB}) and silica (C_{TSi}) in equation 6, we get the concentration of total dissolved carbonic species C_T of each sample. Then using equation 5, the concentration of individual carbonic species is calculated as given in Table 3.

If we look at the values of alk and HCO_3^-, it can be observed that the values reported in earlier studies are not consistent. The samples 1 and 2 have nearly same values of pH and concentration of B and SiO_2, but the sample 2 has alkalinity of 13.3 meq/l, which is 3 times high than that of sample 1. But both the samples have the same HCO_3^- (even less in the sample 2). This is theoretically incorrect. However, the value of HCO_3^- for sample 2 calculated with the present method is about 3 times higher than that of sample 1, which is theoretically consistent.

The analytical errors in the measurements of boron and silica also contribute to the errors in the measurements of carbonic species according to this method. Verma and Santoyo (2002) discussed the reasons for higher errors in the silica determinations in geothermal waters and suggested that it was a necessity to improve the analysis quality. Similarly, there may be some polymerization of silica at the time of titration. It can also produce some analytical errors. Additionally, the geothermal water samples contain other alkalinities like ammonium and sulfide alkalinities. We are still working on these aspects.

4. CONCLUSIONS

The important contributions of this study on the acid-base titration to determine carbonic species concentration in natural waters are the following:

- It is important to plot the whole titration curve. The equivalence points are near the respective points of inflexion in the curve. The fixed pH end points (equivalence points) produce an analytical error depending on the amount of total dissolved carbonic concentration.

- The use of Gran functions F_1 and F_4 is reliable and sufficient for the determination of carbonic species concentration in rainwater.

- The titration procedure (Method 2) used in the geothermal industry is conceptually incorrect. A theoretical analysis indicates that there is 14 % analytical error in the determination of carbonic species concentration in Na_2CO_3 solution and the error increases with decreased concentration.

- There is a need to locate at least two equivalence points out of three in a biprotic acid-base system.

- The revised method based on the location of one equivalence point and initial pH works well for geothermal waters which have boric and silicic alkalinities together with carbonic alkalinity. There is still need to improve the method for other types of alkalinity.

REFERENCES

Arnorsson, S.: Isotopic and chemical techniques in geothermal exploration, development and use: sampling methods, data handling, interpretation. IAEA, Vienna, (2000).

Giggenbach, W.F., and Goguel, R.L.: Collection and analysis of geothermal water and volcanic water and gas discharges. *Laboratory Manual*, 4th Edition. Department of Scientific and Industrial Research, Petone, New Zealand, (1989).

Gran, G.: Determination of the equivalence point in potentiometric titration, part II, *The Analyst*, (1952).

Parr, R.M., and Clements, S.A.: Intercomparison of enriched stable isotope reference materials for medical and biological studies, *Report*, IAEA, Vienna, (1991).

PNOC (Philippine National Oil Company): Bicarbonate, carbonate and total carbon dioxide, *Laboratory Procedure Manual*, Philippines, (2001).

Stumm, W., and Morgan, J.J.: Aquatic chemistry:- an introduction emphasizing chemical equilibria in natural waters. Wiley, New York, (1981).

Verma, M.P.: A revised analytical method for HCO3- and CO32- determinations in geothermal waters: An assessment of IAGC and IAEA interlaboratory comparisons, *Geostandards and Geoanalytical Research* in press (2004a)

Verma, M.P.: Reactvessl: an ActiveX component in Visual Basic for numerical simulation of H_2O-CO_2 interaction in a geothermal reservoir, This volume (2004b)

Verma, M.P., Quijano, J.L., Johnson, C. Gerardo, J. , and Arellano, V.: Origin of acidity nearby Los Azufres geothermal System, *Geothermics*, (1999).

Verma, M.P., and Santoyo, S.: An assessment of the results of the IAEA interlaboratory comparisons for geothermal water chemistry, *Proceedings*, 27th Workshop on Geothermal Reservoir Engineering. Stanford University, Stanford, CA (2002).

Verma, M.P., Santoyo, S.; Aragón, A., Fernández, Ma.E, Tello, E., Tovar, R., Barrera, V., and Sandoval, F.: Determinación de la alcalinidad y especies carbónicas en la lluvia por el método de titulación de Gran, *Ingeniería Hidráulica en México*, (2002)