

# A New Approach to Carbonate Alkalinity

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### Abstract

The article provides experimental data applied to the determination of carbonate alkalinity (CAM) according to modified Gran II functions. CAM is related to the mixtures NaHCO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> + NaOH. In addition to the determination of equivalence volumes, one of the main novelties of the proposed method is the possibility of determining the activity coefficient of hydrogen ions ( $\gamma$ ). Moreover, CAM can be used to calculate the dissociation constants (K<sub>1</sub>, K<sub>2</sub>) for carbonic acid and the ionic product of water (K<sub>W</sub>) from a single pH titration curve. The parameters of the related functions are calculated according to the least squares method.

## Keywords

Carbonate Alkalinity, pH Titration, Mathematical Modelling

## **1. Introduction**

In the papers [1] [2] published recently, the new approaches to the measurement of total alkalinity (TAL) and carbonate alkalinity (CAM) were presented. In particular, CAM refers to titrimetric analysis of two systems ( $V_0$  mL): NaHCO<sub>3</sub> ( $C_{01}$ ) + Na<sub>2</sub>CO<sub>3</sub> ( $C_{02}$ ) (System I), and Na<sub>2</sub>CO<sub>3</sub> ( $C_{02}$ ) + NaOH ( $C_b$ ) (System II). The results {( $V_j$ , pH<sub>j</sub>) | j = 1, ..., N} obtained from pH titration of the corresponding systems with C mol/L HCl, undertaken under isothermal conditions, are presented according to a modified Gran II method. The CAM concept is fully compatible with the TAL concept, in which other species with acid-base properties are also included.

The equivalence volumes  $V_{eqi}$  (i = 1, 2, 3) referring to the corresponding components in Systems I and II are involved in the following relationships:

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$$\mathbf{C} \cdot \mathbf{V}_{ea1} = \mathbf{C}_{01} \cdot \mathbf{V}_0, \ \mathbf{C} \cdot \mathbf{V}_{ea2} = 2\mathbf{C}_{02} \cdot \mathbf{V}_0 \text{ for System I and}$$
 (1)

$$\mathbf{C} \cdot \mathbf{V}_{ea2} = 2\mathbf{C}_{02} \cdot \mathbf{V}_0, \ \mathbf{C} \cdot \mathbf{V}_{ea3} = \mathbf{C}_b \cdot \mathbf{V}_0 \text{ for System II}$$
 (2)

Subsequently, the carbonate alkalinities (CAM, mmol/L) are calculated from the formulae:  $CAM(I) = 10^3 \cdot (C_{01} + 2C_{02})$  or  $CAM(II) = 10^3 \cdot (2C_{02} + C_b)$ , *i.e.*,

$$CAM(I) = 10^{3} \cdot C(V_{eq1} + V_{eq2}) / V_{0} \quad \text{for System I}$$
(3)

$$CAM(II) = 10^{3} \cdot C(V_{eq2} + V_{eq3}) / V_{0} \text{ for System II}$$
(4)

The present paper provides a new approach to the problem in question. This approach enables equivalence volumes ( $V_{eqi}$ ) to be calculated and the following physicochemical data to be evaluated: dissociation constants ( $K_1$  and  $K_2$ ) of H<sub>2</sub>CO<sub>3</sub>, the ionic product of water ( $K_w$ ), and the activity coefficient ( $\gamma$ ) of hydrogen ions—not only in aqueous media, but also in binary-solvent systems [3]. The functions derived for this purpose have a form similar to those ascribed to Gran II method. The validity of the models proposed was confirmed experimentally by pH titration of synthetic samples referring to Systems I and II.

#### 2. The Gran-Type Functions

The Gran functions applicable for determination of CAM(I) (Equation (3)) and CAM(II) (Equation (4)) are detailed in **Table 1** [2]. The notations applied there are as follows: ph = -logh,  $h = \gamma \cdot [H^+]$  - activity, and  $\gamma$  - the activity coefficient of hydrogen ions;  $K_1^* = \gamma \cdot K_1$ ,  $K_2^* = \gamma \cdot K_2$ ,  $K_W^* = \gamma \cdot K_W$  - hybrid values for  $K_1 =$  $[H^+][HCO_3^-]/[H_2CO_3]$ ,  $K_2 = [H^+][CO_3^{-2}]/[HCO_3^-]$ , and  $K_W = [H^+][OH^-]$ . The pH intervals, in which the corresponding Gran-like functions are valid, are denoted by b, c, d for System I, and by a, b, c, d for System II.

Interval a is not included in System I in **Table 1**; simply because the data  $\{(V_j, pH_j) | j = 1, ..., N\}$  do not cover this pH range in System I. Regarding System II, the experimental points may not cover interval a at lower  $C_b$  values.

The case where  $V_0$  mL of  $C_{02}$  mol/L  $Na_2CO_3$  is titrated with V mL of C mol/L HCl is a particular case of System I (at  $C_{01} = 0$ ) or System II (at  $C_b = 0$ ). Note that the formulae related to Systems I and II are identical in pH intervals d and c (see **Table 1**), but the formulae are different in interval b. However, at  $V_b = V_{eq1} = 0$  and  $V_a = V_{eq3} = 0$ , both formulae are simplified into the following form:

$$V \cdot 10^{ph} = \left(K_2^*\right)^{-1} \cdot \left(V_{eq2}/2 - V\right)$$
(5)

In the data handling step referring to simulated or experimental data  $\{(V_j, pH_j) | j = 1, ..., N\}$ , the Gran functions are applied to the sequences of pH intervals, such as those specified in Table 1. The use of other possible sequences is not advised.

The parameters:

- $V_{eq1}$ ,  $V_{eq2}$ ,  $K_1^*$ ,  $K_2^*$  and  $\gamma$  (and then  $K_1 = K_1^*/\gamma$ ,  $K_2 = K_2^*/\gamma$ ) for the modified Gran functions referring to System I, or
- V<sub>eq2</sub>, V<sub>eq3</sub>, K<sub>1</sub><sup>\*</sup>, K<sub>2</sub><sup>\*</sup> and γ (and then K<sub>1</sub> = K<sub>1</sub><sup>\*</sup>/γ, K<sub>2</sub> = K<sub>2</sub><sup>\*</sup>/γ) for the modified Gran functions referring to System II,

can be found according to the least squares method (LSM) [4] [5] applied to the experimental points:

$$\left\{ \left( V_{j}^{x}, ph_{j}^{x} \right) \middle| j = 1, \cdots, N_{x} \right\}$$

referring separately to particular x intervals: x = b, c, d (System I), or x = a, b, c, d (System II) in **Table 1**, with the set of N<sub>x</sub> points, related to the x-th pH interval. It is worth noting that the ph, referring to activity h of H<sup>+</sup> ions, is measured in experimental titrations. The ph = -logh as variable (not pH =  $-log[H^+]$ ) is involved in all relationships specified in **Table 1**.

### **3. Calculation Procedure**

The functions in Table 1 can be presented in a unified form of the linear regression equation:

Table 1. The Gran functions related to Systems I and II.							
N.	pH interval —	Gran type functions					
NO.		System I	System II				
а	$pH > pK_2 + \Delta$	-	$\left(V_{0}+V\right)\cdot10^{ph}=C/K_{W}^{*}\cdot\left(V_{a}-V\right)$				
b	$pK_2 = \Delta < pH \approx pK_2$	$\left(V_{b}+V\right)\cdot10^{ph}=\left(K_{2}^{*}\right)^{-1}\cdot\left(V_{c}-V\right)$	$\left(V-V_a\right)\cdot 10^{ph} = \left(K_2^*\right)^{-1}\cdot \left(V_b-V\right)$				
с	$pK_1 = \Delta \leq pH \leq pK_1 + \Delta$	$\left(V_{d}-V\right)\cdot10^{-ph}=K_{1}^{*}\cdot\left(V-V_{c}\right)$	$\left(V_{d}-V\right)\cdot 10^{-ph}=K_{1}^{*}\cdot\left(V-V\right)_{c}$				
d	$pH < pK_1 - \Delta$	$(V_0 + V) \cdot 10^{-ph} = \gamma \cdot C \cdot (V - V_d)$	$\left(V_{0}+V\right)\cdot 10^{-ph}=\gamma\cdot C\cdot \left(V-V_{d}\right)$				
Sequence of operations		$d \rightarrow c$ and $b$	$d \rightarrow c \text{ and } b, a$				
Relationships		$\begin{aligned} \mathbf{V}_{d} &= \mathbf{V}_{eq1} + \mathbf{V}_{eq2} \\ \mathbf{V}_{c} &= \mathbf{V}_{eq2}/2 \\ \mathbf{V}_{b} &= \mathbf{V}_{eq1} \end{aligned}$	$\begin{split} \mathbf{V}_{d} &= \mathbf{V}_{eq2} + \mathbf{V}_{eq3} \\ \mathbf{V}_{c} &= \mathbf{V}_{b} = \mathbf{V}_{eq2}/2 + \mathbf{V}_{eq3} \\ \mathbf{V}_{a} &= \mathbf{V}_{eq3} \end{split}$				

$$y_{j}^{x} = A_{x} \cdot V_{j}^{x} + B_{x} + \varepsilon_{j}^{x} \quad (j = 1, \dots, N_{x}; x = a, b, c, d)$$
(6)

Subsequently, applying LSM to the sum of squares

$$SS(x) = \sum_{j=1}^{N_x} \left( \varepsilon_j^x \right)^2 \tag{7}$$

where *j* refers to the points  $\{(V_j^x, ph_j^x) | j = 1, \dots, N_x\}$  related to x-th subset (x = a, b, c, d), we obtain the formulae:

$$A_{x} = \frac{N_{x} \cdot \sum_{x} V_{j}^{x} y_{j}^{x} - \sum_{x} V_{j}^{x} \cdot \sum_{x} y_{j}^{x}}{N_{x} \cdot \sum_{x} \left(V_{j}^{x}\right)^{2} - \left(\sum_{x} V_{j}^{x}\right)^{2}}, \quad B_{x} = \frac{\sum_{x} \left(V_{j}^{x}\right)^{2} \cdot \sum_{x} y_{j}^{x} - \sum_{x} V_{j}^{x} \cdot \sum_{x} V_{j}^{x} y_{j}^{x}}{N_{x} \cdot \sum_{x} \left(V_{j}^{x}\right)^{2} - \left(\sum_{x} V_{j}^{x}\right)^{2}}$$
(8)

where the sum  $\Sigma_x$  covers the points taken from the x-th interval,  $V_j^x$  is the j-th V-value taken from the x-th interval.

As stated above, calculation of the parameters is possible in a defined sequence of operations. For example, the sequence  $d \rightarrow c$  applied in **Table 1** for System I means that  $V_d$  value, obtained according to LSM for the data  $\{(V_j^d, ph_j^d) | j = 1, \dots, N_d\}$  composing the subset of the points taken from interval d (Figure 1), is inserted on the left side of the relationship referring to interval c and LSM is applied to the data

 $\{(V_j^c, ph_j^c)| j = 1, \dots, N_c\}$  taken from interval c; in this way, the V<sub>c</sub> value is obtained. From V<sub>d</sub> and V<sub>c</sub>, one can calculate:

$$V_{eq1} = V_d - 2V_c = 2 \cdot \frac{B_c}{A_c} - \frac{B_d}{A_d} \quad \text{and} \quad V_{eq2} = 2 \cdot \frac{B_c}{A_c} \quad \text{for System I (Table 1)}$$
(9)

$$V_{eq2} = 2 \cdot \left(V_d - V_c\right) = 2 \cdot \left(\frac{B_c}{A_c} - \frac{B_d}{A_d}\right) \text{ and } V_{eq3} = \frac{B_d}{A_b} - 2 \cdot \frac{B_c}{A_c} \text{ for System II (Table 1)}$$
(10)

Moreover, we obtain:

$$\gamma = \frac{A_d}{C}, \quad pK_1^* = -\log A_c, \quad pK_1 = \log \frac{A_d}{A_c} - \log C \quad \text{for Systems I and II (Table 1)}$$
(11)

From **Table 1**, System I, no. b, for the point  $(V_j^b, ph_j^b)$  we get



**Figure 1.** Plots related to NaHCO<sub>3</sub> (C<sub>1</sub>) + Na<sub>2</sub>CO<sub>3</sub> (C<sub>2</sub>) system: y (**Table 1**, System I) vs V relationships in (a) d interval; (b) c interval; (c)  $pK_2^*$  vs. V, and (d)  $pK_2^*$  vs. ph plots.

$$pK_{2j}^{*} = ph_{j}^{b} + \log \frac{V_{b} + V_{j}^{b}}{V_{c} - V_{j}^{b}} = ph_{j}^{b} + \log \frac{V_{eq1} + V_{j}^{b}}{V_{eq2}/2 - V_{j}^{b}}$$
(12)

where  $V_{eq1}$  and  $V_{eq2}$  are expressed by Equation (1). Similarly, from Table 1, System II, no. b and a, we get

$$pK_{2j}^{*} = ph_{j}^{b} + \log \frac{V_{j}^{b} - V_{a}}{V_{b} - V_{j}^{b}} = ph_{j}^{b} + \log \frac{V_{j}^{b} - V_{eq3}}{V_{eq2}/2 + V_{eq3} - V_{j}^{b}}$$
(13)

$$pK_{Wj}^{*} = ph_{j}^{a} + \log \frac{V_{0} + V_{j}^{a}}{V_{a} - V_{j}^{a}} - \log C = ph_{j}^{a} + \log \frac{V_{0} + V_{j}^{a}}{V_{eq3} - V_{j}^{a}} - \log C$$
(14)

respectively, where  $V_{eq2}$  and  $V_{eq3}$  are expressed by Equation (2). On the basis of Equation (5), we obtain the relationship:

$$pK_{2j}^{*} = ph_{j}^{b} + \log \frac{V_{j}^{b}}{V_{eq2}/2 - V_{j}^{b}}$$
(15)

We then calculate:

$$pK_2^* = \frac{1}{N_b} \cdot \sum_{j=1}^{N_b} pK_{2j}^*$$
 and  $pK_2 = pK_2^* + \log\gamma$  (16)

$$pK_{W}^{*} = \frac{1}{N_{a}} \cdot \sum_{j=1}^{N_{a}} pK_{Wj}^{*} \text{ and } pK_{W} = pK_{W}^{*} + \log\gamma$$
(17)

and

$$pK_1 = pK_1^* + \log\gamma \tag{18}$$

where  $\gamma$  is defined in Equation (11). The nearly constant ionic strength value, required during the titration, can be secured by the addition of a basal electrolyte on the stage of D and T preparation.

As revealed from Equations (3), (4), it is necessary to know the sum of equivalence volumes:  $V_{eq1} + V_{eq2}$  or  $V_{eq2} + V_{eq3}$ , to calculate CAM(I) or CAM(II) value. However, determination of  $V_{eqi}$  values (i = 1, 2 or 2, 3) from a single pH titration curve is also possible.

#### 4. Experimental Part

#### 4.1. Apparatus and Solutions

The pH titrations were carried out in a 30 mL thermostated, self-made measuring cell, equipped with magnetic stirrer and PT 1000 temperature sensor. The pH measurements and titrations were taken at 22°C with a Cerko Lab System microtitrator, equipped with 5 mL syringe pump, 3-way valve, and pH electrode (Hydromet, type ERH-13-6). The electrode was standardized with aqueous standard buffers of pH 5.00, 7.00 and 10.00, purchased from the Chempur Company. When not in use, the electrode was stored in 3 mol/L KCl solution. Titrant was added into  $V_0 = 4.00$  mL of D stepwise, in aliquots of 0.01 mL, with 6-8-sec. pauses, and the experimental points  $\{(V_i, ph_j) | j = 1, \dots, N\}$  were recorded.

The reagents: HCl, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, NaOH of p.a. grade, purchased from Chempur Company, were used for the preparation of stock and diluted solutions in doubly distilled (freshly prepared, with conductivity of approx. 0.18  $\mu$ S/cm) water. Stock solution of hydrochloric acid (HCl) as T, was standardized against Na<sub>2</sub>CO<sub>3</sub>, obtained after prior calcination (220°C, 5 hrs) of commercial disodium carbonate. The NaOH solution was standardized against potassium hydrogen phthalate (p.a., from Merck). Methanol (p.a. grade, 99.5%, supplied by POCH S.A.) was applied for titrations made in binary-solvent media.

Stock titrands were prepared by dilution of weighed portions of  $Na_2CO_3$  and  $NaHCO_3$  in water, or by addition of a weighed portion of  $Na_2CO_3$  into a standardized NaOH solution. In other titrations, mixed solvent was prepared from appropriate volumes of water and CH<sub>3</sub>OH, and cooled before preparation of HCl and  $Na_2CO_3$  solutions. The HCl solution (10% v/v CH<sub>3</sub>OH) was standardized as described previously. Concentrations of HCl, NaHCO<sub>3</sub>,  $Na_2CO_3$  and NaOH in the corresponding solutions are specified below.

#### 4.2. Results and Discussion

The approach was applied first to the results of titrations of Systems I and II, with HCl solution as the titrant, T. Titration in System I was carried out at pre-assumed values ( $V_0$ ,  $C_{01}$ ,  $C_{02}$ , C) = (4.000, 0.01012, 0.02011, 0.10078);  $V_{eq1} = 0.01012 \cdot 4/0.10078 = 0.4017$ ;  $V_{eq2} = 2 \cdot 0.02011 \cdot 4/0.10078 = 1.5963$ . The results of exemplary titration are graphically presented in **Figure 1**. The data obtained for  $V_d = 2.0122$ ,  $V_c = 0.8017$  (**Figure 1(a**), **Figure 1(b**)) are in good agreement with the expected values: 1.9980 and 0.7982 (see **Table 2**). Moreover, we get here:  $\gamma = 0.9283$  and  $pK_1^* = 6.379$ . The p $K_{2j}^*$  values, calculated on the basis of Equation (13), are plotted in **Figure 1(c**), **Figure 1(d**), with V and ph as the variables on the abscissa, respectively. Some discrepancies in  $V_{eq1}$  value can result from the poor knowledge of NaHCO<sub>3</sub> concentration, which is not a primary standard.

Titration in System II was carried out at pre-assumed values ( $V_0$ ,  $C_{02}$ ,  $C_b$ , C) = (4.000, 0.0200, 0.0209,

0.10078). The results obtained from repeated titrations are detailed in **Table 3**; 2·0.0200·4/0.10078 = 1.5876 and 0.0209·4/0.10078 = 0.08295 are the expected values for  $V_{eq2}$  and  $V_{eq3}$ , respectively. Exemplary data are plotted in **Figure 2**. As can be seen, the sum  $V_d = V_{eq2} + V_{eq3}$  is very well reproducible in repeated titrations and is in good agreement with the expected value of 2.4171 (**Figure 2(a)**). The values for  $V_{eq2}$  are slightly smaller than 1.5876, while the values for  $V_{eq3}$  are slightly greater than 0.08295. The repeatability of values for  $\gamma$  and  $pK_1^*$  is lower. The  $pK_{Wj}^*$  (**Figure 2(c)**) and  $pK_{2j}^*$  (**Figure 2(d)**) values vary regularly (not stochastically) from point-to-point, although the range of ph values covered by the points close to ph  $\approx$  pK<sub>2</sub> = 10.1 is narrow (but in a wider pK range than in **Figure 1(c)**, **Figure 1(d)**); also  $pK_1^*$  (and  $pK_1 = pK_1^* + \log\gamma$  values are close to 6.3). The  $pK_{Wj}^*$  values are distinctly higher than 14.0; this may be ascribed to the non-linear characteristics of the glass electrode in alkaline media. Smaller  $pK_{Wj}^*$  values at lower ph support this opinion.

Another option for System II is also possible *a priori* and starts from equation a in **Table 1** (System II) and finds  $V_a (=V_{eq3})$  and  $K_w^*$  on the basis of the points  $\{(V_j^a, ph_j^a) | j = 1, \dots, N_a\}$ . The  $V_a$  value is then inserted in equation b in **Table 1** (System II) and  $V_b (=V_{eq2}/2 + V_{eq3})$  and  $K_2^*$  values are determined on the basis of the



Figure 2. Plots related to Na<sub>2</sub>CO<sub>3</sub> (C<sub>2</sub>) + NaOH (C<sub>b</sub>) system: y (Table 3) vs. V relationships in (a) d interval; (b) c interval; (c)  $pK_W^*$  vs. V, (d)  $pK_2^*$  vs. V plots.

points  $\{(V_j^b, ph_j^b)| j = 1, \dots, N_b\}$ . The  $V_{eq2}$  (= 2( $V_b - V_a$ )) and  $V_{eq3}$  values can be compared with those obtained on the basis of the experimental points in intervals d and c. This procedure could be regarded as a kind of internal validation of the results. However, it should be borne in mind that the results of ph measurements obtained in alkaline media could be loaded by systematic error resulting from the alkaline error of the glass electrode. The errors involved with ph measurements in the a range affect the  $V_a$  value, subsequently applied in the ( $V - V_a$ )·10<sup>ph</sup> vs. V relationship related to interval b; an improper  $V_a$  value causes this relationship to be a nonlinear one. Therefore, it is advisable to use the experimental points from interval b (for System I) or from intervals a and b (for System II) only for the determination of the related equilibrium parameters, see Equations (12)-(18).

On the basis of known values for  $V_d$  found in interval d for Systems I and II (see **Table 1**), the alkalinities: CAM(I) (Equation (3)), and CAM(II) (Equation (4)) can be calculated; obtaining:

 $CAM(I) = 0.10078 \cdot 2.0122/4 = 0.0507$  (from Table 2, no. 1),

CAM(II) = 0.10078.2.4123/4 = 0.0608 (from Table 3, no. 3).

#### **5. Final Comments**

This article provides the new consistent formulation for alkalinities referring to  $NaHCO_3 + Na_2CO_3$  (System I) and  $Na_2CO_3 + NaOH$  (System II) solutions, titrated with HCl. The related formulae, specified in **Table 2**, are valid in defined pH intervals, denoted as b, c, d or a, b, c, d. The approach based on these new formulae has been called "carbonate alkalinity in a modified version" (CAM). All the formulae are closely relevant to the recently formulated total alkalinity (TAL) [1] [2]. The formulae for CAM are valid within defined pH ranges, in which the relationships between variables are expressed by the functions specified in **Table 1**.

The CAM approach enables equivalence volumes to be calculated, as well as the following physicochemical data: the activity coefficient ( $\gamma$ ) of hydrogen ions; the hybrid values for dissociation constants:  $K_1^*$ ,  $K_2^*$  for H<sub>2</sub>CO<sub>3</sub>, and  $K_W^*$  for the ionic product of water. One of the main novelties of the method is the possibility of determining  $\gamma$ . Moreover, the common equilibrium constants: K<sub>1</sub>, K<sub>2</sub> and K<sub>w</sub> are also calculated. The possibility of calculating  $\gamma$  is also inherent in the TAL method [1] [2]. Another interesting option is the determination of the related parameters in binary solvent media [6].

The pH-intervals assumed for calculation of the analytical and physicochemical data are confined (see [2], p. 229) in comparison with the ones pre-assumed with use of the  $\Delta = 1.9$  value. The narrowing of the pH-range taken for calculations results from the scale of (C<sub>01</sub>, C<sub>02</sub>, C) or (C<sub>02</sub>, C<sub>03</sub>, C) values applied in the experiments.

The procedure applied here can also be extended to salts other than carbonates. To extend the pH range covered by pH titration, it is suggested that the option involving the addition of a pre-dose is used [2]. When weak acid is considered, the strong base solution can be used as titrant or, after addition of the base as the pre-dose, the mixture can be titrated with a strong acid, as above.

The CAM method was tested experimentally. The results for the dissociation constants of  $H_2CO_3$  are close to those found in literature [7]. The values for  $\gamma$  are more scattered.

This article attempts to provide an introductory step for further studies about the determination of alkalinity

Table 2. Results obtained from repeated fitrations made in System I.							
No.	$V_d$	Vc	$V_{eql}$	$V_{eq2}$	γ	$pK_1^*$	$pK_1$
1	2.0122	0.8017	0.4088	1.6034	0.928	6.379	6.351
2	2.0152	0.8043	0.4066	1.6086	0.874	6.427	6.369
3	2.0167	0.8046	0.4075	1.6092	0.891	6.453	6.403
Table 3. Results obtained from repeated titrations made in System II.							
						*	

able 5. Results obtained nom repeated thrations made in System 11.							
No.	$\mathbf{V}_{d} = \mathbf{V}_{eq2} + \mathbf{V}_{eq3}$	$V_{eq2}$	$V_{eq3}$	γ	$pK_1^*$	$pK_1$	
1	2.4096	1.5729	0.8367	0.8438	6.421	6.347	
2	2.4105	1.5703	0.8402	0.7978	6.459	6.361	
3	2.4123	1.5789	0.8334	0.7635	6.467	6.350	

according to the proposed TAL method [1] [2] for examination of natural, municipal and industrial waters, carbonated soft drinks and wines, as well as different biological systems.

The CAM presented here completes the list of modifications of the Gran methods presented in previously published articles [8]-[12], referring to different areas of titrimetric analysis.

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#### **Symbols Used**

CAM—carbonate alkalinity [mmol/L] in modified version; D—titrand (solution titrated);  $\gamma = h/[H^+]$ —activity coefficient for H<sup>+</sup> ions; h—activity of H<sup>+</sup> ions; LSM—least squares method; pH = -log[H<sup>+</sup>]; ph = -logh; T—titrant; TAL—total alkalinity; V—volume [mL] of T; V<sub>0</sub>—volume [mL] of D; V<sub>eqi</sub>—volume [mL] of titrant, referring to the equivalence point (V<sub>eqi</sub>, pH<sub>eqi</sub>); [X]—concentration [mol/L] of the species X. Scientific Research Publishing (SCIRP) is one of the largest Open Access journal publishers. It is currently publishing more than 200 open access, online, peer-reviewed journals covering a wide range of academic disciplines. SCIRP serves the worldwide academic communities and contributes to the progress and application of science with its publication.

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