



Accurate approach for determining fresh-water carbonate (H_2CO_3^*) alkalinity, using a single H_3PO_4 titration point

Liat Birnhack, Sara Sabach, Ori Lahav*

Faculty of Civil and Environmental Engineering, Technion, Haifa 32000, Israel

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ABSTRACT

A new, simple and accurate method is introduced for determining H_2CO_3^* alkalinity in fresh waters dominated by the carbonate weak-acid system. The method relies on a single H_3PO_4 dosage and two pH readings (acidic pH value target: $\text{pH} \sim 4.0$). The computation algorithm is based on the concept that the overall alkalinity mass of a solution does not change upon the addition of a non-proton-accepting species. The accuracy of the new method was assessed batch-wise with both synthetic and actual tap waters and the results were compared to those obtained from two widely used alkalinity analysis methods (titration to $\text{pH} \sim 4.5$ and the Gran titration method). The experimental results, which were deliberately obtained with simple laboratory equipment (glass buret, general-purpose pH electrode, magnetic stirrer) proved the method to be as accurate as the conventional methods at a wide range of alkalinity values ($20\text{--}400 \text{ mg L}^{-1}$ as CaCO_3). Analysis of the relative error attained in the proposed method as a function of the target (acidic) pH showed that at the range $4.0 < \text{pH} < 4.5$ the error was minimal. A suggested experimental setup for continuous alkalinity measurement is also described.

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1. Introduction

Determination of acid-base characteristics of aqueous solutions typically involves pH and alkalinity measurements. Alkalinity analysis is exceptionally common in all aquatic-related scientific and engineering branches. The term alkalinity is defined as the proton accepting capacity of a solution relative to a predetermined reference species, i.e. the mass (in equivalent units) of H^+ ions titrated to a solution until the pH reaches a given reference pH point (termed “equivalence point”). The term alkalinity can be alternatively defined as the mass of OH^- ions added to an aqueous solution which is at the equivalence point (prior to the addition of OH^-). Accordingly, when strong base (e.g. NaOH) is dosed to an equivalent H_2CO_3^* solution, the following proton balance equation can be defined [1]

$$[\text{Na}^+] + [\text{H}^+] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] \quad (1)$$

where [] stands for analytical concentration (mol L^{-1}) rather than activity.

Since the dosed NaOH mass is known, the alkalinity concentration with H_2CO_3^* as a reference species (denoted ‘Alk H_2CO_3^* ’ or simply ‘alkalinity’ in the current paper), has to be identical to the Na^+ concentration added to the water (since following base dosage the mass of H^+ that can be titrated to the solution to

re-attain the H_2CO_3^* equivalence point is equal to the equivalent mass of strong base that was dosed). Accordingly, the well-known alkalinity term can be derived from Eq. (1)

$$\text{Alk}(\text{H}_2\text{CO}_3^*) = \text{alkalinity} = [\text{Na}^+] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+] \quad (2)$$

where alkalinity is expressed in equivalent units (N or eq L^{-1}).

Other alkalinity terms (i.e. alkalinity with respect to other reference species) can be defined in a similar manner. For example, in case H_3PO_4 equivalent solution is titrated with a strong base (e.g. NaOH), the mathematical alkalinity term (in this case with H_3PO_4 as reference species), is defined as follows:

$$\text{Alk}(\text{H}_3\text{PO}_4) = 3[\text{PO}_4^{3-}] + 2[\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{OH}^-] - [\text{H}^+] \quad (3)$$

Likewise, when a solution contains more than one weak-acid system, the corresponding alkalinity term is defined with respect to one reference species from each system. This principle is exemplified in the development of the alkalinity measurement technique described in this paper.

Two batch-type titration methods (titration to $\text{pH} \sim 4.5$ and the Gran titration method) are in wide use, to-date, to measure alkalinity concentrations in the laboratory. Since these methods cannot be easily adapted for continuous measurements, different methods have been developed to determine alkalinity in a continuous fashion; however, each of these methods suffers from certain shortcomings (see elaboration in the following sections), making for an incentive for developing a new, simple, precise and

* Corresponding author. Tel.: +972 4 8292191; fax: +972 4 8228898.
E-mail address: agori@tx.technion.ac.il (O. Lahav).

accurate method which could be used for batch and continuous alkalinity analysis, alike.

This paper presents a new method for fresh water alkalinity determination (in which the carbonate weak-acid system dominates), which is based on a single acid dosage and two pH readings: the original pH of the sample (denoted pH_0) and the pH attained after acidification with a known mass of concentrated H_3PO_4 solution to a pH value close to pH 4 (denoted pH_x). The two pH measured values, along with the known mass of dosed acid are used to accurately calculate the total inorganic carbon concentration (C_T , defined as the sum of the molar concentrations of H_2CO_3^* , HCO_3^- and CO_3^{2-}) and thereby to determine the H_2CO_3^* alkalinity concentration.

The following sections describe the advantages and disadvantages of the commonly-applied alkalinity laboratory batch and continuous on-line measurement methods. This brief literature review was included in order to justify the need for a new method, and to distinguish the suggested technique from the currently practiced methods.

1.1. Standard alkalinity analysis based on strong acid titration to $\text{pH} \sim 4.5$

The most common technique for H_2CO_3^* alkalinity determination is based on strong acid titration to $\text{pH} \sim 4.5$, using either a pH meter or a changing-color indicator [2]. The indicators used are weak acids which change or acquire coloration upon conversion from the protonated to the un-protonated form (or vice versa) [3]. The change in indicator color is usually within $+/-1$ pH unit of the corresponding pK_a -value. This technique (either when it is based on pH reading or on color alteration) suffers from two drawbacks: the first and more significant of which relates to the fact that the location of the H_2CO_3^* equivalence point can be as much as half a pH unit away from the target titration endpoint, within the typical C_T concentration range encountered in natural waters (the higher the C_T , the more acidic is the location of the equivalence point – see [1]). As a result, for water with a high C_T concentration (e.g. $> 500 \text{ mg L}^{-1}$ as CaCO_3), titration to pH 4.5 does not serve to neutralize all the proton accepting carbonate species and the alkalinity value is under-estimated, whereas in the case of low C_T (e.g. $< 50 \text{ mg L}^{-1}$ as CaCO_3), the neutralization of the acid by reaction with bicarbonate and carbonate is completed at a pH higher than 4.5, hence titrating to pH 4.5 results in overestimation of the alkalinity value. The second (less essential) disadvantage is associated with the predisposition of CO_2 to be stripped to the atmosphere during the titration procedure. CO_2 volatilization does not affect the alkalinity value directly (CO_2 is not a proton accepting species (Eq. (2)), but it reduces C_T and acidity concentrations, thereby increasing pH. The rise in pH is then compensated by the analyst by increasing the dosed acid volume, leading to over-estimation of the true alkalinity value. The common solution to this problem is to perform the titration while stirring the sample slowly, to minimize CO_2 stripping. While this procedure manages to reduce the error, it makes the analysis somewhat cumbersome. Another option is to perform the titration using a (almost) sealed beaker.

The Gran method [4], described below, was developed in order to bypass the lack of knowledge regarding the precise location of the equivalence point.

1.2. The Gran titration method

The Gran titration method [4] is widely used for determining H_2CO_3^* alkalinity (as well as other forms of alkalinity), particularly in the context of seawater, but also for fresh waters and wastewater streams. The method is based on titration to several (three

to four) pH points that are more acidic than the presumed location of the equivalence point (commonly for H_2CO_3^* this term is translated into titration to between pH 4.0 and pH 3.5). At such low pH values the concentrations of CO_3^{2-} , HCO_3^- and OH^- may be considered negligible compared to the H^+ concentration (see Eq. (2)) and the precise volume of acid required to attain the equivalence point is obtained from extrapolation of the titration data obtained in this pH range. The Gran method is perceived more accurate than the $\text{pH} \sim 4.5$ titration method particularly for low alkalinity waters, since (1) alkalinity is calculated with respect to the exact equivalence point (rather than to an arbitrary pH value which may be close or not to the true equivalence point) while precise knowledge regarding the exact location of the equivalence point is not required; and (2) since at the measured pH range the carbonate system is composed predominantly of $\text{CO}_2(\text{aq})$, pH readings are only minimally (if at all) affected by carbon dioxide stripping and C_T drop during the titration.

However, one inherent inaccuracy of the Gran method stems from neglecting the CO_3^{2-} and HCO_3^- concentrations in the algorithm, at high C_T values [5]. When C_T is high (e.g. $10^{-2.5} \text{ mol L}^{-1}$), recording the first titration point at a “too high” pH value (pH 3.90, for example), might, per this example, leads to $\sim 10\%$ error. In parallel, if the choice of titration points is too far below the equivalence point (i.e. overly acidic points), an error may occur due to a too large H_2O buffering capacity, which, may demand more H^+ mass than the carbonate system itself. It emanates from these two points that a rough estimation regarding the location of the equivalence point is essential, since such knowledge allows the analyst to choose the appropriate titration pH range for a given sample, which will lead to a minimal error [5].

1.3. Continuous alkalinity measurements

The Gran method, being a multiple-titration-point method, and the direct method, being a titration to a specific pH value, cannot be readily applied for continuous alkalinity measurement. Four alternative methods have been hitherto proposed for this purpose:

1.3.1. Photometric method

This method's principle is to reduce the sample's pH to 4.3 by mixing it at a predetermined ratio with a strong acid (typically HCl), in which a colorimetric pH indicator is immersed. The acidified solution is then analyzed by light absorbance to determine the ratio between the absorbance of the protonated and un-protonated forms of the indicator. The main drawback appears to be high equipment costs (relative to simple titration apparatus) and relatively low accuracy of $\pm 5\%$ [3].

1.3.2. Mid infrared spectroscopy

This method is based on the fact that each compound has a unique absorbance pattern in terms of band shape and band position in the infrared absorption spectrum. Comparing a sample spectrum with the reference spectra and using Beer–Lambert's law it is possible to calculate the alkalinity of the sample. Advantages include (a) no demand for chemicals and low maintenance; and (b) accurate and reliable results outside the calibration range [6]. Drawbacks include (a) expensive equipment; (b) collection of reference spectra, a crucial step in the analysis, is time consuming; and (c) the method requires sample filtration in order to remove any suspended solids that might absorb or scatter the light and interfere with the measurement. It is noted that Steyer et al. [6] focused their work on monitoring of anaerobic digesters, in which the most important parameter is

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