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

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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: pH~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 pH~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 (20–400 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 $4.0 < pH < 4.5$ 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]

$$[Na^+] + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] \qquad (1)$$

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)

$$Alk(H_2CO_3^*) = alkalinity = [Na^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] \qquad (2)$$

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:

$$Alk(H_3PO_4) = 3[PO_4^{3-}] + 2[HPO_4^{2-}] + [H_2PO_4^-] + [OH^-] - [H^+] \qquad (3)$$

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 pH~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

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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 $pH \sim 4.5$

The most common technique for $H_2CO_3^*$ alkalinity determination is based on strong acid titration to $pH \sim 4.5$, 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 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 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 $H_2CO_3^*_{alk}$ 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 $pH \sim 4.5$ 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 $CO_{2(aq)}$, 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. $10^{-2.5}$ 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 apparati) 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

the sum of the short chain volatile fatty acids concentration (VFA) – the accuracy of the mid infrared spectroscopy approach for this purpose was indeed satisfactory, i.e. ± 10–20 mg L^{-1} as CH$_3$COOH, but from the pure alkalinity accuracy standpoint, and in comparison with alternative alkalinity measurement methods, this method cannot be considered very accurate.

1.3.3. Sample acidification and subsequent measurement of CO$_{2(g)}$ volume emitted

The method consists of bubbling CO$_{2(g)}$ to the sample until saturation is reached, followed by acid addition for converting HCO$_3^-$ to the H$_2$CO$_3^*$ species. Finally, the original HCO$_3^-$ concentration of the sample is calculated according to the measured CO$_{2(g)}$ emitted volume. An accuracy of $\pm 5\%$ was reported using this technique [6]. Advantages include (a) relatively inexpensive method and (b) does not rely on pH measurement, thus the problem of probes fouling (frequently encountered in wastewater measurements) is avoided, as well as the need for routine calibration. Drawbacks include [7] (a) dependence on aqueous-gaseous processes makes the method time dependent and cumbersome, relative to methods that rely solely on aqueous equilibrium, which leads to less accurate results; (b) the method is based on several assumptions that result in inherent inaccuracies (see [7]) and (c) response time is relatively long, in the order of 15–20 min per sample.

1.3.4. Single addition technique (SAT)

Several alkalinity measurement techniques are based on the SAT principle, i.e. on measuring the pH of a sample before and after its acidification with a strong acid (typically HCl) to a single pH point (e.g. [8]). In these methods, alkalinity is computed from the knowledge of the amount of acid added (i.e. the amount of alkalinity destroyed), assuming that no CO$_2$ was stripped from the sample (constant C_T). Kimoto et al. [9] and Watanabe et al. [10] developed a SAT-based flow-through analyzer, which measured seawater alkalinity with good precision and high time resolution. This method has several advantages (a) it is simple and relatively inexpensive (e.g. a pH electrode is much cheaper than a spectrophotometer); and (b) it provides data with a high time resolution (1 min approximately) and good precision (± 2 μmol kg^{-1} in seawater, see [9]). The main drawbacks of this technique are that it requires precise laboratory work (accurately prepared solution, accurate volumes of sample etc.), and it is highly dependent on the pH measurement, which, particularly with solutions with low buffering capacity (i.e. low C_T and alkalinity values), may induce a relatively large error.

The main difference between the previously published SAT methods and the technique proposed in this paper lies in the use of a weak-acid as the titrant, whose main advantage is a more accurate low-pH-value measurement, as shown in the Results and discussion Section.

2. Method introduction and development of the interpretation algorithm

The method was developed for determining the alkalinity value of fresh-water solutions comprising carbonate as a sole (or highly dominant) weak-acid system. Such water types abound in all the continents. When other weak acid systems are present, their thermodynamic data can theoretically be included in the algorithm in a similar fashion without changing the computation principle, however, in such case the analyst should know the total concentration of that additional system, or acquire this information by adding a second titration point. Such approach, although possible, was not attempted in this paper, making the presented method restricted to carbonate-dominated solutions.

The method can be applied in either batch or flow-through continuous modes which (excluding technical inaccuracies), should yield identical results. The main advantages of the presented method are simplicity, low cost apparati (standard pH electrode, glass buret, magnetic stirrer, etc.), high accuracy and precision due to the usage of a weak acid (rather than a strong acid) which approximately doubles the solution's buffer capacity close to the target pH range, in which CO$_{2(g)}$ stripping does not affect the pH reading, the electrode's response is rapid and standard calibration solutions are available.

2.1. Computation algorithm

From the technical standpoint the method consists of dosing a known mass of dissolved H$_3$PO$_4$ to a water sample and recording pH, electrical conductivity (EC) and temperature values before and after the dosage. H$_3$PO$_4$ is added to the sample to reduce the pH value. Since the reference species of the alkalinity term of the acidified solution (Alk$_{new}$) are H$_2$CO$_3^*$ and H$_3$PO$_4$, the addition of H$_3$PO$_4$ does not change the overall alkalinity mass (see Eq. (3)), consequently Alk$_0 \cdot V_0 =$ Alk$_{new} \cdot (V_0 + V_a)$, where Alk$_0$ and V_0 represent the alkalinity and the volume of the original solution and the volume of the dosed H$_3$PO$_4$ solution is represented by V_a.

The equation representing the value of alkalinity with H$_2$CO$_3^*$ as reference species is shown in Eq. (2). Derived from a proton balance equation, the term for alkalinity with both H$_3$PO$_4$ and H$_2$CO$_3^*$ as reference species is

$$\text{Alk}(\text{H}_3\text{PO}_4, \text{H}_2\text{CO}_3^*) = 3\left[\text{PO}_4^{3-}\right] + 2\left[\text{HPO}_4^{2-}\right]$$
$$+ \left[\text{H}_2\text{PO}_4^-\right] + 2\left[\text{CO}_3^{2-}\right] + \left[\text{HCO}_3^-\right] + \left[\text{OH}^-\right] - \left[\text{H}^+\right] \quad (4)$$

Each species of a weak acid system can be expressed explicitly by the pH value, the sum of the concentration of the relevant weak acid system species (i.e. C_T, P_T, etc.) and the apparent equilibrium constants. Explicit development of such terms is given, for example, in Moosbrugger et al. [11]. Substituting the explicit terms of the carbonate and orthophosphate weak acid species in the right hand side of Eqs. (2) and (4) yields

$$\text{Alk}(\text{H}_2\text{CO}_3^*) = 2\frac{K'_{C1}K'_{C2}C_T}{K'_{C1}K'_{C2} + K'_{C1}10^{-\text{pH}} + 10^{-2\text{pH}}}$$
$$+ \frac{K'_{C1}10^{-\text{pH}}C_T}{K'_{C1}K'_{C2} + K'_{C1}10^{-\text{pH}} + 10^{-2\text{pH}}}$$
$$+ \frac{K'_W}{10^{-\text{pH}}} - \frac{10^{-\text{pH}}}{\gamma_m} \quad (2a)$$

$$\text{Alk}(\text{H}_3\text{PO}_4, \text{H}_2\text{CO}_3^*)$$
$$= 3\frac{P_T K'_{P1}K'_{P2}K'_{P3}}{K'_{P1}K'_{P2}K'_{P3} + K'_{P1}K'_{P2}10^{-\text{pH}} + K'_{P1}10^{-2\text{pH}} + 10^{-3\text{pH}}}$$
$$+ 2\frac{P_T 2K'_{P1}K'_{P2}10^{-\text{pH}}}{K'_{P1}K'_{P2}K'_{P3} + K'_{P1}K'_{P2}10^{-\text{pH}} + K'_{P1}10^{-2\text{pH}} + 10^{-3\text{pH}}}$$
$$+ \frac{P_T K'_{P1}10^{-2\text{pH}}}{K'_{P1}K'_{P2}K'_{P3} + K'_{P1}K'_{P2}10^{-\text{pH}} + K'_{P1}10^{-2\text{pH}} + 10^{-3\text{pH}}}$$
$$+ \frac{2K'_{C1}K'_{C2}C_T + K'_{C1}10^{-\text{pH}}C_T}{K'_{C1}K'_{C2} + K'_{C1}10^{-\text{pH}} + 10^{-2\text{pH}}} + \frac{K'_W}{10^{-\text{pH}}} - \frac{10^{-\text{pH}}}{\gamma_m} \quad (4a)$$

Where γ_m stands for the activity coefficient of monovalent ions $(-)$; K'_W, K'_C and K'_P represent the apparent equilibrium constants of H$_2$O, carbonate and orthophosphate weak acid systems, respectively, after adjustment for ionic strength and temperature. Since pH is defined as the negative logarithm of the activity of H$^+$, the explicit expression for [H$^+$] is $10^{-\text{pH}} \cdot \gamma_m^{-1}$. Representing the concentration of the dosed H$_3$PO$_4$ solution as C_a (mol L^{-1}) the

total orthophosphate concentration in the acidified solution (P_T, in mol L^{-1}) becomes

$$P_{\mathrm{T}} = \frac{C_a V_a}{V_0 + V_a} \tag{5}$$

The EC and the temperature (T, in $^\circ$K) of both the original and acidified solutions are measured. Based on these, the ionic strength (I) may be calculated using the approximation suggested by Kemp [12] (1971)

$$I = \left(2.5 \times 10^{-5}\right) \cdot (\mathrm{EC}) \cdot 670 \tag{6}$$

where EC is expressed in mS cm^{-1} at 20 $^\circ$C and I in mol L^{-1}.

The calculated ionic strength is used for approximating the activity coefficients, γ (dimensionless), using the Davies equation

$$\log \gamma_{m,d,t} = -AZ^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2 \cdot I\right) \tag{7}$$

where; m, d, t are the absolute values of the valence of the relevant ion (i.e. γ_m refers to monovalent ions, γ_d for divalent ions, γ_t for trivalent ions). A is $1.82 \cdot 10^6 (DT)^{-3/2}$; D is dielectric coefficient of water, whose value is usually 78.3; and Z is the charge of the ions (1 for monovalent ions, 2 for divalent ions, etc.).

Using the activity coefficients the thermodynamic equilibrium constants of the carbonate system ($K_{C1,2}$), the phosphate system ($K_{P1,2,3}$) and H$_2$O (K_W) can be converted into their corresponding apparent constants, e.g.

$$K_{P1} = \frac{(\mathrm{H}^+)(\mathrm{H_2PO_4^-})}{(\mathrm{H_3PO_4})} = \frac{(\mathrm{H}^+)(\gamma_m[\mathrm{H_2PO_4^-}])}{[\mathrm{H_3PO_4}]} = \gamma_m \frac{(\mathrm{H}^+)[\mathrm{H_2PO_4^-}]}{[\mathrm{H_3PO_4}]}$$

$$= \gamma_m K'_{P1} \Rightarrow K'_{P1} = \gamma_m^{-1} K_{P1} \tag{8}$$

Based on the known P_T (Eq. (5)) and pH$_x$ values (the subscript x represents the conditions in the sample following H$_3$PO$_4$ dosage) and the apparent equilibrium constants, the concentrations of PO$_4^{3-}$, HPO$_4^{2-}$ and H$_2$PO$_4^-$ can be calculated, using the terms shown in Eq. (4a). The concentrations of the carbonate system species, however, cannot be calculated, since C_T is still unknown. Instead, these species concentrations are expressed as a function

$$[\mathrm{CO_3^{2-}}]_0 = \frac{K'_{C1,0} K'_{C2,0}}{K'_{C1,0} K'_{C2,0} + K'_{C1,0} 10^{-\mathrm{pH_0}} + 10^{-2\mathrm{pH_0}}} \cdot C_{T0} = [\widetilde{\mathrm{CO_3^{2-}}}]_0 \cdot C_{T0} \tag{9}$$

$$[\mathrm{HCO_3^-}]_0 = \frac{K'_{C1,0} 10^{-\mathrm{pH_0}}}{K'_{C1,0} K'_{C2,0} + K'_{C1,0} 10^{-\mathrm{pH_0}} + 10^{-2\mathrm{pH_0}}} \cdot C_{T0} = [\widetilde{\mathrm{HCO_3^-}}]_0 \cdot C_{T0} \tag{10}$$

where the subscript 0 stands for the conditions in the sample prior to H$_3$PO$_4$ addition and the superscript $\sim$ represents the concentration of each carbonate species divided by the (thus far unknown) C_{T0} concentration. Expressions in Eqs. (9) and (10) are now plugged in Eq. (2a) to yield

$$\mathrm{Alk}(\mathrm{H_2CO_3^*})_0 = \left(2[\widetilde{\mathrm{CO_3^{2-}}}]_0 + [\widetilde{\mathrm{HCO_3^-}}]_0\right) \cdot C_{T0} + \frac{K'_{W0}}{10^{-\mathrm{pH_0}} \gamma_{m0}} - \frac{10^{-\mathrm{pH_0}}}{\gamma_{m0}} \tag{2b}$$

Since the overall mass of the carbonate system species remains constant following the H$_3$PO$_4$ dosage (assuming a closed system, i.e. minute CO$_{2(g)}$ stripping to the gas phase), the following equation holds true

$$C_{T0} \cdot V_0 = C_{Tx} \cdot (V_0 + V_a) \tag{11}$$

Isolation of C_{Tx} (the total inorganic carbon concentration in the acidified solution)

$$C_{Tx} = \frac{C_{T0} \cdot V_0}{V_0 + V_a} \tag{12}$$

Expressions similar to those shown in Eq. (9) and Eq. (10) can be developed to describe the concentrations of carbonate species following the addition of H$_3$PO$_4$, i.e. $[\mathrm{CO_3^{2-}}]_x$ and $[\mathrm{HCO_3^-}]_x$ by substituting the adjusted apparent equilibrium constants and the value of pH$_x$ instead of $K'_{C1,0}, K'_{C2,0}$ and pH$_0$, respectively. The resulting expressions for $[\mathrm{CO_3^{2-}}]_x$ and $[\mathrm{HCO_3^-}]_x$, in addition to the expression for C_{Tx} (Eq. (12)), were plugged into Eq. (4a), to yield

$$\mathrm{Alk}(\mathrm{H_2CO_3^*, H_3PO_4})_x$$
$$= \left(2[\widetilde{\mathrm{CO_3^{2-}}}]_x + [\widetilde{\mathrm{HCO_3^-}}]_x\right) \frac{C_{T0} \cdot V_0}{V_0 + V_a} + 3[\mathrm{PO_4^{3-}}]_x$$
$$+ 2[\mathrm{HPO_4^{2-}}]_x + [\mathrm{H_2PO_4^-}]_x + \frac{K'_{Wx}}{10^{-\mathrm{pH_x}} \gamma_{mx}} - \frac{10^{-\mathrm{pH_x}}}{\gamma_{mx}} \tag{4b}$$

From Eq. (3) it stems that the addition of H$_3$PO$_4$ does not change the Alk (H$_3$PO$_4$, H$_2$CO$_3^*$) mass (since the species H$_3$PO$_4$ does not form a part of this alkalinity term). Therefore, as stated above, the mass of alkalinity prior to the acid dosage equals the mass of alkalinity of the acidified solution

$$\mathrm{Alk}(\mathrm{H_2CO_3^*})_0 \cdot V_0 = \mathrm{Alk}(\mathrm{H_2CO_3^*, H_3PO_4})_x \cdot (V_a + V_0) \tag{13}$$

Inserting the alkalinity concentration terms (Eq. (2b) and (4b)) into Eq. (13), yields

$$\left\{\left(2[\widetilde{\mathrm{CO_3^{2-}}}]_0 + [\widetilde{\mathrm{HCO_3^-}}]_0\right) \cdot C_{T0} + \frac{K'_{W0}}{10^{-\mathrm{pH_0}} \gamma_{m0}} - \frac{10^{-\mathrm{pH_0}}}{\gamma_{m0}}\right\} V_0$$
$$= \left\{\left(2[\widetilde{\mathrm{CO_3^{2-}}}]_x + [\widetilde{\mathrm{HCO_3^-}}]_x\right) \frac{C_{T0} \cdot V_0}{V_0 + V_a} + 3[\mathrm{PO_4^{3-}}]_x + 2[\mathrm{HPO_4^{2-}}]_x \right.$$
$$\left. + [\mathrm{H_2PO_4^-}]_x + \frac{K'_{Wx}}{10^{-\mathrm{pH_x}} \gamma_{mx}} - \frac{10^{-\mathrm{pH_x}}}{\gamma_{mx}}\right\}(V_a + V_0) \tag{14}$$

Hence,

$$C_{T0} = \frac{\left(3[\mathrm{PO_4^{3-}}]_x + 2[\mathrm{HPO_4^{2-}}]_x + [\mathrm{H_2PO_4^-}]_x + \frac{K'_{Wx}}{10^{-\mathrm{pH_x}} \gamma_{mx}} - \frac{10^{-\mathrm{pH_x}}}{\gamma_{mx}}\right) \frac{V_a + V_0}{V_0} - \left(\frac{K'_{W0}}{10^{-\mathrm{pH_0}} \gamma_{m0}} - \frac{10^{-\mathrm{pH_0}}}{\gamma_{m0}}\right)}{\left(2[\widetilde{\mathrm{CO_3^{2-}}}]_0 + [\widetilde{\mathrm{HCO_3^-}}]_0\right) - \left(2[\widetilde{\mathrm{CO_3^{2-}}}]_x + [\widetilde{\mathrm{HCO_3^-}}]_x\right)} \tag{15}$$

Since all the terms of the weak acid species can be exchanged with the explicit terms (as demonstrated in Eqs. (2a) and (4a)) the only unknown in Eq. (15) is C_{T0}. After solving C_{T0}, its value can be plugged into Eq. (2b) to determine the original alkalinity value of the sample.

Note that the described procedure does not rely on neglecting any of the species at any point in the calculation.

2.2. Advantages and limitations of the new approach

As mentioned previously, the reason that the addition of a weak acid was preferred in the suggested method over the addition of a strong acid relates to the fact that an appropriate weak acid dosage may serve to increase the solution's buffer capacity by 36% near the target pH range (0.376 meq L^{-1} vs. 0.276 meq L^{-1} at pH 4.00, in the presence and absence of orthophosphate dosage, respectively), resulting in increased pH measurement accuracy. Fig. 1 shows the buffer capacity value of a
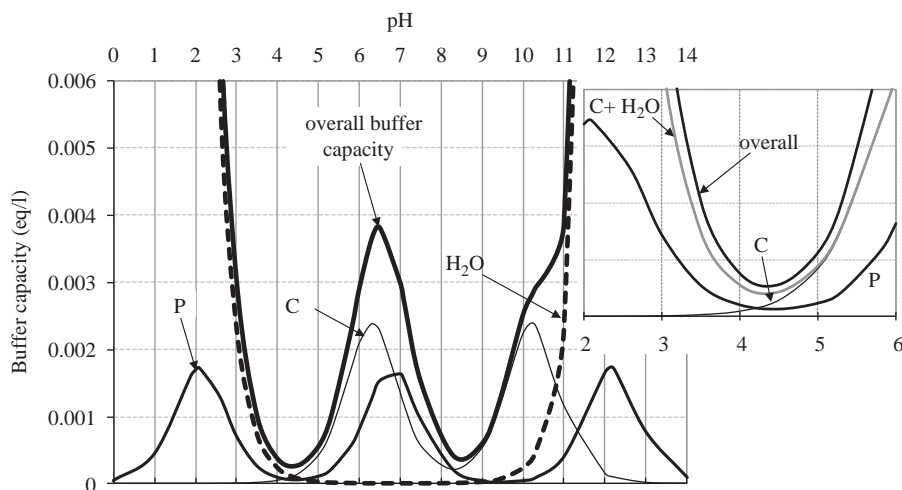
Fig. 1. Buffer capacity curves for the water (H$_2$O), carbonate- (C) and phosphate (P) systems, and a curve representing the overall buffer intensity. Right hand side: zoom in of the buffer capacity curves at the vicinity of the target pH range.

carbonate-containing solution with a C_T concentration typical in natural waters (i.e. $\sim 4 \cdot 10^{-3}$ mol L^{-1}). In addition, it shows the buffer capacity value of a solution containing the orthophosphate weak-acid system at a P_T value typical to that in the mixed stream in the proposed process assuming $C_{T\,0} \approx 4 \cdot 10^{-3}$ mol L^{-1} (i.e. $P_T = 3 \cdot 10^{-3}$ mol L^{-1}), and also the buffer capacity of a solution comprising both weak-acids at similar concentrations. From Fig. 1 it is clear that the buffer capacity of the mixed stream (near the target pH range) is increased relative to that of the original solution (more specifically, the buffering capacity is approximately doubled). Note that in the current method the amount of H$_3$PO$_4$ dosed to the solution is proportional to the sample's buffer capacity. Therefore, the contribution to the buffer capacity of the mixed solution would always be of the same order.

Due to the elevation of the buffer capacity in the proposed method, the control over the reduction in the pH value during the titration is relatively good; consequently, it is possible to reach the pH target (pH$\sim$4.00), relatively precisely. At pH 4.00 the accuracy of the pH measurement should theoretically be the highest, since the (low-pH) electrode calibration is typically performed exactly at this pH value. Moreover, at pH 4, the loss of a certain CO$_2$ mass to the atmosphere cannot affect the pH value, due to the (typically) negligible HCO$_3^-$ concentration at this pH. Alternatively, in case a strong acid is used, the buffer capacity of the acidified stream is described by line 'C+H$_2$O' in Fig. 1. It is hence obvious that a small overdose of strong acid would lead to a significant pH reduction, due to the relatively low buffer capacity at pH < 4, as compared to the buffer capacity of a solution typical to the suggested method, which is represented by the overall buffer capacity line in Fig. 1. To conclude, the main advantage of the proposed method over the method which is based on single addition of a strong acid (e.g. HCl), is that when the latter is used, it is very difficult from the practical standpoint to reduce the pH to the required endpoint (close to pH 4), and more importantly to obtain there a stable pH reading, due to the low buffering capacity at this target pH area. This advantage is particularly significant when the methods are utilized in a flow-through (continuous) manner in order to measure minute variations in alkalinity. Such practice would typically consist of constant acid dosage and measurement of the resultant pH$_x$, and since the accuracy of the pH reading determines the accuracy of the method, the ability to work around stable and accurate pH-reading zone is crucial.

In theory, any weak-acid can be used in the suggested method as long as it complies with the following requirements: (1) pK

value roughly between 1.5 and 3.5. In case pK is higher than 3.5, a high weak-acid dosage would be required in order to reduce the pH of the mixed solution to pH$\sim$4.5. In case the pK is lower than 1.5, the buffer capacity of the mixed stream at the pH range close to pH 4 (the required titration endpoint) will not be high enough and therefore the main advantage associated with the usage of the weak-acid will be lost. (2) It does not react with other species in the solution to precipitate solids (e.g. K_{sp}(Ca$_3$(PO$_4$)$_2$) = $2.07 \cdot 10^{-33}$, thus [PO$_4^{3-}$] at saturation is $\sim$three orders of magnitude higher than the [PO$_4^{3-}$] in the mixed stream, in case [Ca^{2+}] = 1 mmol L^{-1}, therefore, the solution is at all times undersaturated with respect to Ca$_3$(PO$_4$)$_2$). (3) It has low tendency to be stripped to the atmosphere i.e. a low Henry constant value. (4) Finally, as the proposed alkalinity determination procedure relies on calculating the concentration of the carbonate system as well as the species of the weak acid titrant, its accuracy depends on the extent of formation of complexes involving these species. Thus, an additional requirement is that the target pH value would not be significantly affected by formation of ion pairs between titrant species and cations in solution. As shown in the Results and discussion Section, H$_3$PO$_4$ complies with this requirement in fresh water samples. In contrast, in seawater or brines ion pairs are expected to form and application of the method will result in less accurate results.

The paper presents results obtained by applying the suggested method to fresh water samples, in a batch fashion. The underlying assumption in the presented method is that the measured solutions contain the carbonate system as the sole or highly dominant weak-acid system, or in other words, that the sum of the concentrations of alkalinity species of weak-acid systems other than carbonate (e.g. B(OH)$_4^-$; OCl$^-$; NH$_3$; organic acids, etc.) can be considered negligible (< 2%) relative to the carbonate alkalinity. Such conditions prevail in fact in many natural fresh waters, such as the three samples analyzed in this paper. In seawater, the value of the B(OH)$_4^-$ species ($\sim$0.062 meq L^{-1}) is also very low relative to the carbonate alkalinity concentration ($\sim$2.4 meq L^{-1}) but due to the effect of complexes on pH the described method is not adequate for determining seawater alkalinity. It is stressed that the algorithm, as presented, should not be applied when other weak acids are present at > 2% of the overall alkalinity value as determined to pH$\sim$4.5 (e.g. waste-waters or natural terrestrial streams with low alkalinity and relatively high organic acids content, as encountered, for example, on the eastern seaboard region of all the continents in the southern hemisphere [13]).

Furthermore, results of continuous alkalinity determination are not reported in this paper, but it is stressed that from a purely chemical standpoint the conditions prevailing at steady state under continuous flow are identical to those prevailing in batch tests (following the addition of the acid and attainment of steady state). The authors therefore believe that the presented batch test procedure can be reliably repeated in a continuous fashion, using the described algorithm and the physical setup recommended at the end of the text.

The results presented in this paper are shown in order to validate the developed algorithm and to establish the accuracy of the method in comparison to the two most commonly used methods. The accuracy and precision of the technique, as well as its sensitivity to various parameters, are shown and discussed.

3. Material and methods

3.1. Theoretical calculations

Calculations related to formation of ion pairs and their effects on the accuracy of the method were performed using the PHREEQC software [14]. The database selected in all PHREEQC calculations for estimating activity coefficients was the Specific Interaction Theory (SIT) [15].

3.2. Reagents and analyses

All reagents used were of analytical grade. All solutions were prepared using double distilled water: H_3PO_4 solution was prepared by diluting 11 mL of H_3PO_4 85% (Frutarum, Israel) in 500 mL double distilled water (empirically confirmed concentration 0.327 mol L^{-1}). Weights were determined using Precisa model 205A (resolution 0.1 mg). The general purpose pH glass electrode (CyberScan 510, Eutech Instruments, resolution 0.01 pH units) was calibrated at 4.01 and 7.00 using NBS (Carlo Erba) buffers. A 1 eq L^{-1} analytical ampoule (Carlo Erba) was used to generate the HCl solution used in the conventional alkalinity measurements. CyberScan con 510 (Eutech Instruments) was used to measure EC and temperature. Coupled plasma-atomic emission spectrometry (ICP-AES) was used to determine the ionic composition of groundwater. Cl^- concentration was measured by the argenometric method [2].

3.3. Batch apparatus

The apparatus used for applying the proposed method consisted of a 210 mL sealed beaker with five optional lid openings for electrodes (Metrohm beaker: 6.1415.250, lid: 6.1414.010).

The sealing of the beaker ensured no $CO_{2(g)}$ stripping to the atmosphere, imperative since the methodology is based on calculating the C_T value of the sample (i.e. C_{T0}). The beaker was filled with 200 mL of sample, in order to leave a minimal head space volume, and sealed. A pH electrode and a titration buret were inserted into the beaker through two built in lid openings. The sample was stirred slowly throughout the titration procedure. Note that a glass buret was used to assess the method's accuracy and precision, rather than an automatic titrator, to test the new methodology with simple laboratory instruments.

EC and temperature values of each sample were measured twice: before and after H_3PO_4 dosage. To simulate normal alkalinity measurement conditions, the temperature was not maintained constant during the titration. However, since the titration procedure typically lasted merely 2 min, the temperature remained roughly constant.

The following solutions were analyzed for $H_2CO_3^*$ alkalinity: (a) four synthetic $NaHCO_3$ solutions (termed "synthetic solutions") with various alkalinity values (Table 1), prepared by dissolving dried $NaHCO_3$ in 2 L RO de-ionized water (EC=15.5–30 μS cm^{-1}); and (b) three actual tap water sources: desalinated, ground and surface water. Moreover, the alkalinity of the three water sources was spiked by a concentrated $NaHCO_3$ solution and the alkalinity concentration was re-measured to yet again assess the accuracy of the method in a wide range of alkalinity values.

4. Results and discussion

4.1. Determining the alkalinity value of synthetic solutions

The alkalinity value of the synthetic solutions was determined using (a) direct titration to pH 4.5 (denoted "direct alkalinity"); (b) Gran's titration procedure; (c) the suggested method; and (d) by the knowledge of the precise analytical weight of $NaHCO_3$ that was dissolved in the water (termed "weighed alkalinity"). The latter concentration was used as reference and the accuracy of the three other methods was compared to it, using Eq. (16) and results are presented in Table 1.

$$\%error = \frac{alkalinity - weighed\ alkalinity}{weighed\ alkalinity} 100\% \qquad (16)$$

where, the term "alkalinity" represents each of the three analytical methods.

Table 1 shows that the proposed method was both highly accurate (error ≤ 1.5%) and precise (STDV ~0.5 and 2.25 mg L^{-1} as $CaCO_3$ for alkalinity values of < 200 and 400 mg L^{-1} as $CaCO_3$, respectively). The results of the proposed method were also compared with those obtained using the pH 4.5 titration method (Table 1). Based on the relative errors attained, the two methods

Table 1
Average (± STDEV) alkalinity concentrations obtained via the various methods tested in the work (n=3).

Solution		Alkalinity concentration					
#	Description	"Weighed" alkalinity mg L^{-1} as $CaCO_3$	Direct method (pH 4.5)		Gran's method	Suggested method	
			mg L^{-1} as $CaCO_3$	Error %	mg L^{-1} as $CaCO_3$	mg L^{-1} as $CaCO_3$	Error %
1		5.017	5.83 ± 0.07	16.2		4.01 ± 0.13	−21.1
2		10.035	11.58 ± 0.14	15.4		8.79 ± 0.27	−12.5
3	Synthetic solutions	20.30	20.42 ± 0.36	0.60		20.19 ± 0.40	−0.53
4		100.35	98.54 ± 0.36	−1.80		100.41 ± 0.41	0.12
5		200.57	195.83 ± 0.36	−2.36		203.85 ± 0.54	1.22
6		400.93	392.71 ± 0.96	−2.05		406.66 ± 2.25	1.43
7	Desalinated water	–	32.5 ± 1.3		29.3 ± 0.3	32.58 ± 1.20	
7	Surface water	–	125.8 ± 1.4		122.24 ± 2.4	124.12 ± 0.99	
8	Groundwater	–	300.0 ± 0		300.3 ± 1.3	305.5 ± 1.82	

can be considered to have approximately the same accuracy and also analogous standard deviation ranges.

An example of one explicit calculation procedure is shown in the Supporting information (SI-1) file.

4.2. Quantification of the relative error attained as a function of the chosen target acidic pH (pH_x)

As explained previously, the accuracy of the pH measurement was logically expected to be the highest in the vicinity of the pH at which the electrode was calibrated, i.e. pH 4.01. This assumption was tested empirically and the results are shown in Fig. 2 for two synthetic bicarbonate solutions (triplicate measurements). Comparing the accuracy of the method obtained at different pH_x values against a given known alkalinity ("weighed alkalinity") Fig. 2 shows that the lowest relative error (Eq. (16)) was obtained in the range $4.0 < pH_x < \sim 4.7$. Below pH 4.0 the error increased significantly, probably due to inaccurate electrode reading outside its calibration range. Relatively large errors were obtained also at pH_x values higher than pH 4.7. In this region the error was very likely attributed to a small increase in pH caused by $CO_{2(g)}$ stripping to the headspace of the measurement apparatus. Since at this pH range the HCO_3^- concentration is still significant, the loss of CO_2 to the atmosphere instigated reaction between H^+ and HCO_3^- to form $CO_{2(aq)}$, resulting in pH increase triggering the error. At $pH < 4.5$ the effect of this phenomenon is minimal, and consequently, the operation range recommended by the writers is $4.0 < pH_x < 4.5$.

4.3. Determining the alkalinity value of three actual tap water sources

The alkalinity values of three water types (desalinated, surface and ground water) were determined using both the conventional
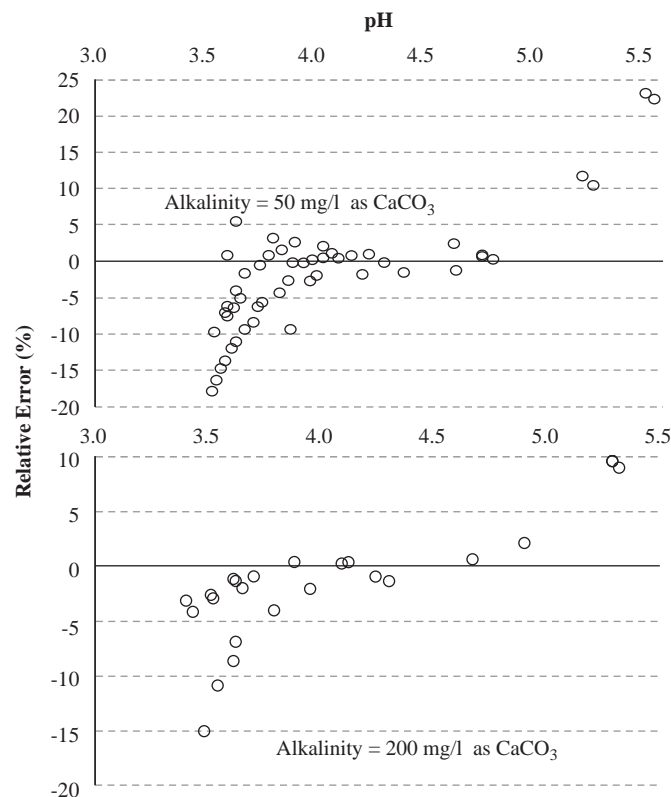
methods and the proposed method. The three water types were selected in order to examine the proposed method over a wide range of alkalinity and EC values. The three water samples, which were collected directly from the water distribution system and represent the majority ($> 95\%$) of fresh waters supplied in Israel, contained, in practical terms, no other weak-acids apart from the carbonate system. The results of executing the methods are shown in the bottom rows of Table 1, indicating, as was the case with the synthetic solutions, that the new method produced alkalinity concentrations that fell normally within $1 - 3\%$ of the results obtained by the Gran and direct alkalinity methods, over the entire concentration range tested. The only place where a larger error was encountered was with the desalinated water, for which the Gran method yielded a result $\sim 10\%$ lower than both the new method and the direct titration method. Having said this, the difference between the results (in absolute terms) was low, i.e. $\sim 6 \cdot 10^{-5}$ eq L^{-1}.
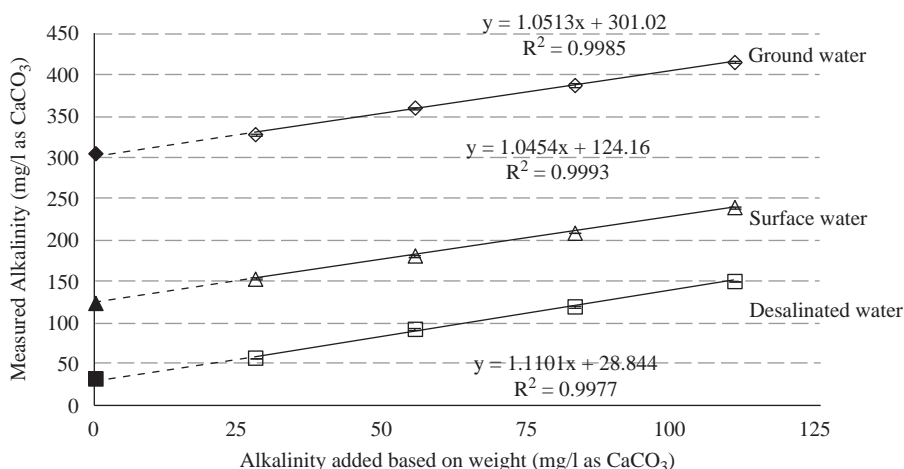
To further asses the accuracy of the new method, each of the three water sources was spiked with varying volumes of a concentrated bicarbonate solution and the alkalinity values of the 'spiked' solutions were re-measured using the proposed method. Fig. 3 shows the measured 'spiked' alkalinities plotted against the spiked alkalinity values. The high linear regression correlation coefficients (R^2) obtained (Fig. 3) indicate that the method returned very accurate results within the alkalinity range tested. Moreover, the alkalinity values of the raw waters could be in fact obtained relatively and accurately based on the regression lines of the alkalinity values extrapolated from the results of the spiked solutions. For example according to the linear regression, the alkalinity of the surface water was 124.16 mg L^{-1} as $CaCO_3$ (Fig. 3) as compared with a value of 125.12 mg L^{-1} obtained directly in the un-spiked solution by the proposed method (Table 1).

### 4.4. Possible extension of the proposed method to continuous alkalinity analysis

Fig. 4 shows the setup proposed by the authors for continuous alkalinity measurement. The setup comprises two pH, EC and temperature electrodes, a static mixer and two accurate (digital) pumps, all connected to a computer. The analyst can control the value of pH_x by changing the relative flow rate of the two pumps, so that pH_x will remain in the required range. The data required for executing the algorithm consists of the two pump flow rates, C_a, and the pH, EC and temperature values at the two measuring points.

5. Conclusions

- A new, simple and accurate fresh-water carbonate alkalinity analysis method, which can be carried out either batch-wise or continuously, was presented. The method is based on single (H_3PO_4) titration and two pH readings, and can be carried out with elementary laboratory equipment.
- The method's interpretation algorithm was developed based on the understanding that the alkalinity mass (per the alkalinity term developed with $H_2CO_3^*$ and H_3PO_4 as reference species) does not change upon the addition of H_3PO_4 to the analyzed sample.
- The accuracy of the method was found equivalent to that of the Gran and the standard "titration to pH 4.5" methods, in the alkalinity range 20–400 mg L^{-1} as $CaCO_3$. At the very low concentration range (5–10 mg L^{-1} as $CaCO_3$) the accuracy of both the new and the standard (pH 4.5) methods was approximately ± 1 mg L^{-1} as $CaCO_3$. In percentage terms the error may seem high (because of the very low background) but for most practical purposes it can be considered satisfactory. It also appears that at the very low alkalinity concentration

Fig. 2. Relative error in alkalinity determination by the new method as a function of the target pH (pH_x) attained with 50 and 200 mg L^{-1} as $CaCO_3$ bicarbonate solutions (results from three different runs).

Fig. 3. Measured alkalinity (using the new method) vs. the alkalinity spiked to desalinated, surface and ground water. Full symbols represent alkalinity analysis of un-spiked solutions.
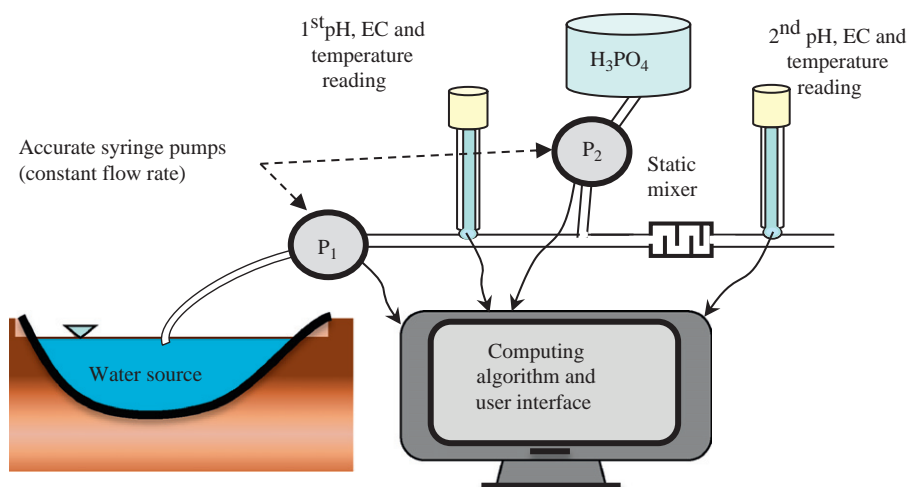
Fig. 4. Proposed setup for continuous alkalinity measurement apparatus.

range (i.e. $< \sim 10$ mg L^{-1} as $CaCO_3$) the Gran technique is superior over the other methods, if executed correctly, i.e. to a titration range roughly between pH 4.5 and pH 4.0 (i.e. below, but not excessively far down from the "true" equivalence point).

- The (acidic) target pH range at which the accuracy of the method is maximized was found to be $4.0 < pH < 4.5$.
- Limitations of the method include: (1) it is accurate only when the carbonate system is the highly dominant weak acid system (sum of all other weak acid systems should not exceed 2% of the $H_2CO_3^*$ alkalinity value); (2) the method does not take into account complexation (ion-pairing) equilibrium reactions and is thus restricted to fresh waters (i.e. TDS $< \sim 1500$ mg L^{-1}); and (3) the pH scale used should be the NBS scale, which again limits the application to water with TDS value not exceeding ~ 1500 mg L^{-1}.
- Future work should focus on technical issues related to the continuous application and sensitivity analysis, particularly in the presence of minute concentrations of organic acids and other weak acid systems (ammonia, orthophosphate, sulfides, etc.).

Supplementary data accessible via the internet

(1) Example of one explicit calculation procedure

(2) An excel file comprising the program compiled to calculate the alkalinity value, according to the algorithm described in the paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.08.024.

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