

Online Novel Techniques for Selective Simultaneous Determination of Alkalinity/Bicarbonate and Hardness in Drinking Water by Skalar San++ Segmented Flow Analysis.

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The procedures of the current novel automated technique for the determination of hardness, Carbonate, bicarbonate and alkalinity in drinking water have been modified from both classical batch titration and the method of the flow analysis Skalar San++ method (classical scalar current). The forms of standards in the current methods have been modified. The calcium chloride used previously in the current method for the determination of both calcium and total hardness was replaced by a mixed standard that contains calcium and magnesium carbonate in an aqueous solution. Likewise, calcium carbonate and sodium bicarbonate standards currently used in determination of alkalinity and bicarbonate respectively were replaced by using only one standard of calcium, sodium carbonate salt, and the required bicarbonate concentrations were derived from the same calcium carbonate formula mathematically in the stoichiometry equation. The new approach method was validated and applied successfully for analysis of drinking water and proficiency tests samples (PTS). The technique is used for an automatic online analysis of total, calcium hardness, total alkalinity and bicarbonate in drinking water covering a range of 10 - 100 ppm for total hardness and calcium hardness and a range of 5-100 ppm for alkalinity and bicarbonate mg/L as CaCO₃. The method gave a distinct merit over the manual titration method and the current skalar method, with enhanced detection limit, high precision (RSD) which was found to be less than 1%) and accuracy of ($\pm 1-2\%$), as well as a high spectral peak resolution and sample throughput.. Moreover, additional merits of the proposed method over the classical skalar one, other than being economic in use, as there is some chemical cut off, is the feasibility of the automatic determination of carbonate ions concentrations in the same run, which could not be achieved automatically by the classical skalar method, as it always needs mathematical subtraction of bicarbonate

concentration from alkalinity concentrations from multi runs. The latter approach is tedious, involved lots of reagents and procedures, time consuming, and could impact the overall method precision and accuracy. The method–demonstrated selectivity as online automated approach for selective determination of total hardness and calcium hardness in one run and determination of total alkalinity and bicarbonate from the same standard in the second run, when keeping all of the four chemistry reagents aspirated automatically. Sole analysis for every parameter as in the current method was achieved demonstrating simultaneous analysis without discernment, the recovery was found to be comparable with the novel proposed method, but the latter gave a marked enhancement in precision and peak resolution.. Analysis for drinking water samples gave quantitative results with Z score of less than ± 1.2 . Accuracy of the automated analysis was investigated by multiple techniques including recovery by standard addition method, run of CRM and t test statistical analysis. The merit of the accuracy for this proposed method has been demonstrated successfully through applications to real samples.

Keywords: *segmented flow analysis, alkalinity/bicarbonate, hardness, drinking water, online calibration curve, Selectivity, Evaluation of carbonate concentration, Smart systems; Continuous Flow techniques.*

1. Introduction

The salts of the alkali and alkaline earth metals are the species richly found in natural waters, to which they provide its characteristics and properties [1]. Their control is of importance as their vital impact could affect the quality of drinking water [1]. Total alkalinity can be defined as the concentration of treatable bases in water [2]. Number of techniques have been utilized in determination of total alkalinity and bicarbonate alkalinity.³ The advantage and disadvantage of the commonly used batch or continuous methods in alkalinity and bicarbonate alkalinity H_2CO_3^+ determination were reviewed earlier[3]. Batch type titration methods, the standard alkalinity analysis, and the Gran titrimetric one, are commonly used to date, to measure alkalinity concentrations in the routine analysis. Since these methods cannot be easily implemented for continuous determinations, different method have been developed such as potentiometric method, Infrared spectroscopy, sample acidification and subsequent measurement of $\text{CO}_2(\text{g})$, single addition technique(SAT) but still each of them suffers from certain limitations [3,4]. The hardness of water is expressed as the contribution of individual ions. For instance, calcium hardness, and the combined contribution of all ions is called total hardness. It is regarded as one of the most viable components for assessing drinking and other sources of water quality [1]. The expression water hardness apparently resulted from the observation that CaCO_3 precipitates when water with appreciable concentrations of HCO_3^- and Ca^{2+} is heated².



This phenomenon is predominantly troublesome in boilers and conduits transmitting heated water, because the precipitate forms hard deposits tend to reduce the efficiencies of boilers and causes clogging pipes. Factors for converting calcium hardness to total hardness is used in this study in preparing total and calcium hardness mixed calibrating standard. Where a rapid determination for continuous water quality is desired in most of application and quality wise, the chelatometric titrations remains the commonly used methods [1,5]. The latter approach is tedious and time consuming and unsuitable for continuous monitoring. A more rapid method based on polarographic reduction of magnesium ions as a displacement reaction of Mg-EDTA complex and others based on potentiometric divalent ion selective electrode were utilized in continuous monitoring [6].

2. Literature Review

Recently, several methods for determination of hardness, alkalinity have been reported by flow injection analysis (FIA). Flow methods have provided a marked degree of integration of all steps of the analytical procedure, from sample collection to acquisition of signals, on a single setup frame. Moreover, have been consolidated as routine techniques of analysis, allowing a high degree of automation and leading to the concept of the total analytical approach. Flow analysis has played a considerable role on research and development for monitoring of key indicators, it also has delivered a broad spectrum of operational and cost-effective methodologies based on automation for determination of many parameters .Francisco et al reported a method for simultaneous determination of magnesium and calcium, alkalinity by flow injection [7]. Yamane and Kamijo [8] determined water hardness with EDTA using hydroxynaphthol blue as an indicator, the change in absorbance was measured at wave length 645nm. Wada et al. synthesized dihydroxyazo compounds and used them in the determination of calcium and magnesium by spectrophotometer [9]. Basson and Van Staden [10] proposed the simultaneous determination of alkali and alkaline earth and alkalinity in water with FIA using an FIA configuration with splitting of the sample stream to feed both the dual-channel detector, the latter device was coupled with flame and atomic absorption spectrometers as detectors. Other workers[10] have proposed methods for the determination of calcium in water with an ion-selective electrode, a fibre optic sensor using fluorescent transduction and a polyether antibiotic has been reported for detection of Ca^{2+} and Mg^{2+} demonstrating good detectability and selectivity, but the method suffers from drawbacks of a short

lifetime and long assay time[12,13] Numata et al[1,2] described a divalent cation selective electrode, with nearly equal selectivity to Ca^{2+} and Mg^{2+} , and the electrode was applied to tap water and upland soil extracts and validated with standard method using chelatometric titration. Large interferences from heavy metal and transition metal ions are, however, observed, although interference from Na^+ and K^+ ions were very small [14] Saurina et al[15] reported on the use of potentiometric sensor arrays for the determination of calcium and total hardness in neutral waters, and the authors presented a very interesting, novel approach to improve selectivity of the calcium and magnesium ISEs, eliminating the effect of interference from other cation species by using chemo metric data treatment for the multivariate sensor array. Alkalinity, Calcium water hardness in natural waters has been measured by digital colorimetry as a ready-to-use method using Chromogenic model based on reaction color change (RGB, Red-Green-Blue) reacting with acid chrome Potential of RGB basic colors and color related parameters have been evaluated[16] In a previous study, flow injection method detection water used for leather-making hardness, the operation method was simple and reliable, and can be used in water used for leather-making hardness as online fast detection[17]. Flow Injection combined with Multivariate Analysis for determining the concentration of Calcium and Magnesium in Water has been reported by chelation of dye Arsenazo III ions and subsequently changes color .They used the dye Arsenazo III, which complexes with these two metal ions and subsequently changes color, that was measured with spectrometer for calcium at around 600-670 nm and for magnesium from 580-630 nm[18]. Recently, the development of microfluidic paper-based analytical devices (μPADs) for the chelate titrations of Ca^{2+} and Mg^{2+} in natural water has been reported [18]. The μPAD component were ten reaction on ten detection zones that were connected through narrow channels to a sample zone Buffer solutions with a pH of 10 or 13, were applied to all surfaces of the zones with addition of variables concentrations of (EDTA) to the reaction zones and a consistent amount of a metal indicator (Eriochrome Black T) was added to the detection zones). The μPADs allowed the determination of Ca^{2+} and Mg^{2+} in mineral water, river water, and seawater samples immediately using only the naked eye without the need of instruments [19]. To date investigations and studies have assessed the hardness and alkalinity in terms of toxicity as independent variables as 97% of global run off is influenced by dissolution of CaCO_3 , both of alkalinity and hardness are correlated in aquatic ecosystem that necessitate to understand the effects of simultaneous changes in alkalinity and water hardness [20]. Recently, in a patented work, method for analysis and controlling water hardness was invented; the present invention is related to methods, apparatuses, and compositions of a resin material being loaded with a plurality of cations for controlling water hardness and reducing scale formation[21] in aquatic ecosystem. Skalar from Skalar Analytical BV- the Netherlands Company Enterprise, is at present, the world leader in wet chemistry technology, offers over 300 proven applications utilizing various combinations of recent technologies such as automatic dilutions, additions, mixing, heating, dialysis, extractions, and more. Skalar has developed a proven systematic approach to provide a quality system starting with complete applications engineered on customer samples to provide the best possible configuration to the customer needs and requirements. Only recently, it was reported, to be used for the analysis of Canonical Component of diatoms water chemistry with batch and simultaneous analysis for some parameters including calcium and magnesium. Analysis was carried out to classify the samples, based on their chemical characteristics, results of analysis with skalar was used to explore the geological history of the island in combination with the climate and the specific environmental features of the main habitat , that was most likely shaped the composition of the actual diatom communities [22]. This brief introduction and literature review was included in this paper in order to justify the sincere need and making an incentive to develop a new selective, simple precise accurate and cost effective to distinguish the suggested technique from the currently practiced methods.

3. Experimental Section

3.1 Materials and Method

All chemicals are of analytical grade, and from Sigma Aldrich, and solutions were prepared in double distilled water. Detailed Chemical methods and preparation procedures are found in-“Skalar Reactors, Series SA552X and 25509XX User Manual, and references [2, 24, and 25].

3.2 Reagents and Chemicals

3.2.1 Total hardness (TH)

Ammonium chloride NH_4Cl , ammonium Hydroxide NH_4OH , Calmagite ($\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_5\text{S}$), HCl, Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$ (abs.)), Magnesium Triplex® ($\text{C}_{10}\text{H}_{12}\text{K}_2\text{MgN}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$, Brij 35 (30%).

3.2.2 Calcium Hardness CaH

Potassium hydrogen phthalate $\text{C}_8\text{H}_5\text{KO}_4$, Boric acid H_3BO_3 , buffer solution (*di-Ethyl amine* ($\text{C}_4\text{H}_{11}\text{N}$), *Potassium cyanide*), (*KCN*, 8-Hydroxyquinoline solution, Cresolphthalein complexions (C.P.C.).

3.2.3 Total Alkalinity (TA)

Potassium hydrogen phthalate $\text{C}_8\text{H}_5\text{KO}_4$, Boric acid H_3BO_3 , Hydrochloric acid HCl. Sodium Chloride Solution NaCl, Methyl orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$, Brij 35%.

3.2.4 Bicarbonates

Sodium carbonate Na_2CO_3 , Sodium hydrogen carbonate (NaHCO_3 , Phenolphthalein $\text{C}_{20}\text{H}_{14}\text{O}_4$ (1% in ethanol), Antifoam.

3.3 Standards

3.3.1 Mixed Standards for Alkalinity & Bicarbonate

Stock solution 10,000 mg CaCO_3 /liter (1 liter):

Sodium Carbonate Na_2CO_3 salt is used for preparation of stock alkalinity and bicarbonate standard instead of CaCO_3 due to the low solubility of the latter salt. No standardization was required.

3.3.2 Mixed Standards for Total and Calcium Hardness

The mixed standard for calcium and total hardness were prepared from a mixture that contains 0.5 g of CaCO_3 and 0.42g of magnesium Carbonate, they were dissolved in a minimum amount of 5% Conc. HNO_3 and dilute to 1L with deionized water. The solution will contain 1000 ppm Total hardness and 500 ppm calcium hardness. For sole determination, standard of 10,000 mg/L total and calcium hardness are prepared from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salts.

3.3.3 Proficiency Test (PTS) and Samples

Round AQ 477LGC 1&2 Soft water, Sample No. A10067917001, Round AQ 445, Ref No.2013/63809, AQ Round 453, Ref No.2013/68254.

3.3.4 CRM for Total Alkalinity

WC-ALK-10X-1 Alkalinity mg/L as CaCO_3 lot 214125054

3.4 Instrumentation

Skalar SAN++ flow analysis instrument (FA) Skalar Analytical BV- the Netherlands, guide and procedure for instrument operation, calibration procedures are found in Skalar Reactors, Series SA552X and 25509XX User Manual. The chief principle of continuous flow analysis CFA is to disregard chemical analysis by manually hand-mixing the reagents in individual items and to substitute a constantly flowing stream of liquid reagents circulating through a closed system. Therefore, in CFA the sample is transformed into a flowing stream via the means of a pumping system and the essential reagent accompaniments are made by uninterrupted pumping and merging of the sample and reagent streams. The mixing along with the chemical reactions take place while the sample solution is on its way toward a low-through cuvette, where the analytical signal is monitored on continuous basis, and accordingly recorded. A CFA diagram, of its simplest form, is shown in Figure 1-a. The same consists of: a pump (P) that is used to propel the carrier stream through a thin tube; a coil of tubing (i.e. reaction coil; RC) in which the sample zone disperses and reacts with the components of the carrier, resulting in the formation of species that are detected by a flow-through detector; a recorder and/or personal (PC) computer which registers the CFA signals. Figure 1- b and Figure 1-c show skalar flow access.

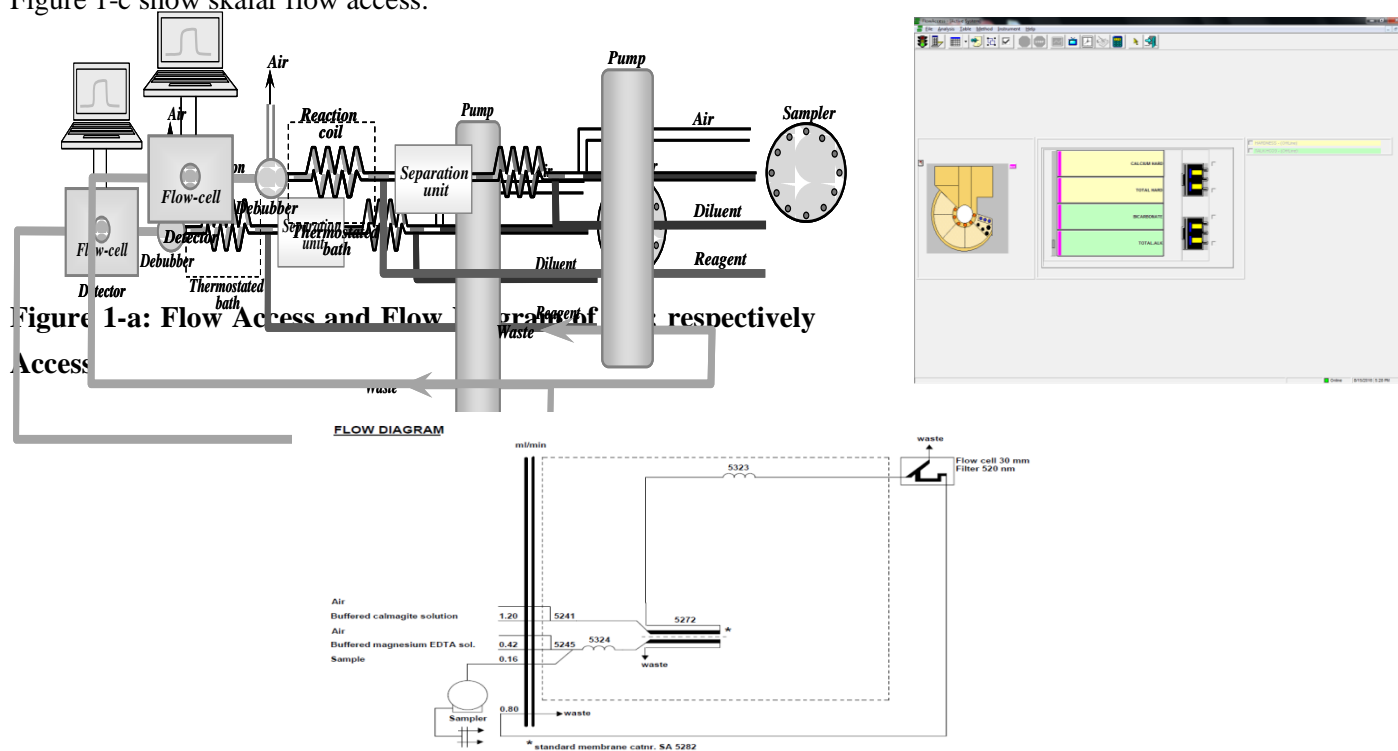
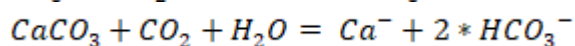
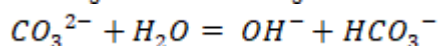
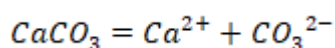


Figure 1-c: Flow Diagram for Hardness as an example

3.5 Method development

Figure 1-a is a schematic diagram for determination of the four parameters, figure 1-b is a representation of skalar robotic flow diagram. On analysis, after switching on the mains, the four parameters are checked, the reagents were passed and consequently the base line was monitored until plateau shape is evident. Analysis is started with analysis of vials of standards which were placed on the auto sampler followed by the analysis of vials of samples. Figure 1-c is an example for the flow diagram for total hardness. In Total Alkalinity, the methyl orange is mixed in a weak buffer solution at a pH of 3.1, just below the equivalence point. The color decrement is measured at 550 nm. for both alkalinity and bicarbonate comprising carbonate as a sole weak acid system or water solution.



For Total hardness the free magnesium reacts with Calmagite at a pH of 10.0 to give a red-violet complex, which is measured at 490 nm. Calcium is complexes with cresolphthalein complex one in alkaline media, this complex is measured at 580 nm. The measured spectra at this particular wave length are taken for calculation for the tested parameters that obeyed from Beer's law equation from calibration Curve.

3.6 Procedure of Analysis

The automated procedure for the determination of total alkalinity **TA**, Bicarbonate, **HCO₃⁻**, total hardness **TH**, Calcium hardness **CaH**, in the auto sampler, position A1-A5 is normally reserved for standards, and the Auto-sampler needle takes the liquid and splitted to each 4 chemistries at a flow rate for TA(0.6ml/min), HCO₃(0.8ml/min), TH (0.16m/min) and Ca Hardness (0.23ml/min), then the sample will be analyzed by different techniques as by pH shift at 550nm decolonization of methyl orange, pH shift at 550 nm decolonization of phenolphthalein, calmagite reaction of chelated EDTA at 520 nm and complexon of Calcium with cresolphtaelin at 580 nm respectively. Prior to analysis, the reagents must be prepared according to the Skalar methods described on each chemistry. A stabilization period of 20mins must be done and ensure the baseline is relatively stable and according to expected absorbance when passing reagent water. Mixed standard that contains *total and* calcium hardness standard was prepared as mentioned in experimental section. The working standard for total hardness contains double concentration of calcium hardness. For alkalinity and analysis, standards are prepared from Na₂CO₃ solution, likewise, the bicarbonate concentrations is derived mathematically from the same standard of Na₂CO₃ as discussed below and shown in Table 1.

Table 1: Calibration Standards at various concentrations

Alkalinity as mg/L CaCO ₃	Equivalent mg/L as CaCO ₃	Bicarbonate
10	6.1	
20	12.2	
40	24.4	
60	36.6	
80	48.8	
100	61	
Total Hardness mg/L as CaCO ₃	Calcium Hardness mg/L as CaCO ₃	
20	10	
40	20	
60	30	
80	40	
100	50	

4. Results & Discussion

4.1 Method Performance

Solution of high concentrations of 500mg/l of the parameters under investigations was utilized in method optimization, such as flow rate, instrument stabilization, which was found to have no significant effect on the method

performance. It was observed that increasing concentrations of methyl orange in analysis of alkalinity from 0.05% as adopted in the current method, up to 0.5% has an enhanced effect on the increasing sensitivity of the method and good peak resolution was evidently higher concentration above 0.5% did not change the sensitivity of the method, so 0.5% of methyl orange was used in analysis of alkalinity. The word “total” is added to alkalinity since the influence of different ions to total alkalinity may sometimes be reflected separately, for instance, bicarbonate alkalinity which takes concerns in this study. In most natural waters, almost all of the alkalinity will derive from HCO_3^- , CO_3^{2-} , and OH^- . Therefore, alkalinity is described sometime as $\text{Alkalinity} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] + [\text{H}^+]$, where the brackets indicate measured molar Concentrations and Supposed that water contains 61 mg/L HCO_3^- , 2.81mg/L CO_3^{2-} . The concentration of a divalent cation multiplied by the ratio CaCO_3 : atomic weight of the divalent cation is the contribution of that ion to hardness; for instance, Ca^{2+} concentration multiplied by $\text{CaCO}_3:\text{Ca}^{2+}$ (100.08:40.08) or 2.5 gives the calcium hardness. Elements for converting other divalent cation concentrations to a CaCO_3 basis can be used in the following: $\text{Hardness (mg/L as CaCO}_3) = (\text{Ca}^{2+} \times 2.5) + (\text{Mg}^{2+} \times 4.12)$. From the above discussion, the present novel mixed standards techniques have used the above formula for calculation in standard preparation as presented in Table 1.0.

4.2 Calibration

Calibration Curve

The calibration peaks observed by the proposed flow method given in figure 2.0(a) and 2.0(b) are used in calibration as presented in figure 3.0. Figures 2-a&b show the real time spectra of calibration curve for selective analysis of hardness, alkalinity and bicarbonate in water. The method gained its specificity and selectivity as being wave length and pH dependent for the selective analysis of bicarbonate and alkalinity by pH shift at 550nm -decolorization of methyl orange for bicarbonate, pH shift at the same wave length 550 nm- decolorization of phenolphthalein for alkalinity, calmagite reaction of chelated EDTA at 520nm for total hardness and complexon of Calcium to cresolphthalein at 580nm. Figure 3.0 showed a curve of a linearity of $\geq R^2$ 99.9% coefficient of determination for the all the tested parameters at the tested concentration, Even lower concentration range as from 5.0 ppm and 10 ppm was evident in the calibration of bicarbonate and alkalinity respectively. In alkalinity determination better resolution of spectra was evident when methyl orange concentration is increased from 0.05% up 0.5 %.

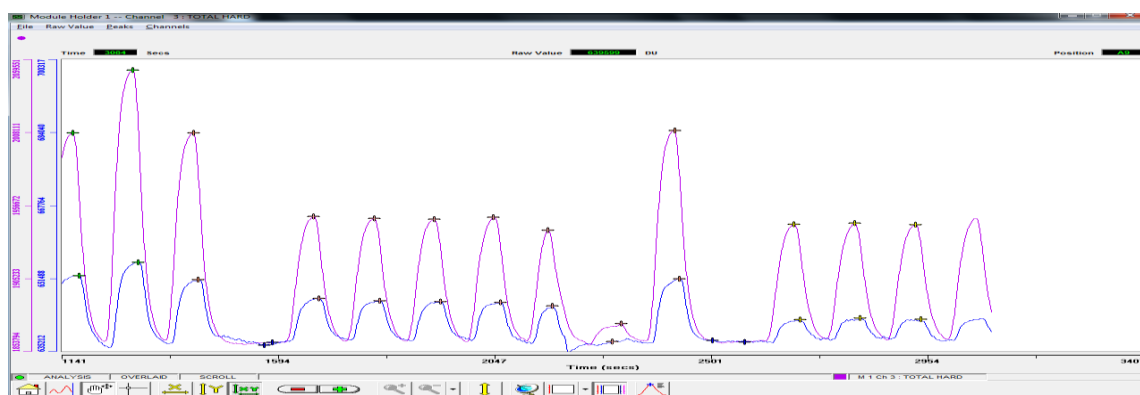


Figure 2-a Register of the signals displayed by the standards used for calibration of total and calcium hardness

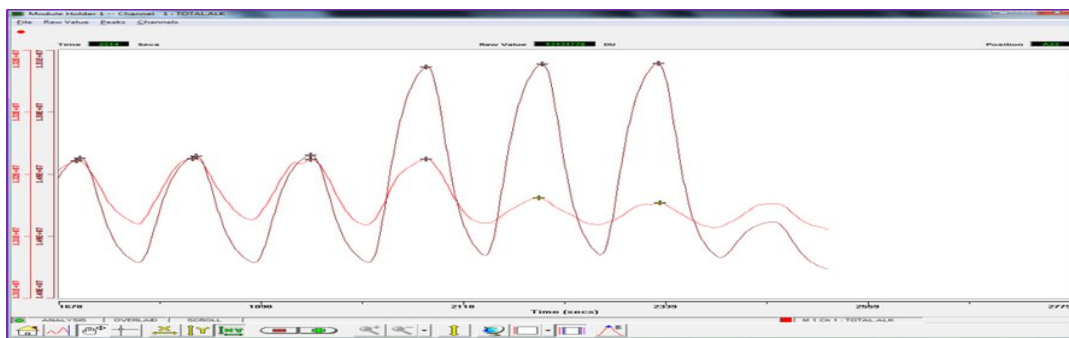


Figure 2-b. Register of the signals displayed by the standards used for calibration of mixed total alkalinity and bicarbonate

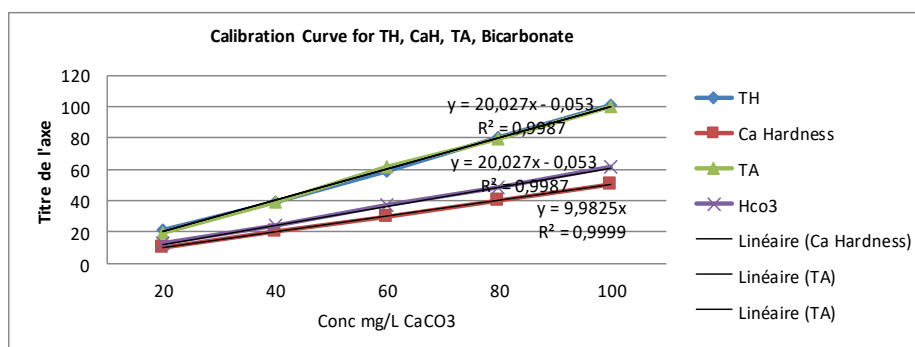


Figure 1: Calibration Curves for Hardness, TA, HCO_3^-

4.3 Precision

Spectral reproducibility is decisive in multi component analysis in order to check the proposed application. Interferences as well as matrix effects and irreproducibility seriously affect the accuracy of the analysis [15]. Figure 4.0 and Figure 5.0 show real time for Total hardness and Total alkalinity respectively. The reproducibility was investigated by repetitive analysis of at least three times for each standard (20-100mg/L). The precision of the method is assessed by calculating the % relative standard deviation RSD which is found to be $\leq 1\%$. E.Gomez¹⁰ used a selective chromatographic reagent PAR for simultaneous determination of calcium and magnesium in environmental samples using a personal microcomputer running software. The High %RSD value for magnesium as well for calcium in the latter study [11] was related to the resolution due to the high absorbance from PAR reagent and also to the lower wave length of the magnesium maxima. In the present study, Spectral peaks obtained for all parameters are sharp and consistent, with an excellent resolution as shown in Figure 4.0 and Figure 5.0 for total hardness total alkalinity respectively.

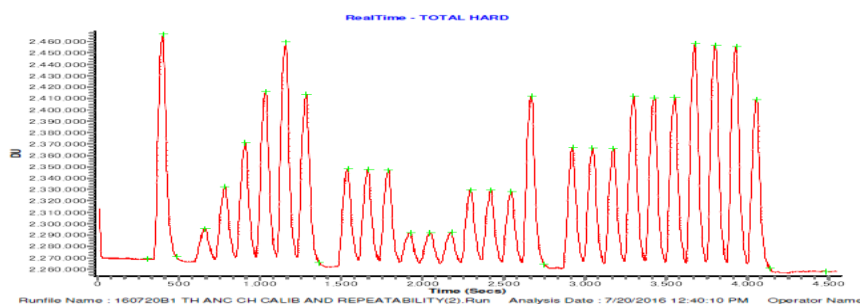


Figure 2: Reproducibility of Total Hardness

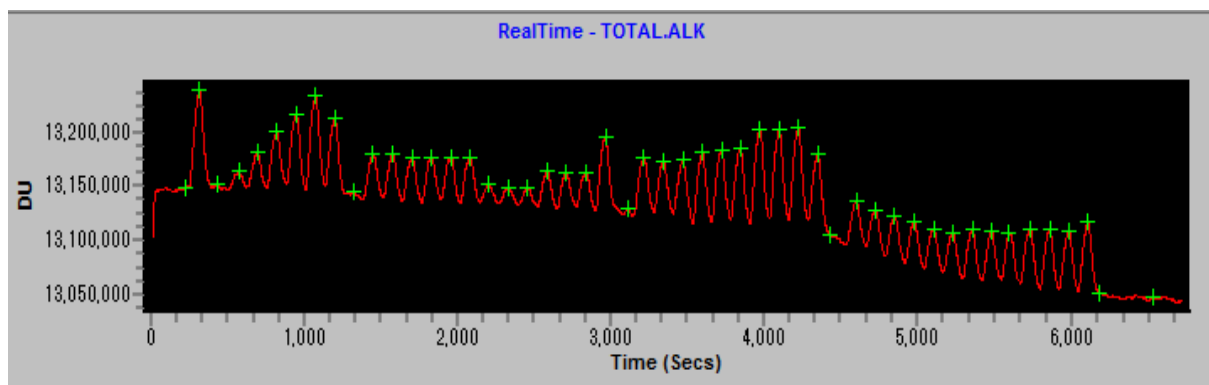


Figure 3: Real time Total Alkalinity Precision

Study of comparing precision found with our proposed method to that with the manual batch titration method, of comparable concentration, was presented in Figure 6.0. Histogram of Fig 6.0 (a-d) present results of the method precision for TA, HCO_3^- and TH as % RSD, which was further compared with % RSD produced by manual titration. From the histogram, it is cleared that the %RSD for the proposed method was almost $\leq 1.0\%$ for all of the concentration tested, which is taken as one of the major advantages of the present technique and it is even highly précised compared to the classical titrimetric manual method for all parameters by 4-5 fold of precision enrichment. Figure 6(e) shows the result of comparing precision of the current method with this our proposed one by analysis in-house reference material IHRM of 50mg/L as CaCO_3 for all tested parameters, the result reflected the high precision in the proposed method compared to the current method.

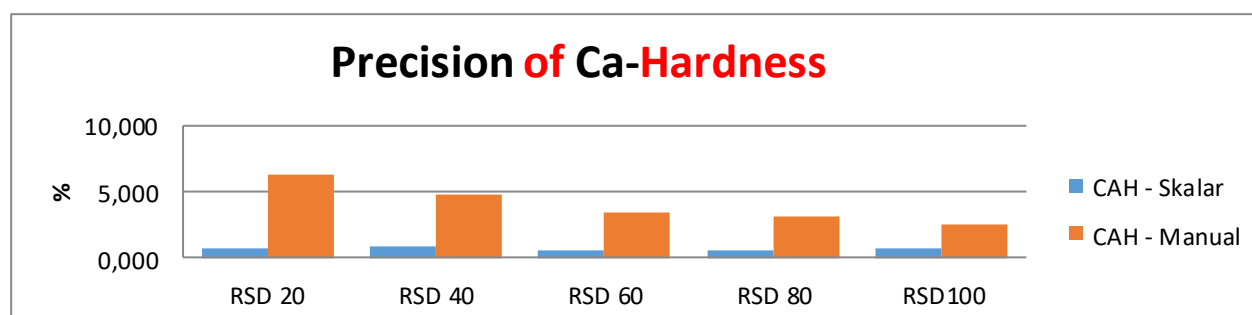


Figure 4-a: Precision of Calcium Hardness of Skalar vs Manual

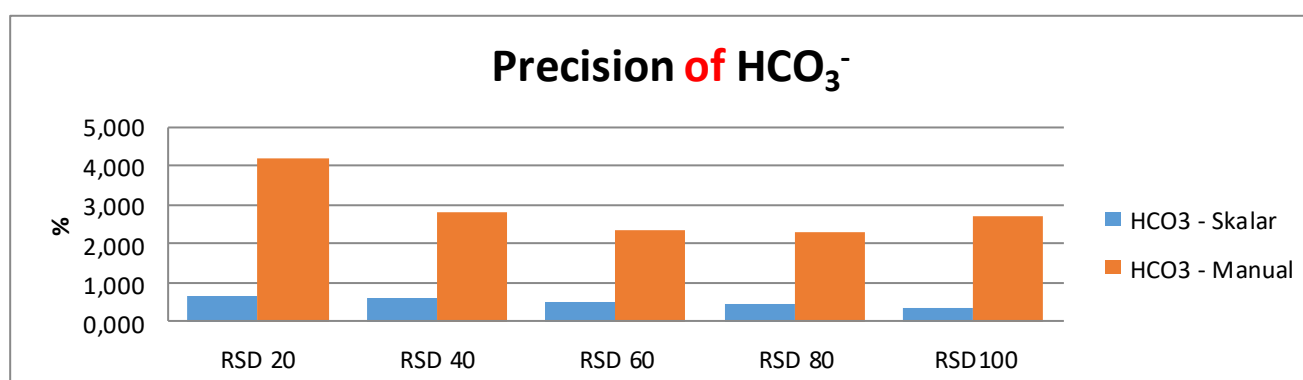


Figure 6-b: Precision of Bicarbonate of Skalar vs Manual

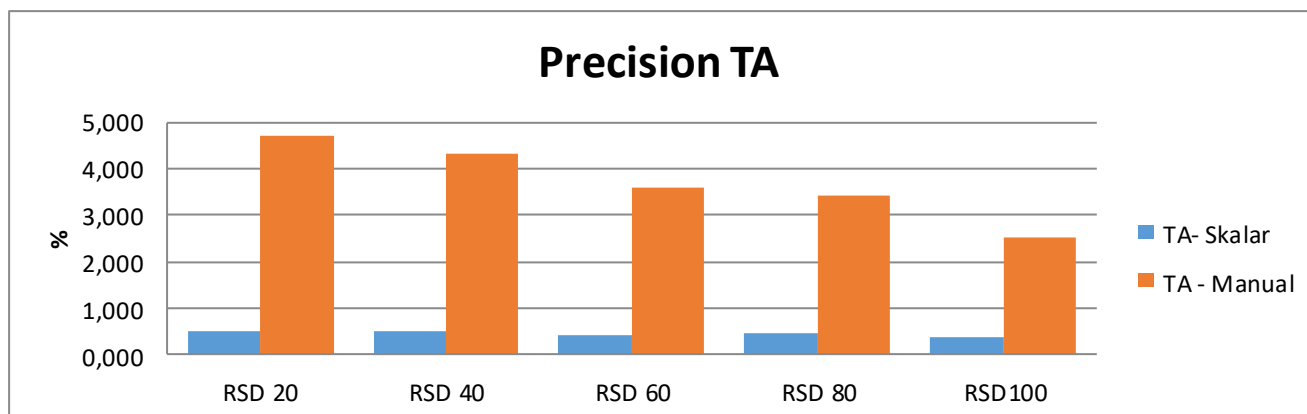


Figure 6-c: Precision of Total Alkalinity of Skalar vs Manual

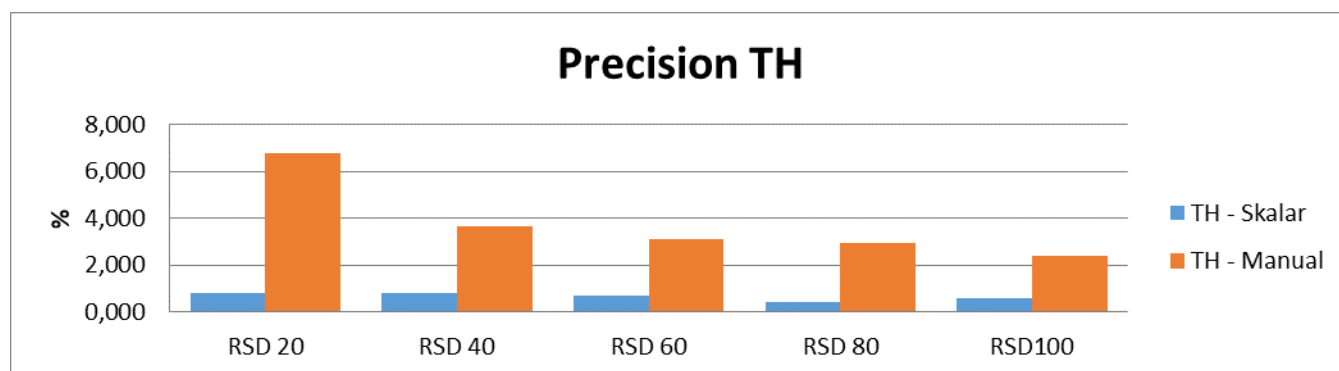


Figure 6-d: Precision of Total Hardness of Skalar vs Manual

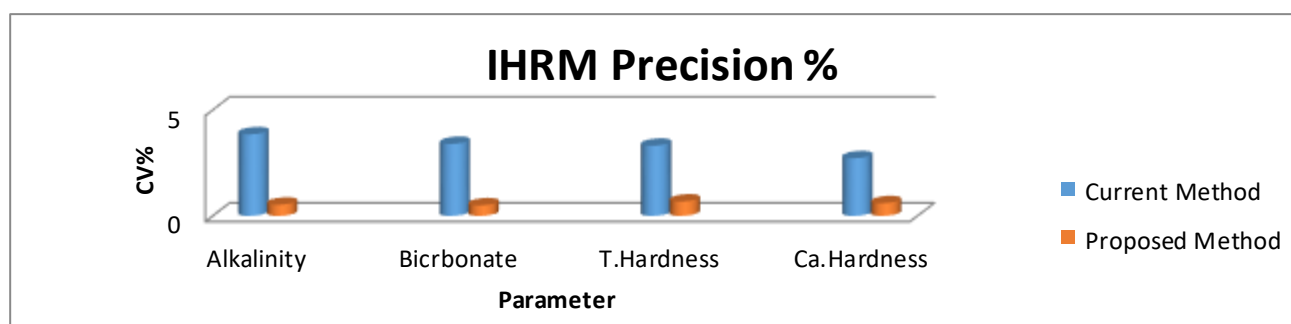


Figure 6-e: precision (IHRM, 60 mg/L as CaCO₃ with current and proposed method)

Table 2.0 (a-b) listed the result for reproducibility of this method for the selective determination of total/calcium hardness and for alkalinity/bicarbonate. The problem of malicious precision in batch titration could be related to the phenomena of pH changes during titration in inconsistent manner due to dissolution of CO₂ from atmosphere. These pHs are significantly less than pHs predicted from enunciations in the titration curves. Although CO₂ is lost from samples during titration, the quantities lost alter with alkalinity concentration, stirring method, and duration for which titration is completed. The reason for this is associated with the removal of dissolved CO₂ by reaction with CaCO₃ which allows more atmospheric CO₂ to enter the water and react with CaCO₃ to attain equilibrium.²

Table 2-a: Method Reproducibility – Total Alkalinity and HCO₃⁻ Mixture

1	Position	Type 1	Identity 1	Total Alkalinity mg CaCO ₃	Bicarbonate mg CaCO ₃
2	WT	IW	Initial Wash	5.14	1.1
3	A26	T	Tracer Standard 5 100 PPM	100.86	60.08
4	Wt	W	Wash	5.14	1.11
5	A22	S1	Standard 1 20 PPM TA	19.66	12.75
6	A23	S2	Standard 2 40 PPM TA	39.46	24.03
7	A24	S3	Standard 3 60 PPM TA	61.95	35.95
8	A25	S4	Standard 4 80 PPM TA	79.09	49.03
9	A26	S5	Standard 5 100 PPM TA	99.84	61.24
10	A25	D	Drift Standard 4 80 PPM	77.86	50.71
11	Wt	W	Wash	5.14	1.11
12	A28	Q1	Quality Control 1 50 PPM	44.12	30.67
13	A28	Q1	Quality Control 1 50 PPM	45.82	31.4
14	A28	Q1	Quality Control 1 50 PPM	42.91	31.84
15	A35	Q1	Quality Control 1	45.6	27.8
16	A35	Q1	Quality Control 1	46.42	28.9
17	A35	Q1	Quality Control 1	47.92	29.1
18	A22	U	Standard 1 20 PPM TA	21.36	15.16
19	A22	U	Standard 1 20 PPM TA	18.99	14.19
20	A22	U	Standard 1 20 PPM TA	19.77	14.42
21	A23	U	Standard 2 40 PPM TA	39.59	25.9
22	A23	U	Standard 2 40 PPM TA	37.65	26.56
23	A23	U	Standard 2 40 PPM TA	38.85	26.35
24	A25	D	Drift Standard 4 80 PPM	73.89	50.02
25	Wt	W	Wash	5.14	1.11
26	A24	U	Standard 3 60 PPM TA	59.29	38.25
27	A24	U	Standard 3 60 PPM TA	56.95	38.94
28	A24	U	Standard 3 60 PPM TA	60.38	38.81
29	A25	U	Standard 4 80 PPM TA	70.7	50.23
30	A25	U	Standard 4 80 PPM TA	74.26	51.17
31	A25	U	Standard 4 80 PPM TA	77.91	50.83
32	A26	U	Standard 5 100 PPM TA	97.64	62.41
33	A26	U	Standard 5 100 PPM TA	97.64	63.4
34	A26	U	Standard 5 100 PPM TA	101.59	63.65
35	A25	D	Drift Standard 4 80 PPM	82.88	52.2
36	Wt	W	Wash	5.14	1.11

Table 2-b: Method Reproducibility – Total and Calcium Hardness

1	Position	Type 1	Identity 1	Total Hardness mg CaCO ₃	Calcium Hardness mg Ca Hardness / L
2	WT	IW	Initial Wash	9.53	-2.3
3	A5	Type 1	Tracer Standard 5 100PPM TH 50 CH	102.98	49.67
4	Wt	W	Wash	9.53	-2.3
5	A1	S6	Tracer Standard 1 20PPM TH 10 CH1	21.39	9.96
6	A2	S7	Tracer Standard 2 40PPM TH 20 CH2	39.41	20.07
7	A3	S8	Tracer Standard 3 60PPM TH 30 CH3	58.17	28.69
8	A4	S9	Tracer Standard 4 80PPM TH 40 CH4	79.85	39.93
9	A5	S10	Tracer Standard 5 100PPM TH 50 CH5	101.17	50.03
10	A4	D	Tracer Standard 4 80PPM TH 40 CH4	79.58	40.15
11	Wt	W	Wash	9.53	-2.3
12	A7	Q1	Quality Control 1 50PPM TH 25 CH	48.86	24.24
13	A7	Q1	Quality Control 1 50PPM TH 25 CH	48.63	26.75
14	A7	Q1	Quality Control 1 50PPM TH 25 CH	48.3	27.6
15	A1	U	Tracer Standard 1 20PPM TH 10 CH1	22.25	11.18
16	A1	U	Tracer Standard 1 20PPM TH 10 CH1	22.3	11.01
17	A1	U	Tracer Standard 1 20PPM TH 10 CH1	22.56	11.29
18	A2	U	Tracer Standard 2 40PPM TH 20 CH2	40.3	22.42
19	A2	U	Tracer Standard 2 40PPM TH 20 CH2	40.18	22.06
20	A2	U	Tracer Standard 2 40PPM TH 20 CH2	39.65	22.13
21	A4	D	Tracer Standard 4 80PPM TH 40 CH4	79.86	42.1
22	Wt	W	Wash	9.53	-2.3
23	A3	U	Tracer Standard 3 60PPM TH 30 CH3	58.3	28.2
24	A3	U	Tracer Standard 3 60PPM TH 30 CH3	58.22	30.88
25	A3	U	Tracer Standard 3 60PPM TH 30 CH3	58.3	28.55
26	A4	U	Tracer Standard 4 80PPM TH 40 CH4	80.07	38.07
27	A4	U	Tracer Standard 4 80PPM TH 40 CH4	79.63	37.22
28	A4	U	Tracer Standard 4 80PPM TH 40 CH4	79.99	36.73
29	A5	U	Tracer Standard 5 100PPM TH 40 CH5	102.44	45.99
30	A5	U	Tracer Standard 5 100PPM TH 40 CH5	101.88	47.11
31	A5	U	Tracer Standard 5 100PPM TH 40 CH5	101.46	48
32	A4	D	Tracer Standard 4 80PPM TH 40 CH4	80.04	39.9
33	Wt	W	End Run	9.53	-2.3
34	Wt	E	End Run	8.24	5.34

4.4 Method Accuracy

4.4.1 Total Alkalinity//and Bicarbonate HCO_3^-

The accuracy of the proposed method for alkalinity was assessed with analysis of known samples with Alain sister water lab, batch method, student paired t-test for equal means was used in comparing difference in mean

concentration, the result revealed that there was no significant difference between the two means. It is worth to note that Titration of alkalinity in batch method is not as simple as it appears in the common practice. The pH reduces gradually as the titration proceeds, and the inflection point in the titration curve at the endpoint is not sharp (i.e. the titration ends at a preset pH which is determined by the change of color of the utilized indicator or the response of a pH electrode) [3]. The theoretical endpoint for titration of HCO_3^- would seem to be at the same pH as the pH of a sample of freshwater in equilibrium with atmospheric CO_2 . In batch method the titration dilemma is that the titration endpoint and the sharpness of the endpoint depends on the dissolved CO_2 concentration in the sample as the endpoint is approached. But under usual laboratory conditions, dissolved CO_2 is produced faster during the titration than it is lost by diffusion from the sample to the atmosphere, and CO_2 accumulates in the sample and shifts the apparent endpoint pH down.²⁷⁻²⁹, he titrated sodium carbonate (Na_2CO_3)-sodium bicarbonate (NaHCO_3) solutions and determined the endpoints from the steepest portion of the inflections in the titration curves. These data were used to show the relationship between alkalinity concentration and pH at endpoints as alkalinity increased from 17.56 to 167.24 mg/L, amounts of CO_2 released during titrations increased and lowered pH of endpoints from 4.98 to 4.63 [3]. The concept of explanation would be used extensively in future work for this study on simultaneous determination of the four parameters in a single run which was tested to be not possible at present due to CO_2 dissolution problem, which needs further investigations. However, the latter approach of the end point titration dilemma disaster do not exist, that adds additional merits on accuracy of the proposed method Moreover, some samples have alkalinity from ions other than HCO_3^- and CO_3^{2-} that do not release CO_2 when neutralized. It is not surprising that recommendation of endpoint pHs for different total alkalinity concentrations has been simplified over the years. Eaton et al¹¹ gave the following alkalinity-pH endpoint recommendation: 30 mg/L, pH4.9; 150 mg/L, pH4.6; 500 mg/L, pH 4.3. They also suggested pH4.5 to be the endpoint pH for routine analyses irrespective of sample alkalinity In previous work [23] the alkalinity value of a synthetic solution was determined using four methods, direct method at pH 4.5 denoted as direct alkalinity, (b) the grans titration method, (c) the proposed method, (d) and by the knowledge of the precise analytical weight of bicarbonate NaHCO_3 that was dissolved in the water termed weighed alkalinity. The latter concentration was used as a reference and the accuracy of the latter methods was compared to the proposed method which is the determination of fresh water measured by H_2CO_3 weak acid system. The method relies on a single titration with H_3PO_4 and two pH readings, acidic PH value target: pH ~ 4.0. The calculation is based on the conception that the overall alkalinity mass of a solution does not vary upon the introduction of non-proton accepting species. The results showed that the accuracy of their finding was comparable with present study although this method showed a precise value compared to the previous work [23] that suffered from dilemma of titration problem.

4.4.2 Accuracy by Recovery in Mixed TA/ HCO_3

Accuracy by recovery was evaluated by analysis of in-house reference material IHRM of 50 mg/L or by analysis of CRM sample WC-ALK-10X-1, CRM sample was not available for HCO_3 , spiking addition standard method was performed instead, the results appear on Table 3 and Figure 7.0. Recovery of IHRM sample is found to be 99%. Moreover, Table 3(b) show results obtained by analysis of CRM material (WC-ALK-10X-1 for TA as CaCO_3) and IHRM of 50.00 mg/L for HCO_3 as CaCO_3 . Recovery was found to be quantitative as shown in Table 3 a-b.

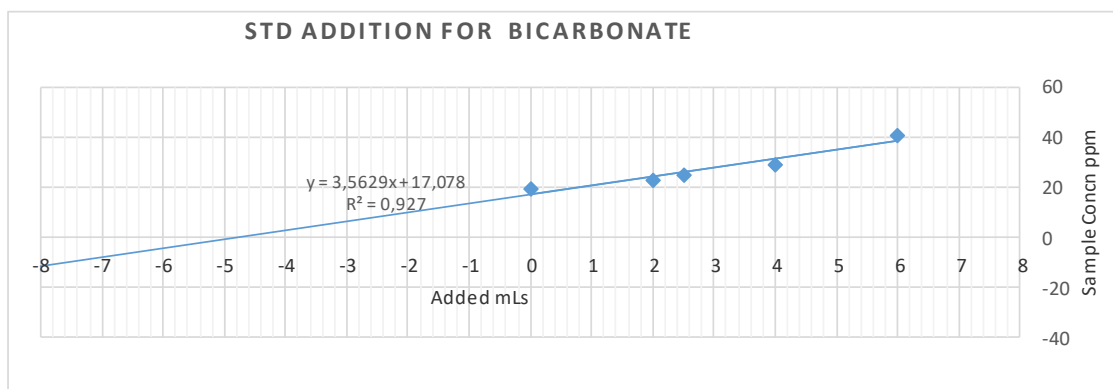


Figure 7: Recovery STD Addition for Bicarbonate

Table 3-a: IHRM Analysis as CaCO₃

1	Position	Type 1	Identity 1	Total Alk mg CaCO ₃	Bicarbonate mg CaCO ₃
10	A25	D	Drift standard 4 80PPM TA 48.8 PPM HCO ₃	78.87	48.9
11	Wt	W	Wash	5.08	-1.14
12	A28	Q1	Quality Control 1 50PPM TA 30.5 HCO ₃	49.83	29.72
13	A28	Q1	Quality Control 1 50PPM TA 30.5 HCO ₄	50.71	30.63
14	A28	Q1	Quality Control 1 50PPM TA 30.5 HCO ₅	51.18	30.75
15	A25	D	Drift standard 4 80PPM TA 48.8 PPM HCO ₃	75.69	48.47
16	Wt	W	Wash	5.08	-1.14
17	ST3	Q1	Quality Control 1 50PPM TA 30.5 HCO ₃	49.13	51.4
18	A25	Q1	Quality Control 1 50PPM TA 30.5 HCO ₄	52.49	52.04
19	ST3	Q1	Quality Control 1 50PPM TA 30.5 HCO ₅	51.62	52.62
20	ST3	Q1	Drift standard 4 80PPM TA 48.8 PPM HCO ₃	49.79	53.2
21	ST3	Q1	Quality Control 1 50PPM TA 30.5 HCO ₃	49.11	52.9
22	ST3	Q1	Quality Control 1 50PPM TA 30.5 HCO ₄	50.22	53.57
23	ST3	Q1	Quality Control 1 50PPM TA 30.5 HCO ₅	50.3	53.49
24	ST3	Q1	Quality Control 1 50PPM TA 30.5 HCO ₄	48.95	53.51
25	ST3	Q1	Quality Control 1 50PPM TA 30.5 HCO ₅	52.5	53.27
26	ST3	Q1	Quality Control 1 50PPM TA 30.5 HCO ₅	51.26	52.59
27	A25	D	Drift standard 4 80PPM TA 48.8 PPM HCO ₃	80.99	49.42
28	Wt	W	Wash	5.08	-1.14
29	Wt	W	End Run	5.08	-1.14
30	Wt	E	End Run	5.08	-1.14

Table 3-b: CRM of Alkalinity and Bicarbonate (x 10 replicate analyses)

Test	Alkalinity CRM	Bicarbonate IHRM
Average*	50.54	52.86
SD	1.36	0.71
Recovery	101.08	105.74

*Average of 5 determinations

4.5 Results for Evaluation of carbonate Concentrations from alkalinity and bicarbonate values

The proposed novel technique is used to automate evaluation of the carbonate content in some of spiked standard and some samples of known contents provided by Abu Dhabi distribution company (ADDC). The computation formula used is the subtraction of bicarbonate concentration from alkalinity values obtained by this method, assuming concentration of hydroxides ions are negligible [3]. Table 4-a shows the results for carbonate determination.

Table 4: Online carbonate evaluation mg/L as CaCO₃

	Alkalinity	Bicarbonate	Carbonate
Drinking water Sample 1	41.77	27.07	14.70
	44.23	30.02	14.21
	44.7	29.68	15.02
Drinking water sample 2	34.64	31.00	3.64
	34.75	31.00	3.75
	34.00	30.30	3.70
	33.5	29.8	3.70
Drinking water Sample 3	63.16	38.56	24.60
	62.8	37.7	25.10
	62.98	38.06	24.92

The results are compared with the results obtained by the manual batch method. The procedure of analysis by the manual method was adopted from below Table 4(-b) [1].

Table 4-b: Alkalinity Relationships¹

	Hydroxide	Carbonate	Bicarbonate
Result of	Alkalinity	Alkalinity	Alkalinity
Titration	as CaCO ₃	as CaCO ₃	as CaCO ₃
P = 0	0	0	T
P < ½T	0	2P	T – 2P
P = ½T	0	2P	0
P > ½T	2P – T	2(T – P)	0
P = T	T	0	0

***Note 1: Key: P – phenolphthalein alkalinity; T – total alkalinity.**

It was found that the results are comparable with the manual with minimal error, for all carbonate analysis as shown in Table 5.0 the precision of the batch method is somewhat lacking as tested with RSD% and Fisher man test (F-test) (data are shown in Table 5 (b-d) with batch method, the analysis for bicarbonate and carbonate is tedious, involves multi-steps titration and fairly depends on pH values as cited earlier, as well as it needs multi calculation steps.¹. On the manual method as shown in table 4-b, if the phenolphthalein alkalinity is less than half total alkalinity, So result for carbonate was essential to be multiplied by two that could have complicate the analysis sequence. The advantage

of this proposed method results for bicarbonate was taken directly from the instrument and no need for mathematical calculation to determine carbonate concentration, here the method gained selectivity and probable specificity as subtraction procedure was computed automatically. The samples investigated for this analysis, were samples that contain a mixture of known amount of carbonate and bicarbonate (Table 5). Accuracy for both methods was assessed by Recovery and precision was assessed by %RSD. The new proposed method demonstrated high superior recovery and lower %RSD. Further comparison with the current skalar method was not feasible. The current method was not practical for the analysis and evaluation of bicarbonate directly because it necessitate manual calculation to subtract the bicarbonate concentration value in a single run from that of alkalinity value in another run for the same sample, assuming the hydroxide value is minimal [3] This is very tedious and rise concern on error propagation, as more than two methods of analysis is considered involved for one sample analysis. The latter approach raised concern over error propagation that could be evident. So, a distinct merit of this proposed method over the current skalar method is demonstrated.

Table 5-a: Comparison Results for evaluation of carbonate concentration

Carbonate mg/L	Proposed Method	Manual Method
Sample 1	14.7	12.8
	14.21	13.9
	15.02	13.2
Mean	14.64	13.30
SD	0.41	0.56
RSD%	2.79	4.19
Recovery	97.62	88.67
Sample 2	3.64	3.08
	3.75	2.88
	3.7	3.08
Mean	3.7	3.2
SD	0.06	0.12
%RSD	1.49	3.61
Recovery	92.42	80
Sample 3	24.6	22.3
	25.1	23.6
	24.92	22.8
Mean	24.87	22.14
SD	0.25	0.66
%RSD	1.02	2.96
Recovery=	99.49	88.56

Table 5-b Evaluation of carbonate concentration mg/Las CaCO₃ for sample 1

t-Test: Paired Two Sample for Means		
<i>Sample 1</i>	<i>Proposed</i>	<i>Manual</i>
Mean	14.64	13.30
Variance	0.17	0.31
Observations	3	3.00
Pearson Correlation	-0.72	
Hypothesized Mean Difference	0	
df	2.0	
t Stat	2.59	
P(T<=t) one-tail	0.06	
t Critical one-tail	2.92	
P(T<=t) two-tail	0.121	
t Critical two-tail	4.30	
F-Test Two-Sample for Variances		
Mean	14.643	13.30
Variance	0.166	0.31
Observations	3.00	3.0
df	2.00	2.00
F	0.54	
P(F<=f) one-tail	0.35	

Table 5-c: Evaluation of carbonate concentration Las CaCO₃ mg/L for sample 2

t-Test: Paired Two Sample for Means		
Sample 2	Proposed	Manual
	3.64	3.08
Mean	3.725	2.98
Variance	0.0013	0.02
Observations	2	2.00
Pearson Correlation	-1	
Hypothesized Mean Difference	0	
df	1	
t Stat	5.96	
P(T<=t) one-tail	0.053	
t Critical one-tail	6.314	
P(T<=t) two-tail	0.106	
t Critical two-tail	12.706	
F-Test Two- Sample or Variances		
	3.64	3.08
Mean	3.725	2.98
Variance	0.0013	0.02
Observations	2	2
df	1	1
F	0.063	
P(F<=f) one-tail	0.156	
F Critical one-tail	0.0062	

Table 5-d: Evaluation of Carbonate concentration mg/L Las CaCO₃ for Sample 3

t-Test: Paired Two Sample for Means		
Sample 3	Proposed	Manual
	24.6	22.3
Mean	25.01	23.2
Variance	0.0162	0.32
Observations	2	2
Pearson Correlation	1	
Hypothesized Mean Difference	0	
df	1	
t Stat	5.838	
P(T<=t) one-tail	0.054	
t Critical one-tail	6.314	
P(T<=t) two-tail	0.108	
t Critical two-tail	12.706	
F-Test Two-Sample for Variances		
Sample 3	24.60	22.30
Mean	25.010	23.20
Variance	0.016	0.32
Observations	2	2.00
df	1	1.00
F	0.051	
P(F<=f) one-tail	0.141	
F Critical one-tail	0.006	

However, one inherent inaccuracy of the Gran method stems from neglecting the CO₃²⁻ and HCO₃⁻ concentrations in the algorithm, at high Total alkalinity values has been reported [25] On analysis, an error may occur due to a too large H₂O buffering capacity, which may requires more pH mass than the carbonate system itself , however recording the first titration point at extremely high pH value might, leads to about 10% error. It originates from these two points that a rough estimation regarding the location of the equivalence point is essential, to choose the suitable pH range for a given sample, which will result in a minimal error [26] .This could justify the lower recovery for manual titration done in this study [26]. The manual or batch technique[26,30], whatever the base on, suffers from some drawbacks: the more significant one relates to the location of the H₂CO₃ n equivalence point can be as much as half a pH unit away from the target titration end point, consequently, with a high concentration (e.g. 4500 mgL⁻¹ as CaCO₃), titration to pH 4.5 does not serve to neutralize all the proton accepting carbonate species and the alkalinity value is underestimated, whereas in the case of too lower concentration range , the neutralization of the acid by reaction with bicarbonate and carbonate is completed, therefor, titrating to pH4.5 results in over estimation of the alkalinity value. Moreover, relatively fewer disadvantages are associated with the pre disposition of CO₂ to be stripped to the atmosphere during the titration procedure. CO₂ volatilization does not affect the alkalinity value directly (CO₂ is not a proton accepting species as shown in below equation, but its 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 [3].

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

4.6 Study of Accuracy for calcium and total hardness

For evaluation of accuracy for both total and calcium hardness, PT Sample No. 477 for mg calcium/L and PT No.445 for total hardness in a separate run was performed. The below table shows the results of the two parameters which are quite satisfactorily with acceptable Z score, Table 6. As t-statistic is less than t-critical (two tailed), so it is concluded that there is no significant difference in means between the two methods.

4.7 Study for sequential analysis of a sole parameter

Unmixed concentrations for Sole parameter were analyzed with the same method. The respective method chemistry is used, $CaCl_2 \cdot 2H_2O$ and Na_2CO_3 , $NaHCO_3$ were used for preparation of working standards for hardness, alkalinity and bicarbonate respectively. Figure 8 shows the calibration curve for each parameter for the same concentration. Recovery was found to be quantitative for the tested parameters using 50mg/L in house reference material IHRM for each the recovery obtained is shown in Table 8.0. Method detection limit was compared with manual using 3 standard deviations of reagent blank as Table 9 shows.

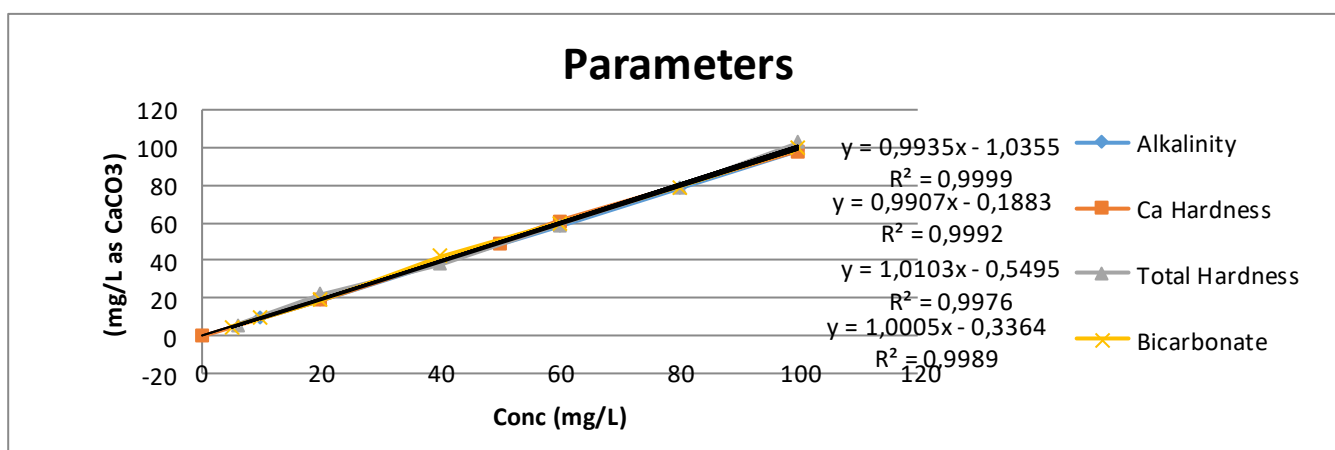


Figure 8: Sequential analysis of Total Alkalinity Hardness and Bicarbonate

Table 6: Recovery for IHRM

Parameter	Current Method	
Alkalinity	Bias (Recovery)	5.00%
Bicarbonate	Bias (Recovery)	-3.70%
Total Hardness	Bias (Recovery)	4.22%
Calcium Hardness	Bias (Recovery)	2.95%

Table 9: Method Detection Limit

	Detection Limit manual mg/L as CaCO ₃	Detection Limit manual mg/L as CaCO ₃	Enhancement
Total alkalinity	5.00	2.20	2.30
HCO ₃ ⁻	5.00	2.00	2.50
Total hardness	5.00	2.80	~2.00
Calcium	6.00	3.00	2.00
Hardness			

4.8 Analysis of Drinking Water Samples

Assuming data is normally distributed, the below equation was used to calculate the z-score assuming only 5% variation from the manual method from the skalar method. Standard deviation SD was quoted as 5% result from the manual [1].

$$Z = \frac{Results_{manual} - Results_{skalar}}{5\% \text{ of manual Results}}$$

$$z = \frac{(x - \bar{x})}{s}$$

Results of Real Sample Analysis shows as Table 10.

Table 10: Results of Real Sample Analysis (Z score Fit for Purpose)

Serial	Sample No	Titration Method	SKALAR	5%Manual	Z score as 5% variation
Total Alkalinity					
1	A10093223001	22.0	23.2	1.1	-1.091
2	A10093734001	49.50	50.41	2.47	-0.368
3	A10093732002	56.00	54.20	2.80	0.643
4	A10093732005	32.00	34.30	1.60	-1.438
8	A1009949001	56.00	54.00	2.80	0.714
9	A10089187002	69.00	67.7	3.45	0.377
10	A10089187003	67.40	69.61	3.37	-0.656
11	A10089188004	67.00	63.34	3.35	1.093
12	A10089188001	68.00	64.17	3.40	1.126
13	A10089187001	66.00	64.43	3.30	0.476
Total hardness					
14	10109101001	53.00	53.76	2.65	-0.287
15	10109101002	53.00	51.51	2.65	0.562
16	10109101003	52.00	47.55	2.35	1.700
17	A10109054001	56.00	59.11	2.80	-1.100
18	A10109054002	60.20	54.49	3.01	1.897
19	A10109054003	69.20	64.38	3.46	1.393
20	A10109054004	67.20	60.14	3.36	2.101
Calcium Hardness					
22	10109101001	50.00	48.93	2.5	0.440
23	10109101002	47.00	44.31	2.35	1.270
24	10109101003	49.60	47.00	2.48	1.050
25	A10109054001	52.00	54.00	2.60	-0.770
26	A10109054002	47.00	52.00	2.35	-2.120
27	A10109054003	56.00	52.00	2.80	0.710

5. Conclusion

Determination of acid-base characteristics of aqueous solutions and corrosivity of water typically involves pH, hardness and alkalinity measurements in a continuous fashion; however, each of these methods suffers from certain shortcomings (making for an incentive for developing a new, simple, accurate method which could be used for continuous analysis). The method gains its superiority by giving a new approach to automate determination of carbonate contents in water sample with high accuracy and precise manner in one single run that could not have been achieved by either the classical titration method or even the sequential scalar current method. Additionally, method gains its simplicity as its being simultaneous and demonstrated its feasibility with reagents cut off by eliminating usage of some standards such as NaHCO_3 one, high sample throughput was evident and its technical specificity as being wave length dependent with no multi titration steps that normally is a concern of error propagation. The current study results raise concern over rapid, accurate and precise new approach in the four parameter determination in a simultaneous manner with special selectivity of calcium and total hardness in one cycle run and for total alkalinity in the second cycle run. The method potential application in this field is illustrated through representative examples covering four parameters and sample matrices, e.g. drinking water and environmental samples such as PT samples. The method did not facilitate online simultaneous determination for the four parameters at the same time, only two related parameters are determined selectively and the other two are detected in the second run, this is due to the fact that the bicarbonate exhibit the problem of drift shift for decolonization absorbance wave length had dramatically limit and impact the determination of total and calcium hardness, this needs further investigations and among future work, alternatively, while the four chemistries were running, the method can selectively determine total and hardness in one run first, then the method shift to determine both of total alkalinity and Bicarbonate in the second run. The Selectivity and simultaneous determination for total /calcium hardness and alkalinity/bicarbonate in one sample gave a distinct merit of simplicity, sensitivity, selectivity and increase sample throughput over the classical manual method.

We suggest future regulators considering developing a guide line for water hardness and alkalinity particularly for Ca^{2+} , $\text{HCO}_3^-/\text{CO}_3^{2-}$ and CaCO_3 precipitation risk. Previous toxicological studies have largely focused separately on the effects of declining or an increase water hardness or alkalinity alone [25]

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