

Measurement of pH, alkalinity and acidity in ultra-soft waters

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Abstract

Conventional characterisation of low alkalinity waters via pH measurement and titration of total alkalinity to a prescribed end-point invariably leads to large errors. These errors result from instability of the pH probe and an unknown titration end-point. In this paper two indirect methods (termed the “double Gran function” and the “blend” method) for the characterisation of such waters are evaluated critically. A blend composed of the raw water, sodium chloride (to increase conductivity), and standard bicarbonate (to increase buffering capacity) was titrated with standard strong acid in two pH regions: $6.3 < \text{pH} < 7.0$, and $3.5 > \text{pH} > 4.0$. In both methods, total alkalinity was determined using the latter set of points, and the first Gran function. In the double Gran function method the upper set of titration points was used to determine CO_2 acidity using the second Gran Function. In the “blend” method, equilibrium chemistry data were used to calculate total acidity for each point based on the known total alkalinity, pH reading, temperature and ionic strength. The two methods gave excellent results (in terms of both repetition and accuracy) as compared to characterisation based on total alkalinity and inorganic carbon analysis. A detailed procedure for the execution of the two approaches is given in an appendix.

Introduction

Natural terrestrial waters on the eastern seaboard region of all the continents in the southern hemisphere have low alkalinity and hardness and are usually slightly acidic; incidents of such waters arise also in most of the northern hemisphere continents.

In South Africa such waters occur from just south of Durban to Cape Town. These waters are corrosive to metals and aggressive to cement materials. Consequently, stabilisation is required prior to distribution. Usually stabilisation is effected via lime (to increase calcium and alkalinity concentrations) and CO_2 addition to obtain a slight supersaturation with respect to CaCO_3 (Loewenthal and Marais, 1976). Dosages to be applied depend on the initial characteristics of the water, i.e. pH, total alkalinity (referred to here as Alkalinity, referring specifically to the alkalinity associated with a H_2CO_3^* reference solution) and Ca^{2+} concentration. In this regard Alkalinity and pH measurements for these waters pose problems. The difficulty with measuring Alkalinity arises from its low value (usually less than 10 mg/l as CaCO_3 and sometimes as low as 1 mg/l) and an unknown titration end-point. For pH the problem is one of instability of the probe in the low buffer/low ionic strength waters. These problems are highlighted in Table 1 below in which are listed results from five analytical laboratories on the eastern seaboard for Alkalinity and pH analyses of a particular water. The magnitude of the differences between the “true” values and the variable results measured by the laboratories is best presented by comparing the total acidity (referred to here as Acidity, referring specifically to the Acidity associated with an CO_3^{2-} reference solution) values of the water calculated from the measured data with their “real” Acidity value calculated from an Alkalinity (measured via Gran function) and total dissolved inorganic carbon (measured using inorganic carbon analyser). The large errors likely to arise in characterisation from “conventional” Alkalinity and pH observations lead to extreme

problems in design and control of water treatment plants in soft water regions.

The problems that arise in these measurements can be summarised briefly as set out below:

Alkalinity measurement problem

Currently most laboratories measure Alkalinity by titration to a fixed end-point (i.e. to a colorimetric or pH end-point) [*The term Alkalinity is used here to define the proton-accepting capacity with respect to carbonic acid as reference point*]. For low Alkalinity waters, this is unsatisfactory because of the difference between the true titration end-point and that used (or reflected by the indicator used). For these waters *Standard Methods* (1998) propose an approximate method based on titration to an arbitrary end-point (anywhere between 4.3 and 4.7). However, this results in large relative errors.

Less often used is a Gran titration (Gran, 1952). The method is accurate, easily effected and independent of a titration end-point.

pH measurement problems

The problem of pH instability in low Alkalinity waters can be partially resolved using glass and reference pH electrodes specifically designed for these waters. However, these are expensive and fragile and most laboratories are not equipped with them. It should be noted, however, that even with these electrodes measurements are still not necessarily reliable as discussed below.

Characterisation of the carbonate system (i.e. the weak acid system controlling pH) in terrestrial waters requires measuring any two independent parameters for this system in water (in addition to temperature and ionic strength). The independent parameters available include Alkalinity, Acidity, CO_2 acidity, total dissolved inorganic carbon (C_T) and pH [*The terms Acidity and CO_2 acidity are used here to define the proton-donating capacity with respect to CO_3^{2-} and HCO_3^- as reference species respectively*]. Recognizing that Alkalinity can be measured accurately using a Gran titration,

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and that (i) Acidity cannot be measured directly (Loewenthal and Marais, 1976), (ii) measurement of C_T requires an expensive inorganic carbon analyser, and (iii) pH measurement is impractical for reasons described above, measurement of the remaining parameter, i.e. CO_2 acidity also should be considered. *Standard Methods* (1998) proposes titration to pH 8.3 using a standardised base, but does not propose a method for CO_2 acidity measurement in very poorly buffered waters where the problem of pH measurement arises. Such consideration is effected in this paper and shown to be acceptable, provided that sodium chloride and standard bicarbonate are added to the test solution.

In this paper, an in-depth investigation is effected into the various means of characterising low-alkalinity waters. The methods investigated include:

- Direct characterisation via measurement of Alkalinity (using Gran function) and pH using various probes available on the market.
- Indirect characterisation where a blend of sample, standard bicarbonate solution and sodium chloride is used. Characterisation of the blend is then effected via:
 - Measurement of Alkalinity using the first Gran function and CO_2 acidity using the second Gran function. From these analyses, the characteristics of the raw water are determined.
 - Measurement of Alkalinity (as above) and measurement of pH of the blend after addition of standard acid to adjust to a well-buffered zone ($6.3 < pH < 7.0$). From these analyses, the characteristics of the raw water are determined.

Before dealing with these methods, it is necessary to review briefly the capacity parameters for the carbonate system (i.e. various forms of alkalinity and acidity) and their interactions with pH via equilibrium equations.

Theory

System parameters

pH in natural terrestrial waters is governed principally by the carbonate system. Equilibrium relationships for this system in water are:

$$(H^+) [HCO_3^-] / [H_2CO_3^*] = K'_1 \quad (1)$$

$$(H^+) [CO_3^{2-}] / [HCO_3^-] = K'_2 \quad (2)$$

$$(H^+) / [OH^-] = K'_w \quad (3)$$

where:

- (x) = activity of species x;
- [x] = molarity of species x;
- K'_1, K'_2 = thermodynamic equilibrium constants adjusted for Debye-Huckel affects;
- $[H_2CO_3^*] = [H_2CO_3] + [CO_{2(aq)}]$.

The three equations above include five weak acid parameters – this observation forms the basis for the need to measure two independent parameters in order to characterise a water. In addition to the above equilibrium equations, a number of proton balance (alkalinity and acidity) equations and a mass balance equation for the dissolved carbonate species can be developed in terms of weak acid species concentrations, giving:

$$\text{Alkalinity} = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] \quad (4)$$

$$CO_2 \text{ acidity} = 2[H_2CO_3^*] - 2[CO_3^{2-}] + [H^+] - [OH^-] \\ = -CO_2 \text{ alkalinity} \quad (5)$$

$$\text{Acidity} = 2[H_2CO_3^*] + [HCO_3^-] + [H^+] - [OH^-] \quad (6)$$

$$\text{Total inorganic carbon} = C_T = [H_2CO_3^*] + [HCO_3^-] \\ + [CO_3^{2-}] \quad (7)$$

These mass and capacity parameters are interdependent as follows:

$$\text{Alkalinity} + \text{Acidity} = 2C_T \quad (8)$$

$$\text{Alkalinity} + CO_2 \text{ acidity} = C_T \quad (9)$$

Clearly, each equation incorporates an extra parameter so that the initial problem remains unchanged, that is, two independent parameters need to be measured.

Usually (H^+) can be measured via operational pH observation (i.e. the pH value measured relative to National Bureau of Standards buffer solutions). The remaining parameter is obtained by considering various alkalinity and acidity capacity parameters applicable to the system. Of these capacity parameters, Alkalinity and CO_2 acidity normally are considered to be easily measurable via strong acid/base titration to a prescribed end-point (about 4.5 and 8.3 respectively) with minimal error involved.

Measurement of Alkalinity and CO_2 acidity using Gran titrations

Gran (1952) showed that functions can be formulated for alkalimetric and acidimetric titrations and used for determining the various capacity parameters independent of a titration end-point. Detailed formulation of these functions is set out in **Appendix A**.

In brief, determination of Alkalinity is effected from standard strong acid titration data effected in a pH region below the H_2CO_3 equivalence point. The appropriate Gran function, F_{1x} , in this region being:

$$F_{1x} = -10^{-pH_x} \cdot (V_s + V_x) = C_a \cdot (V_e - V_x) \quad (10)$$

where:

- V_e = the unknown volume of standard strong acid to be added to reach the H_2CO_3 equivalence point (mL),
- V_x = the volume of standard strong acid added to a point x with pH equal to pH_x (mL),
- C_a = concentration of standard strong acid (mol/L), and
- V_s = volume of sample analysed (mL).

Values for F_{1x} are obtained by inserting titration data in the region $3.5 < pH < 4$ in the left-hand side of Eq. (10), i.e. Plotting F_{1x} vs. V_x gives a linear relationship and its extrapolation to $F_{1x}=0$ (i.e. where the line intercepts with the vertical axis) gives the value of V_e . The desired Alkalinity is thus determined as:

$$\text{Total alk}_{(moles/l)} = \frac{V_e \cdot C_a}{V_s} \quad (11)$$

Determination of CO_2 acidity is effected from titration data in the region $6 < pH < 7$. The appropriate Gran function, F_{2x} , in this region is:

$$F_{2x} = 10^{-(pH)_x} \cdot (V_e - V_x) = -K'_1(V_f - V_x) \quad (12)$$

where:

- V_f = the unknown volume of standard strong acid/base to be added to reach the HCO_3^- equivalence point (mL).

Values for F_{2x} are obtained by inserting titration data into the left-

hand-side term of Eq. (12), after V_e has been determined via the first Gran function. Inspection of the right-hand-side term shows that a plot of F_{2x} vs. V_x is linear and extrapolation to $F_{2x} = 0$ (i.e. where the line intercepts with the vertical axis) gives V_f , that is the volume of strong acid/base to reach the HCO_3^- equivalence point. The desired CO_2 acidity is determined as:

$$\text{CO}_2 \text{ acidity (moles/l)} = \frac{V_f \cdot C_a}{V_s} \quad (13)$$

It should be noted that for low alkalinity waters, the second Gran function is not useful because of pH instability. In order to obtain stable pH observations one may increase both C_T (to increase buffer capacity) and ionic strength (to increase conductivity). Increase in C_T can be effected by addition of a standard bicarbonate solution, termed “a spike” in this paper. The standard bicarbonate solution is designed as an equivalent bicarbonate solution in equilibrium with the air, i.e. Alkalinity = Acidity, and CO_2 acidity = 0 (this is attained ONLY at 96.5 mg/l NaHCO_3 , that is Alkalinity = Acidity = 57.5 mg as CaCO_3 or 1.15 mmol/l). This standard solution remains unchanged with time enabling a long usage period. The modified Gran functions for the blend of sample and standard bicarbonate are as below (the full development of these functions is given in **Appendix A**):

$$F_{1x} = -10^{-\text{pH}_x} \cdot (V_s + V_H + V_x) = C_a \cdot (V_e - V_x) \quad (14)$$

$$F_{2x} = 10^{-(\text{pH})_x} \cdot (V_e - V_x) = -K_1' \cdot (V_f - V_x) \quad (15)$$

where:

$$V_H = \text{volume of spike added to the sample (ml)}$$

From a measurement standpoint, V_e and V_f are obtained as before from strong acid titration data in the relevant pH regions. Note that the V_e and V_f data determined above refer to those for the blend of raw water sample and bicarbonate spike. The raw water Alkalinity and Acidity values are then determined using Eqs. (8) and (9) and simple stoichiometric considerations giving:

$$\text{Alkalinity raw} = [\text{Alkalinity blend} \cdot (V_H + V_s) - V_H \cdot \text{spike}_{\text{alk}}] / V_s \quad (16)$$

$$\text{Acidity raw} = [\text{Acidity blend} \cdot (V_H + V_s) - V_H \cdot \text{spike}_{\text{acd}}] / V_s \quad (17)$$

where:

$$\text{spike}_{\text{alk}} = \text{spike}_{\text{acd}} = 57.5 \text{ mg/l as CaCO}_3 \text{ (standard bicarbonate solution)}$$

With the above basic considerations in mind, it is possible to evaluate critically the various methods for characterising low-alkalinity waters in the laboratory. Note that determination of V_f (to calculate CO_2 acidity) is effected by extrapolation of data based on pH measurements in the region $6 < \text{pH} < 7$. It will be shown that this extrapolation is sensitive to small pH uncertainties. This arises due to the extremely large extrapolation of a plot in which the slope of the regression line is six orders of magnitude greater than the V_f value. Nevertheless, recognising that CO_2 acidity of these waters is usually very low ($< 3 \text{ mg/l as CaCO}_3$), even an error of 50% in this determination has a relatively minor effect on Acidity. This is important, because the chemical dosing to be applied to the water in the treatment works is based on Acidity value and not CO_2 acidity.

Alternatively, the data points can be used individually and the drawback of extrapolation is circumvented. This constitutes the second indirect option of characterisation described in the introduction.

It is to be noted that characterisation via a double Gran function

leads to measurement of two capacity parameters – an approach which is independent of factors affecting potentiometric observations and equilibrium constants such as temperature, pressure, and ionic strength. In contrast, the second approach utilises pH measurements directly (on a sample modified to allow stable pH readings), and depends on all factors affecting equilibrium constants.

Materials and methods

Acidity and Alkalinity measurements were carried out on two low-alkalinity waters originating from the southern coast of South Africa (Port Elizabeth and Knysna). The water samples were initially processed for humic acids removal using $\text{Fe}_2(\text{SO}_4)_3$ and NaOH and their pH was set at approximately pH 6 prior to characterisation.

Standard bicarbonate and hydrochloric acid solutions and standardisation of these is described in detail in **Appendix B**.

Inorganic carbon was measured by means of a Shimadzu TOC – 5000A analyser.

Instruments used: Metrohm digital titrator 715, Metrohm pH meter 744 with combined electrode 6.0228.000, Schott pH meter model CG816 with Orion reference electrode model 90-01 and glass electrode Ag/AgCl 9101SC. Calibration of pH was effected with pH 4 and pH 7 NBS buffers.

Results and discussion

Two low-alkalinity water samples (from Knysna and Port Elizabeth) were used to assess three methods of characterisation. These were:

- Alkalinity and pH measurement of the raw water sample.
- Alkalinity and CO_2 acidity measurements (effected via Gran functions) for a blend of the raw water, standard bicarbonate solution, and sodium chloride.
- Alkalinity measurement and pH measurement (in the region $6.3 < \text{pH} < 7.0$) effected on the blend described in (b) above. Note that the pH – strong acid titration data used to effect the analysis for CO_2 acidity determination in (b) above, are used also in this approach.

Characterisation via Alkalinity and pH measurements on the raw water

Determination of Alkalinity for the two samples was effected via the first Gran function (Eq. (14)). The results of these are listed in Table 2.

pH measurement of the raw samples was attempted using a “general purpose” combined electrode (Metrohm, 6.0228.000), and a specialised glass electrode plus a rapid-flow reference electrode (Orion, model Ag/AgCl 9101SC and 90-01 respectively), recommended for pH measurement in low-conductivity waters. Neither probe gave stable pH observations for the two samples analysed (Fig. 1). Consequently, this option was abandoned.

The observed drift in pH probably reflects the broad spectrum of pH data reported by various analytical laboratories for the Port Elizabeth water samples sent to them for analysis (Table 1).

Alkalinity and CO_2 acidity measurement via Gran functions (the double Gran function method)

Samples of the two waters to be analysed were each blended with standard bicarbonate solution (see **Appendix B**) in the volumetric

Laboratory	pH	Alkalinity (mg/l as CaCO ₃)	Calculated Acidity* (mg/l as CaCO ₃)	"True" Alkalinity (via Gran titration) and Acidity (via IC measurement) (mg/l as CaCO ₃)
1	6.0	2.0	10.9	Alkalinity = 2.80 Acidity = 5.78
2	5.9	4.0	13.3	
3	6.9	2.0	3.1	
4	5.43	2.8	105.2	
5	6.1	2.8	4.3	

* calculated @ 25 °C, EC = 10 ms/m

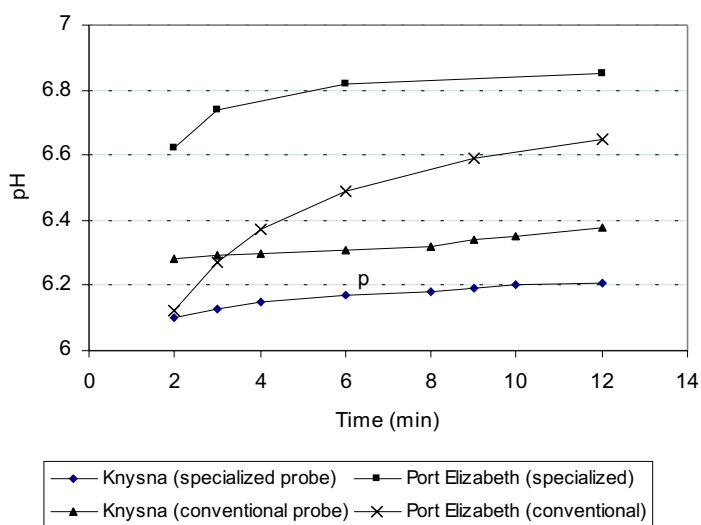


Figure 1

pH measurement with time for Knysna and Port Elizabeth samples, with specialised (Orion) and conventional (Metrohm) probes

ratio 4 to 1 (Knysna) and 6.78 to 1 (Port Elizabeth). The solutions were then titrated with standard acid (for a selection of blending ratio and titration information, see **Appendix B**) to obtain four pH data points in the region $6.3 < \text{pH} < 7.0$ (to be used with the second Gran function), and another 5 points in the region $3.5 < \text{pH} < 4.0$ (to be used with the first Gran function).

The raw titration data (in duplicate, for each water sample) are listed in Table 3. Excellent repeatability was obtained between the duplicates (normally within ± 0.01 pH units).

Alkalinity and CO₂ acidity results calculated from these data via the first and second Gran functions (and the accuracy of the linear regressions) are listed in Table 4.

Figures 2 and 3 show plots of the first and the second Gran functions for a blended sample of the Knysna water. In all cases, linearity was excellent (with $R^2 > 99.7\%$). Comparing Acidity determined for repetitions (i.e. precision), the values determined are close in terms of concentrations, i.e. 4.33 and 5.15 mg/l as CaCO₃ for Knysna, and 4.31 and 4.01 mg/l as CaCO₃ for Port Elizabeth. In order to assess accuracy of the method, results were compared with Acidity determined from observed Alkalinity and

Sample	Alkalinity (mg/l as CaCO ₃)	Average linear regression (R ²)
Knysna	1.13 ± 0.05	0.9998
Port Elizabeth	2.80 ± 0.04	0.9999

	Standard acid addition (mℓ)	pH 1	pH 2
Knysna	1.485	6.93	6.91
	2.905	6.71	6.71
	4.025	6.55	6.56
	5.485	6.36	6.37
	21.620	3.98	3.98
	23.775	3.90	3.90
	26.895	3.81	3.81
	30.190	3.73	3.72
	34.715	3.66	3.66
	Port Elizabeth	1.845	6.78
3.015		6.57	6.57
4.025		6.40	6.39
5.140		6.22	6.21
18.790		3.96	3.95
21.350		3.86	3.85
23.700		3.79	3.79
27.260		3.70	3.70
32.600		3.61	3.61

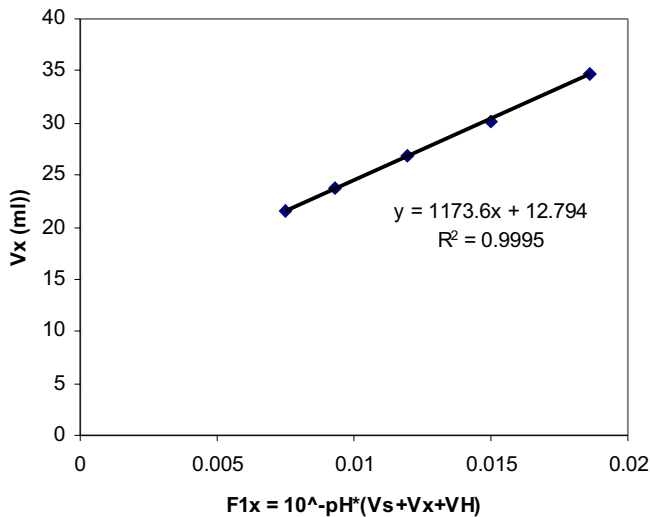


Figure 2

First Gran function regression curve for Knysna water blend, Sample 1 ($V_e=12.794$ ml, $R^2=0.9995$)

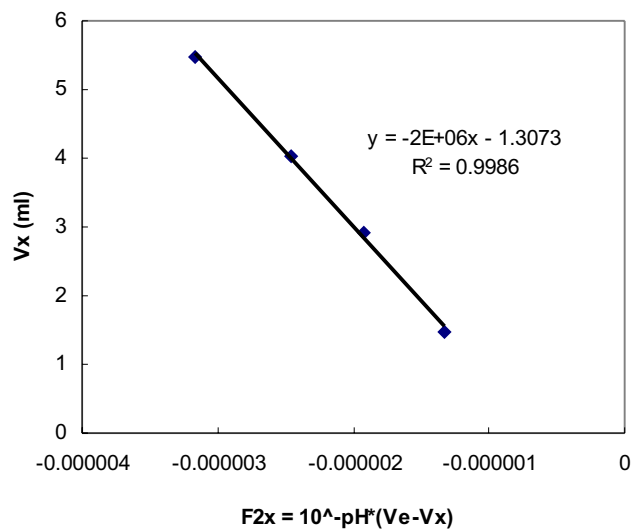


Figure 3

Second Gran function regression curve for Knysna water blend Sample 1 ($V_i = 1.307$ ml, $R^2 = 0.9986$)

Sample	Alkalinity – blend (mg/l as CaCO ₃) (in brackets – R ²)	CO ₂ acidity - raw water (mg/l as CaCO ₃) (in brackets – R ²)	Acidity – raw water (mg/l as CaCO ₃)
Knysna 1	12.61 (0.9995)	1.62 (0.9986)	4.33
Knysna 2	12.63 (0.9999)	2.03 (0.9967)	5.15
Port Elizabeth 1	10.58 (0.9998)	0.75 (0.9980)	4.31
Port Elizabeth 2	10.26 (0.9995)	0.61 (0.9971)	4.01

C_T obtained from a total inorganic carbon analyser. Again, Acidity results are very close (i.e 4.87 mg/l as CaCO₃ from Alkalinity and C_T data vs. 4.33 and 5.15 for Knysna, and 5.78 mg/l as CaCO₃ versus 4.31 and 4.01 for Port Elizabeth).

As previously noted, determination of CO₂ acidity is extremely sensitive to small differences in pH (which result in very small differences in the slope of the regression curve) and as such may create large errors in utilising the second Gran function because of the large extrapolation involved. This phenomenon is shown for the titration results obtained from the blend effected for Knysna

water, Sample 1. For this sample, four pH observations were effected in the pH region used for CO₂ acidity determination. The sensitivity of the second Gran function was then assessed as follows: accepting that the four data points did not give 100% linearity, the data were grouped into four sets of three-point data combinations on which Gran analyses were effected. Referring to these analyses in Table 5, CO₂ acidity varies from 1.30 to 1.80 mg/l as CaCO₃ compared with 1.62 mg/l as CaCO₃ obtained from 4 points. Although the percentage differences appear large, Acidity values calculated from these vary only between 3.70 to 4.69 mg/l respectively, and the pH value of the raw water calculated from these Acidity data (and Alkalinity of 1.13 mg/l as CaCO₃) gives 6.32 and 6.19 respectively.

Points combination	V_f (ml)	CO ₂ acidity (blend) (mg/l as CaCO ₃)	CO ₂ acidity (raw water) (mg/l as CaCO ₃)	R ²
Four points	1.31	1.295	1.62	0.9986
Points 1, 2, 3	1.45	1.44	1.80	0.9985
Points 2, 3, 4	1.05	1.04	1.30	1
Points 1, 3, 4	1.37	1.36	1.70	0.9995
Points 1, 2, 4	1.31	1.29	1.62	0.9987
Average			1.61 ± 0.19	

Alkalinity and pH observations using a bicarbonate blend (The “blend” method)

Samples of the two waters were created as in (b) above, and titrated with standard acid to obtain pH titration data in the regions $6.3 < \text{pH} < 7.0$ and $3.5 < \text{pH} < 4.0$ (i.e. exactly the same experimental data as in (b) above were utilised here). However, the titration data are now analysed differently. In a particular titration, the Alkalinity (in the form of V_e of the blend derived from the first Gran function) is used together with the various pH titration data to calculate Acidity. In this calculation, in addition to the titration data one will

TABLE 6 Raw water Acidity determination using the "blend" method					
Sample	V _x (mℓ)	pH _x	Alkalinity _x ¹ (blend) (mg/ℓ as CaCO ₃)	Acidity _x ² (blend) (mg/ℓ as CaCO ₃)	Acidity raw ³ (mg/ℓ as CaCO ₃)
Knysna 1 (Sample to bicarbonate ratio: 4 to 1)	1.485	6.93	10.84	16.22	4.66
	2.905	6.71	9.22	16.81	4.26
	4.025	6.55	8.00	17.53	4.31
	5.485	6.36	6.48	18.45	4.42
Knysna 2 (Sample to bicarbonate ratio: 4 to 1)	1.485	6.91	10.85	16.50	5.02
	2.905	6.71	9.23	16.84	4.30
	4.025	6.56	8.01	17.34	4.06
	5.485	6.37	6.49	18.21	4.09
PE 1 (Sample to bicarbonate ratio: 6.78 to 1)	1.845	6.78	8.43	13.81	5.90
	3.015	6.57	7.16	14.60	5.90
	4.025	6.40	6.10	15.50	6.21
	5.14	6.22	4.97	16.62	6.76
PE 2 (Sample to bicarbonate ratio: 6.78 to 1)	1.845	6.78	8.12	13.30	5.29
	3.015	6.57	6.85	13.97	5.14
	4.025	6.39	5.79	14.95	5.53
	5.14	6.21	4.68	15.92	5.87

¹ Alkalinity_x = (V_e-V_x)*C_a/(V_s+V_H+V_x), C_a in this calculation = 0.000992 M, V_e (blend) = 12.74, 12.754, 10.686, and 10.358 mℓ for the four samples respectively.

² Acidity_x was calculated using STASOFT, with TDS = 1000 mg/ℓ for all samples, temperature = 23 °C and 25 °C for Knysna and Port Elizabeth respectively.

³ Acidity raw = [(V_s+V_H+V_x)*Acidity_x-V_H*57.5-V_x*0.000992*50000]/V_s

TABLE 7 Summary of Acidity results obtained from the various methods			
Sample	Acidity via "blend" method (mg/ℓ as CaCO ₃)	Acidity via double Gran function method (mg/ℓ as CaCO ₃)	Acidity via inorganic carbon analyzer (mg/ℓ as CaCO ₃)
Knysna 1	4.41 ± 0.18	4.33	4.87
Knysna 2	4.36 ± 0.44	5.15	4.87
Port Elizabeth 1	6.19 ± 0.40	4.31	5.78
Port Elizabeth 2	5.45 ± 0.32	4.01	5.78

also use equilibrium constants adjusted for temperature and ionic strength effects. Results of this calculation are listed in Table 6. Referring to Table 6, for each pH value in a particular titration one can calculate an Acidity value (and CO₂ acidity value). Acidity results for each titration point together with the average and standard deviation for the duplicates of the two waters are given in Table 7. Comparing these Acidity results with those determined using the double Gran function and results obtained from the inorganic carbon analyser, the results are very similar (i.e. an accuracy of approximately ± 1 mg/ℓ as CaCO₃).

Conclusions

- Conventional characterisation of low alkalinity waters, i.e. via pH measurement and Alkalinity measurement via titration to a prescribed end-point invariably leads to large errors due to instability of the pH probes and an unknown titration end-point. This problem was highlighted by the large variability in results obtained from commercial analytical laboratories for a given sample of water, and by the inability to obtain stable pH readings in such waters even with specialised probes (see Fig. 1).
- Full characterisation of terrestrial waters requires a reliable measurement of at least two independent parameters. Recognising that Alkalinity can be accurately measured using a Gran titration, and that:
 - Acidity cannot be measured directly;
 - measurement of C_T requires an expensive inorganic carbon analyser; and
 - pH measurement is impractical for reasons described above;
 direct and indirect measurement of CO₂ acidity through a second Gran function, as well as indirect Acidity measurement were considered.
- Regarding direct CO₂ acidity measurement, it was concluded that the second Gran function is not applicable because of pH instability. In order to obtain stable pH observations one may

increase both C_T (to increase buffer capacity) and ionic strength (to increase conductivity). Increase in C_T was effected by addition of a standard bicarbonate solution, termed in this paper “spike”.

Two indirect characterisation methods were assessed with regard to the blended sample: Measurement of Alkalinity using the first Gran function and CO_2 acidity using the second Gran function (termed the “double Gran function” method); and measurement of Alkalinity (as above) and measurement of pH of the blend after addition of standard acid to adjust the solution into a well-buffered zone ($6.3 < pH < 7.0$) (termed the “blend” method). From these analyses, the characteristics of the raw waters were determined.

- The CO_2 acidity and Acidity results obtained from the two methods were very similar to each other and also similar to the Acidity results calculated using Alkalinity and C_T measurement obtained using an inorganic carbon analyser. Acidity values for all three methods fell between 4.33 and 5.15 mg/l as $CaCO_3$ for the Knysna sample (Alkalinity = 1.13 mg/l as $CaCO_3$), and between 4.01 to 6.19 for the Port Elizabeth sample (Alkalinity = 2.8 mg/l as $CaCO_3$).
- The Double Gran function method was found to be sensitive to small pH differences (although the linear regression was in all cases above 99.7%) due to an extremely large extrapolation involved in the calculation of V_f . Nevertheless, sensitivity tests showed that this phenomenon, although resulting in relatively large fluctuation in the CO_2 acidity result, has only a small affect on the Acidity value.
- It would appear that use of either of the two indirect methods will reduce the errors involved in characterisation of low Alkalinity waters and, consequently, improve control of water treatment plants dealing with these waters.
- It is recommended that soft waters be characterised via Alkalinity and either CO_2 acidity or Acidity measurement. pH is then determined from equilibrium considerations. In this regard, any of various computer programs can be used. In this research, STASOFT4 (Loewenthal and Morrison, 2000) was utilised.
- A detailed procedure to facilitate the execution of the two approaches is presented in **Appendix B**.

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Appendix A

Development of modified Gran functions for the ‘spiked’ sample

Development of modified first Gran function for Alkalinity of spiked sample

Total alkalinity is measured via addition of standard acid to a volume of sample (V_s) to which V_H ml of standard bicarbonate has been added (i.e. “blend”). At any point in the titration, after V_x ml of standard acid has been added, the Alkalinity of the blend can be represented as follows:

$$\text{Alkalinity}_x = (V_e \cdot C_a - V_x \cdot C_a) / (V_s + V_H + V_x) \quad (1)$$

where:

- alkalinity_x = concentration of alkalinity after the addition of V_x ml of standard strong acid (mol/l)
- V_e = the unknown volume of standard strong acid to be added to the alkalimetric end point of the blend (ml)
- V_H = volume of bicarbonate spike added (ml),
- V_x = the volume of standard strong acid added to a point x with pH equal to pH_x (ml)
- C_a = concentration of standard strong acid (mol/l)
- V_s = volume of raw water sample analysed (ml).

Alternatively Alkalinity can be written in terms of weak acid species concentration. Equating this with Eq. (1) gives:

$$\text{Alkalinity}_x = \{ [HCO_3^-]_x + 2[CO_3^{2-}]_x + [OH^-]_x - [H^+]_x \} \quad (2)$$

$$= (V_e \cdot C_a - V_x \cdot C_a) / (V_x + V_s + V_H)$$

where $[y]_x$ indicates concentration of species y after addition of x ml of standard acid.

In the pH region of the titration where $pH < 4$, the species CO_3^{2-} , HCO_3^- and OH^- are negligible and Eq. (2) reduces to:

$$\text{Alkalinity}_x = -[H^+]_x = (V_e \cdot C_a - V_x \cdot C_a) / (V_x + V_s + V_H) \quad (3)$$

Rearranging terms gives:

$$-10^{-pH_x} (V_s + V_H + V_x) = C_a \cdot (V_e - V_x) \quad (4)$$

which is defined as the first Gran function F_{1x} . Values for F_{1x} are then determined from the left-hand side of Eq. 4, i.e.

$$F_{1x} = -10^{-pH_x} (V_s + V_H + V_x)$$

Plotting F_{1x} vs. V_x gives a linear relationship which interception with the vertical axis (i.e. where F_{1x} equals zero) gives the value of V_e for the blend. The Alkalinity of the original water is thus calculated using Eq. (5):

$$\text{Alkalinity}_{(\text{moles/l})} = \frac{V_e \cdot C_a - V_H \cdot [\text{spike}_{\text{alk}}]}{V_s} \quad (5)$$

where:

- $\text{spike}_{\text{alk}}$ = Alkalinity of standardised HCO_3^- solution (1.15 mmol/l)

Development of modified second Gran function for CO_2 acidity for the ‘spiked’ sample

Recognising that the CO_2 acidity of the standardised bicarbonate solution is zero and following the procedure set out above, the total CO_2 acidity equation can be written as follows:

$$CO_2 acid_x = \{ [H_2CO_3^*]_x - [CO_3^{2-}]_x - [OH^-]_x + [H^+]_x \}$$

$$= (V_f \cdot C_a - V_x \cdot C_a) / (V_x + V_s + V_H) \quad (6)$$

where:

- $CO_2 acid_x$ = CO_2 acidity after addition of V_x mL standard bicarbonate solution (mol/L) and
- V_f = the unknown volume of standard strong base to be added to reach the HCO_3^- equivalence point at pH 8.3 (1).

Acknowledging that CO_2 acidity = - CO_2 alkalinity, Eq. (6) can be rewritten as follows:

$$CO_2 alk_x = \{ -[H_2CO_3^*]_x + [CO_3^{2-}]_x + [OH^-]_x - [H^+]_x \}$$

$$= -(V_f \cdot C_a - V_x \cdot C_a) / (V_x + V_s + V_H) \quad (7)$$

In the pH range between 7 and 6, Eqs. (2) and (7) are respectively reduced to:

$$Alkalinity_x = [HCO_3^-]_x = (V_e \cdot C_a - V_x \cdot C_a) / (V_x + V_s + V_H) \quad (8)$$

$$CO_2 alk_x = -[H_2CO_3^*]_x = -(V_f \cdot C_a - V_x \cdot C_a) / (V_x + V_s + V_H) \quad (9)$$

Recognising that $[HCO_3^-] / [H_2CO_3^*] = K_1' / (H^+)$, dividing Eqs. (8) and (9) yields:

$$\frac{Alkalinity_x}{CO_2 alk_x} \cong -\frac{[HCO_3^-]_x}{[H_2CO_3^*]_x} = \frac{V_e C_a - V_x C_a}{V_f C_a - V_x C_a} = -\frac{K_1'}{(H^+)} \quad (10)$$

Rearranging gives the desired equation for CO_2 alkalinity:

$$F_{2x} = 10^{-(pH)_x} \cdot (V_e - V_x) = -K_1' \cdot (V_f - V_x) \quad (11)$$

where F_{2x} is the second Gran function used for determining CO_2 acidity as follows:

Plotting F_{2x} vs. V_x gives a linear relationship the interception of which with the vertical axis (i.e. where F_{2x} equals zero) gives the value of V_f (in this calculation V_f will appear as a negative value due to the representation of CO_2 acidity as $-CO_2$ alkalinity).

The CO_2 acidity of the original water is thus calculated using Eq. (12) (note that CO_2 acidity of the standard bicarbonate solution is zero):

$$CO_2 acid_{(moles/l)} = \frac{V_f \cdot C_a}{V_s} \quad (12)$$

Note that another interesting feature of the second Gran function is that the slope of the curve represents the apparent equilibrium constant K_1' .

Appendix B Procedure for execution of the "double Gran function" and "blend" methods

Apparatus

- 1 pH probe and reference electrode: general purpose combined electrodes cannot be used. In the work reported here an Orion glass electrode and an Orion rapid flow reference electrode were used (see **Materials and methods**). However, one can also use any specialised combined electrode available on the market for use with low conductivity waters.
- 2 Titration apparatus: a micro-burette can be used for the strong acid titration, but rather use an automatic titrator with accuracy of at least ± 0.01 mL.
- 3 Magnetic stirrer: any magnetic stirrer with slow and smooth stirring.

Reagents

- 1 Standard hydrochloric acid: dilute 0.198 mL concentrated HCl (32%) in 2 L with distilled or deionised water. Add 2 g NaCl. Standardise against 20 mL 0.005 N Na_2CO_3 solution by titrating to 4 points at pH values in the region $3.5 < pH < 4$. Execute a first Gran function calculation (see **The double Gran method** below) to calculate the accurate standard acid concentration (Na_2CO_3 concentration is 250 mg/L as $CaCO_3$).
- 2 Standard bicarbonate solution: dissolve 96.5 mg $NaHCO_3$ in 1 L distilled or deionised water. Verify Alkalinity of solution by the first Gran function, using the standard acid. Result of titration should be very close to 57.5 mg/L as $CaCO_3$. If necessary, correct value to 57.5 mg/L, by either diluting with distilled water or by the addition of $NaHCO_3$.
- 3 NaCl can be added to the blend either as powder or as a 250 g/L aqueous solution.

Procedure

- 1 Titrate the raw sample to get 4 to 5 points between pH 4 and 3.5. Analyse Alkalinity using the first Gran function (see **The double Gran method** below).
- 2 Prepare the blended sample according to the following table:

If Alkalinity of raw mg/L is $CaCO_3$	Use raw sample (mL)	Standard bicarbonate (mL)	NaCl (250 g/L) (mL)
0.5 - 2	45	5	0.18
2 - 10	40	10	0.16

Note: the purpose of the bicarbonate to raw sample ratio is to effect pH readings with a minimal C_T of approximately 10 mg/L as $CaCO_3$ while not camouflaging the original acidity value. NaCl is added to maintain a Total dissolved solids (TDS) concentration of approximately 1 g/L throughout the titration.

- 3 Record the temperature of the blend solution.
- 4 Titrate the blend as follows: 4 points evenly distributed between pH 7.0 to pH 6.3. Stir very slowly (to minimise CO_2 exchange with air), and allow the pH to stabilise for at least 40 s before

further addition of acid. After completion of the upper pH region, add acid to reach a pH below 4 and additional volume for another 4 to 5 points down to around pH 3.5. The mixing speed at this stage can be slightly increased as the lower Gran function is not affected by CO₂ loss or gain.

Calculations

The double Gran method

- 1 First Gran function: using the data from the lower pH region, set up the following table (note that if NaCl is added to the sample as powder $V_{NaCl} = 0$ as developed in **Appendix A**):

Point	pH	$F_{1x} = 10^{-pH}(V_x + V_H + V_s + V_{NaCl})$	V_x (mℓ)
1			
2			
3			
4			

- 2 Using Excel, plot F_{1x} (X axis) versus V_x (Y axis), and draw a linear regression curve. The constant of the linear regression formula (i.e. where $F_{1x} = 0$) constitutes V_e (mℓ). R^2 of the regression line should be greater than 0.999.

$$\begin{aligned} \text{Alkalinity of blend (mg/l as CaCO}_3\text{)} \\ = V_e * C_a * 50\,000 / (V_s + V_H + V_{NaCl}) \end{aligned}$$

where:

- V_e = linear regression constant (mℓ),
- C_a = standard acid concentration (mol/l),
- V_s = raw water volume in blend (mℓ),
- V_H = bicarbonate volume in blend (mℓ),
- V_{NaCl} = volume of NaCl 250 g/l solution (mℓ).

Note: For a raw water Alkalinity (No 1 under **Procedure**), V_H and $V_{NaCl} = 0$.

- 3 Second Gran function: using the data from the upper pH region, and V_e from 2 above, set up the following table:

Point	pH	$F_{2x} = 10^{-pH} (V_e - V_x)$	V_x
1			
2			
3			
4			

- 4 Using Excel, plot F_{2x} (X axis) vs. V_x (Y axis), and draw a linear regression curve. The constant of the curve (multiplied by (-1) constitutes V_f (mℓ). R^2 of the regression curve in this case should be greater than 0.996.

Calculation of CO₂ acidity of the raw water is based on the fact that CO₂ acidity of the bicarbonate (and the NaCl solution) solution is zero. Hence:

$$\begin{aligned} \text{CO}_2 \text{ acidity (raw) (mg/l as CaCO}_3\text{)} \\ = (V_f * C_a * 50\,000) / V_s \end{aligned}$$

$$\begin{aligned} \text{Acidity (raw) (mg/l as CaCO}_3\text{)} \\ = [\text{CO}_2 \text{ acidity (raw) + Alkalinity (raw)}] * 2 - \text{Alkalinity (raw)} \end{aligned}$$

The blend method

- 1 Calculate V_e of the blend using the first Gran function as in No 1 under **The double Gran method**.
- 2 For each individual titration point, carry out the following calculation (given in a tabular format):

Point	V_x (mℓ)	pH _x	Alkalinity _x (blend) (mg/l as CaCO ₃)	Acidity _x (blend) (mg/l as CaCO ₃)	Acidity raw (mg/l as CaCO ₃)
1					
2					
3					
4					

- $\text{Alkalinity}_x = (V_e - V_x) C_a / (V_s + V_H + V_{NaCl} + V_x)$
- Acidity_x is calculated using STASOFT or any other software, with TDS = 1 000 mg/l and the measured temperature of the blend, using the measured pH_x and the calculated Alkalinity_x.
- $\text{Acidity raw} = [(V_s + V_H + V_{NaCl} + V_x) * \text{Acidity}_x - V_H * 57.5 - V_x * C_a * 50\,000] / V_s$

- 3 The average of the four points should be reported as the result accompanied by the corresponding standard deviation (e.g., 4.0 ± 0.2 mg/l as CaCO₃).

