Comments on:
"Measurement of pH, alkalinity and acidity in ultra-soft waters"
by
Lahav O, Morgan BE and Loewenthal RE
(*Water SA* **27** (4) 423-432)

This paper is an excellent contribution to the laboratory aspects of the problem of these measurements in low alkalinity waters.

For more than 30 years I too have grappled with this problem, from both a research perspective and a pragmatic approach more suited to a water quality treatment and monitoring laboratory.

Summary

The paper is a very welcome addition to improving these measurements of natural waters, not only because of the techniques used but also because the approach is based on a detailed analysis of the fundamentals of carbonate chemistry in these waters.

However, the paper appears to overlook the significance of errors introduced by not considering the oversaturation of carbon dioxide that is typical of natural surface waters. In particular, the loss of this excess carbon dioxide during sample handling, storage (if any), and laboratory measurement.

Further, consideration of the loss of excess carbon dioxide suggests that not all of the drift in measuring pH is due to probe problems; rather it is at least in part due to the loss of carbon dioxide.

Other issues raised include:

- The effect of the choice of value for the partial pressure of CO_2 in air in determining the concentration of the standard bicarbonate solution.
- Limitations in the accuracy of measuring total inorganic carbon in some analysers.
- The desirability of automating the Gran titration method.
- Whether the *Standard Methods* double endpoint method for measuring alkalinity might be sufficiently accurate.

The effects of oversaturation with carbon dioxide

There is another aspect to the problem of these measurements that is not covered in the paper – the likely presence of excess carbon dioxide (that is, oversaturation) in the sampled waters. Calculations on data from around the world show that (because of respiration of organic material to carbon dioxide) river, lake, and reservoir waters can be up to 30 x oversaturated and groundwaters up to 100 x oversaturated (see also Stumm and Morgan, 1996, pp 189, 191). Waters in the Perth, Western Australia, supply system, some of which have alkalinities in the range below 0.2 mequiv l^{-1} (10 mg CaCO$_3$ l^{-1}), are up to 60 x oversaturated. Of course, anaerobic bottom waters of lakes and reservoirs can be even more oversaturated in carbon dioxide.

Firstly, the elevated carbon dioxide levels lower the pH compared with what would be expected from a consideration of the other constituents of water that effect pH. Measurements we made show increases of up to 0.8 pH units in source waters when excess CO_2 is allowed to escape to the atmosphere. This is close to the theoretical value (~1.1 pH units) for water with alkalinity of 10 mg CaCO$_3$ l^{-1} and 30 x oversaturated with CO_2.

Secondly, the initial loss of carbon dioxide from a freshly taken water sample is sufficiently fast such that ideally pH should be measured directly in the field. In practice, this is not only difficult and costly to arrange, but also presents many instrumental difficulties that are not easily solved. For example, few instruments seem to adjust quickly when taken from a hot vehicle and then placed into relatively cold water. Nevertheless, the exchange of carbon dioxide across the water-air interface is a relatively slow process, and becomes particularly slow as equilibrium is approached. Thus, equilibration can take up to a half-hour in even a small sample in a well-stirred beaker.

After much experimentation, I adopted the following approach as a practical compromise:

- Use multiple sample bottles (new, LDPE plastic), with one (completely filled) set aside only for pH and major component analyses.
- Transport in cooled containers, and within a few hours, to the laboratory.
- Measure pH as soon as possible, at least the same day.
- Measure pH on groups of samples that are similar. Thus, the probe is already more or less equilibrated as it goes from sample to sample.
- Measure pH by inserting a combination electrode directly into the sample bottle, taking the *first reasonably stable* reading (within about 30 s). This requires not only a suitable electrode, but also one that is in good condition (that is, has a rapid response and shows a slope very close to the correct value). A few years ago, even expensive probes would last only about six months. I understand from my former colleagues that probes now last somewhat longer.

The habit of many laboratories (driven by economic considerations) to use pH meters in combination with auto-samplers is easily shown to lead to significantly erroneous results (that is, measured pH higher than actual in these types of samples), and yet this source of error is often ignored. This may explain some of the different values reported for the Knysna and Port Elizabeth samples by the different laboratories.

Carbon dioxide saturation in your Knysna and Port Elizabeth samples

Using the pHs reported in your paper, both those measured directly and those calculated from the double Gran function method, I calculated the levels of carbon dioxide given in the table. To calculate the degree of oversaturation, I used equilibrium $H_2CO_3^* = ca\ 1 \times 10^{-5}$ (pCO_2 = 316 ppm).

Note, however, that it is not clear if in the reported measurements some CO_2 has already been lost to the atmosphere. Thus, the degree of oversaturation in the water bodies may be higher than given in the table.

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Reported pH	Calculated $H_2CO_3^*$	Oversaturation
Knysna (alkalinity 2.26 x 10^{-5} M)		
6.32 (calc)	2.42 x 10^{-5} M	2.4 x
6.1	4.02 x 10^{-5} M	4.0 x
6.3	2.54 x 10^{-5} M	2.5 x
6.4	2.01 x 10^{-5} M	2.0 x
Port Elizabeth (alkalinity 5.6 x 10^{-5} M)		
6.19 (calc)	8.09 x 10^{-5} M	8.1 x
6.1	9.96 x 10^{-5} M	10 x
6.6	3.15 x 10^{-5} M	3.2 x
6.8	1.99 x 10^{-5} M	2.0 x

The directly measured pH values were approximated from the 2 and 12-min readings for the conventional and specialised probes.

Note that calculated values for oversaturation at the 12-min readings are lower than at the 2-min readings, and all trend towards 2 x oversaturation. These data illustrate:

- Significant oversaturation exists in these waters.
- If excessive loss of carbon dioxide occurs before or during measurements, the amounts of treatment chemicals required will be underestimated.
- pH readings taken within the first minute are likely to more accurately reflect the true pH values.
- Reaching equilibrium levels of carbon dioxide is a relatively slow process, especially as equilibrium is approached.

Your standard bicarbonate solution

As part of my work in providing more appropriate calibration solutions for pH in low alkalinity waters, I developed solutions based on calculations and compared the calculated pH values with those measured after equilibration with atmospheric carbon dioxide. The composition of these solutions are available from the author in a document entitled *Quality Assurance Test Solutions - pH Measurement*.

This document shows that the concentration of bicarbonate for a solution in equilibrium with atmospheric carbon dioxide varies significantly with the value used for the partial pressure of the gas in air. Note, however, that the pH varies only very slightly (for a given temperature and ionic strength).

At 25°C, with no added NaCl:
For pCO_2 = 316 ppm, 0.932 mM $NaHCO_3$ is in equilibrium, pH 8.265, $CO_{2(aq)}$ 1.076 x 10^{-5}.
For pCO_2 = 355 ppm, 1.055 mM $NaHCO_3$ is in equilibrium, pH 8.268, $CO_{2(aq)}$ 1.208 x 10^{-5}.

At 20°C, with 1 000 mg l^{-1} NaCl:
For pCO_2 = 350 ppm, 1.0925 mM $NaHCO_3$ is in equilibrium, pH 8.215, $CO_{2(aq)}$ 1.366 x 10^{-5}.

All calculations were made with the PHREEQC program (using the WATEQ4F.dat database) available from the US Geological Survey.

Limitations in measuring low values of total inorganic carbon

A known limitation in the instrumental measurement of total inorganic carbon (TIC) is the difficulty of sparging carbon dioxide at low concentrations.

Measurement of TIC is usually based on converting the carbonates to CO_2 and then measuring the CO_2 stripped from the solution. The problem arises depending on the actual stripping technique used. Those that use a 'continuous-flow' technique may show low results, especially at low levels, because of the difficulty in stripping all the CO_2. On the other hand, those that use a 'closed-loop' technique are less prone to this problem.

Thus, the approach that includes the measurement of TIC may not be as accurate as inferred in the paper.

pH probes and meters

In the early 1980s we conducted a rather large test wherein we gathered every type of pH meter (from about $100 - $1 500) and probe (from about $50 - $200) readily available where I worked at the time. We tested every combination with a range of drinking waters and buffers. To cut a long story short, there were little differences between the pH meters used (at least when measuring to two decimal places – all were modern, solid state designs) but big differences between the probes.

After much discussion, including with representatives from both Radiometer and Orion, and testing every 'cleaning' procedure that we could find (none were successful), we concluded that the main problem was in clogging of the semi-permeable, liquid-liquid junction. As a result, it was necessary to replace probes frequently (about every 6 months) to maintain a fast response and an acceptable value for the mV/H$^+$ relationship. In due course, we tested specialised probes (including those of the 'rapid-flow' type) and low ionic-strength buffers, without changing the main conclusions. I understand, from my former colleagues, that probes available in recent years maintain fast response and good slope for longer.

The Gran titration method

I have no argument with the superiority of the Gran titration method.

However, for practical use of the "double Gran function" method with a large and on-going number of samples it would need to be brought under computer control to enable automation of both the measurement and calculation procedures.

The *Standard Methods* double end-point method for alkalinity

This method corrects for acid needed to titrate the 'water' of the sample to the chosen endpoint. This amount of acid is significant in low alkalinity waters and is the method we chose for routine measurement of alkalinity in water samples at the Water Corporation of Western Australia.

This double endpoint method is easily implemented with at least some commercially available autotitrators. The additional calculations were performed within the laboratory data management system.

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Response to comments made by Dr. Ronald Rosich on the paper
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The authors express their pleasure that the topic of characterisation of soft waters has elicited such an enthusiastic response from many readers. In particular, the comments of Dr. Rosich indicate that the measurement problems encountered in the Western Cape of South Africa appear to be ubiquitous wherever such soft waters are encountered.

In response to some of the many comments and experiences of Dr. Rosich:

- With regard to onsite pH measurement: while the authors are in agreement with the sampling methods proposed by Dr. Rosich, accurate and stable pH observations on-site have not proved successful for soft waters. Indeed, it is resolving just this problem that inspired the investigation published.

- With regard to the double endpoint method for alkalinity measurement as proposed by *Standard Methods*: the required adjustment of 0.3 units of pH below the end point is difficult to execute, unless an autotitrator that is capable of making such a double endpoint titration is available, and therefore we do not recommend this procedure. Furthermore, this method involves a "short-cut" to the complete Gran titration for measuring alkalinity. In our paper we fully endorse use of the Gran titration for effecting such measurements; however, our problem lay in the fact that two independent measurements are needed to characterise the water, that is alkalinity plus some extra parameter requires measurement. We point out that initial pH (usually in the region $5 < \mathrm{pH} < 7$) cannot be measured simply using standard (or even specialised) potentiometric (pH) measurement. We propose measuring the acidity (with reference species HCO_3^-) using a second Gran function. In order to successfully carry out such measurement the C_T and pH of the sample need to be increased – this we suggest is best achieved using a standard bicarbonate solution (see paragraph 4).

- With regard to CO_2 expulsion from samples grossly supersaturated with CO_2 (i.e. certain waters from underground and from anaerobic sediments), the comments of Dr. Rosich are correct and should CO_2 escape occur, this will lead to an error in characterisation. As commented by Dr. Rosich, special precautions need to be adopted both in sampling of, and in dealing with these waters. Principally, no splashing and minimal turbulence should be induced in taking and transferring of samples. Large samples should be taken ($\pm$ 1 l) and bottle should be filled completely; analysis should be done on fresh samples adopting stirring techniques suggested in the paper. However, it is to be noted that the work reported in our paper was carried out on and referred to "normal" soft terrestrial waters that were equilibrated with the atmosphere and certainly not supersaturated with respect to CO_2. Therefore, the exercise presented in the second paragraph is theoretically correct (based on the premise of Dr. Rosich that the initial direct pH measurements were correct), but in our opinion irrelevant to these particular measurements.

- Regarding the "standard bicarbonate solution": a stable bicarbonate solution as defined in the paper is a solution that does not adsorb nor release CO_2 to the atmosphere, i.e. that is close to equilibrium with CO_2 in the air. The solution is made up of 57.5 mg/l $NaHCO_3$ + 1000 mg/l NaCl to increase the ionic strength of the samples measured. Our computation, carried out at 20 ℃ and $CO_{2(g)}$ partial pressure of 0.00035 atmospheres, using STASOFT 4 (a software available from the WRC of South Africa) gives the following results: alkalinity = 57.500 mg/l as $CaCO_3$ and acidity = 57.494 mg/l as $CaCO_3$, i.e. 1.15 mM. We found this accuracy satisfactory.
  A temperature of 20 ℃ was assumed a common laboratory temperature. The error introduced in the procedure by a deviation of 1 to 3 ℃ in the actual temperature of the solution, is totally negligible.

- With regard to "limitations in measuring low values of total inorganic carbon": in the paper no recommendation is made regarding stripping of CO_2. In the paper, we used TIC measurements for comparison purposes only and took precautions to lose as little CO_2 as possible in the sampling and measurement procedure. However, we do not recommend this procedure as means of routine measurement.

- With regard to automation of the Gran method: when measuring a large number of samples, it is always better to have a programmable automated titrator. Such titrators are widely available on the market. For example titrators from Mettler-Toledo and Metrohm.

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