Comments on:
"Measurement of pH, alkalinity and acidity in ultra-soft waters"
by
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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.

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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