

## Response to comments made by Dr. Ronald Rosich on the paper “Measurement of pH, alkalinity and acidity in ultra-soft waters”

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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  $5 < \text{pH} < 7$ ) cannot be measured simply using standard (or even specialised) potentiometric (pH) measurement. We propose measuring the acidity (with reference species  $\text{HCO}_3^-$ ) 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  $\text{CO}_2$  expulsion from samples grossly supersaturated with  $\text{CO}_2$  (i.e. certain waters from underground and from anaerobic sediments), the comments of Dr. Rosich are correct and should  $\text{CO}_2$  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  $\text{CO}_2$ . 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  $\text{CO}_2$  to the atmosphere, i.e. that is close to equilibrium with  $\text{CO}_2$  in the air. The solution is made up of 57.5 mg/l  $\text{NaHCO}_3$  + 1000 mg/l NaCl to increase the ionic strength of the samples measured. Our computation, carried out at 20 °C and  $\text{CO}_2$  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  $\text{CaCO}_3$  and acidity = 57.494 mg/l as  $\text{CaCO}_3$ , i.e. 1.15 mM. We found this accuracy satisfactory. A temperature of 20 °C was assumed a common laboratory temperature. The error introduced in the procedure by a deviation of 1 to 3 °C 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  $\text{CO}_2$ . In the paper, we used TIC measurements for comparison purposes only and took precautions to lose as little  $\text{CO}_2$  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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