

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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