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Estimating the organic acid contribution to coastal seawater alkalinity by potentiometric titrations in a closed cell

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ARTICLE INFO

Article history:

Received 21 November 2007

Received in revised form

6 February 2008

Accepted 7 May 2008

Published on line 16 May 2008

Keywords:

Alkalinity

Organic acids

Organic bases

Potentiometric titrations

Coastal waters

ABSTRACT

This paper examines the performance of a previously reported, closed cell, potentiometric titration technique [J.M. Hernández-Ayón, S.L. Belli, A. Zirino, *Anal. Chim. Acta* 394 (1999) 101] for the simultaneous determination of pH, total inorganic carbon (TCO₂), total alkalinity (TA), and organic alkalinity (OA) in coastal seawater samples. A novel interpretation of the titration data, as recently proposed by Hernández-Ayón et al. [J.M. Hernández-Ayón, A. Zirino, A.G. Dickson, T. Camiro-Vagas, E. Valenzuela-Espinoza, *Limnol. Oceanogr.: Methods* 5 (2007) 225] who applied it to waters of unusually high organic matter content, was applied here to fjord surface waters collected over the duration of a phytoplankton bloom. The parameters pH and TCO₂ – combined with knowledge of boric, phosphate and silicate species concentrations – allowed calculation of all inorganic species that contributed to TA. This inorganic alkalinity term was then subtracted from TA to produce an estimation of OA. Although the OA values obtained were very small ($2\text{--}22 \pm 3 \mu\text{mol L}^{-1}$), they showed a reproducible trend over time in two simultaneous experiments. The organic acids that may have contributed to OA were characterised in back titrations of acidified and CO₂-stripped samples with CO₂-free NaOH. Two classes of organic titratable species, with pK_a values around 4.0 ± 0.2 and 9.1 ± 0.2 were detected. The first occurred in concentrations that co-varied linearly ($r^2 = 0.75$) with protein-like fluorescence, indicating a marine biological source, but were only weakly correlated ($r^2 = 0.46$) to OA. By contrast, Class 2 organic species were not significantly correlated to any fluorescence component of either marine or terrestrial origin but were linearly correlated to OA ($r^2 = 0.69$). These new results reveal that the method proposed by Hernández-Ayón et al. [J.M. Hernández-Ayón, A. Zirino, A.G. Dickson, T. Camiro-Vagas, E. Valenzuela-Espinoza, *Limnol. Oceanogr.: Methods* 5 (2007) 225] for estimating OA can provide a powerful and hitherto unused tool for analysing DOM dynamics and sources in most coastal environments, i.e. as a complement to the more widely used optical tools.

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1. Introduction

As the concentration of atmospheric CO₂ continues to rise, it is estimated that the size of the total inorganic carbon (TCO₂) reservoir in the surface ocean is increasing at a rate of approx-

imately $1 \mu\text{mol kg}^{-1}$ per year [1]. The magnitude of this change can in principle be estimated by measuring either air–sea CO₂ fluxes at sufficient temporal and spatial resolutions, or TCO₂ concentrations in the surface ocean with a precision and accuracy better than $1 \mu\text{mol kg}^{-1}$. Total carbon dioxide dissolved

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0003-2670/\$ – see front matter © 2008 Elsevier B.V. All rights reserved.

doi:10.1016/j.aca.2008.05.018

in seawater (TCO_2) can be obtained directly by automated potentiometric titration of seawater with hydrochloric acid, or indirectly from independent measurements of pH and total (titration) alkalinity (TA) [2,3]. Whichever method is used, the evaluation of the titration data is usually done by the modified Gran functions methodology [2,4,5] which requires defining proton conditions at the two main end points corresponding to the titration of CO_3^{2-} and HCO_3^- species, respectively. Deciding upon the individual contributions of minor inorganic species, such as that of H_2PO_4^- at the HCO_3^- end point for example, can introduce some ambiguities [5]. For example, attempts to correct the TCO_2 results obtained by the modified Gran method for the presence of relatively large concentrations of phosphate ($\sim 60 \mu\text{mol L}^{-1}$) have led to negative errors of 1–2% in the estimation of TCO_2 [5]. Departure from a simple inorganic composition of the water, as may be the case in coastal ocean waters [6], may also prevent a reliable estimate of one of both equivalence points to be obtained if the (unrecognized) protonation reactions of the organic acids present overlap measurably with those of CO_3^{2-} or HCO_3^- . In practice, this overlap is likely to cause serious difficulties in the derivation of the corresponding Gran function when the pK_a of the unknown organic acid differs from that of CO_3^{2-} or HCO_3^- by less than about 1 log unit [7]. In turn, these analytical errors will compromise the accuracy and precision of the CO_2 system parameters such as TCO_2 and carbonate alkalinity (CA). The unknown contribution of organic acids to the measured alkalinity together with the natural variability of CO_2 dynamics in coastal regions, are major reasons why the carbon cycle in these regions is still poorly understood. To overcome these difficulties, Hernández-Ayón et al. [8] proposed a method based on the potentiometric titration with HCl of a known amount of coastal seawater contained in a closed cell. The use of a closed cell ensures that TCO_2 remains constant during the titration—apart from the effect of dilution. Provided a discrete pH measurement is made before the start of the titration, the titration curve then allows pH, TCO_2 and TA to be evaluated on the same sample. Total dissolved inorganic carbon and total alkalinity are evaluated from the position of the two inflection points in the pH vs. volume of added HCl titration plot. These inflection points, which are due to the titration of CO_3^{2-} and HCO_3^- species, respectively, are converted into two well-defined peaks by plotting the slope $\text{dpH}/\text{d}V_{\text{HCl}}$ against V_{HCl} . The end points are then taken as the points where the slope of the titration curve shows a maximum. Unlike the modified Gran approach where the contributions of competing protonation reactions involving protolytes other than CO_3^{2-} or HCO_3^- must be taken into account in an iterative procedure [2], the derivative method does not require an appropriate zero level of protons to be defined at each end point. A further advantage of the derivative method of Hernández-Ayón et al. [8] is that it provides an estimation of the confidence limits of TCO_2 and TA. Titration data from natural water samples containing unpredictable concentrations of uncharacterised organic constituents are therefore best analysed using the derivative method. Furthermore, using a closed titration system adapted from one first described by Dickson and Goyet [3] enables the simultaneous determination of pH, TCO_2 and TA. By detecting a mismatch between the measured alkalinity and that calculated from pH and TCO_2 , it should be

possible in principle to evaluate any organic contribution to TA, such as may occur in estuarine or coastal waters. Only recently, this line of enquiry was followed by Hernández-Ayón et al. [9]. These authors found surprisingly large concentrations ($50\text{--}800 \mu\text{mol L}^{-1}$) of acid–base species that were not consistent with known, inorganic species in seawater and that manifested themselves through (i) large shifts in the position of each titration derivative peak towards greater HCl volumes and (ii) depression and broadening of the first peak (carbonate peak). However, their study was performed in microalgal culture media as well as coastal waters of very high organic content. Whether their technique [8] and methodology [9] is applicable to more typical situations encountered in the coastal ocean remains therefore of considerable interest.

The present study was motivated by the need to examine the precision and limit of detection of this technique in order to assess its geographic range of applicability and thus its usefulness for obtaining accurate values of the carbonate system in the coastal ocean. Given the findings that the separation between the two peaks in the derivative method was relatively insensitive to organic interferences below $300 \mu\text{mol L}^{-1}$ [8], our hypothesis was that TCO_2 in coastal seawater could still be accurately determined from the distance between these two peaks. From TCO_2 and pH, therefore, CA could be calculated. If we knew, or could estimate, the contribution to TA of inorganic bases formed from weak acids with $\text{pK}_a < 4.5$ other than H_2CO_3 and HCO_3^- , it would then be possible to obtain the contribution of the organic species (OA) by difference between the measured alkalinity (TA) and the sum of its inorganic terms according to [10]

$$\begin{aligned} \text{TA} = & \text{CA} + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] \\ & + [\text{SiO}(\text{OH})_3^-] + [\text{HS}^-] + [\text{NH}_3] + \text{OA} - [\text{H}^+] - [\text{HSO}_4^-] \\ & - [\text{HF}] - [\text{H}_3\text{PO}_4] \end{aligned} \quad (1)$$

This possibility was explored in the present study, which was performed during a 21-day nutrient stimulation experiment in a Norwegian fjord [11,12]. The results of this study showed that

- The methodology developed by Hernández-Ayón et al. [8,9] was applicable to a much wider range of coastal waters than might be inferred from their recent field validation study [9], and enabled refined estimates of TA to be extracted in the presence of low levels of organic acid–base species.
- The term defined as ‘organic alkalinity’ (OA) varied in a continuous and reproducible way during the experimental period and turned out to be produced by two groups of organic species that were back titrated after removal of the carbonate system, demonstrating that OA is indeed a chemically meaningful quantity.
- The first group of organic acids correlated very significantly with phytoplankton bloom dynamics and protein-like fluorescence but not with OA itself, indicating that different components of the DOM pool can be detected by potentiometric vs. spectrophotometric methods.

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