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Bárbara Anes, Ricardo J.N. Bettencourt da Silva, Cristina Oliveira, M. Filomena Camões

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UNCERTAINTY EVALUATION OF ALKALINITY MEASUREMENTS ON SEAWATER SAMPLES

Bárbara Anes, Ricardo J. N. Bettencourt da Silva,*
Cristina Oliveira, M. Filomena Camões
Centro de Química Estrutural, Faculdade de Ciências da Universidade de Lisboa,
C8 Campo Grande, 1749-016 Lisboa, Portugal
*bvanes@fc.ul.pt

ABSTRACT

Alkalinity and pH are chemical parameters that, once measured in seawater, allow the calculation of the concentration of the carbonate system species CO_3^{2-}, HCO_3^-, H_2CO_3 and CO_2 which tend to be in equilibrium. Hence, these are key parameters used in oceanic carbon cycle models. The interpretation of the measured values depends on their respective uncertainties.

This work presents a bottom-up evaluation of the uncertainty associated with measurements of total alkalinity, carbonate and bicarbonate concentrations in seawater samples by acid-base titration, with potentiometric detection, using as titrant a hydrochloric acid solution, 0.01 mol L^{-1} HCl in 0.67 mol L^{-1} NaCl, in order to approach working conditions to those of real seawater, with average ionic strength I = 0.67 mol L^{-1}. The precision of the endpoint identification is estimated by the difference between the standard deviation of measurements repeatability and the combination of the repeatability of volumetric operations. Endpoint identification is the major uncertainty component that can be reduced by estimating alkalinity and concentration of the titrant solution, using a larger number of replicates. Total alkalinity was evaluated with a relative standard uncertainty of 1.5 % from triplicate measurements enabling distinction of relative differences larger than 6.3 % on a pair of seawater samples.

A validated spreadsheet for estimating seawater alkalinity, carbonate and bicarbonate equivalent concentrations with respective uncertainty is made available as Electronic Supplementary Material.

KEY WORDS: Alkalinity; carbonate system; uncertainty; seawater; potentiometric titration.