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## Open-cell Titration of Seawater for Alkalinity Measurements by Colorimetry Using Bromophenol Blue Combined with a Non-linear Least-squares Method

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The open-cell titration of seawater was studied for alkalinity measurements by colorimetry.

1) The colorimetric pH of free hydrogen ion concentration,  $\text{pH}_{\text{F(ind)}}$ , was calculated from the ratio of the absorbances at 436 and 590 nm ( $R = \frac{590\text{nm}A}{436\text{nm}A}$ ), along with the molar absorption coefficient ratios ( $e_1$ ,  $e_2$  and  $e_3/e_2$ ) and a tentative acid dissociation constant value ( $\text{p}K_{\text{a}_2}$ ). 2) The perturbation of hydrogen ion was evaluated from the change in titration mass ( $\Delta m$ ). The total hydrogen ion concentration at  $m + \Delta m$ ,  $\text{pH}_{\text{T(at } m+\Delta m)}}$ , was calculated using  $\text{pH}_{\text{F(ind)}}$  for a mass  $m$  and constants for sulfate ( $S_{\text{T}}$ ) and fluoride ( $F_{\text{T}}$ ). 3) The alkalinity ( $A_{\text{T}}$ ) was computed from the titrant mass ( $m + \Delta m$ ) and the corresponding  $\text{pH}_{\text{T(at } m+\Delta m)}}$  through a non-linear least-squares approach using the  $\text{p}K_{\text{a}_2}$  value as a variable parameter. Seawater sample at 2000 m depth from the West Pacific was analyzed. The resulting  $A_{\text{T}}$  ( $2420.92 \pm 3.35 \mu\text{mol kg}^{-1}$ ) was in good agreement with the  $A_{\text{T}}$  measured by potentiometric electric force ( $2420.46 \pm 1.54 \mu\text{mol kg}^{-1}$ ). The resulting  $\text{p}K_{\text{a}_2}$  was 3.7037, in close proximity to that reported by King *et al.* ( $\text{p}K_{\text{a}_2} = 3.695$ ).

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