Potentiality for Over-Estimation of Total Alkalinity observed in Arctic Ocean by Spectrophotometric Method

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Total alkalinity is an important component of oceanic carbonate system, which deeply affects and is infected to the oceanic chemistry, and also oceanic biology. Measurement of total alkalinity is conducted by potentiometric or spectrophotometric method. Potentionetric method is a traditional method that has been employed for a long time, while spectrophotometric method, that avoids problems attributed to glass-made pH electrodes and has higher precision than potentiometric method, was developed in 1990’s and goes into use in this century. A spectrophotometric method was introduced to the laboratory of Research and Development Center for Global Change, Japan Agency for Marine-Earth Science and Technology (JAMSTEC) and the onboard measurement has been conducted for around a decade. Observations were also done in Arctic Ocean, where low alkalinity with its value under 2000 μmol kg^{-1} was often observed especially in sea surface. However, spectrophotometric method is suitable for the measurement of oceanic seawater with its alkalinity values ranges from about 2000 μmol kg^{-1} to about 2500 μmol kg^{-1}, and its application for lower alkalinity has not been examined. In this study, we prepared some seawater samples with their alkalinity under 2000 μmol kg^{-1}, and measured their value by spectrophotometric method.

Reliability of low alkalinity value measured by the spectrophotometric alkalinity system is evaluated by measurements of CRM and its dilutions with ultra pure water under assumption that alkalinity of ultra pure water is 0 μmol kg^{-1}. Ten types of dilutions with its dilution ratio from 0 % (stock solution) to 90 % are prepared for measurements. Titration should be terminated at pH ~ 3.8 –4.2 in the case of using BCG as pH indicator. To examine the pH termination ranges are appropriate for analysis of seawater with low alkalinity, the CRM dilutions were analyzed at their pH termination ~ 3.1 - 4.7.

Measured alkalinity is not necessarily equal for the designated terminated pH ~ 3.8 - 4.2. The difference of measured alkalinity is in 2 - 3 μmol kg^{-1} for the dilution ratio under 40 % (over alkalinity of 1341.9 μmol kg^{-1}), however, the difference of alkalinity in this pH range increases as the dilution ratio increase (lower alkalinity). The difference becomes about 10 μmol kg^{-1} with its dilution ratio of 50 % (1118.3 μmol kg^{-1}), and over 20 μmol kg^{-1} with its ratio of 80 % (447.3 μmol kg^{-1}). Trueness of measured alkalinity is then discussed. Figure 2 shows the difference between the measured alkalinity and theoretical alkalinity. The difference is related to their alkalinity and shows a convex distribution. Around alkalinity of 2250 μmol kg^{-1}, the averaged alkalinity and theoretical value has good agreement. Below 2250 μmol kg^{-1}, the difference increases with decrease of alkalinity and measured alkalinity is higher than theoretical alkalinity. Its difference is about 10 μmol kg^{-1} around the alkalinity of 1500 μmol kg^{-1}. Lower than the alkalinity of 1500 μmol kg^{-1}, the difference decreases as the alkalinity decrease, and the measured value and the theoretical value is nearly equal again at around alkalinity of 750 μmol kg^{-1}. Lower than the alkalinity of 750 μmol kg^{-1}, the measured alkalinity turns to be lower than the theoretical alkalinity and its absolute difference increases with alkalinity decrease.

In Arctic Ocean, where sea-ice melting and increase of inflow of river water has a lot of attention in these decades, alkalinity less than 2000 μmol kg^{-1} was often observed. On edge of sea-ice melting area, alkalinity less than 1700 μmol kg^{-1} is occasionally observed. Our analysis shows that measured alkalinity with its value of around 1300 - 1800 μmol kg^{-1} is considered to be overestimated with its difference of around 10 μmol kg^{-1}. The degree of overestimation is less at external side of this range.

Keywords: Alkalinity, Spectrophotometric Method, Arctic Ocean

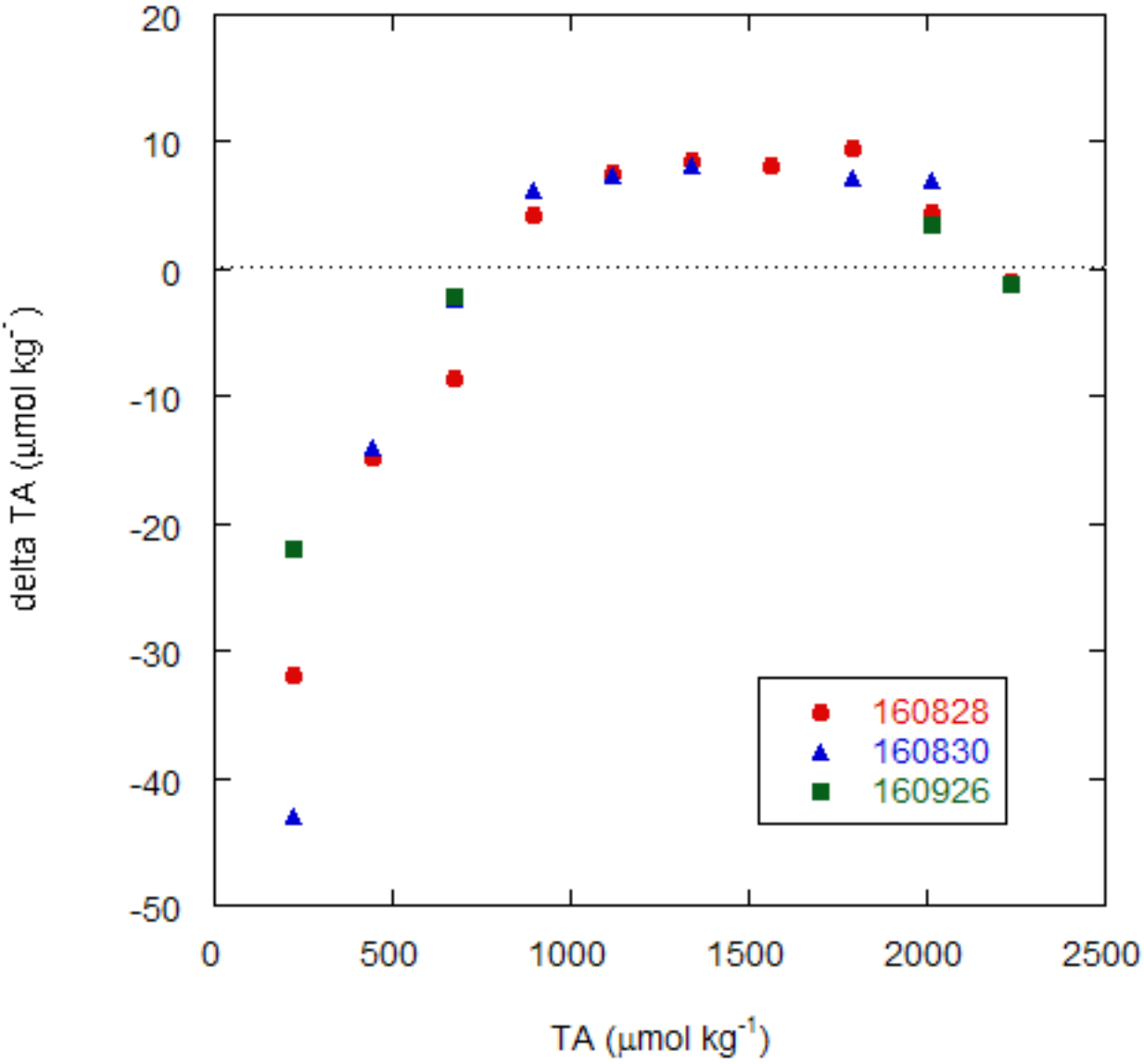

Fig. 1 Difference of alkalinity between measured value and theoretical value. Numeric characters of legend represent the date of analysis (yymmdd).

