5.19   pH of sampled water

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(2) Objective

In order to solve the mechanism of the Madden-Julian Oscillation (MJO) development, the vertical distribution of salinity, dissolved oxygen, nutrients, Chlorophyll-a and pH were measured in the equatorial Indian Ocean. We here report on board measurements of pH during MR11-07 cruise.

(3) Methods, Apparatus and Performance

(3)-1 Seawater sampling

Seawater samples were collected by 12 liter Niskin bottles mounted on the CTD/Carousel Water Sampling System and a bucket. Seawater was sampled in a 100 ml glass bottle that was previously soaked in 5 % non-phosphoric acid detergent (pH13) solution at least 3 hours and was cleaned by fresh water for 5 times and Milli-Q ultrapure water for 3 times. A sampling silicone rubber tube with PFA tip was connected to the Niskin bottle when the sampling was carried out. The glass bottles were filled from the bottom smoothly, without rinsing, and were overflowed for 2 times bottle volume (about 10 seconds) with care not to leave any bubbles in the bottle. The water in the bottle was sealed by a glass made cap gravimetrically fitted to the bottle mouth without additional force. After collecting the samples on the deck, the bottles were carried into the lab and put in the water bath kept about 25 deg C before the measurement.

(3)-2 Seawater analyses

pH ($-\log[H^+]$) of the seawater was measured potentiometrically in the glass bottles.   The pH / Ion meter (Radiometer PHM240) is used to measure the electromotive force (e.m.f.) between the glass electrode cell (Radiometer pHG201) and the reference electrode cell (Radiometer REF201) in the sample with its temperature controlled to 25 +/- 0.05 deg C.

Ag, AgCl reference electrode | solution of KCl || test solution | H^+ -glass electrode.

To calibrate the electrodes, the TRIS buffer (Lot=110525, 100715: pH=8.0910, 8.0906 pH units at 25 deg C, Delvalls and Dickson, 1998) and AMP buffer (Lot=110526, 100720: pH=6.7845, 6.7838 pH units at 25 deg C, DOE, 1994) in the synthetic seawater (Total hydrogen ion concentration scale) were applied. pH_T of seawater sample (pH_{spl}) is calculated from the expression:

$$pH_{spl} = pH_{TRIS} + (E_{TRIS} - E_{spl}) / ER$$

where electrode response ER is calculated as follows:

$$ER = (E_{AMP} - E_{TRIS}) / (pH_{TRIS} - pH_{AMP})$$

ER value should be equal to the ideal Nernst value as follows:

$$ER = RT\, LN(10) / F = 59.16 \text{ mV} / pH \text{ units at 25 deg C}$$

(4) Preliminary results

A replicate analysis of seawater sample was made at 2 layers (ex. 80 and 200 m depth) of cast. The difference between each pair of analyses was plotted on a range control chart (see Figure 5.19-1). The average of the difference was 0.001 pH units (n = 396 pairs) with its standard deviation of 0.001 pH units. These values were lower than the value recommended by Guide (Dickson et al., 2007).

(5) Data Archive

All data will be submitted to JAMSTEC and is currently under its control.

(6) Reference

DelValls, T. A. and Dickson, A. G., 1998. The pH of buffers based on 2-amino-2-hydroxymethyl-1,3-propanediol ('tris') in synthetic sea water. Deep-Sea ResearchI 45, 1541-1554.

Dickson, A. G., C. L. Sabine and J. R. Christian, Eds. (2007): Guide to best practices for ocean CO_2 measurements, PICES Special Publication 3, 199pp.
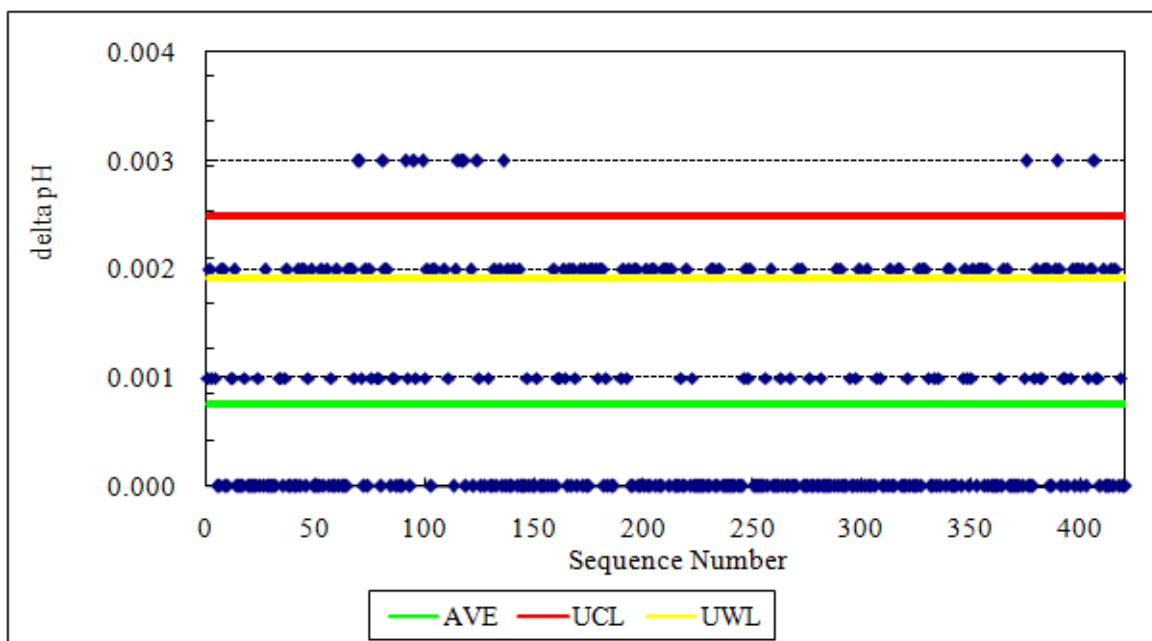

Figure 5.19-1: Range control chart of the absolute differences of replicate measurements of pH carried out during the cruise. AVE represents the average value, UCL upper control limit (UCL = AVE * 3.267), and UWL upper warning limit (UWL = AVE * 2.512) (Dickson et al., 2007).