

2.7 Certified reference materials (CRMs) and working standards

We examined the repeatability of the pH_T measurements for a variety of time ranges from a day to a few years using batches of certified reference materials (CRMs; provided by Andrew Dickson; <http://andrew.ucsd.edu/co2qc/>) used as standards for TCO_2 and TA analyses in seawater. We analysed the CRMs at the beginning and the end of each run of pH_T measurements. Since TCO_2 and TA of a CRM are certified, its pH_T is expected to be stable at constant temperature, although its pH_T value has not been certified yet. In addition, we prepared several batches of reference seawaters as working standards, by a method similar to that used to create the CRMs (Dickson, 1991). These reference seawaters were sterilized with HgCl_2 , sealed as described above, and stored in 250 cm³ borosilicate glass bottles.

3. Onboard measurements

We first evaluated the repeatability of onboard pH_T measurements in the laboratory on land by analysing seawater stored in a large-volume polyethylene container (20 dm³). This seawater was a mixture collected at stations along the equator from 145° E to 160° W during cruise MR00-K08 and kept in the dark at room temperature after the addition of HgCl_2 . The average pH_T (with standard deviation) of this test seawater was 7.8598 ± 0.0002 ($n = 32$). The standard deviation was attributable to the baseline fluctuation of the spectrophotometer.

We then examined the repeatability of onboard pH_T measurements at sea from the standard deviations of pH_T data measured when the ship was stopped at several stations during cruise MR02-K06. Although the number of measurements was limited to 5 at most, the standard deviations of pH_T data ranged from 0.0001 to 0.0011 (Table 1). As evident from fluctuations in salinity, seawater samples taken at each station were not as homogeneous as the seawater mixed in a polyethylene container in the laboratory. However, the standard deviations of the pH_T data in onboard measurements suggest that measurement repeatability was comparable to that obtained in the laboratory on land.

Table 1. Repeatability of onboard pH_T measurements of near-surface waters along the equator during cruise MR02-K06.

Date	Longitude	pH_T	Salinity (psu)
2003/1/17	164°29.4'E – 164°33.6'E	8.1345 ± 0.0006 ($n = 5$)	34.434 ± 0.010
2003/1/18	169°59.1'E – 169°59.3'E	8.1396 ± 0.0001 ($n = 4$)	34.337 ± 0.005
2003/1/21	179°17.0'E – 179°18.8'E	8.1472 ± 0.0002 ($n = 5$)	34.101 ± 0.005
2003/1/22	175°38.3'W – 175°37.5'W	8.1557 ± 0.0003 ($n = 4$)	34.143 ± 0.012
2003/1/24	169°59.5'W – 169°57.2'W	8.1001 ± 0.0011 ($n = 3$)	34.170 ± 0.009
2003/1/25	164°48.2'W – 164°47.8'W	8.0934 ± 0.0002 ($n = 4$)	35.321 ± 0.003
2003/1/28	159°58.9'W – 159°58.4'W	8.0689 ± 0.0006 ($n = 3$)	35.265 ± 0.003

Such onboard measurements of pH_T with good repeatability, taken every 45 minutes at an interval of about 12 nautical miles, can be used to find fine structures of pH_T distribution in near-surface seawater. During cruise MR02-K06, a clear boundary was observed near 172°W at the east end of the western Pacific warm pool (Fig. 4). In the warm pool, pH_T was higher than 8.120. It exceeded 8.140 in the region from the international dateline to 172°W . In the divergence zone to the east of 160°W , pH_T decreased towards the east (minimum 8.069 at 160°W). The results of these observations will be described in a future report.

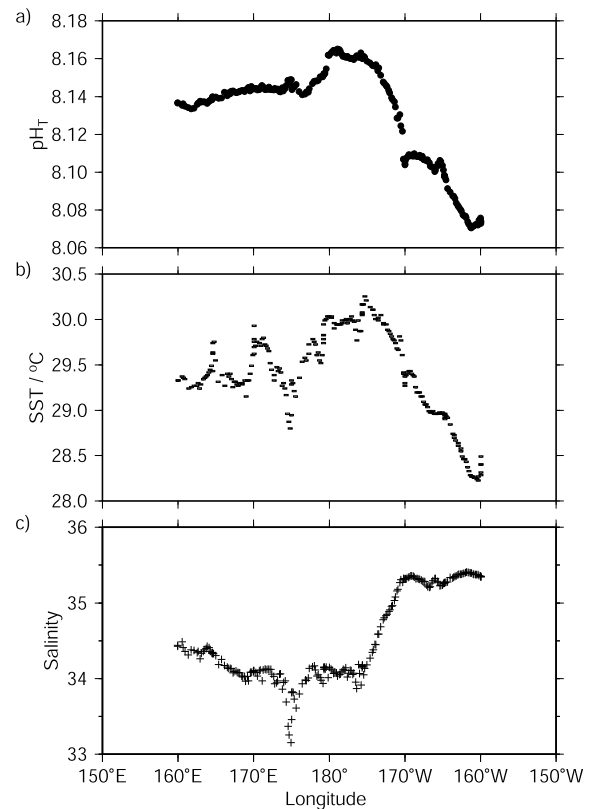


Fig. 4 Horizontal distributions of a) pH_T , b) temperature and c) salinity in near-surface water along the equator observed in January 2003 during the R/V *Mirai*'s MR02-K06 cruise.

4. Measurements of bottle samples taken at depth

For pH_T analysis of bottle samples collected at depths with the CTD/carousel sampler, it has been recommended that the seawater samples be directly withdrawn from Niskin bottles into the optical cells (DOE, 1994). However, it is not convenient to prepare and handle many optical cells during fieldwork. Therefore, we examined the use of sampling bottles and the effect of sterilization with HgCl_2 .

In our study, ca. 500 cm^3 of water sample was drawn with a silicone rubber tube, which was connected to the outlet cock of a Niskin bottle, into a 250 cm^3 borosilicate glass bottle (250 cm^3 was overflowed). After the temperature of the sample was adjusted to $25.0_0 \pm 0.05^\circ \text{C}$ in a water bath, the sample was introduced into the sample loop of the measurement system with a peristaltic pump (see Fig. 1). During cruise MR02-K06, bottle samples were taken in duplicate from a Niskin bottle. The repeatability for the measurement of bottle samples as inferred from duplicate measurements (Fig. 5) was 0.0011 (1σ , $n = 32$). Problems associated with the comparability and precision of pH_T measurements of bottle samples