Table 2 pH_T of CRMs.
Mean ± standard deviation (bottles, measurements) during individual cruises

Experiment periods (ddmmyy)	Apparatus	Dye soln. batch	WS batch	Batch 58	Batch 62	Batch 65	Batch 72
140103-190303	1	784C	V	7.9118 ± 0.0007 (2, 4)			
301003-111103	1	826C	W		7.8760 ± 0.0011 (3, 8)		
170304-210404	1	826C	W		7.8740 ± 0.0007 (3, 6)		
270804-100904	2	837C	W,X		7.8747 ± 0.0007 [a] (1, 2)		
241004-271204	1	837C	X		7.8709 ± 0.0014 (3, 6)		
180805-180805	2	957C	X,Y		7.8747 ± 0.0005 [a] (1, 2)		
091105-290306	2	957C	Y		7.8712 ± 0.0016 (3, 6)	7.9155 ± 0.0006 (2, 4)	7.9009 ± 0.0001 [a] (1, 2)
130706-140806	2	957C	Y,Z		7.8690 ± 0.0001 [a] (1, 2)	7.9079 ± 0.0001 [a] (1, 2)	7.8962 ± 0.0006 [a] (1, 2)
131206-200107	2	957C, 1058C	27				7.8949 ± 0.0022 (3, 7)
Whole period				7.9118 ± 0.0007 (2, 4)	7.8731 ± 0.0025 (16, 34)	7.9129 ± 0.0039 (3, 6)	7.8956 ± 0.0027 (7, 15)
Calculated from TCO_2 and TA [b]				7.9119 ± 0.0010	7.8735 ± 0.0014	7.9189 ± 0.0015	7.8986 ± 0.0017
Measured – Calculated				–0.0001	–0.0005	–0.0059	–0.0029

[a] Mean ± standard deviation for the difference in analytical results between duplicate measurements.
[b] Means ± standard deviations of pH_T calculated from certified values of TCO_2 and TA using dissociation constants for carbonic acid in seawater reported by Lueker et al. (2000).

6. Procedure to measure pH_T with high comparability and precision

On the basis of our experimental results, we recommend the following experimental procedure for pH_T measurements at sea and on land. CRMs should be measured at the beginning and the end of a cruise or a series of experiments. Working standards should be measured at the beginning and the end of each day of pH_T measurements during a cruise. Prior to data collection during a cruise, we recommend making a property control chart of measured pH_T values (SOP 22 in DOE (1994)) and calculating the mean and standard deviation from at least 12 data points obtained from working standards measurements. If a newly measured value is out of the range of mean ± 2σ, an additional bottle of working standard should be analysed. If a couple of measured values are out of the range of mean ± 3σ, another batch of working standards or CRMs should be analysed. If the results are out of the range of each mean ± 3σ, the apparatus or reagents should be checked to determine the reason for discrepancy. The mean and standard deviation are updated by adding newly accepted data.

The following data processing method is recommended:

1) pH_T is calculated from spectrophotometric data by means of Eqs. (4) and (5).
2) pH_T should be corrected for the perturbation induced by the addition of dye and saturated $HgCl_2$ solutions to the sample. Dye correction is expressed by the term ΔR and expressed as a quadratic function of R_1 (Eqs. (7) and (8)). The coefficients in equation (8) should be determined for each batch

of indicator solution. To correct for the perturbation caused by the addition of saturated $HgCl_2$ solution, the constant value of 0.0012_3 is added to the pH_T data of a sample that has been sterilized with $HgCl_2$.

3) pH_T measured at temperature t (°C) is normalized at temperature of 25.00 ºC by means of Eq. (9).

7. Discussion

7.1 Standard deviation of pH_T in reference materials

The averages and standard deviations of the pH_T values of CRMs and working standards for a single cruise and for several cruises are listed in Tables 2 and 3, respectively. The standard deviations for working standards (0.0004–0.0059) during each cruise were on the whole larger than those for CRMs (0.0006–0.0022), except the values from duplicate measurements. The standard deviations were somewhat larger than the repeatability of bottle sample measurements described in Section 4.3 (0.0011). This result indicates that the CRMs and, in particular, working standards were somewhat inhomogeneous. Working standard batch W is likely to be more inhomogeneous than others, because the standard deviation of pH_T for working standard W was larger than that for working standard V and X, which was measured in the same periods of experiments with same apparatus (Table 3). If we exclude the results of working standard batch W, we can conclude that the repeatability of our measurements within a cruise or a series of experiments was better than 0.002.

Table 3 pH_T of working standards.
Mean ± standard deviation (bottles, measurements) during individual cruises

Experiment periods (ddmmyy)	Apparatus	Dye soln. batch	Batch V	Batch W	Batch X	Batch Y	Batch Z
140103 –190303	1,	784C	7.7776 ± 0.0011 (43, 43)				
171003 –221003	1	826C	7.7756 ± 0.0015 (7, 9)	7.8613 ± 0.0059 (7, 9)			
301003 –111103	1	826C	7.7810 ± 0.0025 (4, 4)	7.8704 ± 0.0057 (40, 41)			
170304 –210404	1	826C		7.8640 ± 0.0038 (45, 45)			
270804 –100904	2	837C		7.8718 ± 0.0040 (3, 5)	7.9576 ± 0.0020 (23, 27)		
300904 –011004	1	837C			7.9494 ± 0.0013 (6, 6)		
041004 –081004	2	837C			7.9550 ± 0.0020 (8, 11)		
241004 –271204	1	837C			7.9504 ± 0.0015 (31, 32)		
180805 –180805	2	957C			7.9550 ± 0.0004 (7, 7)		
091105 –290306	2	957C				7.9177 ± 0.0021 (93, 101)	7.8356 ± 0.0013 (7, 7)
130706 –140806	2	957C				7.9187 ± 0.0010 (5, 5)	7.8348 ± 0.0021 (40, 40)
131206 –200107	2	957C, 1058C				7.9169 ± 0.0001 [a] (2, 2)	7.8358 ± 0.0021 (6, 6)
Whole period			7.7776 ± 0.0017 (54, 56)	7.8667 ± 0.0061 (95, 100)	7.9537 ± 0.0037 (75, 83)	7.9177 ± 0.0021 (101, 109)	7.8330 ± 0.0024 (54, 54)

[a] Mean ± standard deviation for the difference in analytical results between duplicate measurements.