

4.4 Uncertainty in pH_T measurements of bottle samples

The pH_T values of bottle samples agreed reasonably with the values measured onboard. The precision of bottle sample measurements as estimated from duplicate sample measurements was 0.0011 (Fig. 5 in Section 4). Taking into account the perturbation due to storage, the uncertainty of bottle sample measurements was 0.001 for surface waters (Fig. 9 in Section 4.3) and a maximum of 0.006 for deep waters (Fig. 10 in Section 4.3) over a period of 50 days.

5. Consistency of measured and calculated pH_T values for CRMs and comparability of pH_T data among several cruises

We measured pH_T values of several batches of CRMs used as standards for TCO_2 and TA analyses to investigate the consistency of pH_T measurements obtained by means of our system with the calculated pH_T values of CRMs certified for TCO_2 and TA. Although the CRMs were not certified for pH_T , their pH_T values could be calculated from the certified TCO_2 and TA values because these values are stable. We compared our measured pH_T values with the values calculated from the certified TCO_2 and TA values of the CRMs using the dissociation constants of carbonic acid in seawater reported by Lueker et al. (2000). We adopted the dissociation constants of Lueker et al. (2000) for the following reasons:

- a) The fugacity of CO_2 ($f\text{CO}_2$) calculated from TCO_2 and TA using these dissociation constants agreed well with measured values in the range up to 500 μatm (Lueker et al., 2000).
- b) The dissociation constants of Lueker et al. (2000) are based on the data of Mehrbach et al. (1973). Lee et al. (2000) reported that $f\text{CO}_2$ calculated from pH_T and TCO_2 using dissociation constants based on the data of Mehrbach et al. (1973) agreed well with measured $f\text{CO}_2$ values.

The pH_T values of CRMs measured during several cruises agreed well with pH_T values calculated from the certified values of TCO_2 and TA (Table 2). Although the difference between the measured and calculated pH_T values for batch 65 was larger than for any other batch, this difference was within the range of experimental error ($\text{mean} \pm 2\sigma$). We concluded that the pH_T values obtained by our measurement system were consistent with certified TCO_2 and TA values and that the pH_T measurements we obtained during the different cruises (in which different dye solutions and working standards were used) were comparable.

Table 2 pH_T of CRMs.Mean $\pm$ 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 $\pm$ 0.0007 (2, 4)			
301003-111103	1	826C	W		7.8760 $\pm$ 0.0011 (3, 8)		
170304-210404	1	826C	W		7.8740 $\pm$ 0.0007 (3, 6)		
270804-100904	2	837C	W,X		7.8747 $\pm$ 0.0007 ^a (1, 2)		
241004-271204	1	837C	X		7.8709 $\pm$ 0.0014 (3, 6)		
180805-180805	2	957C	X,Y		7.8747 $\pm$ 0.0005 ^a (1, 2)		
091105-290306	2	957C	Y		7.8712 $\pm$ 0.0016 (3, 6)	7.9155 $\pm$ 0.0006 (2, 4)	7.9009 $\pm$ 0.0001 ^a (1, 2)
130706-140806	2	957C	Y,Z		7.8690 $\pm$ 0.0001 ^a (1, 2)	7.9079 $\pm$ 0.0001 ^a (1, 2)	7.8962 $\pm$ 0.0006 ^a (1, 2)
131206-200107	2	957C, 1058C	27				7.8949 $\pm$ 0.0022 (3, 7)
Whole period				7.9118 $\pm$ 0.0007 (2, 4)	7.8731 $\pm$ 0.0025 (16, 34)	7.9129 $\pm$ 0.0039 (3, 6)	7.8956 $\pm$ 0.0027 (7, 15)
Calculated from TCO ₂ and TA ^b				7.9119 $\pm$ 0.0010	7.8735 $\pm$ 0.0014	7.9189 $\pm$ 0.0015	7.8986 $\pm$ 0.0017
Measured – Calculated				–0.0001	–0.0005	–0.0059	–0.0029

^a Mean $\pm$ standard deviation for the difference in analytical results between duplicate measurements.^b Means $\pm$ standard deviations of pH_T calculated from certified values of TCO₂ 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 $\pm$ 2 σ , an additional bottle of working standard should be analysed. If a couple of measured values are out of the range of mean $\pm$ 3 σ , another batch of working standards or CRMs should be analysed. If the results are out of the range of each mean $\pm$ 3 σ , 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 HgCl₂ 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