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 °C by means of Eq. (9).

#### 7. Discussion

### 7.1 Standard deviation of pH<sub>T</sub> 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.

| Experiment<br>periods<br>(ddmmyy) | Apparatus | Dye soln.<br>batch | Batch V                         | Batch W                          | Batch X                               | Batch Y                                | Batch Z                         |
|-----------------------------------|-----------|--------------------|---------------------------------|----------------------------------|---------------------------------------|--|---------------------------------|
| 140103 –190303                    | 1,        | 784C               | $7.7776 \pm 0.0011$<br>(43, 43) |                                  |                                       |  |                                 |
| 171003 -221003                    | 1         | 826C               | $7.7756 \pm 0.0015$<br>(7, 9)   | $7.8613 \pm 0.0059$<br>(7, 9)    |                                       |  |                                 |
| 301003 -111103                    | 1         | 826C               | $7.7810 \pm 0.0025$<br>(4, 4)   | $7.8704 \pm 0.0057$<br>(40, 41)  |                                       |  |                                 |
| 170304 - 210404                   | 1         | 826C               |                                 | $7.8640 \pm 0.0038$<br>(45, 45)  |                                       |  |                                 |
| 270804 - 100904                   | 2         | 837C               |                                 | $7.8718 \pm 0.0040$<br>(3, 5)    | $7.9576 \pm 0.0020$<br>(23, 27)       |  |                                 |
| 300904011004                      | 1         | 837C               |                                 | (-,-)                            | $7.9494 \pm 0.0013$<br>(6, 6)         |  |                                 |
| 041004 081004                     | 2         | 837C               |                                 |                                  | $7.9550 \pm 0.0020$<br>(8, 11)        |  |                                 |
| 241004 - 271204                   | 1         | 837C               |                                 |                                  | $7.9504 \pm 0.0015$<br>(31 32)        |  |                                 |
| 180805 - 180805                   | 2         | 957C               |                                 |                                  | (51, 52)<br>7.9550 ± 0.0004<br>(7, 7) |  |                                 |
| 091105 -290306                    | 2         | 957C               |                                 |                                  | (', ')                                | $7.9177 \pm 0.0021$<br>(93, 101)       | $7.8356 \pm 0.0013$             |
| 130706 - 140806                   | 2         | 957C               |                                 |                                  |                                       | (55, 101)<br>7.9187 ± 0.0010<br>(5, 5) | $7.8348 \pm 0.0021$<br>(40, 40) |
| 131206 - 200107                   | 2         | 957C,<br>1058C     |                                 |                                  |                                       | $7.9169 \pm 0.0001^{a}$<br>(2, 2)      | $7.8358 \pm 0.0021$<br>(6, 6)   |
| Whole period                      |           |                    | $7.7776 \pm 0.0017$<br>(54, 56) | $7.8667 \pm 0.0061$<br>(95, 100) | $7.9537 \pm 0.0037$<br>(75, 83)       | $7.9177 \pm 0.0021$<br>(101, 109)      | $7.8330 \pm 0.0024$<br>(54, 54) |

**Table 3**  $pH_T$  of working standards. Mean  $\pm$  standard deviation (bottles, measurements) during individual cruises

 $^{a}$  Mean  $\pm$  standard deviation for the difference in analytical results between duplicate measurements.

In contrast, cruise-to-cruise differences were observed in the  $pH_T$  measurements. The standard deviations in  $pH_T$  measurements of CRMs for the whole period (0.0007–0.0039) were larger than those for each cruise (0.0006–0.0022) (Table 2). For example, the standard deviations of the  $pH_T$  values in CRM batch 62 and in working standard batch X measured during the same cruises were 0.0025 and 0.0037, respectively. When we analysed the CRMs and working standards at the same time, both  $pH_T$  values tended to change similarly. This result suggests that the variations of  $pH_T$  were caused not by changes in the quality of the CRMs or working standards but by changes in the conditions of apparatus or indicator solutions. If we corrected the  $pH_T$  values to reflect the amount of change we commonly observed for the CRM and working standard measurements, the standard deviation of the measured  $pH_T$  values of working standard batch X decreased from 0.0037 to 0.0023; therefore we can expect to obtain more precise measurements than present measurements. However, there is no guarantee that we can apply this correction to the whole  $pH_T$  range in seawater, because the  $pH_T$  range of the CRMs or working standards was limited between 7.8 and 7.9. We would be able to confirm the possibility to correct for the cruise-to-cruise difference by measuring several sets of working standards with different  $pH_T$  values.

For precise  $pH_T$  measurements, it is important to satisfy the requirements for analyses of reference materials before measuring a series of samples, as described in Section 6. Our experimental results suggest that the procedure described here for analysing reference materials effectively enables us to obtain  $pH_T$  measurements with an uncertainty of less than 0.003 during different cruises.

## 7.2 Origin of the pH<sub>T</sub> perturbation caused by the addition of HgCl<sub>2</sub>

To determine the reasons for the  $pH_T$  decrease of -0.0024 to -0.0003 caused by the addition of HgCl<sub>2</sub> solution (see Section 4.2), we calculated  $pH_T$  from TCO<sub>2</sub> and TA before and after addition of the HgCl<sub>2</sub> solution. In this calculation, we took into account the effect of dilution and the effect of complexation of Hg<sup>2+</sup> with OH<sup>-</sup> and with CO<sub>3</sub><sup>2-</sup> ions (see Appendix B for details).

The result of this calculation supports the experimental results that the addition of HgCl<sub>2</sub> solution reduced the pH<sub>T</sub> in seawater. The change in pH<sub>T</sub> calculated for the addition of 0.2 cm<sup>3</sup> of saturated HgCl<sub>2</sub> solution to 250 cm<sup>3</sup> of seawater ranged from -0.0039 to -0.0015, depending on the combination of the values of TCO<sub>2</sub> and TA of seawater (Fig. 8). These calculated results of the negative differences and the negative correlation to pH<sub>T</sub> were consistent with experimental results. Although the calculated results differed significantly from the experimental results at a 99% confidence level ( $p = 6 \times 10^{-9}$ ), the magnitude of the calculated change in pH<sub>T</sub> was within the same order as that of the experimental data. A change in TA

(-3.8  $\mu$ mol/kg) due to hydrolysis of Hg<sup>2+</sup> and HgCO<sub>3</sub> formation corresponded to a change in pH<sub>T</sub> of -0.0025. Most of the experimentally observed changes in pH<sub>T</sub> caused by HgCl<sub>2</sub> addition could be accounted for by the change in TA and dilution. The difference between experimental and calculated values might be derived from uncertainty in the stability constants of Hg<sup>2+</sup> complexes.

# 7.3 Internal consistency of CO<sub>2</sub> system parameters

When we measure three of four parameters controlling the CO<sub>2</sub> system (TCO<sub>2</sub>, TA, pH<sub>T</sub> and pCO<sub>2</sub>), we can examine each data point by comparing measured values and the one parameter calculated from the other two parameters (e.g., Lee and Millero, 1995; McElligott et al., 1998; Lee et al., 2000). We calculated pCO<sub>2</sub> from measured pH<sub>T</sub> and TCO<sub>2</sub> and compared the results with measured pCO<sub>2</sub> using the calculation procedure described in DOE (1994). Various dissociation constants for carbonic acid, including those reported by Lueker et al. (2000), Mojica Prieto and Millero (2002), Roy et al. (1993), Dickson and Millero (1987), Goyet and Poisson (1989), Mehrbach et al. (1973) and Hansson (1973), were used for these calculations and were compared on the scale of pH<sub>T</sub>.

The  $pH_T$ , TCO<sub>2</sub> and  $pCO_2$  values in surface water were measured simultaneously during the cruise MR02-K06. Seawater samples for onboard measurements of these three parameters were obtained from the same onboard pumping system. TCO<sub>2</sub> was determined by the coulometric method described by Ishii et al. (1998) and calibrated with the same CRMs described above.  $pCO_2$ was measured by the method described by Inoue (2000) and was calibrated by the MRI87 scale that is traceable to the WMO scale.

The difference between measured and calculated  $pCO_2$ ,  $\Delta pCO_2 = pCO_2^{\text{meas}} - pCO_2^{\text{calc}}$ , ranged from -6 to +18 µatm (< 4%), depending on the dissociation constants used (Fig. 11). The  $\Delta pCO_2$  value calculated with



**Fig. 11** Comparison of  $pCO_2$  values observed and calculated from measured pH<sub>T</sub> and TCO<sub>2</sub> using dissociation constants for carbonic acid given by Mehrbach et al. (1973; diamond), Hansson (1973; bar), Dickson and Millero (1987; plus), Goyet and Poisson (1989; circle), Roy et al. (1973; triangle), Lueker et al. (2000; box) and Mojica Prieto and Millero (2002; cross).

dissociation constants reported by Lueker et al. (2000) was in the middle of these differences. Taking into account the uncertainties of  $\pm 2 \mu atm$  for  $pCO_2^{meas}$  and  $\pm 2 \mu atm$  for  $pCO_2^{calc}$  derived from onboard measurements of pH<sub>T</sub> ( $\pm 0.0002$ ) and TCO<sub>2</sub> ( $\pm 2 \mu mol kg^{-1}$ ),  $pCO_2^{calc}$  calculated with dissociation constants reported by Lueker et al. (2000) was approximately equivalent to  $pCO_2^{meas}$ .

Lee et al. (2000) reported that  $pCO_2$  and TA calculated from measured TCO<sub>2</sub> and pH<sub>T</sub> showed the best agreement with measured values when the dissociation constants of Mehrbach (1973), which were given as functions of temperature and salinity by Dickson and Millero (1987), were used. In the study of Lee et al. (2000), the difference in fugacity,  $\Delta fCO_2 = fCO_2^{\text{meas}} - fCO_2^{\text{calc}}$ , was  $\pm 1.4 \pm 1.4 (1\sigma) \% (\pm 5.2 \pm 5.2 \mu atm at 370 \mu atm)$  for seawater collected at the 170° W meridian. For our pH<sub>T</sub> results, the calculation with dissociation constants of Mehrbach (1973) gave  $\Delta pCO_2$  of  $\pm 2.3 \pm 0.4 (1\sigma) \% (\pm 8.7 \pm 1.4 \mu atm)$ . This value of  $\Delta pCO_2$  differed insignificantly from the value described by Lee et al. (2000).

Although further consideration may be required to the comparability of  $pH_T$  measurements and to the variability of calculation caused by the uncertainty of dissociation constants of carbonic acid, the  $pCO_2$ values measured in the equatorial Pacific Ocean were reproduced within the range of ±11 µatm by calculation from our measured  $pH_T$  and  $TCO_2$  values.

#### 8. Summary

We developed an automated, precise  $pH_T$  measurement system based on a spectrophotometric technique with the indicator dye *m*-cresol purple. We proposed a procedure for precise  $pH_T$  measurement involving the analysis of reference materials, and we evaluated the uncertainty of the  $pH_T$  values obtained with our analytical procedure. We also examined the effects of bottling and storage, as well as the effect of the addition of HgCl<sub>2</sub> solution, on the  $pH_T$  measurements obtained from bottle samples.

The standard deviations of  $pH_T$  measurements obtained with our system were 0.0002 for onboard measurements, 0.002 for bottle samples of surface waters and 0.006 for deep waters after 50 days of storage. Our measured  $pH_T$  values for CRMs were consistent with those calculated from certified TCO<sub>2</sub> and TA values with the dissociation constants of carbonic acid reported by Lueker et al. (2000). The onboard  $pH_T$  measurements were consistent with those derived from TCO<sub>2</sub> and *p*CO<sub>2</sub> measurements in the field study.