## Total Alkalinity (TA)

## 30 September 2023

### Personnel

AKAMATSU Mio

MASUDA Shinji

TANI Masanobu

### Station occupied

A total of 42 stations (Leg 1: 27, Leg 2: 15) were occupied for total alkalinity (TA). Station location and sampling layers of them are shown in Figures C.7.1 and C.7.2, respectively.



Figure C.7.1. Location of observation stations of TA. Closed and open circles indicate sampling and no-sampling stations, respectively.



Figure C.7.2. Distance-depth distribution of sampling layers of TA.

### Instrument

The measurement of TA was carried out with DIC/TA analyzers (Nihon ANS Co. Ltd., Japan). The methodology that these analyzers use is based on an open titration cell. We used two analyzers concurrently. These analyzers are designated as apparatus A and B.

### Sampling and measurement

The procedure of seawater sampling of TA bottles and poisoning with mercury (II) chloride (HgCl2) were based on the Standard Operating Procedure (SOP) described in PICES Special Publication 3 (Dickson et al., 2007). Details are shown in Appendix A1 in C.6.

TA measurement is based on a one-step volumetric addition of hydrochloric acid (HCl) to a known amount of sample seawater with prompt spectrophotometric measurement of excess acid using the sulfonephthalein indicator bromo cresol green sodium salt (BCG) (Breland and Byrne, 1993). We used a mixed solution of HCl, BCG, and sodium chloride (NaCl) as reagent. Details of measurement are shown in Appendix A1.

### Calculation

#### (5.1) Volume of sample seawater

The volumes of pipette *V*S using in apparatus A and B was calibrated gravimetrically in our laboratory. Table C.7.1 shows the summary.

Table C.7.1. Summary of sample volumes of seawater *V*S for TA measurements.

|  |  |
| --- | --- |
| Apparatus | *V*s / mL |
| A | 42.0355 |
| B | 43.0459 |

#### (5.2) pHT calculation in spectrophotometric measurement

The data of absorbance *A* and pipette temperature *T* (in °C) were processed to calculate pHT (in total hydrogen ion scale; details shown in Appendix A1 in C.8) and the concentration of excess acid [H+]T (mol kg−1) in the following equations (C7.1)–(C7.3) (Yao and Byrne, 1998),

pHT = − log10([H＋]T)

 = 4.2699 + 0.02578 ∙ (35 − *S*) + log{(*R*25 − 0.00131) / (2.3148 − 0.1299 ∙ *R*25)}

 − log(1 − 0.001005 ∙ *S*) (C7.1)

 *R*25 = *R*T ∙ {1 + 0.00909 ∙ (25 − *T*)} (C7.2)

 $R\_{T}={\left(A\_{616}^{SA}-A\_{616}^{S}-A\_{730}^{SA}+A\_{730}^{S}\right)}/{\left(A\_{444}^{SA}-A\_{444}^{S}-A\_{730}^{SA}+A\_{730}^{S}\right)}$. (C7.3)

In the equation (C7.1), *R*T is absorbance ratio at temperature *T*, *R*25 is absorbance ratio at temperature 25 °C and *S* is salinity. $A\_{λ}^{S}$ and $A\_{λ}^{SA}$ denote absorbance of seawater before and after acidification, respectively, at wavelength ** nm.

#### (5.3) TA calculation

The calculated [H＋]T was then combined with the volume of sample seawater *V*S, the volume of titrant *V*A added to the sample, and molarity of hydrochloric acid *HCl*A (in mmol L−1) in the titrant to determine to TA concentration *A*T (in mol kg−1) as follows:

 *A*T = (−[H+]T ∙ (*V*S + *V*A)∙ **SA + *HCl*A ∙ *V*A) / (*V*S ∙ **S) (C7.4)

**S and **SA denote the density of seawater sample before and after the addition of titrant, respectively. Here we assumed that **SA is equal to **S, since the density of titrant has been adjusted to that of seawater by adding NaCl and the volume of titrant (approx. 2.5 mL) is no more than approx. 6 % of seawater sample.

Finally, the value of *A*T was multiplied by 1.00067 (= 300.2 / 300.0) to correct dilution effect in *A*T induced by addition of HgCl2 solution.

### Standardization of HCl reagent

HCl reagents were prepared in our laboratory (Appendix A2) and divided into bottles (HCl batches). *HCl*A in the bottles were determined using measured CRMs provided by Dr. Andrew G. Dickson in Scripps Institution of Oceanography. Table C.7.2 provides information about the CRM batch used during this cruise.

Table C.7.2. Certified *A*T and standard deviation of CRM. Unit of *A*T is μmol kg–1. More information is available at the NOAA web site (https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/oceans/Dickson\_CRM/batches.html).

|  |  |
| --- | --- |
| Batch number | 150 |
| *A*T | 2214.71±0.87 |
| Salinity | 33.343 |

The CRM measurement was carried out at every station. The apparent *HCl*A of the titrant was determined from CRM using equation (C7.4).

*HCl*A was assigned for each HCl batches for each apparatus, as summarized in Table C.7.3 and detailed in Figure C.7.3.

Table C.7.3. Summary of assigned *HCl*A for each HCl batches. The reported values are means and standard deviations. Unit is mmol L−1.

|  |  |  |
| --- | --- | --- |
| Apparatus | HCl Batch | *HClA* |
| A | A\_1 | 49.9489±0.0395 (N=33) |
| A\_2 | 49.9847±0.0303 (N=34) |
| A\_3 | 49.9924±0.0342 (N=33) |
| A\_4 | 50.0075±0.0213 (N=32) |
| B | B\_1 | 50.0684±0.0401 (N=35) |
| B\_2 | 50.0617±0.0400 (N=35) |
| B\_3 | 50.0652±0.0235 (N=17) |
| B\_4 | 50.0491±0.0313 (N=33) |
| B\_5 | 50.0937±0.0390 (N=33) |



Figure C.7.3. Results of *HCl*A measured by apparatus (a) A and (b) B. The HCl batch names are indicated at the top of each graph, and vertical lines denote the day when the HCl batch was switched. The red solid, dashed, and dotted lines denote the mean and the mean ± twice the S.D. and thrice the S.D. for each HCl batches, respectively.

The precisions of *HCl*A, defined as the coefficient of variation (= S.D. / mean), were 0.0426–0.0791 % for apparatus A and 0.0469–0.0801 % for apparatus B. They correspond to 0.94–1.75 mol kg−1 and 1.04–1.77 mol kg−1 in *A*T of CRM batch 150, respectively.

### Quality Control

#### (7.1) Replicate and duplicate analyses

We took replicate (pair of water samples taken from a single Niskin bottle) and duplicate (pair of water samples taken from different Niskin bottles closed at the same depth) samples of TA throughout the cruise. Table C.7.4 summarizes the results of the measurements with each apparatus. Figures C.7.4–C.7.5 show details of the results. The calculation of the standard deviation from the difference of sets of measurements was based on a procedure (SOP 23) in DOE (1994).

Table C.7.4. Summary of replicate and duplicate measurements. Unit is mol kg−1.

|  |  |  |
| --- | --- | --- |
|  | **Apparatus A** | **Apparatus B** |
| **Measurement** |  **Average magnitude of difference ± S.D.** |
| Replicate | 0.7±0.6 (N=54) | 1.0±0.9 (N=68) |
| Duplicate | 0.9±0.9 (N=29) | 1.1±1.1 (N=42) |



Figure C.7.4. Results of (left) replicate and (right) duplicate measurements during the cruise versus (a) station number, (b) pressure, and (c) *A*T determined by apparatus A. The green lines denote the averages of the measurements. The bottom panels (d) show histograms of the measurements.



Figure C.7.5. Same as Figure C.7.4, but for apparatus B.

#### (7.2) Measurements of CRM and working reference materials

The precision of the measurements was monitored by using the CRMs and working reference materials bottled in our laboratory (Appendix A2 in C.6). The measurements of the CRMs and working reference materials were the same those used to measure DIC (see (6.2) in C.6), except that the CRM measurement was repeated 3 times from the same bottle. Table C.7.5 summarizes the differences in the repeated measurements of the CRMs, the mean *A*T of the CRM measurements, and the mean *A*T of the working reference material measurements. Figures C.7.6–C.7.8 show detailed results.

Table C.7.5. Summary of difference and mean of *A*T in the repeated measurements of CRM and the mean *A*T of the working reference material. These data are based on good measurements. Unit is μmol kg−1.

|  |  |  |
| --- | --- | --- |
|  | **CRM** | **Working reference material** |
| **HCl Batches** |  **Average magnitude of difference ± S.D.** | **Mean****Ave. ± S.D.** | **Mean****Ave. ± S.D.** |
| A\_1 | 1.5±1.2 (N=10) | 2214.7±1.5 (N=10) | 2282.8±1.6 (N=5) |
| A\_2 | 1.0±0.8 (N=12) | 2214.6±1.2 (N=12) | 2285.3±1.3 (N=6) |
| A\_3 | 1.9±1.6 (N=11) | 2214.7±0.7 (N=11) | 2284.6±0.5 (N=3) |
| A\_4 | 0.8±0.7 (N=11) | 2214.7±0.8 (N=11) | 2285.1±1.0 (N=5) |
| B\_1 | 1.3±1.0 (N=12) | 2214.7±1.6 (N=12) | 2282.4±3.0 (N=5) |
| B\_2 | 0.9±0.8 (N=12) | 2214.7±1.8 (N=12) | 2285.9±2.8 (N=6) |
| B\_3 | 0.9±0.7 (N=6) | 2214.7±0.9 (N=6) | 2285.5±0.3 (N=3) |
| B\_4 | 1.4±1.1 (N=11) | 2214.8±1.0 (N=11) | 2284.4±1.4 (N=7) |
| B\_5 | 1.4±1.1 (N=11) | 2214.7±1.6 (N=11) | 2285.0±1.7 (N=5) |



Figure C.7.6. The absolute difference (*R*) of *A*T in repeated measurements of CRM determined by apparatus (a) A and (b) B. The solid line indicates the average of *R* ($\overbar{R}$). The dashed and dotted lines denote the upper warning limit (2.512$\overbar{R}$) and upper control limit (3.267$\overbar{R}$), respectively (see Dickson et al., 2007).



Figure C.7.7. The mean *A*T of measurements of CRM. The panels show the results for apparatus (a) A and (b) B. The solid line indicates the mean of the measurements. The dashed and dotted lines denote the upper/lower warning limit (mean ± 2S.D.) and the upper/lower control limit (mean ± 3S.D.), respectively. The gray dashed line denotes certified *A*T of CRM. The labels at the top of the graph and vertical lines have the same meaning as in Figure C.7.3.



Figure C.7.8. Calculated *A*T of working reference material measured by apparatus (a) A and (b) B. The solid, dashed and dotted lines have the same meaning as in Figure C.7.7. The labels at the top of the graph and vertical lines have the same meaning as in Figure C.7.3.

#### (7.3) Comparisons with other CRM batches

At every few stations, other CRM batches (140, 145, 147 and 155) were measured to provide comparisons with batch 150 to confirm the determination of *A*T in our measurements. For these CRM measurements, *A*T was calculated from *HCl*A determined from batch 150 measurement. Figures C.7.9 show the differences between the calculated and certified *A*T.



Figure C.7.9. The differences between the calculated *A*T from batch 150 measurements and the certified *A*T. The panels show the results for apparatus (a) A and (b) B. The labels at the top of the graph and vertical lines have the same meaning as in Figure C.7.3. Colors indicate CRM batches; light blue: 140, blue: 145, green: 147 and red: 155.

#### (7.4) Quality control flag assignment

A quality control flag value was assigned to the TA measurements (Table C.7.6) using the code defined in the IOCCP Report No.14 (Swift, 2010).

Table C.7.6. Summary of assigned quality control flags.

|  |  |  |
| --- | --- | --- |
| Flag | Definition | Number of samples |
| 2 | Good | 1362 |
| 3 | Questionable | 19 |
| 4 | Bad (Faulty) | 9 |
| 5 | Not reported | 0 |
| 6 | Replicate measurements | 122 |
| Total number of samples | 1512 |

### Appendix

**A1. Methods**

**(A1.1) Measurement**

The unit for TA measurements in the coupled DIC/TA analyzer consists of sample treatment unit with a calibrated sample pipette and an open titration cell that are water-jacketed and connected to a thermostated water bath (25 °C), an auto syringe connected to reagent bottle of titrant stored at 25 °C, and a double-beam spectrophotometric system with two CCD image sensor spectrometers combined with a high power Xenon lamp. The mixture of 0.05 N HCl and 40 mol L−1 BCG in 0.65 M NaCl solution was used as reagent to automatically titrate the sample as follows:

(a) A portion of sample seawater was delivered into the sample pipette (approx. 42 mL) following sample delivery into the DIC unit for a measurement. After the temperature in the pipette was recorded, the sample was transferred into a cylindrical quartz cell.

(b) An absorption spectrum of sample seawater in the visible light domain was then measured, and the absorbances were recorded at wavelengths of 444 nm, 509 nm, 616 nm, and 730 nm as well as the temperature in the cell.

(c) The titrant that contains HCl was added to the sample seawater by the auto syringe so that pH of sample seawater altered in the range between 3.85 and 4.05.

(d) While the acidified sample was being stirred, the evolved CO2 was purged with the stream of purified N2 bubbled into the sample at approx. 200 mLmin−1 for 5 minutes.

(e) After the bubbled sample steadied down for 1 minute, the absorbance of BCG in the sample was measured in the same way as described in (b), and pH (in total hydrogen ion scale, pHT) of the acidified seawater was precisely determined spectrophotometrically.

**A2. HCl reagents recipes**

0.05 N HCl and 40 mol L−1 BCG in 0.65 M NaCl solution

Dissolve 0.30 g of BCG and 190 g of NaCl in roughly 1.5 L of deionized water (DW) in a 5 L flask, and slowly add 200 mL concentrated HCl. After the powders completely dissolved, dilute with DW to a final volume of 5 L.

***References***

Breland II, J. A. and R. H. Byrne (1993), Spectrophotometric procedures for determination of sea water alkalinity using bromocresol green, *Deep-Sea Res. I*, 470, 629–641.

Dickson, A. G., C. L. Sabine, and J. R. Christian (Eds.) (2007), Guide to best practices for ocean CO2 measurements. PICES Special Publication 3, 191 pp.

DOE (1994), Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2. *A. G. Dickson and C. Goyet (eds), ORNL/CDIAC-74*.

Yao, W. and R. H. Byrne (1998), Simplified seawater alkalinity analysis: Use of linear array spectrometers. *Deep-Sea Res. I*, 45, 1383–1392.

Swift, J. H. (2010): Reference-quality water sample data, Notes on acquisition, record keeping, and evaluation. *IOCCP Report No.****14****, ICPO Pub. 134, 2010 ver.1.*