B-7.1.2 Factors of analytical errors in the total dissolved inorganic Carbon and total alkalinity measurements in seawater samples.

Contact person Koh Harada
Head of Marine Environment Division
Environmental Assessment Department
National Institute for Resources and Environment
National Institute of Advanced Industrial Science and Technology
Ministry of Economy and Industrial Technology
Onogawa 16-1, Tsukuba, Ibaraki, 305-8569 Japan
Tel: +81-298-61-8390 Fax: +81-298-61-8357
E-mail: harada.emtech@aist.go.jp

Abstract International inter-comparison works for total inorganic carbon (TC) and total alkalinity (TA) measurements in seawater were conducted in 1999 and 2000. For the TC measurement, systematic differences existed between the participated organizations, although precisions of the data in each organizations were relatively good in the 1999 activity. It suggested there were some problems in calibration method. In the 2000 activity, the differences became smaller and data obtained by the all organizations participated were within acceptable range to discuss an increase of TC from the industrial revolution. The difference of TA in the organizations in 1999 were extremely large and it was hardly acceptable. However, the difference became small in the 2000 activity, and the data were comparable when they were corrected against the certified reference materials (RCMs) which were measured simultaneously with the samples. From those results, it is strongly suggested that usage of the RCM for checking of accuracy of the measurement.

Key Words   total inorganic carbon, total alkalinity, seawater, inter-comparison

1. Introduction

   It is said that about 2 giga-ton (Gt) of carbon is absorbed in the ocean from the atmosphere annually. To predict climate change in future world, understanding of carbon cycles on the Eartt is very important and more accurate and precise data set of carbonate chemistry in the ocean are needed. Recently, oceanographic researches for the carbon cycle are conducted by many countries and organizations. The data obtained by many organizations should be compatible and be always in high quality. Inter-comparison using the same samples is one of the best ways to check the data quality.

2. Research Objective

   The objectives of the research are to organize the inter-comparison of the TC and TA

measurements among researchers who are studying the carbon cycle in the Pacific and to discuss difference of the data holding workshops for the participants of the inter-comparison activities.

3. Research Method

The inter-comparison activities were carried out once a year in 1999 and 2000. In the 1999 activity, four kinds of the seawater samples were distributed organizations of three countries. The samples and the participants were as follows;

Samples:
1. Certified Reference Material prepared by Scripps Institute of Oceanography
2. Uncertified seawater from coastal surface ocean off California prepared by SIO
3. Uncertified Reference Material prepared by Hokkaido University (in this project)
4. Fitered and sterilized deep seawater from the western North Pacific coastal surface prepared by NIES

Participants:
1. Scripps Institute of Oceanography (USA) 2. NOAA/PMEL (USA)
3. NOAA/AOML (USA)   4. University of Washington (USA)
5. Institute of Ocean Science (Canada)   6. CRIEPI (Japan)
7. Hokkaido University (Japan)   8. JAMSTEC (Japan)
9. CREST KNOT team/NIES (Japan)   10. Meteorological Research Institute (Japan)
11. NIRE/KANSO (Japan)   12. SAGE project team (Japan)

In the 2000 activity, the same kinds of the seawater samples were distributed to the almost same organizations as in the 1999 activity. After the measurements in the laboratories, the data were reported and organized. To discuss the results, the workshop was held in Tsukuba once in each year.

All laboratories were used basically same method for the TC measurement. CO_2 in the samples is striped by acidifying and purging of the CO_2 free air, is absorbed in ethernol aminesolution and is detected by coulometric titration. One laboratory used un-automated method, but others were used automated systems.

Analytical methods for TA were categorized in four groups which were the two stage open cell titration, the one stage open cell titration, the closed cell titration and one-point pH measurement method.

4. Results and Discussion

Each laboratory measured four bottles for each four samples. In table 1, the reported data of TC from the laboratories in Japan were listed.

Table 1. Reported concentrations of TC from Japanese laboratories (μmol kg^{-1})

	A		B		C		D		E	
CRM-SIO	1987.9	(0.5)	1992.4	(1.1)	1988.1	(1.4)	1996.9	(1.3)	1995.98	(1.1)
Unknown(SIO)	1985.3	(1.4)	1991.5	(2.1)	1988.3	(0.8)	1995.8	(0.4)	1994.50	(0.5)
RM-HU	2122.1	(0.9)	2126.0	(2.3)	2132.1	(1.6)				
Deep water	2326.8	(1.1)	2336.6	(2.1)	2333.5	(0.4)	2336.3	(0.7)	2339.93	(1.7)

Value in parentheses is 1 σ standard deviation.

From the these results, following summaries were introduces;

1. Each laboratory can measure TC in good precision.
2. However, difference among the laboratories were over (μmol kg^{-1}) and which was not acceptable for discussion of CO2 in the ocean.
3. It suggested there was some trouble in calibration procedures such as purity of NaCO3 standard and preparation method of standard solution.
4. Calibration by CO2 gas using a gas loop should be better than the calibration by the NaCO3 standard solution.
5. Normalization to the CRM value was very useful even if there was some trouble in the calibration method, and it was confirmed that the method can be applied to the high concentration samples from deep ocean.

For the TA measurements, the reported values were listed in Table 2.

Table 2. Results of TA inter-comparison

(μeq. kg^{-1})	A		B		C		D	
CRM-SIO	2209.4	(0.7)	2180.5	(3.4)	2207.7	(3.2)	2192.4	(1.7)
Unknown(SIO)	2194.7	(1.0)	2164.7	(2.6)	2178.7	(4.3)	2181.4	(0.4)
RM-HU	2184.2	(1.1)	2151.3	(1.0)	2170.9	(4.5)		
Deep water	2422.0	(1.3)	2396.6	(0.8)	2417.4	(1.5)	2405.4	(4.1)

Value in parentheses is 1 σ standard deviation.

Precision of the TA measurements was worse than that of the TC. From the comparison between the method, it was suggested that people should pay attention to the week point of the method such as gas exchange when they use the open cell titration or the one-point pH measurement method which are easier and less time-consuming methods rather than the closed titration method. When the values were normalized against CRM, the difference became smaller. This confirmed validity of usage of the CRM.

After the discussion in the workshop in 1999, each laboratory checked their methods and participated to the second inter-comparison in 2000.

The results of TC and TA in the 2000 inter comparison were shown in Fig.1 and 2,
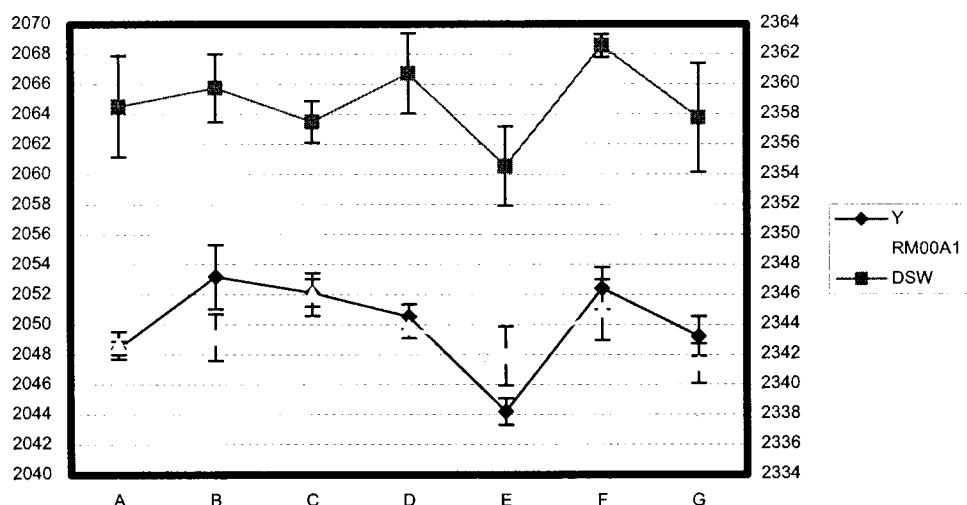
respectively.

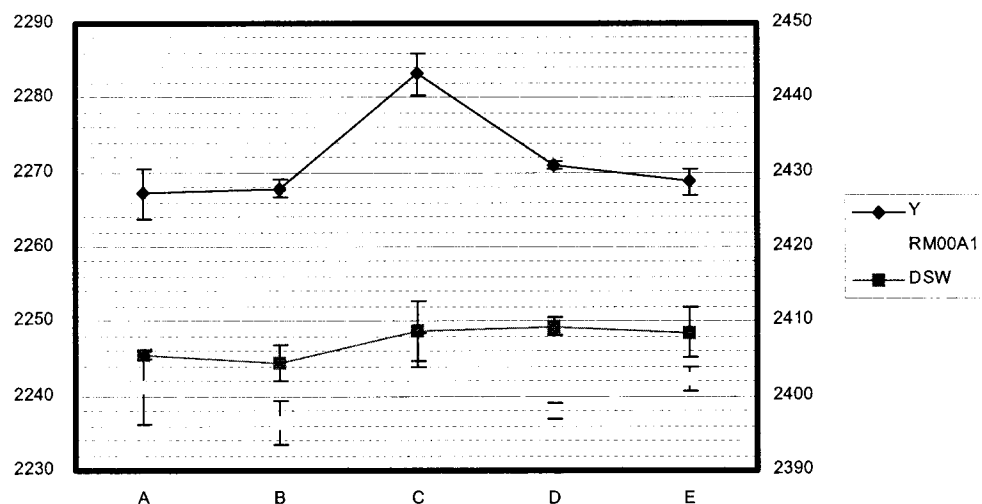Fig. 1 Results of TC comparison in 2000.

Fig. 2 Results of TA comparison in 2000.

Both results were improved very much. When CRM normalization was carried out, difference among the laboratories were less than 2 μmol kg^{-2} for TC and 5 μeq. kg^{-2} for TA. These values were acceptable for the discussion of CO2 absorption into the ocean.

5. Conclusion

To discuss the carbonate chemistry in the ocean, highly accurate and precise are requested. From the first international inter-comparison activity, it is suggested that to keep the high precision can be achieved easily by the effort in each laboratory. However, it is very difficult to keep their accuracy and to keep data obtained different laboratories in same quality. Judging from our activities, the inter-comparison participated by many laboratories is one of the good ways to overcome the difficulty. For the TC and TA measurement, it is suggested that management and usage of the certified reference material were very important.