B-7.1.1 Improvement of on board measurement system for partial pressure of CO_2 with the comparative study of analytical error

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Abstract For the improvement of the accuracy of the partial pressure measurement of CO_2 (pCO_2) in seawater, a precise comparison of existing systems were carried out in 1998 and 1999 with participation of eight Japanese and three foreign institutes utilizing a 170 t indoor seawater pool. The stable temperature and pCO_2 of the pool facilitated for the precise comparison. The results showed 0.8% lower bias in the bubbling equilibrator. It was reasonable bias from the surface tension inside the bubble. By the results of the experiments, an excellent seawater pCO_2 equilibrator of tandem design was developed, which is a combination of bubbling and mixer equilibrators. The results of on board equilibrators in the Japan-Canada ship-of-opportunity monitoring program from 1995 was carefully analyzed using the estimated analytical bias of the bubbling equilibrator. The agreement between the shower head and the bubbling equilibrator on board was excellent after 1997. The on board measurement was improved by the replacement of the bubbling equilibrator to tandem equilibrator. From 1999 November, a new on board pCO_2 system was installed on another cargo ship between Japan and Canada. The use of the updated system gave much reliable observational data with 0.45 μatm accuracy in pCO_2.

Key Words CO_2, Partial pressure in seawater, Air-water equilibrator, accuracy, Inter-comparison

1. Introduction

The estimation of oceanic absorption of anthropogenic CO_2 can be done by the global integration of surface ocean ΔpCO_2 (partial pressure difference between ocean and atmosphere), wind velocity and gas exchange coefficients. The bias in the measurement can give a large uncertainty in the estimation, however, the certification of the analytical accuracy of the on board pCO_2 measurement systems are very difficult. In case the discrete seawater measurement of seawater CO_2 species, such as dissolved inorganic carbon or alkalinity, the

use of certified reference materials is effective way to assure the accuracy of the measurement. Since the surface seawater pCO_2 measurement is carried out as an underway measurement using a continuous flow of seawater, the use of bottled certified reference material is impossible. One of possible way to assure the accuracy of the measurement is to practice inter-method comparison.

In this program, inter-method comparison was carried out by the participation of eight Japanese and four foreign research institutes, gathering their CO_2 systems at a large seawater indoor pool having 170 t of the water volume. It facilitated precise comparison of pCO_2 data. A new design of seawater equilibrator was also developed utilizing the result of the indoor pool test. Finally, the new CO_2 equilibrator was installed for on board pCO_2 measurement.

2. Inter-comparison of seawater pCO_2 system

In January 1998, the 10 types of CO_2 equilibrators were gathered for the seawater indoor pool inter-comparison experiment.

A: bubbling (1.5m length), B: bubbling (1m length), C: static mixer, D: gas exchange membrane, E: shower head, F: shower head, G: gas exchange membrane, H: shower head, I: bubbling (combined)

Because of the small temperature change of the pool, the seawater pCO_2 was kept within 6 ppm for the over night inter-comparison of the equilibrators. The pool pCO_2 was adjusted at 315 or 425 ppm with HCl and NaOH. Fig. 1 is the results of January 27-28 test,

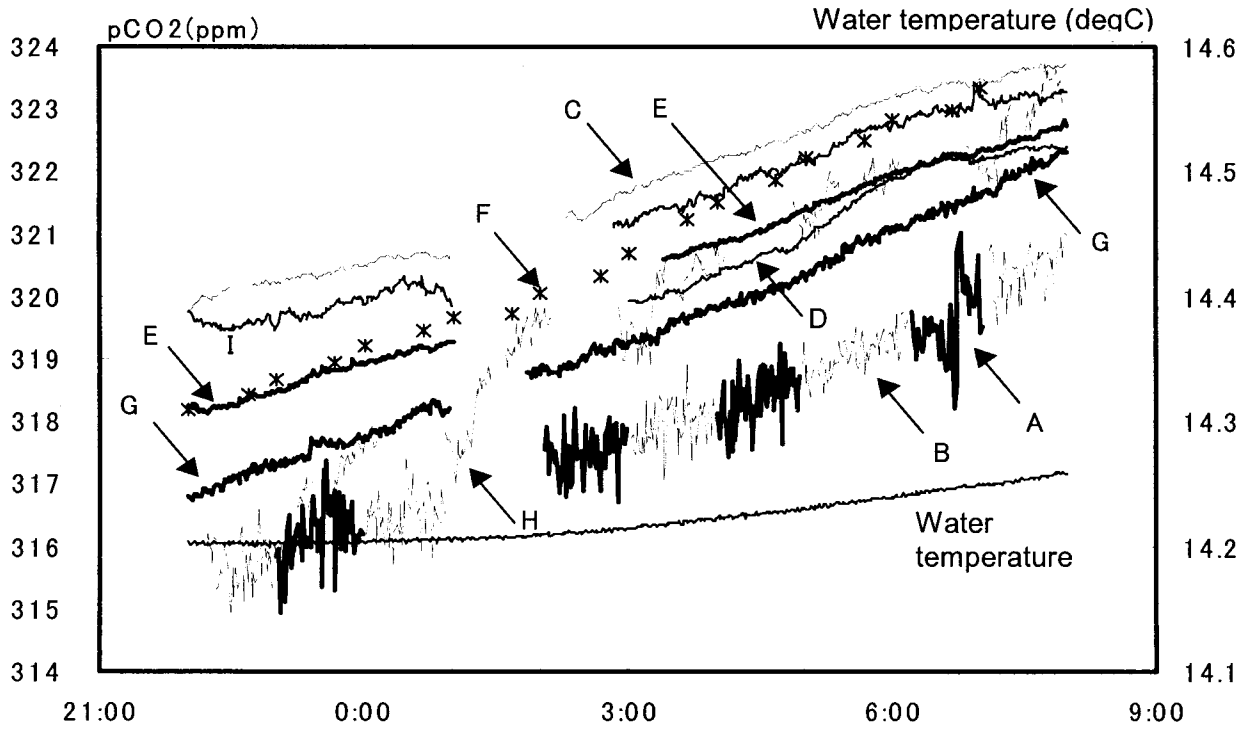

Fig. 1 Result of pCO_2 equilibrators using a seawater indoor pool, January 27-28, 1998. Capitals correspond to the equilibrators in the text.

when the maximum numbers of equilibrators were operated simultaneously. A and B are the result of alternative use of one detection system by the two equilibrators. The noise level of the detection system was larger than the other systems, however the difference of the two equilibrators was not found. The result suggested the bias of the bubbling equilibrators. Other systems gave the results generally within ±2 ppm of pCO_2. Considering the previous inter-comparison of Japanese pCO_2 system at 1995, when results showed much larger discrepancies, the results were reasonably improved and the accuracy of Japanese institutions in pCO2 measurement was confirmed. The range of the agreement of analytical results was comparable to the international inter-comparison on board a research vessel in 1996. At the end of the inter-comparison experiment, a combination of bubbling and static mixer equilibrators was tried and the measured value was within good agreement with other equilibrators.

3. Design of new equilibrator

The trial of combination of bubbling and static mixer equilibrator in 1998 inter-comparison experiment was successful. Then a two-stage equilibrator, which is the direct combination of bubbling and static mixer equilibrators, was designed for on board use. Fig. 2 is the schematic of the new equilibrator.

The most typical pCO_2 equilibrator is shower head design with circulating air flow. The air circulation is necessary because the efficiency of the equilibrator is no so high because the water/gas ratio is small. As the new design is a flow through equilibrator, the CO_2 detection system of the effluent equilibrated air can be a simple one as same as an ordinary atmospheric measurement. The shower head equilibrator frequently suffered from clogging by zooplankton in the ocean of highly productive. The static mixer equilibrator has a large diameter (20 mm) of water inlet, which never clogs in the on board use. The equilibrator pressure inside is strictly same as atmosphere as it has atmosphere vent. It is an important factor to ensure the accuracy of pCO_2 measurement.

The new tandem design equilibrator was used on board the Japan-Canada cargo ship, M/S Skaugran. M/S Skaugran program started in 1995 and used to have 2 pCO_2 systems, one with shower head equilibrator and the other with bubbling equilibrator. After changed from bubbling equilibrator to tandem equilibrator, the pCO_2 results of the two systems agreed well within 2 ppm.

In 1999 March, an indoor pool experiment was again carried out for the purpose of the precise comparison of bubbling and tandem equilibrators. The tandem equilibrator system gave close agreement with the membrane equilibrator system but the bubbling equilibrator gave systematically lower pCO_2. The efficiency of the equilibrators was measured using various pool conditions and changing CO_2 concentration of supplying air to the equilibrators. As the result, the reason of the negative bias of bubbling equilibrator was identified the effect of the surface tension of the bubble inside. The measured bias of 0.8%

was not so far from the predicted bias considering the surface tension inside the bubble. The use static mixer equilibrator as the 2nd stage of the equilibration compensates the 0.8% lower bias comes from the 1st stage bubbling equilibrator. Even the bias exists, the bubbling equilibrator shows highest efficiency of equilibration in flow through operation, which was higher than 99.5%.

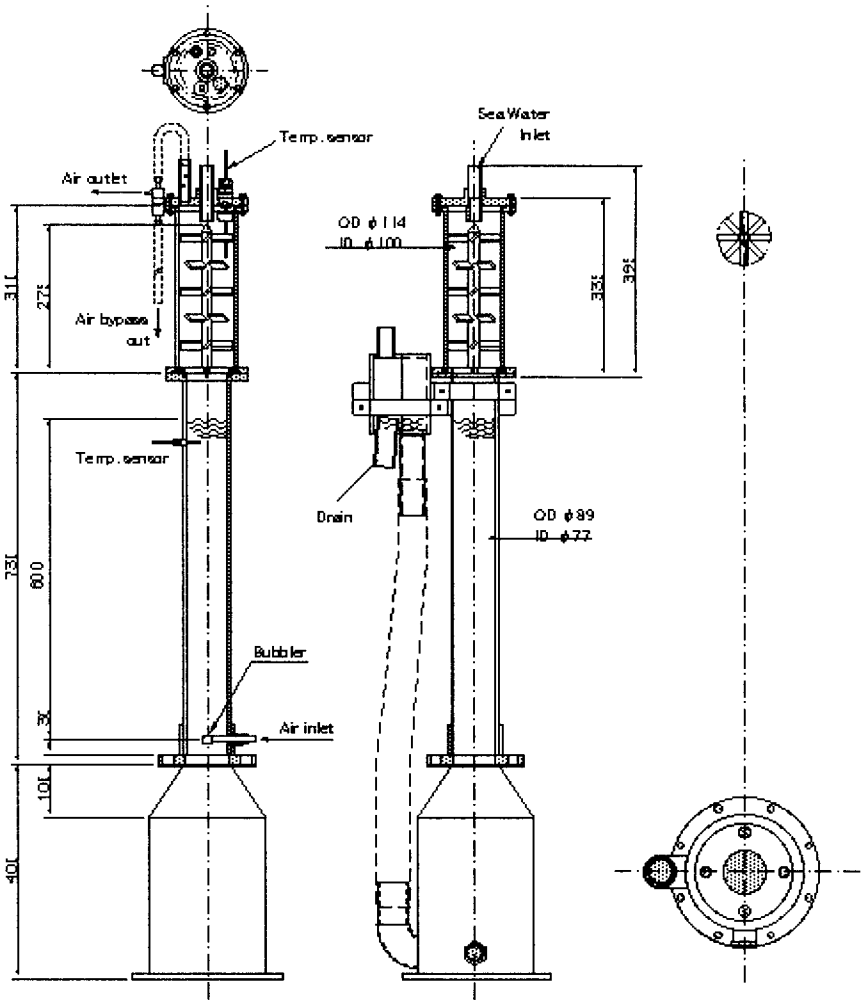

Fig. 2 Schematic of newly designed tandem equilibrator for on board pCO2 measurement

The results of on board pCO_2 systems in the Japan-Canada ship-of-opportunity monitoring program from 1995 was carefully analyzed using the estimated analytical bias of the bubbling equilibrator. The agreement between the shower head equilibrator and the bubbling equilibrator on board was excellent after 1997, however the on board measurement was less accurate before 1996. The replacement of the bubbling equilibrator to tandem equilibrator in 1998 improved the accuracy of the pCO_2 measurement in the ship-of-opportunity program. From 1999 November, a new on board pCO_2 system was installed on another cargo ship between Japan and Canada, M/S Alligator Hope. Due to the automation of the on board pCO_2 system, on board operation was entrusted to a seaman in charge of the program. The use of the updated system gave much reliable observational data with 0.45 μatm accuracy in pCO_2. The establishment of on board pCO_2 system requiring no skillful operator makes it possible to extend the CO_2 observation by the volunteer observation ship program utilizing commercial cargo ships. It is important technical achievement to accumulate ocean pCO_2 data set having good spatial and temporal coverage.