

해수의 총수소이온농도(pH)와 총알칼리도 측정방법에 대한 선상 비교 연구

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On Board Comparison of Total Hydrogen Ion Concentration (pH) and Total Alkalinity Measurements in Seawater

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요 약

해수 중의 수소이온농도(pH)와 총알칼리도(TA) 측정 방법에 대한 선상 비교 연구가 동해 표층에서 저층에 이르는 약 550개의 실제 해수 시료에 대해 이루어졌다. 분광광도법과 전위차법에 대한 pH의 비교가 이루어졌으며, 두 방법에 의한 해수의 pH는 전반적으로 잘 일치하였으나, pH가 낮은 심층의 경우 피펫을 사용한 분광법에 의한 값이 전위차법 보다 높은 값을 보였다. 그러나 피펫을 사용하지 않은 분광법과는 두 방법의 정밀도 내에서 동일한 값을 보였다. 이는 피펫에 의해 해수 내의 이산화탄소가 제거되면서 시료 내의 pH를 증가시키는 것으로 판단된다. TA 측정법의 비교를 위해 폐쇄 용기를 이용한 전위차법과 개방 용기를 이용한 전위차법이 사용되었으며, 개방형 용기를 사용했을 때의 값이 폐쇄형 용기를 사용했을 때의 값에 비해 약 5~10 $\mu\text{mol kg}^{-1}$ 작은 값을 보인다. 이는 폐쇄형 용기를 사용했을 때, 적정 도중에 발생하는 이산화탄소가 용액 속에 남아 적정액인 염산 이외의 산을 용액 속에 추가하는 효과를 내기 때문으로 판단된다. 따라서 pH 혹은 TA의 분석에 있어서 본 연구에서 비교한 어느 방법을 사용할 수도 있지만 각각의 방법에 대해 특별히 요구되는 주의를 기울일 때 만족할 만한 분석결과를 얻을 수 있다.

Abstract – On board comparison of pH and total alkalinity measurement in seawater was carried out during the JES expedition on R/V Roger Revelle in the East Sea using 550 real seawater samples from the surface to the bottom. Spectrophotometry and potentiometry without liquid junction were compared for pH measurement. The pH values of two methods are generally in a good agreement. Spectrophotometry with a pipette provides higher value compare with the potentiometry in the deep layer, where pH values are lower. However, spectrophotometry without a pipette shows same values with potentiometry within their precision range. The pipetting procedure may remove of CO₂ in the sample, which causes increase of pH. Potentiometric titration methods using a closed-cell and an open-cell were compared for the total alkalinity measurement. Values from open cell method are smaller by about 5~10 $\mu\text{mol kg}^{-1}$ than those from closed cell method. This may be caused by the bubble formed in the closed cell during the experiment. Although any analytical method compared in this study for the pH or TA measurement can be applied, special attentions should be paid for satisfactory results.

Keywords: On board comparison(선상비교시험), Total Hydrogen Ion Concentration(총수소이온농도), pH, Total Alkalinity(총알칼리도)

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1. INTRODUCTION

The carbonate system of seawater is one of the most complex topics in marine environment. Recently the fate of fossil fuel CO₂ in the ocean has promoted interests in the study of carbonate chemistry in the ocean. The biogeochemical cycle of CO₂ in the marine environment is controlled by its special pumping mechanism such as solubility, biological, carbonate, and dynamic pumps (Volk and Hoffer [1985], Sarmiento *et al.* [1995]). In order to quantify these pumps, it is essential to understand precisely the distribution of CO₂ parameters.

Four CO₂ parameters, which are total dissolved inorganic carbon (C_T), total alkalinity (TA), fugacity of CO₂ (*f*CO₂), and total hydrogen ion concentration (pH), can be measured. These are used together with ancillary information to obtain a complete description of the carbonate system in seawater. It is only necessary to know two parameters among the four above to have a complete description of the system (Park [1969], Skirrow [1975], Lewis and Wallace [1998]). TA and pH are usually chosen since their analytical procedures are simple to be carried out on board. Especially, pH should be measured immediately after sampling, because pH is very easy to change by the contact with the atmospheric CO₂.

There are several methods to determine TA and pH in seawater. Methods for TA determination are single point titration, open-cell potentiometric titration, closed-cell potentiometric titration, colorimetric titration and so on (Dickson *et al.* [2007]). Spectrophotometric and potentiometric methods are commonly used for pH determination in seawater (Dickson *et al.* [2007]).

The potentiometric titration measuring EMF in a closed cell (Dickson [1981], Bradshaw and Brewer [1988], Millero *et al.* [1993], Dickson and Goyet [1994]) and the spectrophotometry using an indicator dye (Clayton and Byrn [1993]) are generally accepted as modern analytical methods for the measurement of TA and pH in seawater, respectively. Although they are considered to give accurate information about the carbonate chemistry of seawater, they have some disadvantages when are carried out on board. As for pH, the spectrophotometric performance of the instrument, which is one of the most important factors for precise determination of pH (Dickson and Goyet [1994]), is not easy to be occurred on board. It takes long time to analysis TA since the electrode needs times to adjust to changing EMF.

Here, we compared two different methods on board using real seawater samples to identify the optimum method which can be performed on board. Spectrophotometry and potentiometric pH measurement were compared for pH measurement.

Whereas closed-cell potentiometric titration and direct colorimetric titration using an open cell for TA are compared. On board inter-comparison study was carried out during the JES (Japan/East Sea) expedition on R/Vs Roger Revelle and Professor Khromov in the East Sea. Around 550 seawater samples, collected from the surface to the bottom (deeper than 3500 m depth), were analyzed by both methods.

2. METHODS AND MATERIALS

2.1 Total Hydrogen Ion Concentration (pH)

Spectrophotometry is a method to measure pH values in seawater using *m*-cresol purple as an indicator dye (Clayton and Byrn [1993], Dickson *et al.* [2007]). The absorbance of each seawater sample with and without dye are measured at three wavelength (434, 578, and 730 nm); corresponding to the absorption maxima of acid (434 nm) and base (578 nm) forms of the dye, and a non-absorbing wavelength (730 nm). The pH values are calculated from the absorbance of seawater and seawater with adding dye at three wavelength using the following equation.

$$pH = pK_2 + \log \left(\frac{\frac{A_1}{A_2} \frac{\varepsilon_1(HI)}{\varepsilon_2(HI)}}{\frac{\varepsilon_1(I^{2-})}{\varepsilon_2(HI)} - \frac{\left(\frac{A_1}{A_2}\right) \varepsilon_2(I^{2-})}{\varepsilon_2(HI)}} \right) \quad (1)$$

A_1 and A_2 are the corrected respectively absorbances measured at the wavelengths of 578 and 434 nm, respectively. pK_2 is the acid dissociation constant for the species HI⁻ which is a function of salinity and temperature (in *K*);

$$pK_2 = \frac{1245.69}{T} + 3.8275 + 0.00211 \cdot (35 - S) \quad (2)$$

The various extinction coefficient ratios for *m*-cresol purple are as follows;

$$\frac{\varepsilon_1(HI)}{\varepsilon_2(HI)} = 0.0069 \quad (3)$$

$$\frac{\varepsilon_1(I^{2-})}{\varepsilon_2(HI)} = 2.222 \quad (4)$$

$$\frac{\varepsilon_2(I^{2-})}{\varepsilon_2(HI)} = 0.133 \quad (5)$$

All spectrophotometric data reported here are averaged values of duplicate analysis. The average precision of duplicate analysis is 0.006 pH unit as one standard deviation.

Potentiometric method measures potential differences of two electrodes in a potential cell without liquid junction for pH measurements of seawater, since it was reported that unrepro-

ducibility and loss of accuracy of potentiometric pH measurement are caused by liquid junction potential (Tishchenko and Pavlova [1999], Tishchenko *et al.* [2001]).

Glass-electrode-Na⁺ | Test (standard) solution | H⁺-glass-electrode (A)

The cell (A) was calibrated by TRIS-buffer (DelValls and Dickson [1998]) at 25 °C and pH is calculated by formula;

$$pH = 8.0936 + \frac{E_s - E_x}{59.16} \log(\gamma_{Na} m_{Na})_s - \log(\gamma_{Na} m_{Na})_x \quad (6)$$

Where, E , m_{Na} , and γ_{Na} are EMF, sodium ion molality and activity coefficient of sodium ion, respectively; subscript indexes “s”, “x” note standard and test solutions, respectively. Activity coefficients of sodium ion have been calculated by Pitzer method (Pitzer [1992]) and approximated by empirical formula below.

Properties of sodium ion as follows

$$(m_{Na})_s = 0.44618 \quad (7)$$

$$(\gamma_{Na})_s = 0.6382 \quad (8)$$

$$(m_{Na})_x = \frac{13.872 \cdot S}{1000 - 1.00511 \cdot S} \quad (9)$$

$$\ln(\gamma_{Na}) = -0.5163 \cdot I^{\frac{1}{2}} + 0.60845 \cdot I - 0.4521 \cdot I^{\frac{3}{2}} + 0.15499 \cdot I^2 \quad (10)$$

Where S is salinity; I is an ionic strength which calculated by equation

$$I = \frac{19.9273 \cdot S}{1000 - 1.00511 \cdot S} \quad (11)$$

Shift of a standard EMF of the cell (A) was less than 0.5 mV per day. The precision of pH measurement by means of the cell (A) is about ± 0.004 pH unit.

2.2 Total Alkalinity (TA)

Closed cell method is a potentiometric titration measuring EMF in a completely closed cell (Millero *et al.* [1993]). The system is composed by a motor driven piston burette (5 mL, scale ± 0.001 mL) with anti-diffusion tip, titration cell assembly, and personal computer for controlling burette and data acquisition from pH meter. Orion double junction Ag/AgCl reference electrode and ROSS glass electrode are used as reference and EMF electrodes, respectively. The titration cell and burette piston are incorporated with outer water jackets which constant temperature (25.0 ± 0.1 °C) water circulates through. The titration procedure is controlled by a personal computer through serial ports. Total alkalinity is

calculated by non-linear least squares approach method (Dickson [1981], Johansson and Wedborg [1982], Dickson and Goyet [1994]).

Total alkalinity is normalized by Dickson’s CRMs (Batch #46) which are measured at every station. It take 40 to 50 minutes to complete titration including flushing. The average precision of duplicate analysis is 4.5 mmol kg^{-1} in one standard deviation.

Open cell method is a direct colorimetric titration by hydrochloric acid in an open system using a mixed indicator (methylene blue and methyl red). The titration is carried out under CO₂ free condition by flowing of CO₂-free air (or nitrogen). The change of the sample color from green to light-pink at the equivalence point is detected visually. The pH at the end point is about 5.4-5.5. The method is known as Bruevich’s method (Bruevich [1944]) and is recommended as standard operating procedure among Russian oceanographers (Ivanenkov and Borodovsky [1978]). The detailed titration procedure is presented below.

The acid (~ 0.02 N) is standardized daily with Dickson’s CRM. The calibrated volumetric pipette (25 mL) is used to transfer the samples into the cell. Three drops of the mixed indicator are added and the sample is flushed with nitrogen for 3 min to remove all the carbon dioxide. CRM is then titrated with hydrochloric acid using Dosimat 665 motor driven piston burette (5 mL, scale ± 0.001 mL). The solution color at the end point of the titration must be light pink and quite stable (no change for 1 min). The seawater samples are analyzed using the same procedure. Total titration time takes about 7 min. Alkalinity is calculated by formula

$$TA = N_a V_a / (V_{sw} d_{sw}) \quad (12)$$

Here, N_a , and V_a , are normality and volume of acid, respectively; V_{sw} and d_{sw} are volume and density of seawater. Estimated precision is about 0.2% ($4\sim 5 \text{ } \mu\text{mol kg}^{-1}$).

The comparison of both methods are summarized briefly in Table 1.

2.3 Materials

During two cruises of the JES expedition on R/V Roger Revelle from 24th June to 17th July, 1999 and R/V Professor Khromov from 22nd July to 11th August, 1999 in the East Sea, around 550 real seawater samples from the surface to more than 3500 m depth at 92 stations were measured and the results were compared (Fig. 1).

Table 1. Summary of the methods for total alkalinity (TA) and pH for inter-comparison

	Cell type	Closed	Open
TA	End Pt detection	EMF	Visual Indicator
	Calculation	Non-linear Least Square	Algebraic formula
	Titrant	~ 0.25 N HCl	~ 0.02 N HCl
	Acid Standardization	Na ₂ CO ₃ and CRM	Na ₂ CO ₃ and CRM
	Precision*	4.5 μmol kg ⁻¹	4 ~ 5 μmol kg ⁻¹
pH		Spectrophotometry using <i>m</i> CP indicator	Potentiometry using a cell without liquid junction
	Precision**	0.006	0.004

*Values from the results of certified reference material measurements.

**Values from the results of the buffer solution measurements.

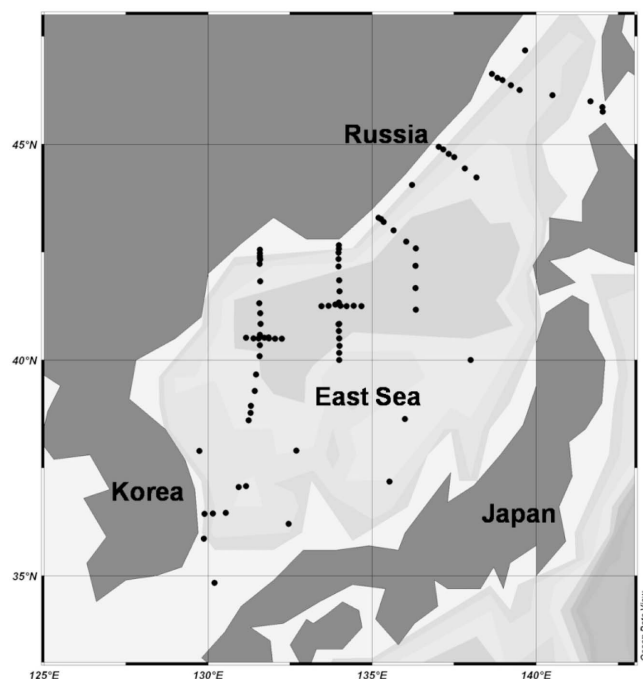


Fig. 1. A map showing the stations for inter-comparison in the East Sea.

3. RESULTS AND DISCUSSION

3.1 Total Hydrogen Ion Concentration (pH)

The pH values of two methods are in a good agreement ($r^2=0.996$, Fig. 2). However, the slope between two data sets is about 3.5% different from the expected equivalence ($pH_{Pot}=1.035 \cdot pH_{Spec} - 0.274$, $r^2=0.996$).

As for the spectrophotometric method, seawater samples were delivered into the cell by a pipette ($V=25$ mL) to maintain the exact volume ratio of $V_{indicator}/V_{sample}$. We compared the effect of the pipetting procedure on the pH measurement as well as two different methods, spectrophotometry and potentiometry.

The slope between potentiometry and spectrophotometry with a pipette is about 1.055 ($pH_{Pot}=1.055 \cdot pH_{Spec} - 0.430$, $r^2=0.996$) and the one between potentiometry and spectropho-

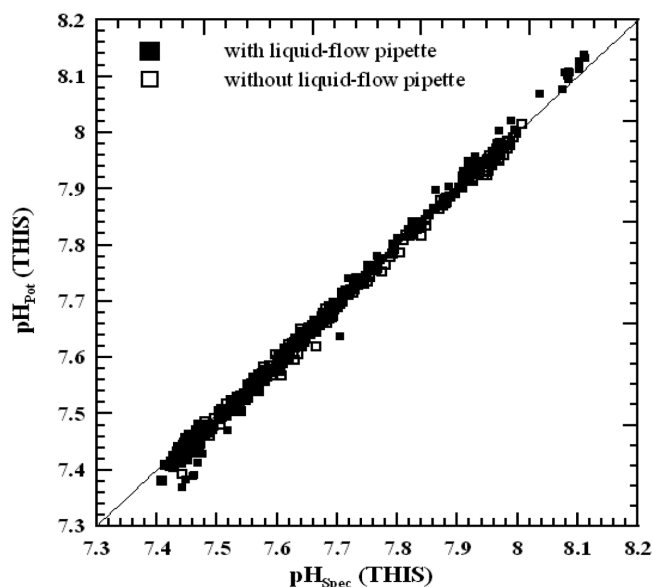


Fig. 2. Comparison of pH values between spectrophotometry and potentiometry. Solid line denoted the equivalence line. The unit is in total hydrogen ion scale (THIS).

tometry without a pipette is about 1.017 ($pH_{Pot}=1.017 \cdot pH_{Spec} - 0.138$, $r^2=0.997$). This shows much closer to the equivalence. The mean difference between the methods with a pipette is 0.014 ($\sigma=0.012$), while the one without a pipette are 0.009 ($\sigma=0.008$), close value to the precision value from the results of the buffer solution measurements.

The results of the spectrophotometry with a pipette show higher value comparing to the results of the potentiometry, when pH value is lower (Fig. 3). Since typical profile of pH in the region (the East Sea) decreases with depth, and shows around 7.5 of pH from 200~300 m depth to the bottom (Fig. 4), the spectrophotometric method gives higher value in the deep layer than the surface.

The pipetting procedure may remove dissolved CO₂ in the samples. Removal of CO₂ causes a decrease of proton concentration in the sample as know as an increase of pH. Since surface samples are mostly equilibrated with atmosphere, there

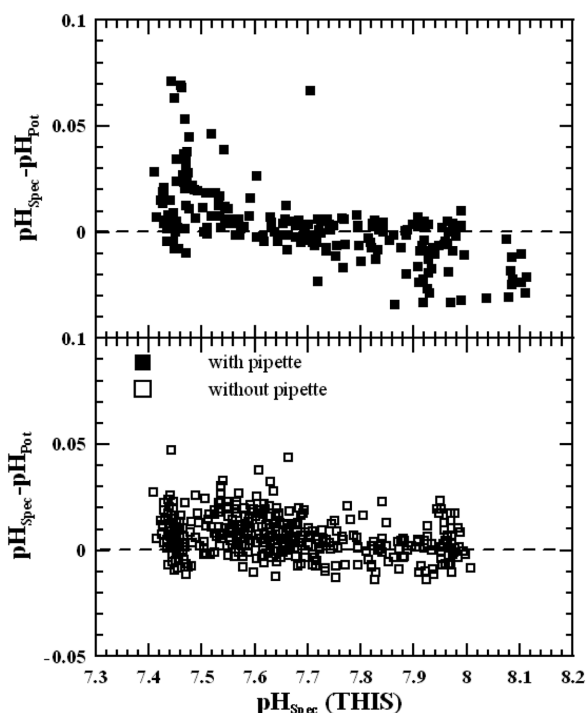


Fig. 3. Plots of pH differences between two methods vs. pH values of spectrophotometry. Results of the experiment without a pipette are also shown in the figure. The units are same as Fig. 2.

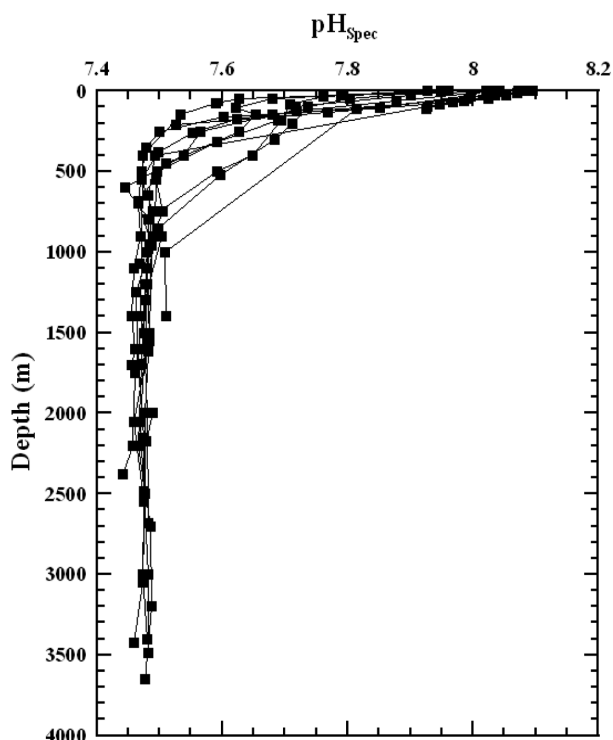


Fig. 4. Typical vertical distributions of pH values measured by spectrophotometry. The units are same as Fig. 2.

were almost no differences between two methods for the surface samples. On the other hand, larger differences were discovered in the deep samples because deep samples are prone to

lose CO_2 . The data from the same procedure without a pipette show much less difference between the two which corresponds to precisions of the methods (Fig. 3). From this result, pipetting procedure should be excluded to get better results.

In general, the spectrophotometric method is the most commonly used to determine pH in seawater. Nevertheless, this method has a distraction. The temperature of the samples and the cell in the spectrophotometer generate a significant error. The difference of 0.1°C in the temperature during the measurement gives 0.014 pH offset which is much higher than the precision of this method. Hence, very special care should be required to maintain the temperature stable during the measurements.

3.2 Total Alkalinity (TA)

In general, salinity normalized total alkalinity ($\text{NTA} = \text{TA} \times 35/S$; S represents salinity) values of the two methods show linear relationship. However, it seems that there is a systematic offset existing between the two methods (Fig. 5). The values from open cell method are lower by $5\text{--}10 \mu\text{mol kg}^{-1}$ than those from closed cell method. No trend of discrepancy between the two methods was found (Fig. 6, Fig. 7).

In the PICES WG13 inter-comparison workshop, which was held at Tsukuba, Japan in April, 1999 and 2000, there were discrepancies of up to $\pm 25 \mu\text{mol kg}^{-1}$ among 13 laboratories in 1999, and up to $\pm 7 \mu\text{mol kg}^{-1}$ in 2000 (Feely *et al.* [2003]). Comparing with this result and considering the precisions of

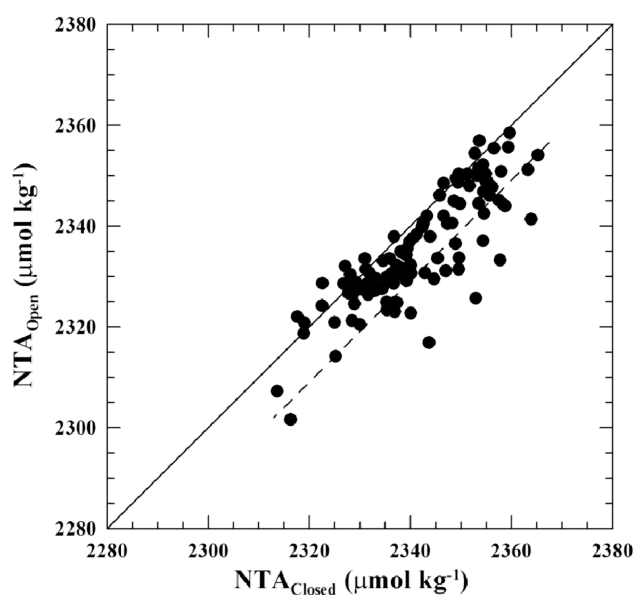


Fig. 5. Comparison of normalized total alkalinity (NTA) values between closed-cell method ($\text{NTA}_{\text{Closed}}$) and open-cell method (NTA_{Open}). Solid and dashed lines denote 1:1 and regression lines, respectively.

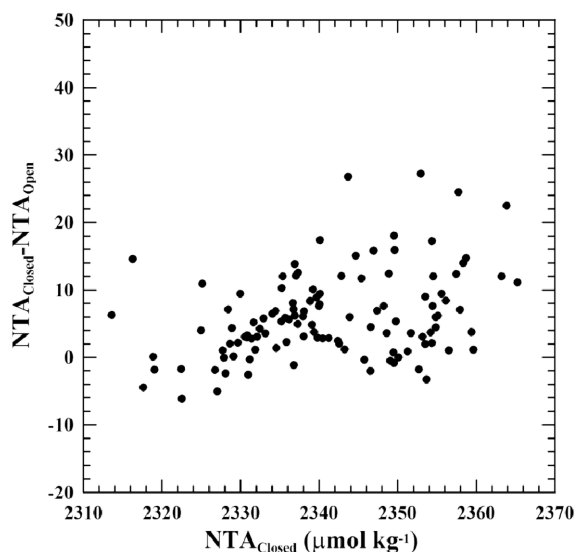


Fig. 6. A plot of NTA differences between closed-cell method and open-cell method vs. NTA values of closed-cell method.

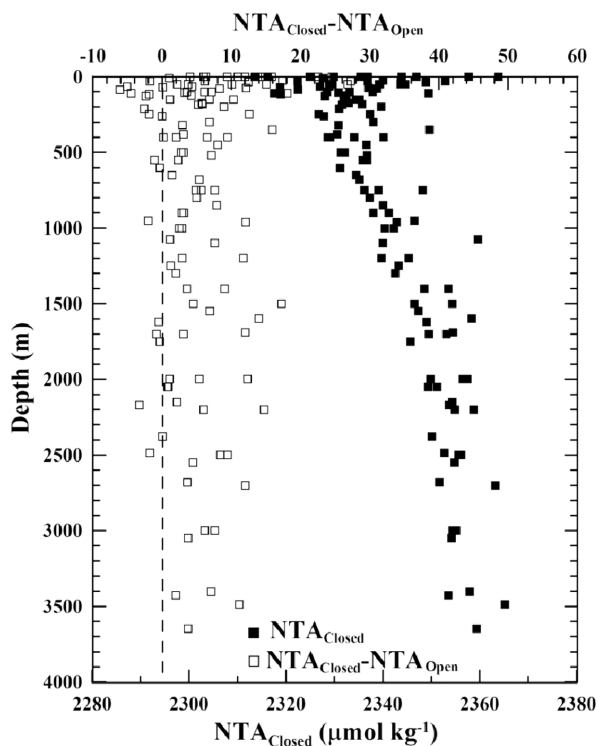


Fig. 7. Vertical distributions of normalized total alkalinity (NTA) measured by closed cell method and difference of NTA between closed-cell method and open-cell method for all stations.

the two methods (Table 1; both are 4~5 $\mu\text{mol kg}^{-1}$), the discrepancy of the two methods is not serious.

Though the reported precision of the open cell method (less than 2 $\mu\text{mol kg}^{-1}$) is generally better than that of the closed cell method (less than 6 $\mu\text{mol kg}^{-1}$) (Dickson *et al.* [2007]), the precision of the open cell method in this study is similar with that of the closed cell method. The detection of the end point by

indicator with the naked eye may cause worse precision.

In the PICES inter-comparison workshop, the closed cell method showed higher values, and the open cell method showed lower mean values for samples of high pCO_2 concentration (Feely *et al.* [2003]). This study also yields similar results to those of the PICES inter-comparison workshop. This may be caused by the bubble formed in the closed cell during the experiment. Usually, in the open cell method, the solution is stirred for a period of time for allowing the evolved CO_2 to escape. However, the CO_2 cannot escape from the cell in the closed cell method. This removal of CO_2 from the solution consumes extra proton in the solution. This raises more acid and titrant for total alkalinity determination. This may cause of little higher value in total alkalinity for the closed cell method.

4. SUMMARY

Two different measurements of pH and total alkalinity were compared for the same seawater samples. Spectrophotometry using *mCP* indicator and potentiometry without liquid junction were compared for pH measurement. The pH values of the two methods are generally in a good agreement. However, the spectrophotometric method yields about 3.5% higher values and pronounces especially for deep seawater with lower pH. This may be caused by using a pipette in the spectrophotometry and the subsequent escape of CO_2 . The results of the experiment without a pipette show better concurrence between the two methods.

Potentiometric titration methods of total alkalinity using a closed cell and an open cell (Bruevich's method) were compared as well. Values from the open cell method are smaller by about 5~10 $\mu\text{mol kg}^{-1}$ than the values from the closed cell method. This may be caused by the CO_2 bubble formed in the closed cell during the experiment.

Although any analytical method compared in this study can be applied for the pH or TA measurement, we should be aware that paying especial attentions is critical to get a satisfactory result. In the case for the pH determination by spectrophotometry, pipetting procedure should be excluded to get better results, and very special care is required to stabilize the temperature during the measurements.

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REFERENCES

- [1] Bruevich, C.V., 1944, "Determination alkalinity of small volumes of seawater by direct titration", In: Instruction of chemical investigation of seawater. Glavsevmorput, Moscow, 83 p.
- [2] Clayton, T.D. and Byrn, R.H., 1993, "Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results", *Deep-Sea Res.*, Vol. 40, 2115-2129.
- [3] Dickson, A.G., 1981, "An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data", *Deep-Sea Res.*, Vol. 28A, 609-623.
- [4] Dickson, A.G. and Goyet, C. eds., 1994, *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water. version 2*, ORNL/CDIAC-74, DOE, Washington DC, 187 p.
- [5] Dickson, A.G., Sabine, C.L., Christian, J.R. eds., 2007, *Guide to best practices for ocean CO₂ measurement*. PICES Special publication 3, PICES Press, Sidney, 191 p.
- [6] Feely, R.A., Nojiri, Y., Dickson, A.G., Sibine, C.L., Lamb, M.F., Ono, T., 2003, *CO₂ in the North Pacific Ocean* (PICES Working Group 13 Final Report). PICES Scientific Report, No. 24, PICES Press, Sidney, 57 p.
- [7] Ivanenkov, V. and Bordovsky, O. 1978, *The methods of hydrochemical investigation of the ocean*. Nauka, Moscow, 271 p (in Russian).
- [8] Johansson, O. and Wedborg, M., 1982, "On the evaluation of potentiometric titrations of seawater with hydrochloric acid", *Oceanol. Acta*, Vol. 5, 209-218.
- [9] Lewis, E. and Wallace, D., 1998, *Program developed for CO₂ system calculations*, Carbon Dioxide Information Analysis Center, Oak Ridge, 31p.
- [10] Millero, F.J., Zhang, J.-Z., Lee, K., Campbell, D.M., 1993, "Titration alkalinity of seawater", *Mar. Chem.*, Vol. 44, 153-166.
- [11] Park, K., 1969, "Oceanic CO₂ system: an evaluation of ten methods of investigation", *Limnol. Oceanogr.* Vol. 14, 179-186.
- [12] Pitzer, K.S., 1991, *Ion interaction approach: Theory and data correlation*. In: Pitzer KS (ed) *Activity coefficients in electrolyte solutions*. 2nd Edition. Roca Raton Ann Arbor, CRC Press, London, pp 75-153.
- [13] Sarmiento, J.L., Murnane, R., LeQuere, C., 1995, "Air-sea CO₂ transfer and the carbon budget of the North Atlantic", *Phil. Trans. R. Soc. Lond. B*, Vol. 348, 211-219.
- [14] Skirrow, G. 1975, *The dissolved gases-carbon dioxide*. In: Riley JP, Skirrow G (eds) *Chemical Oceanography*, v.2., Academic Press, London, pp 1-912.
- [15] Tishchenko, P.Y., Pavlova, G.Y., 1999, *Standardization of pH measurements of seawater by Pitzer's method*. In: "CO₂ in the Oceans", *Extended Abstracts*, Tsukuba.
- [16] Tishchenko, P.Y., Wong, C.S., Pavlova, G.Y., Johnson, W.K., Kang, D.-J., Kim, K.-R., 2001, "The Measurement of pH Values in Seawater Using a Cell without a Liquid Junction", *Oceanology*, Vol. 41, 813-822.
- [17] Volk, T. and Hoffert, M.I., 1985, *Ocean carbon pumps: Analysis of relative strength and efficiencies in ocean-driven atmospheric CO₂ changes*. In: Sundquist ET, Broecker WS (eds) *The carbon cycle and atmospheric CO₂: natural variations archean to present*, *Geophysical Monograph Series*, no.32, AGU, pp 99-110.

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