

# Potentiometric open-cell titration for seawater alkalinity considering temperature dependence of titrant density and Nernst response of pH electrode

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The total alkalinity ( $A_T$ ) of seawater is one of the parameters required to characterize carbonate systems, which are essential for studying the greenhouse effects of carbon dioxide ( $\text{CO}_2$ ) on the Earth's climate. The  $A_T$  of seawater was measured by potentiometric open-cell titration using HCl—without the addition of sodium chloride (NaCl)—and calculated by a nonlinear least-squares regression. In addition, the equation for calculating the titrant density was studied over a range of concentrations and temperatures. The similarity of the pH electrode response to the ideal Nernst value ( $k_s$ ) was measured using pH buffers for seawater and pure water. New methods for the calculation of  $A_T$  using  $k_s$  were proposed. Open-cell titrations for a certified reference material (CRM) were conducted using two electrodes with  $k_s$  of 0.997 and 0.989. The measured values for both electrodes were in good agreement with the CRM value of  $2356.78 \pm 0.26 \mu\text{mol/kg}$ .  $A_T$  was successfully calculated using  $k_s$ . The dilution effect by the titrant, free of NaCl, on electromotive force measurement was also examined and found to be negligible for the calculation of  $\text{CO}_2$  parameters.

Keywords: alkalinity, open-cell titration, potentiometric method, HCl density, Nernst response

## INTRODUCTION

The greenhouse effect of  $\text{CO}_2$  on the Earth's climate has generated considerable interest in understanding the global carbon cycle (Siegenthaler and Sarmiento, 1993). The carbonate system in seawater can be studied by measuring four parameters: pH, total alkalinity ( $A_T$ ), total dissolved inorganic carbon ( $C_T$ ), and fugacity of  $\text{CO}_2$  ( $f_{\text{CO}_2}$ ). At least two of these parameters are required to characterize the carbonate system, while the other interrelated parameters can be calculated using thermodynamic constants (Millero, 1995).

Previously reported analytical methods for the determination of  $A_T$  in seawater include (a) single-step acid addition with the potentiometric determination of excess acid (Anderson and Robinson, 1946; Culbertson *et al.*, 1970; Perez and Fraga, 1987a) and (b) stepwise acid addition to an open- (Dickson *et al.*, 2003) or closed-titration cell (Millero *et al.*, 1993; Hernández-Ayón *et al.*, 1999), combined with the determination of the sample

equivalence point on the titration curve through chemical algorithms. The multistep method has been widely used for shipboard measurements because of its high precision and autonomous operation (Dickson *et al.*, 2007).

In the multistep method, a seawater sample of known weight is titrated with a HCl solution with precalibrated concentration. The titrant (acid) is added to the seawater according to volume rather than weight. Consequently, the density of the titrant must be known in order to calculate the weight of the titrant added. In general, the titrant contains sufficient NaCl to adjust the total ionic strength to approximately that of seawater (approximately 0.7 mol/kg) in order to maintain the activity coefficients constantly during titration. However, it is difficult to control concentrations of both NaCl and HCl simultaneously. Unfortunately, the equation used for the calculation of the density of the NaCl and HCl mixture is only reliable at 25°C (Dickson *et al.*, 2007); therefore, it is necessary to maintain the titrant at 25°C during sample measurements. However, in practice, it is convenient to use the titrant without NaCl and formulate a suitable equation in order to calculate the titrant density at various temperatures.

The titration process is monitored by measuring the electromotive force (EMF) of a combination pH glass electrode/reference electrode cell. In the traditional Gran method,  $A_T$  is computed using the titrant volume and EMF data and a linear least-squares regression calculation

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(Gran, 1952). The nonlinear least-squares calculation has also been used for  $A_T$  measurement (Dickson *et al.*, 2003). In the procedure, the SD of  $A_T$  for each titration step was minimized by adjusting the standard electrode potential,  $E^\circ$ , or related parameters for the pH electrode.

The temperature of the titration cell assembly is generally controlled at 25°C to maintain the temperature of the sample solution (Dickson *et al.*, 2007). The response of a pH electrode obeys the Nernst equation (Bates, 1973), and the calculated pH decreases approximately 0.34% for a 1°C increase in temperature from 25°C. Consequently, it is important to consider the effect of temperature in the calculation of  $A_T$ .

The performance of the pH electrode is paramount for achieving high-quality results and is generally assessed by measuring the  $A_T$  of a certified reference material (CRM) (Dickson *et al.*, 2003). If the certified value is not obtained by  $A_T$  measurement, it may even be necessary to replace the electrode (Dickson *et al.*, 2007). Therefore, the determination of the pH electrode performance prior to the analysis of the reference material is encouraged.

To address these issues, we discuss the use of a HCl solution without the addition of NaCl as the titrant for  $A_T$  determination. The density of the HCl solution at temperatures of 5–40°C and concentrations of 0–2 mol/L was determined, and a suitable equation was formulated to calculate the titrant density over these ranges. Finally, the Nernst response of the electrode, dilution, and temperature effect of the seawater sample during open-cell titration were considered in the subsequent nonlinear least-squares calculation of  $A_T$ .

## THEORETICAL BASIS

### Total alkalinity of seawater $A_T$

The total alkalinity of a seawater sample is defined as the number of moles of hydrogen ions equivalent to the excess of proton acceptors over proton donors in 1 kg of sample (Dickson *et al.*, 2003). Proton acceptors are defined as bases resulting from weak acids with dissociation constants  $K < 10^{-4.5}$  at 25°C and zero ionic strength, while proton donors are defined as acids resulting from bases with  $K > 10^{-4.5}$  (Dickson *et al.*, 2003).

For the open-cell multistep titration of  $A_T$ , a known amount of seawater is first placed in an open cell. The seawater sample is then acidified to pH 3.5–4.0 with a single aliquot of the titrant. The solution is then stirred for a sufficient period to allow the evolved  $\text{CO}_2$  to escape. Titration is continued until a pH value of approximately 3.0 is attained. At each titration point, after a mass ( $m$  kg) of acid at a concentration ( $C$  mol  $\text{kg}^{-1}$ ) of a solution is added to a mass ( $m_0$  kg) of the sample, the analytical concentration of hydrogen ions ( $C_H$  mol  $\text{kg}^{-1}$ ) is given by

$$C_H = \frac{-m_0 A_T + mC}{m_0 + m}. \quad (1)$$

Because the  $\text{CO}_2$  generated by the reaction of the seawater with the acid titrant escapes into the atmosphere during open-cell titration, the majority of terms, except for the sulfate and fluoride terms, can be safely neglected in the evaluation of  $C_H$  at pH 3.0–3.5. Thus,

$$\begin{aligned} & \frac{-m_0 A_T + mC}{m_0 + m} \\ & \approx [\text{H}^+]_{\text{F}(at\ m_0+m)} + [\text{HSO}_4^-]_{(at\ m_0+m)} + [\text{HF}]_{(at\ m_0+m)} \end{aligned} \quad (2)$$

where  $[\text{H}^+]_{\text{F}}$  is the free hydrogen ion concentration at the titration point after a mass ( $m$  kg) of acid has been added to a mass ( $m_0$  kg) of the sample ( $m_0 + m$ ). Consequently, the right-side parameters of Eq. (2) can be rewritten as:

$$\begin{aligned} [\text{H}^+]_{\text{F}(at\ m_0+m)} &= [\text{H}^+]_{\text{T}(at\ m_0+m)} / Z_{(at\ m_0+m)} \\ [\text{HSO}_4^-]_{(at\ m_0+m)} &= \frac{S_{\text{T}(at\ m_0+m)}}{1 + K_{\text{S}(at\ m_0+m)} / [\text{H}^+]_{\text{F}(at\ m_0+m)}} \\ [\text{HF}]_{(at\ m_0+m)} &= \frac{F_{\text{T}(at\ m_0+m)}}{1 + K_{\text{F}(at\ m_0+m)} / [\text{H}^+]_{\text{T}(at\ m_0+m)}}. \end{aligned} \quad (3)$$

Here  $[\text{H}^+]_{\text{T}}$  is the “total hydrogen ion concentration” on the pH scale as defined by Hansson (1973).  $S_{\text{T}}$  and  $F_{\text{T}}$  are the total sulfate and fluoride concentrations, respectively.  $K_{\text{S}}$  and  $K_{\text{F}}$  are the acid dissociation constants of  $[\text{HSO}_4^-]$  and  $[\text{HF}]$ , respectively.  $Z$  is defined as:

$$Z_{(at\ m_0+m)} = 1 + S_{\text{T}(at\ m_0+m)} / K_{\text{S}(at\ m_0+m)}. \quad (4)$$

Subsequently, Eq. (2) can be transformed to:

$$\begin{aligned} A_T &= - \frac{S_{\text{T}(at\ m_0)}}{1 + Z_{(at\ m_0+m)} K_{\text{S}(at\ m_0+m)} / [\text{H}^+]_{\text{T}(at\ m_0+m)}} \\ &\quad - \frac{F_{\text{T}(at\ m_0)}}{1 + K_{\text{F}(at\ m_0+m)} / [\text{H}^+]_{\text{T}(at\ m_0+m)}} \\ &\quad - \frac{m_0 + m}{m_0} \frac{[\text{H}^+]_{\text{T}(at\ m_0+m)}}{Z_{(at\ m_0+m)}} + \frac{m}{m_0} C. \end{aligned} \quad (5)$$

$S_{T(at\ m0)}$  (Riley, 1965) and  $F_{T(at\ m0)}$  (Morris and Riley, 1966) can be expressed relative to the practical salinity of sample  $Sp_{(at\ m0)}$ .  $K_{S(at\ m0+m)}$  (Dickson, 1990) and  $K_{F(at\ m0+m)}$  (Perez and Fraga, 1987b) can be expressed in terms of  $T_{(at\ m0+m)}$ ,  $Sp_{(at\ m0+m)}$ , and  $I_{(at\ m0+m)}$ , which denote the temperature, salinity, and ionic strength of the sample, respectively. The ionic strength is calculated as follows (Dickson, 1990):

$$\frac{I}{m} = \frac{19.924Sp_{(at\ m_0+m)}}{1000 - 1.005Sp_{(at\ m_0+m)}} \quad (6)$$

where  $m^\circ = 1 \text{ mol/kg-H}_2\text{O}^{-1}$ .  $Sp_{(at\ m0+m)}$  can be expressed as the salinity of the initial sample  $Sp_{(at\ m0)}$  as follows:

$$Sp_{(at\ m_0+m)} = \frac{m_0}{m_0 + m} Sp_{(at\ m_0)} \quad (7)$$

$[H^+]_T$  for a pH glass electrode

$[H^+]_T$  for a pH glass electrode/reference electrode cell is given by the ideal Nernst equation (Dickson *et al.*, 2007) as:

$$[H^+]_{T(at\ m_0+m)} = \exp \left( \frac{E_{(at\ m_0+m)} - E^\circ}{RT_{(at\ m_0+m)}/F} \right) / k_s \quad (8)$$

where  $E^\circ$  and  $E$  are the standard potential and EMF of the pH cell, respectively.  $k_s$  is the electrode response factor compared with the ideal Nernst value,  $RT \ln 10 / F$ , calculated from the EMF values,  $E_1$  and  $E_2$ , for the two pH standard solutions,  $pH(S)_1$  and  $pH(S)_2$ , as:

$$k_s = \left( \frac{E_1 - E_2}{pH(S)_1 - pH(S)_2} \right) / (RT \ln 10 / F) \quad (9)$$

Estimation of initial  $E^\circ$  ( $E^\circ_{init}$ )

To appropriately apply the nonlinear procedure for the calculation of  $A_T$ , it is necessary to start with reasonable estimates for the initial  $E^\circ$  ( $E^\circ_{init}$ ) value in order to ensure convergence. A reasonable estimation of  $E^\circ_{init}$  can be achieved using a simple Gran approach (Gran, 1952) or suitable seawater buffer solutions. As we propose for the determination of  $E^\circ_{init}$  using seawater buffer solutions,  $k_s$  is first estimated by the measurement of 2-amino-2-hydroxymethyl-1,3-propanediol (TRIS) and 2-aminopyridine (AMP) buffer solutions by Eq. (9).  $E^\circ_{init}$  is next evaluated by the EMF measurement of the pH electrode ( $E$ ) for TRIS at temperature ( $T$ ) by Eq. (10):

$$[H^+]_{T \text{ for TRIS}} = \exp \left( \frac{E - E^\circ_{init}}{RT / F} \right) / k_s \quad (10)$$

The pH values of TRIS and AMP with salinity ( $S$ ) and temperature ( $T$ ) were calculated according to the method of Dickson *et al.* (2007).

Estimation of  $A_T$

A nonlinear least-squares calculation is typically used to refine the values of  $A_T$  and  $E^\circ_{init}$  by using a multiplier:

$$f = [H^+] / [H'], \quad (11)$$

$$[H'] = \exp \left( \frac{E_{(at\ m_0+m)} - E^\circ_{init}}{RT_{(at\ m_0+m)}/F} \right) / k_s, \quad (12)$$

where estimates of  $[H^+]$  ( $[H']$ ) are computed from  $E^\circ_{init}$  (Dickson *et al.*, 2007). In our proposed calculation, the standard deviation (SD) minimization procedure for the  $A_T$  calculation is performed as follows. The actual data fitting was performed by the nonlinear least-squares method with Eq. (5) by using the solver unit in Microsoft Excel. This software minimizes the SD of  $A_T$  for each titration step by adjusting  $E^\circ$  in Eq. (8). Finally, a correction factor for the dilution by mercuric chloride of the CRM, 1.0002, was multiplied by the resultant  $A_T$ .

## EXPERIMENTAL METHODS

Reagents

TRIS and AMP pH buffers in synthetic seawater with a salinity of 35 ( $pH_T$  buffers) were purchased from Wako Pure Chemical, Japan. For oceanic  $CO_2$  measurements, CRM batch #99 ([http://cdiac.esd.ornl.gov/oceans/Dickson\\_CRM/rmdata/Batch99.pdf](http://cdiac.esd.ornl.gov/oceans/Dickson_CRM/rmdata/Batch99.pdf)) was used to investigate the consistency of the analytical value of  $A_T$  we obtain with its certificated value. The certified  $A_T$  value for the CRM was  $2356.78 \pm 0.26 \mu\text{mol/kg}$ . The HCl concentration used for alkalinity titration was determined by acid-base titration using a  $Na_2CO_3$  solution (Wako, for volumetric analysis). Phthalate and phosphate pH buffers in pure water ( $pH_{NBS}$  buffers) for  $pH = 6.865$  and  $4.008$  at  $25^\circ\text{C}$  were purchased from Wako (Japan Calibration Service System; JCSS grade).

Apparatus

The titration was conducted using an open-cell-type alkalinity analyzer (ATT-05, Kimoto Electric) equipped with a voltmeter with high-input impedance ( $>10^{13} \Omega$ ) and a sensitivity of  $0.01 \text{ mV}$ . The HCl density ( $0.02\text{--}2.0$

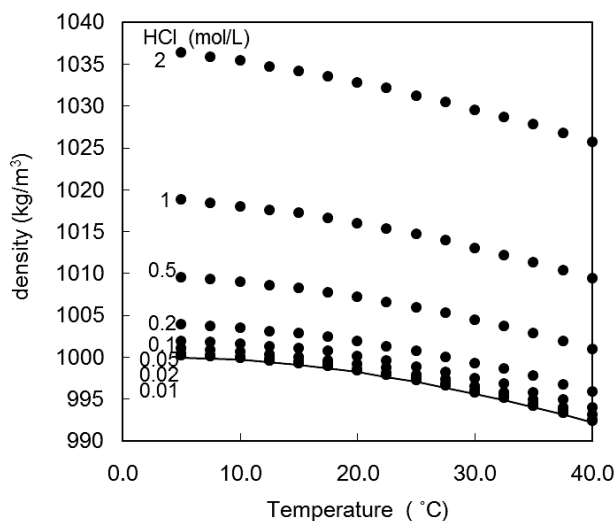


Fig. 1. Density of HCl ( $\text{kg/m}^3$ ) for various concentrations. Density of air-saturated water from Jones and Harris 1992 is shown as a solid line.

mol/L) was measured using a resonant-frequency oscillation-type density meter (DA-640, Kyoto Electric). The EMF was measured using a combination of a glass/reference electrode (PH2401C, Radiometer Analytical) and the alkalinity analyzer ATT-05. The temperatures of the titrant and sample were measured with a resolution of  $0.01^\circ\text{C}$  and a precision of  $0.1^\circ\text{C}$ .

#### Procedure for determination of $A_T$

A seawater sample (approximately 100 g) was weighed in the titration cell, in which it was titrated with HCl in two stages. The seawater was acidified to a  $\text{pH}_T$  slightly more than 3.5 with approximately  $2.5 \text{ cm}^3$  of the titrant (0.1 mol/L HCl), and then the solution was vigorously stirred with air flowing at  $100 \text{ cm}^3/\text{min}$  through the solution for 10 min to allow the evolved  $\text{CO}_2$  to escape. Next, the titration was conducted in a series of approximately 20 additions of  $0.04 \text{ cm}^3$  HCl titrant each until a final  $\text{pH}_T$  of below 3.0 was attained. After each addition, the total dispensed volume was recorded at a resolution of  $0.001 \text{ cm}^3$ ; the EMF of the combination pH electrode was recorded as 0.01 mV, and the sample temperature was recorded as  $0.01^\circ\text{C}$ . The temperature of the titrant was also measured.

A nonlinear least-squares regression was used to calculate  $E^\circ$  and  $A_T$ . The actual data fitting was performed using a solver program with Microsoft Excel spreadsheet software. The initial and final titration points of the data set processed were chosen as those for which the  $\text{pH}_T$  by initial  $E^\circ$  values were the closest to 3.5 and 3.0, respectively. Points that lie outside this region were excluded

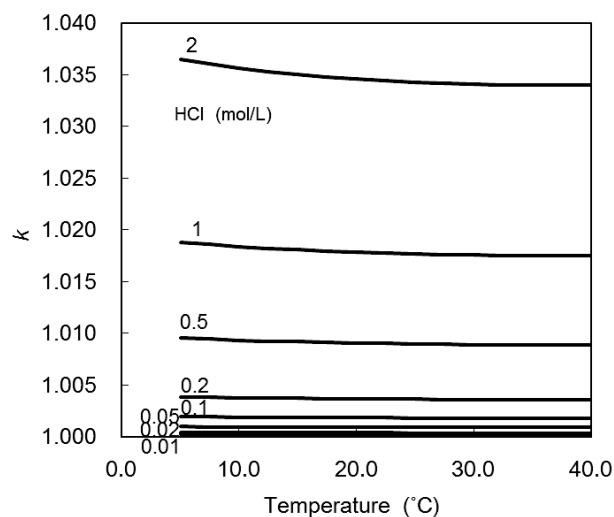


Fig. 2. Value of factor  $k$  in Eq. (14) for various HCl concentrations.

from the calculation. The data fitting was conducted three times by using the adjusted  $E^\circ$  value.

#### Collection of seawater samples

$A_T$  measurements for seawater samples were conducted during the R/V Hakuho-Maru KH11-05 cruise in the northwestern subtropics of the North Pacific about 800 to 1300 km to the south of Japan. Sub-samples for  $A_T$  measurements were collected by an X-Niskin type water sampler attached to a CTD-CMS water sampling system. Water samples were collected in high-density polyethylene bottles and stored temporarily at room temperature. The sample temperature was set at  $25^\circ\text{C}$  before analysis.  $100 \text{ cm}^3$  of the sample was collected and poured into a tall beaker. Sample density was calculated by the equation of Millero and Poisson (1981), using sample temperature and salinity, and then  $A_T$  measurements were conducted onboard the ship.

## RESULTS AND DISCUSSION

#### Equation for the calculation of the density of HCl at various temperatures and concentrations.

The density of the HCl titrant solution at various temperatures ( $5\text{--}40^\circ\text{C}$ , every  $2.5^\circ\text{C}$ ) and concentrations (0.02–2 mol/L) was measured, as shown in Fig. 1. The density of air-saturated water (Jones and Harris, 1992) is also shown for comparison. Using air-saturated water density ( $\rho_w \text{ kg/m}^3$ ), the temperature and concentration dependence of our density results in Fig. 1 ( $\rho_{\text{HCl}} \text{ kg/m}^3$ ) were well described by the following equation:

Table 1. Deviation of calculated density of HCl ( $\text{kg/m}^3$ ) using Eq. (13)

Water temperature ( $^{\circ}\text{C}$ )	HCl (mol/L)							
	0.01	0.02	0.05	0.10	0.20	0.50	1.00	2.00
5.0	0.0	0.1	0.1	0.0	0.1	0.0	0.0	0.0
7.5	0.0	-0.1	0.0	0.0	0.0	0.0	-0.1	0.0
10.0	0.0	-0.1	0.0	0.0	0.0	0.0	-0.1	0.1
12.5	0.0	0.0	-0.1	0.0	-0.1	-0.1	0.0	0.0
15.0	0.0	0.0	0.0	0.0	0.0	-0.1	0.1	0.1
17.5	0.0	0.0	0.0	0.2	0.0	-0.1	0.0	0.1
20.0	0.0	-0.1	0.0	0.1	0.1	0.0	0.0	0.1
22.5	0.1	0.0	0.1	0.1	0.0	0.0	0.0	0.1
25.0	0.0	0.0	0.0	0.0	0.1	-0.1	0.1	0.0
27.5	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.1
30.0	0.0	0.0	0.0	0.0	0.0	-0.1	-0.1	-0.1
32.5	0.1	0.1	0.0	0.1	0.2	0.0	-0.1	0.0
35.0	0.0	0.0	0.0	0.0	0.2	0.0	-0.1	0.0
37.5	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	-0.1
40.0	0.0	-0.1	0.0	0.0	0.1	-0.1	-0.2	-0.2

$$\rho_{\text{HCl}} = k\rho_w. \quad (13)$$

The factor of  $k$  correlated well with the temperature and concentration of HCl,  $t$  ( $^{\circ}\text{C}$ ) and  $C_{\text{HCl}}$  (mol/L), respectively, and described by the following equation (Fig. 2):

$$k = \left( 1.2525 \times 10^{-11} \times t^3 - 7.0835 \times 10^{-9} \times t^2 + 3.1353 \times 10^{-6} \times t - 6.0338 \times 10^{-4} \right) \times C_{\text{HCl}}^2 + \left( -1.5980 \times 10^{-8} \times t^3 + 2.4222 \times 10^{-6} \times t^2 - 1.2067 \times 10^{-4} \times t + 1.9938 \times 10^{-2} \right) \times C_{\text{HCl}} + 1.0000. \quad (14)$$

The density of the air-saturated water in the temperature range 5–40 $^{\circ}\text{C}$  is given by Jones and Harris (1992):

$$\rho_w = 6.943248 \times 10^{-5} \times t^3 - 8.523829 \times 10^{-3} \times t^2 + 6.337563 \times 10^{-2} \times t + 999.84847. \quad (15)$$

For  $t = 25^{\circ}\text{C}$  and  $C_{\text{HCl}} = 0.1000$  mol/L, Eq. (13) provides an estimated  $\rho_{\text{HCl}} = 998.8$   $\text{kg/m}^3$ . The residual data of equation (13) from our Fig. 1 are shown in Table 1. The SD of the data fit represented by Eq. (13) was 0.075  $\text{kg/m}^3$ , and the largest observed residual was 0.2  $\text{kg/m}^3$  ( $\pm 0.02\%$ ).

Electrode response factor,  $k_s$ , and the standard potential of electrode,  $E^{\circ}$

The electrode response factor,  $k_s$ , and the electrode

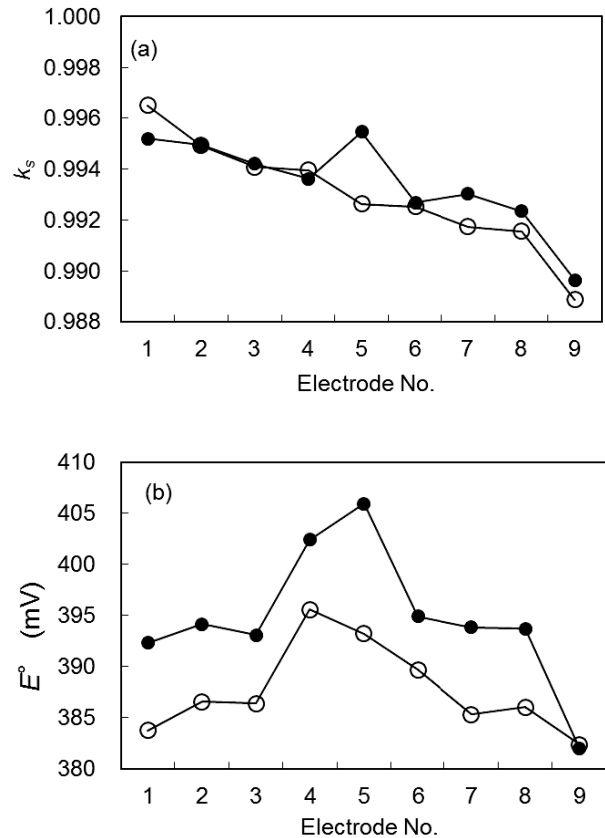


Fig. 3. (a)  $k_s$  and (b)  $E^{\circ}$  value for TRIS–AMP  $\text{pH}_T$  buffers and phthalate and phosphate  $\text{pH}_{\text{NBS}}$  buffers. Open circles: TRIS and AMP  $\text{pH}_T$  buffers; closed circles: phthalate and phosphate  $\text{pH}_{\text{NBS}}$  buffers.

Table 2. Calculation of alkalinity of CRM batch #99 using electrode No. 1

	#1-1	#1-2	#1-3
(a) $E^{\circ}_{\text{init}}$ from the Gran approach, calculation with $f$			
Result for $k_s = 0.997$			
initial $E^{\circ}$ (mV)	383.10	383.29	382.81
initial alkalinity ( $\mu\text{mol/kg}$ )	2352.22	2349.86	2340.69
resultant $E^{\circ}$ (mV)	383.10	383.29	382.81
resultant alkalinity ( $\mu\text{mol/kg}$ )	2356.43	2356.25	2356.52
standard deviation ( $\mu\text{mol/kg}$ )	0.30	0.36	0.42
number of data points	18	19	18
resultant $f$	0.9940	0.9907	0.9766
Result for $k_s = 1$			
initial $E^{\circ}$ (mV)	383.36	383.78	383.30
initial alkalinity ( $\mu\text{mol/kg}$ )	2350.23	2347.93	2338.84
resultant $E^{\circ}$ (mV)	383.36	383.78	383.30
resultant alkalinity ( $\mu\text{mol/kg}$ )	2354.47	2354.36	2354.68
standard deviation ( $\mu\text{mol/kg}$ )	0.23	0.27	0.42
number of data points	19	19	19
resultant $f$	0.9940	0.9907	0.9767
(b) $E^{\circ}_{\text{init}}$ from seawater buffer solutions, SD minimization procedure for $A_T$ calculation			
Result for $k_s = 0.997$			
initial $E^{\circ}$ (mV)	383.75	383.75	383.75
initial alkalinity ( $\mu\text{mol/kg}$ )	2369.73	2362.20	2365.52
resultant $E^{\circ}$ (mV)	383.26	383.54	383.41
resultant alkalinity ( $\mu\text{mol/kg}$ )	2356.43	2356.42	2356.44
standard deviation ( $\mu\text{mol/kg}$ )	0.30	0.35	0.44
number of data points	18	18	18
Result for $k_s = 1$			
initial $E^{\circ}$ (mV)	383.75	383.75	383.75
initial alkalinity ( $\mu\text{mol/kg}$ )	2354.52	2346.86	2350.27
resultant $E^{\circ}$ (mV)	383.75	384.03	383.90
resultant alkalinity ( $\mu\text{mol/kg}$ )	2354.46	2354.45	2354.47
standard deviation ( $\mu\text{mol/kg}$ )	0.23	0.27	0.45
number of data points	18	18	18

standard potential,  $E^{\circ}$ , were measured for 9 pH glass electrodes using TRIS and AMP  $\text{pH}_T$  buffers (Fig. 3). For  $\text{pH}_T$  buffer solutions, the ranges of  $k_s$  and  $E^{\circ}$  were 0.989–0.997 and 382.37–395.55 mV, respectively.  $k_s$  and  $E^{\circ}$  for the phthalate and phosphate  $\text{pH}_{\text{NBS}}$  buffer solutions were also measured. The ranges  $k_s$  and  $E^{\circ}$  for  $\text{pH}_{\text{NBS}}$  buffers were 0.990–0.995 and 381.95–405.94 mV, respectively. The  $k_s$  and  $E^{\circ}$  for  $\text{pH}_T$  and  $\text{pH}_{\text{NBS}}$  buffers showed different values and no regularity. Therefore,  $\text{pH}_{\text{NBS}}$  buffers cannot be used for the determination of  $k_s$  for seawater.

For the following experiment, electrode Nos. 1 and 9 with the highest and lowest  $k_s$ , respectively, were used. Open-cell titrations for the CRM using two electrodes, Nos. 1 and 9, are shown in Supplementary Materials (Supplementary Tables S1 and S2, respectively). Titrations using electrode No. 9 without air bubbling were also conducted for comparison (Supplementary Table S3).

#### Alkalinity calculation using $E^{\circ}_{\text{init}}$ from the Gran approach and multiplier $f$

An  $A_T$  calculation using  $E^{\circ}_{\text{init}}$  from the Gran approach and multiplier  $f$  (Dickson *et al.*, 2007) was conducted (Tables 2a and 3a). The resultant averaged alkalinity for electrode No. 1, with a higher  $k_s$  value of 0.997, was in good agreement with the established CRM value. The third trial for electrode No. 9 was conducted using a smaller weight of 72.18 g (Table 3a); no change of the SD value was observed. However, the alkalinity for electrode No. 9, with a lower  $k_s$  value of 0.989, was slightly lower than that for No. 1, consistent with the CRM value, within  $\pm 0.1\%$ .  $A_T$  was successfully calculated using  $k_s$ .

The alkalinity was also calculated without considering the Nernst response of the electrodes with  $k_s$  set to 1.000 in Eq. (12). The resultant averaged alkalinity was approximately 2354  $\mu\text{mol/kg}$  for electrode No. 1 (Table 2a) and approximately 2349  $\mu\text{mol/kg}$  for electrode No. 9

Table 3. Calculation of alkalinity of CRM batch #99 using electrode No. 9

	#9-1	#9-2	#9-3
(a) $E^{\circ}_{\text{init}}$ from the Gran approach, calculation with $f$			
Result for $k_s = 0.989$			
initial $E^{\circ}$ (mV)	379.74	379.58	382.08
initial alkalinity ( $\mu\text{mol/kg}$ )	2338.53	2338.55	2339.55
resultant $E^{\circ}$ (mV)	379.74	379.58	382.08
resultant alkalinity ( $\mu\text{mol/kg}$ )	2355.69	2355.79	2356.52
standard deviation ( $\mu\text{mol/kg}$ )	0.86	0.55	0.75
number of data points	18	18	15
resultant $f$	0.9746	0.9743	0.9765
Result for $k_s = 1$			
initial $E^{\circ}$ (mV)	381.55	381.38	383.87
initial alkalinity ( $\mu\text{mol/kg}$ )	2331.66	2331.74	2332.04
resultant $E^{\circ}$ (mV)	381.55	381.38	383.87
resultant alkalinity ( $\mu\text{mol/kg}$ )	2348.92	2349.06	2349.08
standard deviation ( $\mu\text{mol/kg}$ )	0.61	0.36	0.89
number of data points	18	18	15
resultant $f$	0.9747	0.9745	0.9767
(b) $E^{\circ}_{\text{init}}$ from seawater buffer solutions, SD minimization procedure for $A_T$ calculation			
Result for $k_s = 0.989$			
initial $E^{\circ}$ (mV)	377.27	377.27	377.27
initial alkalinity ( $\mu\text{mol/kg}$ )	2264.56	2269.81	2185.20
resultant $E^{\circ}$ (mV)	380.43	380.27	382.68
resultant alkalinity ( $\mu\text{mol/kg}$ )	2356.51	2356.59	2356.50
standard deviation ( $\mu\text{mol/kg}$ )	0.78	0.71	0.72
number of data points	18	18	16
Result for $k_s = 1$			
initial $E^{\circ}$ (mV)	377.27	377.27	377.27
initial alkalinity ( $\mu\text{mol/kg}$ )	2200.21	2206.06	2113.30
resultant $E^{\circ}$ (mV)	382.22	382.06	384.47
resultant alkalinity ( $\mu\text{mol/kg}$ )	2349.29	2349.41	2348.88
standard deviation ( $\mu\text{mol/kg}$ )	0.57	0.49	0.87
number of data points	1.8	18	16

(Table 3a). The difference from the CRM value of electrode No. 9 was approximately 8  $\mu\text{mol/kg}$ , which was approximately 5  $\mu\text{mol/kg}$  larger than that of electrode No. 1. The calculation of  $A_T$  using an appropriate  $k_s$  value is essential for the determination of  $A_T$ .

The averaged resultant  $E^{\circ}$  value for electrode No. 1 was 383.07 mV, which was close to the  $E^{\circ}_{\text{init}}$  value of 383.75 mV. For electrode No. 9, the averaged resultant  $E^{\circ}$  value was 380.47 mV, which was approximately 3 mV higher than the initial  $E^{\circ}_{\text{init}}$  of 377.27 mV. This discrepancy was due to the non-Nernst response behavior of electrode No. 9 as compared with that of electrode No. 1.

*Alkalinity calculation using  $E^{\circ}_{\text{init}}$  from seawater buffer solutions and a SD minimization procedure for  $A_T$*

According to the SD minimization procedure for the  $A_T$  calculation we proposed, open-cell titrations for the CRM using two electrodes were studied using  $E^{\circ}_{\text{init}}$  from

seawater buffer solutions and without using multiplier  $f$ . The benefit of removing  $f$  is the simplification of the equation for the  $A_T$  calculation.

The resultant alkalinities for electrode Nos. 1 and 9 from our proposed method are shown in Tables 2b and 3b, respectively. These  $A_T$  values for both electrodes were also in good agreement with the CRM value.  $A_T$  was successfully calculated using  $k_s$  and without  $f$ . SDs for electrode No. 9 (Table 3b) were higher than those obtained for electrode No. 1 (Table 2b). The resultant  $E^{\circ}$  value for electrode No. 1 was approximately 383 mV, which was similar to the  $E^{\circ}_{\text{init}}$  value (383.75 mV). In contrast, the resultant  $E^{\circ}$  value for electrode No. 9 was approximately 381 mV, which was approximately 4 mV higher than  $E^{\circ}_{\text{init}}$  (377.27 mV) because of a lower  $k_s$  than No. 1. These trends for SDs were the same as the  $A_T$  calculation using  $f$ .

The alkalinity was also calculated without consider-

Table 4. Calculation of alkalinity of CRM batch #99 using electrode No. 1 without air bubbling

	#1-4	#1-5
(a) $E^\circ_{\text{init}}$ from the Gran approach, calculation with $f$		
Result for $k_s = 0.997$		
initial $E^\circ$ (mV)	380.82	380.79
initial alkalinity ( $\mu\text{mol/kg}$ )	2326.29	2325.19
resultant $E^\circ$ (mV)	380.82	380.79
resultant alkalinity ( $\mu\text{mol/kg}$ )	2344.88	2342.16
standard deviation ( $\mu\text{mol/kg}$ )	0.89	0.81
number of data points	18	17
resultant $f$	0.9713	0.9755
Result for $k_s = 1$		
initial $E^\circ$ (mV)	381.31	381.28
initial alkalinity ( $\mu\text{mol/kg}$ )	2324.33	2323.26
resultant $E^\circ$ (mV)	381.31	381.28
resultant alkalinity ( $\mu\text{mol/kg}$ )	2343.07	2342.26
standard deviation ( $\mu\text{mol/kg}$ )	0.81	0.74
number of data points	18	17
resultant $f$	0.9713	0.9756
(b) $E^\circ_{\text{init}}$ from seawater buffer solutions, SD minimization procedure for $A_T$ calculation		
Result for $k_s = 0.989$		
initial $E^\circ$ (mV)	377.27	377.27
initial alkalinity ( $\mu\text{mol/kg}$ )	2345.69	2219.66
resultant $E^\circ$ (mV)	381.61	381.43
resultant alkalinity ( $\mu\text{mol/kg}$ )	2345.49	2342.32
standard deviation ( $\mu\text{mol/kg}$ )	0.80	0.79
number of data points	18	18
Result for $k_s = 1$		
initial $E^\circ$ (mV)	377.27	377.27
initial alkalinity ( $\mu\text{mol/kg}$ )	2201.22	2202.04
resultant $E^\circ$ (mV)	382.10	381.92
resultant alkalinity ( $\mu\text{mol/kg}$ )	2344.03	2340.37
standard deviation ( $\mu\text{mol/kg}$ )	0.72	0.72
number of data points	18	18

ing the Nernst response of the electrodes with  $k_s$  set to 1.0000 in Eq. (8). The resultant averaged alkalinity was approximately 2354  $\mu\text{mol/kg}$  for electrode No. 1 (Table 2b) and approximately 2349  $\mu\text{mol/kg}$  for electrode No. 9 (Table 3b). The difference from the CRM value of electrode No. 9 was approximately 8  $\mu\text{mol/kg}$ , which was approximately 5  $\mu\text{mol/kg}$  larger than that of electrode No. 1. The calculation of  $A_T$  using an appropriate  $k_s$  value was again essential for the determination of  $A_T$ .

#### Influence of air bubbling during titration

Alkalinity titrations without air bubbling were conducted for the purposes of comparison (Table S3). The resultant alkalinity from the calculation with  $f$  and our proposed method without  $f$  showed approximately the same value: 2345  $\mu\text{mol/kg}$  and 2342  $\mu\text{mol/kg}$  in the first and second trials, respectively (Table 4). These values were more than 10  $\mu\text{mol/kg}$  lower than that the certified

value of the CRM. Consequently, we conclude it is necessary to blow air into the sample solution to allow the escape of  $\text{CO}_2$  from the sample.

#### Effect of dilution by the titrant without sodium chloride

For this experiment, the titrant was prepared without NaCl. Consequently, the ionic strength and activities of dissolved ions, including the protons in seawater, changed during titration. The ionic strength during titration can be expressed using the initial salinity  $Sp_{(\text{atm}0)}$  and the concentration of titrant  $C$  as:

$$\left(\frac{I}{m^\circ}\right)_{(\text{atm}+m_0)} = \frac{m_0}{m_0 + m} \frac{19.924Sp_{(\text{at}m_0)}}{1000 - 1.005Sp_{(\text{at}m_0)}} + \frac{m_0}{m_0 + m} \frac{1}{2}C. \quad (6')$$



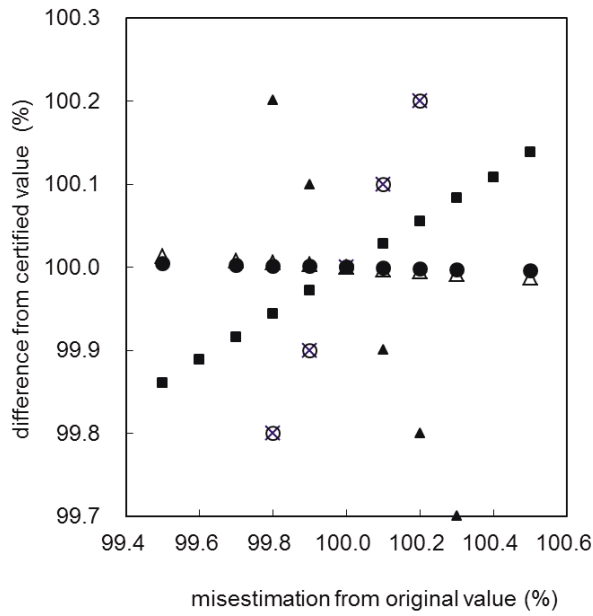


Fig. 4. Effects of the misestimation of parameters on alkalinity measurements by open-cell titration. Open circles, titrant concentration; crosses, dispensed volume of titrant; closed triangles, sample weight; closed squares, pH electrode response compared to the ideal Nernst response; open triangles, temperature of sample in °C; closed circles, titrant temperature in °C.

The value of  $A_T$  calculated using Eq. (6') was approximately 0.01  $\mu\text{mol/kg}$  higher than that determined using Eq. (6), which is equal to approximately 0.005% of the negative error in the  $A_T$  value. The change in pH,  $\Delta\text{pH}$ , by the dilution of the seawater sample with the titrant is defined as:

$$\Delta\text{pH} = -\log\left(\frac{f_H(S_{p_{atm0}})}{f_H(S_{p_{atm+m_0}})}\right) \quad (16)$$

where  $f_H(S)$  is the apparent total hydrogen ion activity coefficient (Whitfield *et al.*, 1985) for seawater at salinity  $S_p$ .

$f_H$  values at salinities of 34.6 and 31.4 at 25°C were approximately 0.709 and 0.705, respectively (Culberson and Pytkowicz, 1973). The change in  $f_H$  with respect to the unit change in salinity was 0.0013. Although different pH electrodes were expected to show a difference in  $f_H$  values, observations revealed that the slope of  $f_H$  for salinity was nearly the same (Whitfield *et al.*, 1985). For the open-cell titration, approximately 100 g of the initial seawater sample was diluted by using approximately 4 g of the titrant. The salinity of the diluted sample at the final step of the titration was approximately 3.8% lower

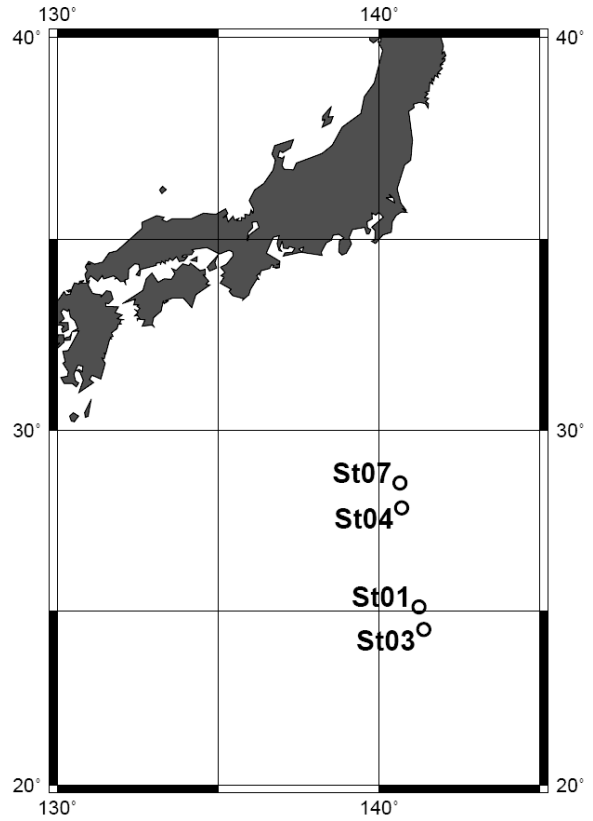


Fig. 5. Sampling point of seawater samples during R/V Hakuho-Maru KH11-05 cruise.

than that of the initial step, i.e., 1.32 lower for CRM #99. For example, if  $f_H$  for CRM #99 were 0.709,  $\Delta\text{pH}$  at the final step of the titration calculated by Eq. (16) would be  $-0.00107$ , which equals an EMF of  $-0.064$  mV. The initial and final sample EMF values in Tables 2 and 3 were approximately  $-85$  and  $205$  mV, respectively, and the difference in the EMF between the initial and final steps was approximately 290 mV. The error of  $-0.064$  mV was equal to  $-0.022\%$  for the 290 mV difference. The error  $-0.022\%$  of EMF was equal to the error of the slope for the Nernst response and  $-0.01\%$  of the alkalinity ( $=-0.2$   $\mu\text{mol/kg}$ ). The error ( $-0.2$   $\mu\text{mol/kg}$ ) was smaller than the SD values for  $A_T$  measurements in Tables 2 and 3 ( $\pm 0.23$  to  $0.89$   $\mu\text{mol/kg}$ ). Therefore, it is negligible for the  $A_T$  measurement in seawater.

#### Effects of error in the measurement of parameters on the computation of alkalinity

The effects of the misestimation of parameters on alkalinity measurements by the open-cell titration and the SD minimization procedure for the  $A_T$  calculation are shown in Fig. 4. Underestimation of the sample weight (closed triangles), temperatures of the sample in °C (open

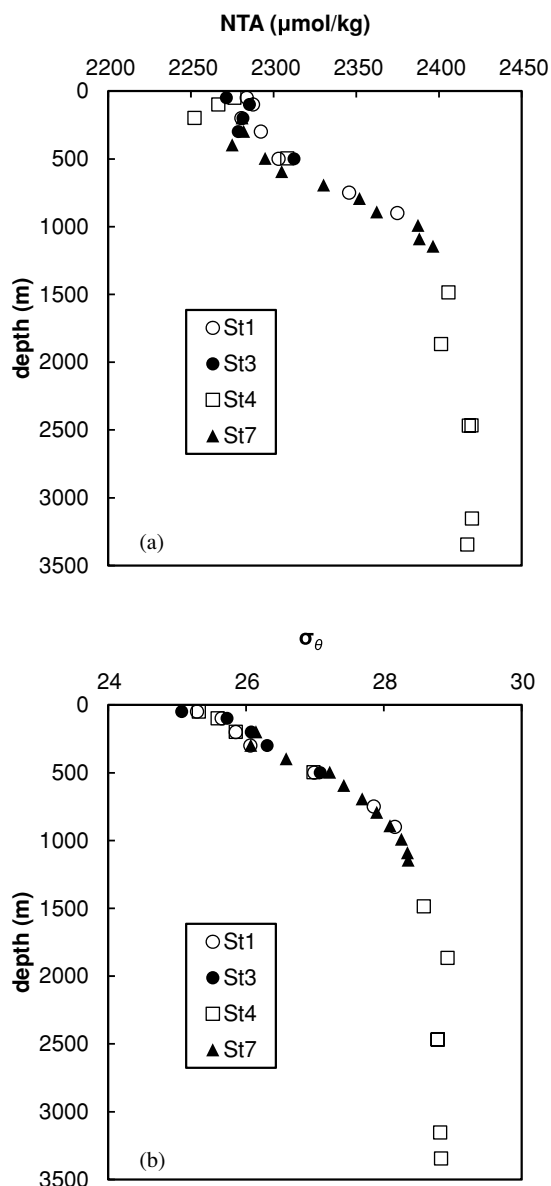


Fig. 6. (a) Vertical profiles of salinity normalized alkalinities (NTA) and (b) potential density ( $\sigma_\theta$ ) from four stations shown in Fig. 5.

triangles) and temperatures of the titrant in  $^\circ\text{C}$  (closed circles) resulted in the positive bias in  $A_T$ . On the other hand, decreasing the concentration of the titrant (open circles), dispensing the volume of the titrant (crosses), and the response of the pH electrode (closed squares) showed a negative error. To achieve the  $A_T$  measurement with smaller error ( $\pm 0.1\%$  error, approximately  $\pm 2 \mu\text{mol/kg}$ ), the tolerance allowed is  $\pm 0.1\%$  of the dispensing volume of the titrant, concentration of the titrant, and weight of the sample, as well as allowed tolerances of

$\pm 0.3\%$  of the pH electrode response,  $\pm 3\%$  of the sample temperature, and  $\pm 10\%$  of the titrant temperature. In the case where 100 g of a seawater sample was titrated using 0.1 mol/L HCl solution at  $25^\circ\text{C}$ , to achieve the  $A_T$  measurement with small error ( $\pm 0.1\%$ ), the tolerances allowed are  $\pm 4 \mu\text{L}$  of the titrant volume dispensed,  $\pm 0.1 \text{ mmol/L}$  of the titrant concentration,  $\pm 0.1 \text{ g}$  of the sample weight,  $\pm 0.75^\circ\text{C}$  of the sample temperature, and  $\pm 2.5^\circ\text{C}$  of the titrant temperature.

#### $A_T$ measurements of seawater samples

Samples were collected from four stations in the northwestern Pacific (Fig. 5). The profiles of salinity normalized  $A_T$ ,  $\text{NTA} = A_T \times 35/S_p$  (Millero *et al.*, 1998), at four stations in the northwestern subtropics of the North Pacific (see Fig. 5) that were calculated from the SD minimization procedure using  $k_s$  are shown in Fig. 6(a). The NTA values at all stations were almost the same, approximately  $2275 \mu\text{mol/kg}$ , at the sea surface, increased at around 500 m in depth, and then reached approximately  $2420 \mu\text{mol/kg}$  at around 2000 m in depth. These profiles are consistent with Geochemical Ocean Section Study (GEOSECS) data (Takahashi *et al.*, 1981). It is known that NTA in the surface layer of the subtropical ocean shows little variability in space and time (Millero *et al.*, 1998). The profiles of potential density ( $\sigma_\theta$ ) of the four stations showed consistency as shown in Fig. 6(b); thus, NTA in the deeper layer also showed little variability. Our proposed method was successfully applied to the seawater sample.

## CONCLUSIONS

Alkalinity measurements of seawater by open-cell titration using a nonlinear least-squares method were successfully performed without the addition of NaCl to the titrant. The density of the titrant was successfully calculated from the equation using the concentration and temperature of the titrant. The precision of the calculated density compared with the measured value was within  $\pm 0.01\%$ . Open-cell titrations for the CRM using the two electrodes with  $k_s$  values of 0.997 and 0.989 were studied. Two nonlinear least-squares methods were studied: one used  $E_{\text{init}}^\circ$  from the Gran method and changed  $f$ , and the other used  $E_{\text{init}}^\circ$  from seawater buffer solutions and directly changed  $E^\circ$ . The resultant averaged alkalinities for the two electrodes directly using the nonlinear least-squares method for  $E_{\text{init}}^\circ$  were in good agreement with the CRM value.  $A_T$  was successfully calculated using  $k_s$ . Further investigations established that the  $k_s$  value should be determined using TRIS–AMP buffers, because  $k_s$  for TRIS–AMP and phthalate–phosphate buffers showed different values.

To achieve the  $A_T$  measurement with smaller error

( $\pm 0.1\%$  error, approximately  $\pm 2 \mu\text{mol/kg}$ ), the tolerances allowed are as follows:  $\pm 0.1\%$  for the dispensing volume of the titrant, titrant concentration, and weight of the sample,  $\pm 0.3\%$  for the pH electrode response,  $\pm 3\%$  for the sample temperature, and  $\pm 10\%$  for the titrant temperature.

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## SUPPLEMENTARY MATERIALS

URL (<http://www.terrapub.co.jp/journals/GJ/archives/data/48/MS296.pdf>)  
Tables S1 to S3