

Absolute salinity measurements of standard seawaters for conductivity and nutrients

Hiroshi UCHIDA^{1*}, Takeshi KAWANO¹⁾, Michio AOYAMA²⁾ and Akihiko MURATA¹⁾

Abstract: We measured the density salinities (ie. absolute salinities) of International Association of the Physical Sciences of the Ocean (IAPSO) Standard Seawater (SSW) batches P144–P152 and Reference Material for Nutrients in Seawater (RMNS) lot BF by using an oscillation-type density meter. Practical Salinity, silicate, nitrate, total alkalinity (TA) and dissolved inorganic carbon (DIC) were also measured. The measured density salinities were compared with the absolute salinities calculated from two models by using measured Practical Salinity, silicate, nitrate, TA and DIC data. The absolute salinities estimated from one model using all of these parameters agreed relatively well with the measured density salinity, especially for the RMNS. However, the absolute salinities of the IAPSO SSW estimated from another model by using Practical Salinity and a simple relationship with silicate were overestimated because of a difference in composition from natural seawater caused by dissolution of silicate from the glass bottles. The rate of increase of the density salinity of the IAPSO SSW caused by dissolution of silicate was estimated to be $0.0005 \text{ g kg}^{-1} \text{ y}^{-1}$. The results suggest that RMNS, in which the composition of real seawater is maintained, has substantial potential as a reference liquid for density measurements.

Keywords: "Density salinity", *International Thermodynamic Equation of Seawater 2010 (TEOS-10)*, *International Association of the Physical Sciences of the Ocean (IAPSO) Standard Seawater, Reference Material for Nutrients in Seawater (RMNS)*

1. Introduction

In June 2009, the International Thermodynamic Equation of Seawater 2010 (TEOS-10) was endorsed by the Intergovernmental Oceanographic Commission (IOC) of the United Nations Educational, Scientific and Cultural Organization (UNESCO) as the replacement for the International Equation of State of Seawater 1980 (EOS-80) (IOC *et al.*, 2010). An-

other substantial change from previous practice is the use of absolute salinity (g kg^{-1}) instead of Practical Salinity (S_P) in TEOS-10 (MILLERO, 2010).

Density of seawater is a function of absolute salinity (S_A) rather than conductivity. To date, however, there is no sensor that can precisely measure absolute salinity in situ (MILLERO, 2006). Therefore, an algorithm to estimate absolute salinity was provided along with TEOS-10 (McDOUGALL *et al.*, 2009). The absolute salinity of International Association of the Physical Sciences of the Ocean (IAPSO) Standard Seawater (SSW) (Ocean Scientific International Ltd., Havant, UK) has been examined and used to define the Reference-Composition Salinity (S_R) scale (MILLERO *et al.*, 2008). Practical Salinity can be converted to Reference-

1) Research Institute for Global Change, Japan Agency for Marine-Earth Science and Technology, Yokosuka, Kanagawa 237-0061, Japan

2) Meteorological Research Institute, Japan Meteorological Agency, Tsukuba, Ibaraki 305-0052, Japan

* Corresponding author:

E-mail: huchida@jamstec.go.jp;

Tel: +81-45-867-9474; Fax: +81-46-867-9455

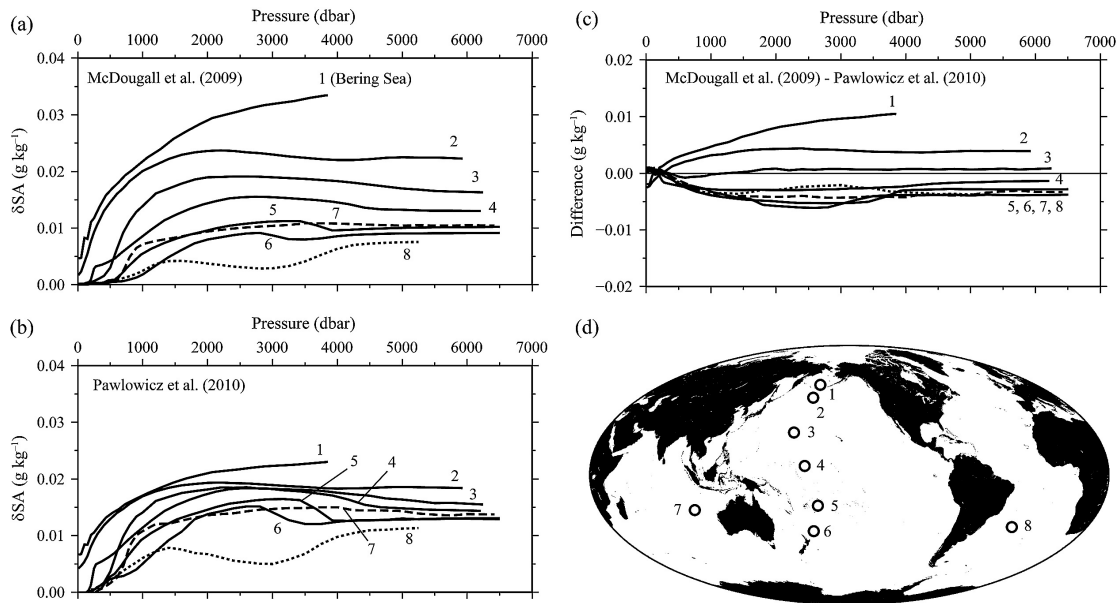


Fig. 1. Vertical profiles of absolute salinity anomalies (δS_A) estimated from the models of (a) McDougall *et al.* (2009) and (b) Pawlowicz *et al.* (2010), and (c) difference of the absolute salinity anomalies between the two models. Locations of the data used for the estimation are shown in (d) with the numbers. High-quality hydrographic data obtained on the R/V Mirai cruises (UCHIDA and FUKASAWA, 2005; KAWANO and UCHIDA, 2007; KAWANO *et al.*, 2009; UCHIDA *et al.*, 2011) were used for the estimation.

Composition Salinity over the range of concentrations where Practical Salinity is defined: $S_R = (35.16504 \text{ g kg}^{-1}/35) \times S_P$.

To estimate the absolute salinity (also called “density salinity”) for a particular seawater sample, the algorithm exploits the correlation between the absolute salinity anomaly (δS_A) relative to the Reference-Composition Salinity and the silicate concentration, making use of the global atlas of silicate concentrations (McDOUGALL *et al.*, 2009, Eqs. [3–6]). However, δS_A estimated from the model from McDougall *et al.* (2009) shows latitude-dependent systematic discrepancy from δS_A estimated from another model from PAWLOWICZ *et al.* (2010) which exploits more precisely the correlation between δS_A and nutrient concentrations and carbonate system parameters based on mathematical investigation using a model relating composition, conductivity, and density of arbitrary seawaters (Fig. 1). A bias in the density data for the North Pacific obtained in the 1970s may partly contribute to the discrepancy by overestimating the latitude-

dependent coefficient in the model from McDougall *et al.* (2009). Therefore, values for absolute salinity as well as Practical Salinity, nutrient concentrations, and carbonate system parameters should be accurately collected for evaluation and future updating of the estimation method, especially in the North Pacific, coastal and marginal seas and oceanic areas in which density salinities have not yet been measured. If certified standard seawater were available as a density reference with an uncertainty on the order of 0.001 kg m^{-3} , seawater density could be measured more accurately relative to this standard seawater with metrological traceability by means of an oscillation-type density meter (PICKER *et al.*, 1974).

In this study, we evaluated standard seawaters used for conductivity and nutrient measurements for their potential as such a reference liquid by measuring their density salinities with an oscillation-type density meter. The density salinities of the standard seawaters were compared with the absolute salinities calculated from the two models

(McDOUGALL *et al.*, 2009; PAWLOWICZ *et al.*, 2010) by using measured Practical Salinity, nutrient concentrations, and carbonate system parameters.

2. Materials and Methods

In this study we used standard seawaters for conductivity (IAPSO SSW batches P144–P152) and for nutrients (Reference Material for Nutrients in Seawater [RMNS] lot BF; Kanso Technos Co., Ltd., Osaka, Japan). Seawater densities were measured with a DMA 5000M oscillation-type density meter with an Xsample 122 sample changer (Anton-Paar GmbH, Graz, Austria). The sample changer was used to load samples automatically from up to ninety-six 12-mL glass vials. Practical Salinity was measured with a salinometer (Autosal 8400B; Guildline Instruments Ltd., Ontario, Canada), which was standardized with IAPSO SSW batch P152. Nutrients were measured with an autoanalyzer (TRAACS 800 system; Bran+Luebbe, Norderstedt, Germany). Total alkalinity (TA) and dissolved inorganic carbon (DIC) were measured with a custom-made spectrophotometer and a total-CO₂ measuring system (Nippon ANS, Inc., Fuchu, Japan), re-

spectively (UCHIDA *et al.*, 2011) (Table 1).

Densities of pure water and standard seawaters were measured at 20.001 °C and atmospheric pressure in the laboratory with a standard deviation of about 0.001 kg m⁻³. Time drift of the density meter was monitored by periodically measuring the density of ultra-pure water (Milli-Q water, Millipore, Billerica, Massachusetts, USA) prepared from Yokosuka (Japan) tap water in July 2010, density standard water (Kyoto Electronics Manufacturing Co., Ltd., Kyoto, Japan), and standard seawaters (Fig. 2).

The true density of the Milli-Q water was estimated from the isotopic composition (MENACHÉ and GIRARD, 1973) and International Association for the Properties of Water and Steam (IAPWS) -95 standard (FEISTEL, 2008). The isotopic composition for hydrogen (δD) and oxygen ($\delta^{18}O$) relative to Vienna Standard Mean Ocean Water (VSMOW) was determined for the Milli-Q water and density standard water by using an isotope-ratio mass spectrometer (IRMS) MAT 252 with an equilibration device (Thermo Fisher Scientific Inc., Waltham, Massachusetts, USA); the true density of the Milli-Q water was estimated to be

Table 1. Concentrations of salinity, nutrient, and carbonate system parameters in standard seawaters. Practical Salinity (S_p) was measured on August 25, 2010, and absolute salinity (S_A) was measured on August 26, 2010 for several bottles of the standard seawaters. Nutrient concentrations were measured on July 14, 2010; average of two measurements for one bottle is listed. Total alkalinity (TA) was measured on September 12, 2010. Dissolved inorganic carbon (DIC) was measured on November 7, 2010 for IAPSO SSW lot P152 and on September 11, 2010 for RMNS.

Lot	Date of	S_p	S_A	NO ₃	SiO ₂	TA	DIC
no.	manufacture	[PSS-78]	[g kg ⁻¹]		[μ mol kg ⁻¹]		
IAPSO SSW							
P152	2010/05/05	34.9926	35.1578	0.04	22.16	2298.9	2055.9
P151	2009/05/20	34.9984	35.1632	0.03	32.39	2303.7	—
P150	2008/05/22	34.9920	35.1572	0.39	38.91	2306.2	—
P149	2007/10/05	34.9945	35.1594	0.04	40.95	2307.4	—
P148	2006/10/01	34.9932	35.1574	0.96	45.16	2307.6	—
P147	2006/06/06	34.9914	35.1581	1.36	69.40	2309.5	—
P146	2005/05/12	34.9898	35.1559	0.47	78.48	2302.6	—
P145	2004/07/15	34.9913	35.1600	0.06	69.77	2317.3	—
P144	2003/09/23	34.9940	35.1626	0.08	90.52	2318.6	—
RMNS							
BF	2007/04/11	34.6138	34.7906	41.39	150.42	2376.3	2218.9

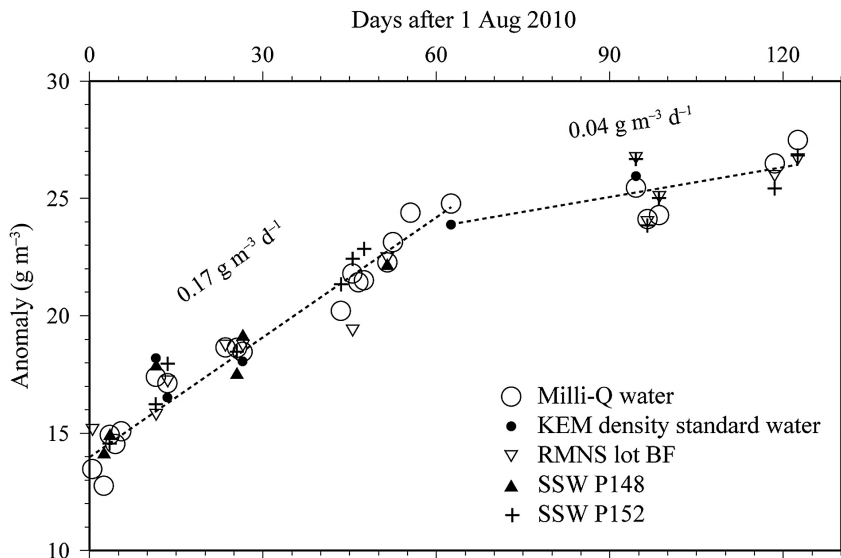


Fig. 2. Time drift of the density meter, as estimated from repeated measurements of pure waters (Milli-Q and density standard water) and standard seawaters (IAPSO SSW and RMNS). Measured values were averaged for each day and density anomalies for Milli-Q water are shown relative to the estimated true value ($998.2038 \text{ kg m}^{-3}$). For the other waters, anomalies from the temporal mean were added to the mean of the anomalies for Milli-Q water measured at the same time. Dashed lines show the regression lines for Milli-Q water before and after day 62.

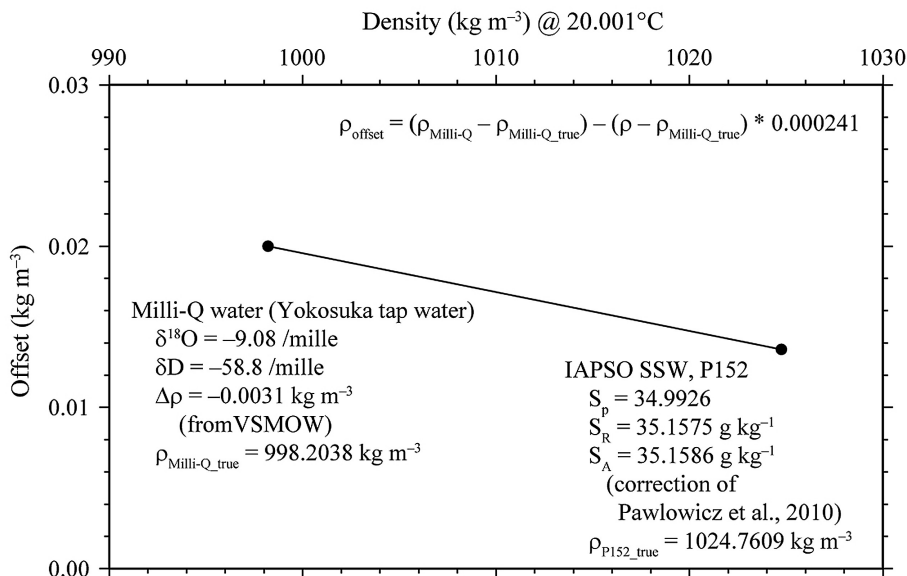


Fig. 3. Mean density offset from the estimated true value for IAPSO SSW batch P152 (first 7 measurements in Fig. 2) and for Milli-Q water measured at the same time. The true density for the Milli-Q water at 20.001°C and atmospheric pressure was estimated from the isotopic composition of water and the IAPWS-95 standard (Vienna Standard Mean Ocean Water [VSMOW]) for the thermodynamic properties of water; for the IAPSO SSW, true density was calculated from absolute salinity calculated by using the model of PAWLOWICZ *et al.* (2010) and TOES-10.

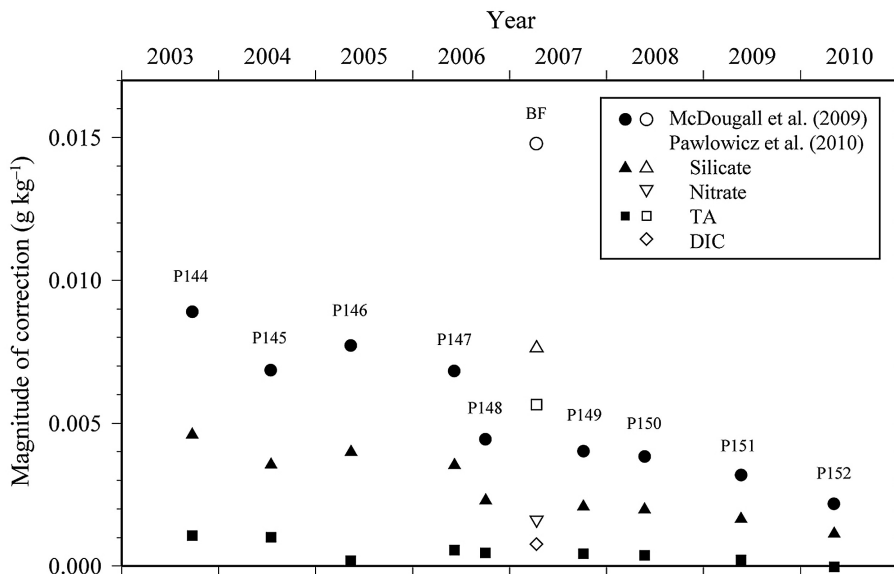


Fig. 4. Magnitude of corrections for the absolute salinity of IAPSO SSW (batches P144–P152) and RMNS (lot BF) from the Reference-Composition Salinity plotted against the date of manufacture. Filled and hollow circles indicate the total corrections for the models of McDougall *et al.* (2009) and Pawlowicz *et al.* (2010), which include corrections for measured silicate, nitrate, TA, and DIC. For the IAPSO SSW, corrections for nitrate and DIC are not shown because they were small (0.00002 ± 0.00002 g kg⁻¹ for nitrate and -0.0001 g kg⁻¹ for DIC in batch P152).

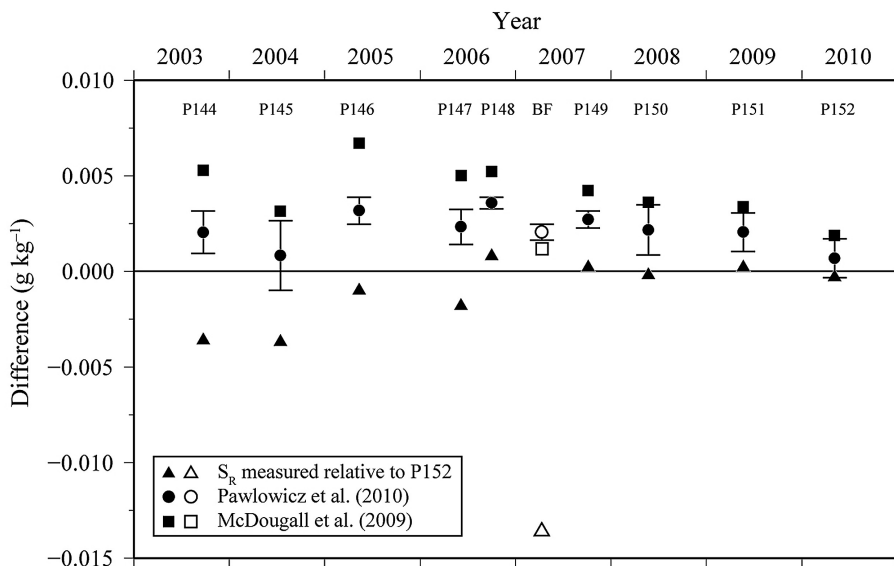


Fig. 5. Differences between the absolute salinities of IAPSO SSW and RMNS, as estimated from the models of McDougall *et al.* (2009) and Pawlowicz *et al.* (2010), and those estimated from the density measurements, plotted against the date of manufacture. Error bars show standard deviation. Also shown is the difference between the Reference-Composition salinity (S_r) and the measured density salinity.

998.2038 kg m⁻³ (Fig. 3). For the density standard water (certified density, 998.204 ± 0.015 kg m⁻³), the true density as estimated from the isotopic composition (998.2050 kg m⁻³) agreed with the measured density (998.2058 kg m⁻³) as corrected with the Milli-Q water measurements.

The true density of IAPSO SSW batch P152 manufactured in May 2010 was estimated from the Reference-Composition Salinity calculated from the labeled Practical Salinity with the slight correction (+0.0011 g kg⁻¹) of PAWLOWICZ *et al.* (2010) for absolute salinity and TEOS-10 (IOC *et al.*, 2010) (Fig. 3); however, there could be some ambiguity (a few mg kg⁻¹ in S_R) in the labeled Practical Salinity (KAWANO *et al.*, 2006).

We used a method similar to the substitution method (WOLF, 2008) to apply an offset correction to the measured density by using the Milli-Q water measurements with a slight modification of the density dependency (Fig. 3), under the assumption that the density meter was stable over about 9 h for a series of measurements of up to 96 samples. We expected the effect of dissolved air on measured densities (about -0.0024 kg m⁻³ at 20 °C; HARVEY *et al.*, 2005) to be cancelled out, as the measured density of pure water was adjusted to the IAPWS-95 standard.

3. Results

By using measured nutrient concentrations and carbonate system parameters, we examined the magnitude of corrections for the absolute salinity anomaly of the IAPSO SSW and RMNS by using two models (Fig. 4). The first model is from McDOUGALL *et al.* (2009) :

$$\delta S_A [\text{g kg}^{-1}] = 9.824 \times 10^{-5} [\text{SiO}_2] \quad (1)$$

and the second is from PAWLOWICZ *et al.* (2010):

$$\delta S_A [\text{g kg}^{-1}] = (5.07 [\text{SiO}_2] + 3.89 [\text{NO}_3] + 5.56 \Delta \text{NTA} + 0.47 \Delta \text{NDIC}) \times 10^{-5}, \quad (2)$$

where [SiO₂] is silicate concentration, [NO₃] is nitrate concentration, ΔNTA is TA anomaly normalized to a salinity of 35 (= TA - [2300 × S_P/35]), and ΔNDIC is DIC anomaly

normalized to a salinity of 35 (= DIC - [2080 × SP/35]) (all in units of μ mol kg⁻¹). Although the algorithm to estimate absolute salinity provided along with TEOS-10 is consisted from latitude-dependent equations for each ocean basin (McDOUGALL *et al.*, 2009, Eqs. 3–6), the simple relationship with silicate obtained by fitting to the data from throughout the world ocean (McDOUGALL *et al.*, 2009, Eq. 2) is used for the standard seawaters, because locations where the source water was taken from are unknown.

For the IAPSO SSW, the magnitude of the corrections for nitrate, TA, and DIC in Eq. (2) was small. However, silicate concentrations were higher in IAPSO SSW with earlier dates of preparation (Table 1), probably as a result of dissolution of silicate from the glass bottles used for SSW. Therefore, the magnitude of the correction for silicate in both Eqs. 1 and 2 was substantially larger for the older batches of the IAPSO SSW, and the rate of increase in silicate concentration was estimated to be 0.0005 g kg⁻¹ y⁻¹, although this rate is about half of the previous estimate (0.0012 g kg⁻¹ y⁻¹) (FEISTEL *et al.*, 2010).

We examined the differences between the absolute salinity of the IAPSO SSW and RMNS estimated from the two models (Eqs. 1 and 2) and the density measurements (Fig. 5). The correction term for DIC in Eq. 2 was excluded for the IAPSO SSW calculation because DIC was not measured, except in batch P152. The absolute salinities estimated from Eq. 2 agreed well with the measured density salinities. However, the absolute salinity of the IAPSO SSW estimated from Eq. (1), which uses a simple relationship with silicate, was overestimated, probably because of a difference in composition from natural seawater caused by dissolution of silicate from the glass bottle. For the RMNS, the difference was relatively small for both models.

4. Discussion

The absolute salinity of the IAPSO SSW estimated from Eq. (1) was overestimated (Fig. 5). The coefficient of Eq. (1) does not represent the effect of SiO₂ alone, and it represents both SiO₂ and the combined effects of TA, DIC, NO₃, and

so on. All of these parameters are relatively correlated in the deep ocean, and so it might be reasonable to empirically correlate the total effect to a single one of them. However, since the chemistry inside the bottle of IAPSO SSW is somewhat different, the coefficient of Eq. (1) can not represent the effect of the aging of the IAPSO SSW.

The discrepancy (0.006 kg m^{-3}) in the density offset between the Milli-Q water and the IAPSO SSW was found (Fig. 3). Uncertainty of the Reference-Composition Salinity Scale for the determination of the absolute salinity of SSW may be as large as 0.05 g kg^{-1} (WRIGHT *et al.*, 2011). Moreover, it is possible that IAPSO SSW now available has a slightly different conductivity/density relationship than the SSW that was used when most of the conductivity/density measurements were made in the 1970s. Therefore, certified standard seawater for density is needed for density measurements. The results we obtained suggest that RMNS has substantial potential as a reference liquid for density measurements, because the RMNS maintains the composition of natural seawater (OTA *et al.*, 2010) and is stable for at least 3 years. The use of a magnetic levitation densimeter (KANO *et al.*, 2007) to measure the absolute density of RMNS could be an effective solution to the problem of finding a reliable density reference.

Acknowledgments

We thank Naoyuki KURITA of the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) for analyzing the isotopic compositions of pure water and RMNS. We also thank the marine technicians of Marine Works Japan, Ltd., who analyzed nutrient concentrations, TA and DIC of the standard seawaters. We are grateful to Rich PAWLOWICZ (University of British Columbia) and Koji SHIMADA (Tokyo University of Marine Science and Technology) for valuable comments, which improved the paper. The RMNS used in this study was provided by Hitoshi MITSUDA (Kanso Technos Co., Ltd.).

References

- FEISTEL, R. (2008) : A Gibbs function for seawater thermodynamics for -6 to 80 °C and salinity up to 120 g kg^{-1} . *Deep-Sea Res. I*, **55**, 1639–1671.
- FEISTEL, R., S. WEINREBEN, H. WOLF, S. SEITZ, P. SPITZER, B. ADEL, G. NAUSCH, B. SCHNEIDER and D. G. WRIGHT (2010) : Density and absolute salinity of the Baltic Sea 2006–2009. *Ocean Sci.*, **6**, 3–24.
- HARVEY, A. H., S. G. KAPLAN and J. H. BURNETT (2005) : Effect of dissolved air on the density and refractive index of water. *Intl. J. Thermophys.*, **26**, 1495–1514.
- IOC, SCOR and IAPSO (2010) : The international thermodynamic equation of seawater – 2010: Calculation and use of thermodynamic properties. Intergovernmental Oceanographic Commission, Manuals and Guides No. 56, United Nations Educational, Scientific and Cultural Organization (English), 196 pp.
- KANO, Y., Y. KAYUKAWA, K. FUJII and H. SATO (2007) : A new method for correcting a force transmission error due to magnetic effects in a magnetic levitation densimeter. *Meas. Sci. Technol.*, **18**, 659–666.
- KAWANO, T., M. AOYAMA, T. JOYCE, H. UCHIDA, Y. TAKATSUKI and M. FUKASAWA (2006) : The latest batch-to-batch difference table of standard seawater and its application to the WOCE onetime sections. *J. Oceanogr.*, **62**, 777–792.
- KAWANO, T. and H. UCHIDA (2007) : WHP P03 Revisit Data Book, JAMSTEC, Yokosuka, Japan, 208 pp.
- KAWANO, T., H. UCHIDA and T. DOI (2009) : WHP P01, P14 Revisit Data Book, JAMSTEC, Yokosuka, Japan, 212 pp.
- MCDUGALL, T. J., D. R. JACKETT and F. J. MILLERO (2009) : An algorithm for estimating Absolute Salinity in the global ocean. *Ocean Sci. Discuss.*, **6**, 215–242.
- MENACHÉ, M. and G. GIRARD (1973) : Concerning the different tables of the thermal expansion of water between 0 and 40 °C. *Metrologia*, **9**, 62–68.
- MILLERO, F. J. (2006) : *Chemical Oceanography*, 3rd ed., CRC Press, Florida, USA, 496 pp.
- MILLERO, F. J. (2010) : History of the equation of state of seawater. *Oceanography*, **23**, 18–33.
- MILLERO, F. J., R. FEISTEL, D. G. WRIGHT and T. J. MCDUGALL (2008) : The composition of standard seawater and the definition of the Reference-Composition Salinity scale. *Deep-Sea Res.*, **1**, 55, 50–72.
- OTA, H., H. MITSUDA, M. KIMURA and T. KITAO (2010) : Reference materials for nutrients in seawater: Their development and present homogeneity and stability. In *Comparability of*

- nutrients in the world's ocean* (M. AOYAMA *et al.*, Eds.), Mother Tank, Tsukuba, Japan, 148 pp.
- PAWLOWICZ, R., D. G. WRIGHT and F. J. MILLERO (2010) : The effects of biogeochemical processes on oceanic conductivity/salinity/density relationships and the characterization of real seawater. *Ocean Sci. Discuss.*, **7**, 773–836.
- PICKER, P., E. TREMBLAY and C. JOLICOEUR (1974) : A high-precision digital readout flow densimeter for liquids. *J. Solution Chem.*, **3**, 377–384.
- UCHIDA, H. and M. FUKASAWA (2005) : WHP P6, A10, I3/I4 Revisit Data Book, Vol. 2, JAMSTEC, Yokosuka, Japan, 129 pp.
- UCHIDA, H., A. MURATA and T. DOI (2011) : WHP P21 Revisit Data Book, JAMSTEC, Yokosuka, Japan, 173 pp.
- WOLF, H. (2008) : Determination of water density: limitations at the uncertainty level of 1×10^{-6} , *Accred. Qual. Assur.*, **13**, 587–591.
- WRIGHT, D. G., R. PAWLOWICZ, T. J. MCDUGALL, R. FEISTEL and G. M. MARION (2011) : Absolute Salinity, “Density Salinity” and the Reference-Composition Salinity Scale: present and future use in the seawater standard TEOS-10, *Ocean Sci.*, **7**, 1–26.

Received: May 17, 2011

Accepted: July 7, 2011