Density Salinity Measurements of the Standard Seawaters for Conductivity and Nutrients

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Abstract – Density salinity of IAPSO Standard Seawater (SSW) batches from P144 to P152 and Reference Materials for Nutrients in Seawater (RMNS) lot BF were measured by using an oscillation-type density meter (DMA 5000M). Practical salinity, nutrients, and total alkalinity for the standard seawaters were also measured. As the date of manufacture was older, more silicate was dissolved in the IAPSO SSW. The density salinity were compared with the absolute salinity calculated from two models by using measured Practical Salinity, silicate, nitrate and total alkalinity. The absolute salinity estimated from one model using Practical Salinity, silicate, nitrate and total alkalinity agreed well with the density salinity. However, the absolute salinity of IAPSO SSW estimated from another model using simple relationship with silicate were overestimated probably due to difference in composition from real seawater, such as dissolution of silicate from glass bottle. The results suggest that RMNS has a significant potential as a reference liquid for density measurements.

I. INTRODUCTION

In June 2009, the International Thermodynamic Equation of Seawater 2010 (TEOS-10) was endorsed by IOC/UNESCO as the substitute for the International Equation of State of Seawater 1980 (EOS-80) [1, 2]. Significant change from previous practice is the use of absolute salinity (g/kg) as opposed to Practical Salinity ($S_p$) [3]. Density of seawater is a function of absolute salinity ($S_a$) rather than a function of the conductivity of seawater [4]. To date, however, there is no sensor to measure absolute salinity precisely in situ [5]. Therefore, an algorithm to estimate absolute salinity was provided along with the TEOS-10 [6]. Absolute salinity of IAPSO Standard Seawater (SSW) (Ocean Scientific International Ltd., UK) was examined and defined as Reference-Composition Salinity ($S_R$) scale [7]. Practical Salinity can be converted to Reference-Composition Salinity over the range of concentrations where Practical Salinity is defined.

To estimate absolute salinity for a particular seawater sample, the algorithm exploits the correlation between the absolute salinity anomaly from the Reference-Composition Salinity and the silicate concentration, and the global atlas of silicate concentration [6]. However, the estimation method is not perfect. Therefore, density salinities ($S_D$) as well as Practical Salinity, nutrients and carbonate system parameters should be gathered accurately for evaluation and future update of the estimation method, especially in coastal and marginal seas and oceanic areas in which density salinity have not yet been measured.

If certified standard seawater can be available as a density reference with an uncertainty on the order of 0.001 kg/m³, seawater density could be measured more accurately relative to this standard seawater with metrological traceability by means of an oscillation-type density meter.

In this study, standard seawaters for conductivity and nutrients were evaluated their potential as a reference liquid by measuring density salinity using an oscillation-type density meter. The density salinity of the standard seawaters were compared with the absolute salinities calculated from two models [6, 8] by using measured Practical Salinity, nutrients and total alkalinity.

II. MATERIALS AND METHODS

Standard seawaters for conductivity, IAPSO SSW batches from P144 to P152, and for nutrients, Reference Materials for Nutrients in Seawater (RMNS, KANSO Technos Co., Ltd.) lot BF, were used. Density were measured with an oscillation-type density meter, DMA 5000M with Xsample 122 sample changer (Anton-Paar GmbH, Austria). The sample changer was used to fill samples automatically from up to 96 glass vials of 12 ml. Practical Salinity were measured with a salinometer, AUTOSAL 8400B (Guildline Instruments Ltd., Canada) which was standardized with IAPSO SSW batch P152. Nutrients were measured with an autoanalyzer, TRAACS 800 system (BRAN+LUEBBE, Germany). Total alkalinity were measured with a total alkalinity titration equipment, ATT-05 (Kimoto Electric Co., Ltd.).
The densities were measured on the density meter at 20.001 °C in the laboratory. The measurements on pure water and standard seawaters were reproducible to about 0.001 kg/m³. Time drift of the density meter was monitored by measuring ultra-pure water (Milli-Q water, Milli-pore, USA) made from Yokosuka tap water on July 2010. Density standard waters (Kyoto Electronics Manufacturing Co., Ltd.) were also measured.

Since the density meter was largely drifted in time (Fig. 1), the measured values were corrected with respect to the Milli-Q water and IAPSO SSW batch P152 manufactured at May 5, 2005 (Fig. 2).

True density of the Milli-Q water was estimated from the isotopic composition [9] and IAPWS-95 standard [3, 10]. Stable isotopic composition for hydrogen and oxygen in the Milli-Q water and the density standard water were measured by an isotope ratio mass spectrometry (IRMS) MAT 252 with equilibrium device (Thermo Fisher Scientific Inc., USA), and true density of the Milli-Q water was estimated to be 998.2038 kg/m³. The isotopic composition (δD and δ¹⁸O) relative to Vienna Standard Mean Ocean Water (V-SMOW) were determined. For the density standard water (leveled density was 998.204 ± 0.03 kg/m³), true density (998.2050 kg/m³) estimated from isotopic composition agreed well with measured density (998.2058 kg/m³) corrected with the Milli-Q water measurements.

True density of IAPSO SSW batch P152 was estimated from the Reference-Composition Salinity (=S_A) [7] calculated from the labeled Practical Salinity and TEOS-10 [1], although the labeled Practical Salinity may have same ambiguity (a few mg/kg in S_A) [11].

Similarly to the substitution method [12], offset correction was applied to the measured density by using the Milli-Q water measurements with slight modification of dependency on magnitude of density (Fig. 2), assuming that the density meter is stable during each day. Effect of dissolved air on density of samples was ignored. Error of the effect is, at the most, about -0.0024 kg/m³ at 20 °C [9, 13].

III. RESULTS AND DISCUSSION

By using measured nutrients and total alkalinity, magnitude of corrections for the absolute salinity of the IAPSO SSW and RMNS from the Reference-Composition Salinity was examined for two models [6, 8] (Fig. 3), although it should be zero by definition for the IAPSO SSW [7].

For the IAPSO SSW, magnitude of correction for nitrate and total alkalinity in the model [8] was quite small, though nitrate concentration is relatively larger for P147 (1.36 μmol/kg) and P148 (0.96 μmol/kg) than that for the other SSW. However, as the date of manufacture was older, more silicate was dissolved in the IAPSO SSW (22.16 μmol/kg for P152 manufactured at May 5, 2010 and 90.52 μmol/kg for P144 manufactured at September 23, 2003), probably due to dissolution of silicate from glass bottle of the SSW. Therefore, magnitude of correction for silicate in the model [8] was significantly large for the old batches of the IAPSO SSW. Meanwhile, magnitude of correction in the model [6] was larger than that in the model [8], even for the recent batch.

For the RMNS lot BF, magnitude correction for silicate, nitrate and total alkalinity in the model [8] was larger than that for the IAPSO SSW, since silicate and nitrate were much more dissolved in the RMNS than northeast Atlantic surface water of the IAPSO SSW as nutrient standards and total alkalinity is smaller than that for the Reference Composition (2300 μmol/kg).

Differences between the Reference-Composition Salinity and the absolute salinity measured by the density meter are shown in Fig. 4. Dependency on the age of the IAPSO SSW estimated from the regression line was 0.0006 g/kg per year. The dependency was about half of the previous study (0.0012 g/kg per year) [15].

Differences between the absolute salinity of the IAPSO SSW and RMNS estimated from the two models [6, 8] and the measured density salinity were examined (Fig. 4).
Fig. 3. Magnitude of corrections for the absolute salinity of the IAPSO SSW (batches from P144 to P152) and RMNS (lot BF) from the Reference-Composition Salinity plotted against the date of manufacture. The model from [6] and from [8] are used with measured silicate, nitrate, and total alkalinity except for dissolved inorganic carbon for the model from [8].

Fig. 4. Difference between the absolute salinity of the IAPSO SSW and RMNS estimated from the model from [6] and [8] and the density salinity measured by the density meter plotted against the date of manufacture. The correction term for dissolved inorganic carbon for the model from [8] was excluded since dissolved inorganic carbon was not measured. Difference between the Reference-Composition Salinity and the density salinity is also shown.

The correction term for dissolved inorganic carbon for the model [8] was excluded since dissolved inorganic carbon was not measured. The absolute salinity estimated from the model [8] using Practical Salinity, silicate, nitrate and total alkalinity agreed well with the measured density salinity. However, the absolute salinity of IAPSO SSW estimated from the model [6] using simple relationship with silicate were overestimated probably due to difference in composition from real seawater, such as dissolution of silicate from glass bottle. For the RMNS which maintain a composition of real seawater, the difference was relatively small for both models. The results suggest that RMNS has a significant potential as a reference liquid for density measurements.

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REFERENCES