Density and derived properties of standard seawater up to high pressure in stable and metastable states

Thermal properties of standard seawater up to high pressure in stable and metastable states

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Abstract

In this work, a consolidated experimental apparatus for measuring the density of liquids, such as high pressure and metastable states, based on the isochoric method, was exploited to measure thermal properties of seawater. Density of standard seawater was measured in a wide range of temperature and pressure, specifically from (261.15 to 313.15) K and up to 110 MPa. All terms contributing to the uncertainty in determining the volume and the mass of the specimen were evaluated, obtaining a relative expanded uncertainty of seawater density around 0.05 % ($k = 2$). Experimental results were fitted by using a 8-parameters function of specific volume as a function of temperature and pressure. Using the obtained expression, density, isobaric thermal expansion, and isothermal compressibility of seawater were calculated from (263.15 to 313.15) K and for pressures between (1 and 105) MPa. A comparison with the predictions obtained by the Thermodynamic Equation of Seawater - 2010 (TEOS-10) shows a general good agreement that worsens when metastable states are considered.

Keywords: seawater, density, pycnometer, metastable states, thermal properties

1. Introduction

Seawater is not only the environment where more than 200 thousands documented species live, but it is also the reservoir of the thermal energy of our planet. The distribution of the energy content is driven by geographical variations of the temperature, the pressure and the density that are at the origin of small and large scale circulations (Wright et al., 2011). Furthermore, the energy exchanges between seawater and the atmosphere significantly contribute to the formation and to the evolution of ordinary and extraordinary climate events. To monitor and provide predictive models for forecast and climate change, accurate measurements of physical and chemical properties of seawater are strongly demanded. Beside the role played to sustain the Earth's ecosystem and climate, seawater is also exploited as cooling fluid in power stations, as heating fluid for the regasification of liquefied natural gas (LNG) and as feed stock to produce fresh water by desalination processes. For all the applications, it is necessary to have accurate predictions for the density of the fluid, at high pressure and at different temperatures, to optimize the production of the industrial plants (Safarov et al., 2009, 2013).

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The density of seawater changes as a function of the depth below sea surface. Specifically, the pressure range in oceanic seawater is from 0.1 MPa at the sea surface to approximately 108.6 MPa at the deepest level. The ocean temperature ranges, on average, approximately from (273.15 to 313.15) K. In addition to density, derived properties are useful to understand real ocean processes. For example, thermal expasivity is needed to figure out great gradients due to hot (close to critical temperature) seawater vents from ocean floor (Safarov et al., 2012).

Seawater freezing point is around 271 K; however, it can be cooled to lower temperatures without crystallization (supercooled seawater). This phenomenon is observed both in Antarctic and Arctic oceans, occurring as a consequence of the melting of ice shelves at depth (ice shelves cavity) and the formation of sea ice at the surface. As shown in Haumann et al. (2020), the deep vertical extent of the supercooled seawater column can be important for both vertical heat transport and for the vertical transport of salt, carbon, oxygen, and nutrients. Furthermore, supercooled seawater is the basis for the creation of the "platelet ice", which forms by nucleation in supercooled layers of seawater near ice shelves, both in Antarctica and Arctic, under particular conditions able to generate and maintain supercooling (Hoppmann et al., 2020). Platelet ice involves both physical processes and biogeochemical cycles, hosting the associated peculiar ecosystem (Katlein et al., 2020).

The thermodynamic modelling of seawater poses many problems since the system is composed by a large number of different dissolved salts in small quantities, but strongly interacting. For this reason, a complete description of the interactions as a function of the composition has been avoided in favor of the adoption of salinity as a new independent variable, defined on the basis of chemical properties. Although the introduction of salinity allowed to solve practical problems, the chosen definition is not unique and still debated, as claimed by Seitz et al. (2011) and Feistel (2018).

Since 2010, the thermodynamic of seawater is described by the Thermodynamic Equation of Seawater - 2010, or TEOS-10 (IOC et al., 2010), in terms of absolute salinity, S_A, defined as the mass fraction of dissolved material per kilogram of seawater. However, the validity of TEOS-10 and the experimental values in the literature do not include the liquid metastable region.

Considering these aspects, in the present work standard seawater density is measured and modeled in a wide range of temperature and pressure. The pseudo-isochoric method (pycnometry) was exploited to carry out density measurements up to 110 MPa, to cover the whole natural range of ocean pressure, and for temperatures down to 261 K, to investigate (even partially) supercooled seawater. These measurements were used to implement a function of density able to operate in the entire range of temperature and pressure here investigated, and to be used to derive the thermal properties, such as isothermal compressibility and isobaric thermal expansivity.

2. Materials and method

To measure the density of seawater, and with the aim of carrying out measurements even in metastable conditions, the isochoric method was exploited. As for the previous work Romeo et al. (2018), the method was chosen because of its versatility and

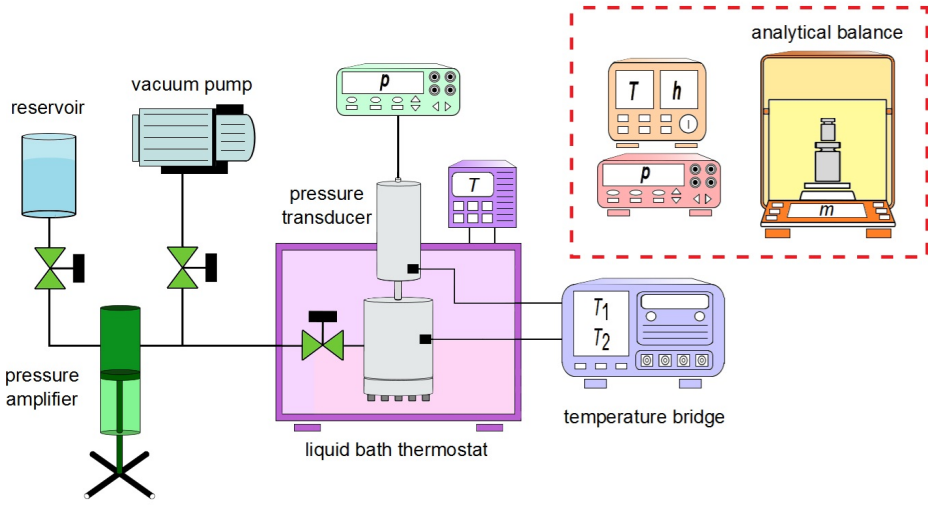

Figure 1: Schematic representation of the experimental apparatus for carrying out density measurements of standard seawater.

capability to operate in hard working conditions without being affected by the physical properties of the fluid (Goodwin et al., 2003).

This technique basically consists in measuring the mass and the volume of the measuring pycnometric cell. The main element of the experimental apparatus, the pycnometer, was designed and realized at Istituto Nazionale di Ricerca Metrologica and used in Romeo et al. (2018), where details on the pycnometer construction features and on the experimental setup can be found. The pycnometer was pressurized several times to test the sealing and the pressure stabilization was obtained up to 120 MPa.

The experimental apparatus schematically represented in Fig. 1 was arranged to control both temperature and pressure. A liquid bath thermostat (with a stabilization of ± 0.01 K), where the pycnometer is placed, is used to control the temperature, which is measured by two platinum resistance thermometers (PT100). The latter are sited one on the pycnometer main body and the other one on the pressure transducer. The thermometers are connected in 4-wire configuration to an industrial thermometer bridge. While the pycnometer is connected to a capacitance high pressure transducer with a full-scale range of 200 MPa for the pressure measurements. A high-pressure circuit consisting of a pressure amplifier and a system of valves are arranged to connect to the tank at ambient conditions, fill the pycnometer, and increase the pressure inside. To complete the measurement, an analytical balance with a resolution of 0.1 mg, stainless steel standard weights to measure the mass, and sensors to monitor ambient temperature, pressure and relative humidity to calculate air density, is used.

To start the measuring procedure, the pycnometer is filled to a certain pressure using the pressure amplifier and the high pressure circuit. Then, it is placed into the thermostatic liquid bath. The temperature is slowly decreased, so that the sample reaches the metastable liquid condition avoiding crystallization. To this scope, it is required from

1 hour up to 3 hours (at the lower temperatures) to change the temperature by 1 K below the triple point. The temperature and the pressure are recorded at the equilibrium: when temperature and pressure stabilization is within 0.01 K and 0.2 MPa, respectively (usually around one hour is required). At the end of the cycle, the pycnometer is taken off the thermostat and carefully cleaned and dried from the thermostatic liquid (ethanol) before the weighing for the mass determination.

Once the measurements were complete, the density of seawater sample was measured by a commercial vibrating tube densimeter at atmospheric pressure, with an uncertainty of 30 ppm as estimated by Romeo et al. (2019), to verify the composition had not changed.

2.1. Determination of the mass

The mass of seawater was determined by means of the gravimetric method. Weighing was performed using a commercial analytical balance employed as a comparator with stainless steel standard masses (Davidson et al., 2004), by the double substitution method (OIML R111-1, 2004). Therefore, the mass M was obtained by the value of the certified standard weights, M_{eq}, and the difference of the readings, ΔR:

$$M = M_{\mathrm{eq}} + \Delta R \,. \tag{1}$$

Seawater mass, m, was obtained by the difference between the mass of the pycnometer filled with the seawater sample, M_{ssw}, and the mass of the empty pycnometer, M_0, corrected for the buoyancy, by the following relation

$$m = M_{\mathrm{ssw}} \left(1 - \frac{\rho_{\mathrm{air}}}{\rho_{\mathrm{std}}}\right) - M_0 \left(1 - \frac{\rho_{\mathrm{air}}}{\rho_{\mathrm{std}}}\right) \,, \tag{2}$$

where ρ_{air} is the density of air during the weighing, and $\rho_{\mathrm{std}} = 8\ \mathrm{g \cdot cm^{-3}}$ is the standard weights density.

2.2. Determination of the volume

The gravimetric method was also adopted to measure the volume of the pycnometer (Lorefice et al., 2014). Thus, the pycnometer was weighted both empty and filled with ordinary bi-distilled water (used as reference fluid) at the temperature T_0 and pressure p_0, corresponding to a thermodynamic state of water density known with low uncertainty (0.003 % for the thermodynamic state here investigated). Water density is provided by the equation of state of the International Association for Properties of Water and Steam, i.e., IAPWS-95 formulation by Wagner and Pruss (2002).

The pycnometer mass (empty and filled with water) was measured by comparison with standard weights by the double substitution method, using the analytical balance as comparator. During the weighing, atmospheric parameters were monitored to correct for the buoyancy in air. So that, the reference volume was determined as

$$V_0\left(T_0, p_0\right) = \frac{M_{\mathrm{ref}} - M_0}{\rho_{\mathrm{ref}}\left(T_0, p_0\right) - \rho_{\mathrm{air}}} \left(1 - \frac{\rho_{\mathrm{air}}}{\rho_{\mathrm{std}}}\right) \,, \tag{3}$$

where M_{ref} is the mass of the pycnometer filled with ordinary water, M_0 is the mass of the empty pycnometer, ρ_{ref} is the reference water density, ρ_{air} is the air density, and $\rho_{\mathrm{std}} = 8\ \mathrm{g\cdot cm^{-3}}$ is the standard weights density. The reference volume of the pycnometer at $T_0 = (293.21 \pm 0.01)$ K and $p_0 = (50.8 \pm 0.2)$ MPa is $V_0 = (11.655 \pm 0.002)\ \mathrm{cm^3}$.

To account for the variation of the volume as a function of temperature, T, and pressure, p, the value of V_0 was corrected by the thermal expansion coefficient and the compressibility coefficient, as follows

$$V\,(T,p) = V_0(T_0,p_0)[1 + \alpha\left(T - T_0\right) + \beta\left(p - p_0\right)]\,, \tag{4}$$

where α and β are the thermal expansion and the isothermal compressibility of the pycnometer, respectively.

The values of α and β were determined experimentally, by performing measuring cycles with a reference fluid, i.e., ordinary water. Measurements were carried out using bi-distilled water, between (275 and 313) K and from (50 to 100) MPa. Considering the change of volume of Eq. 4, a function derived from the definition of density was used (see Romeo et al. (2018) for details). By fitting this linear function of both temperature and pressure, considering the literature density values of the IAPWS-95 formulation for each measurement, the α and β were obtained:

$$\alpha = (2.2 \pm 0.2)\cdot 10^{-5}\ \mathrm{K^{-1}}$$
$$\beta = (7.5 \pm 0.2)\cdot 10^{-5}\ \mathrm{MPa^{-1}}\ .$$

For the studied temperature and pressure range, variations of the elastic properties with temperature and pressure were within the declared uncertainty. For this reason, they are considered constant over the whole examined $T - p$ range.

3. Uncertainty analysis

3.1. Contribution of mass measurement

For the uncertainty analysis, according to Eq. 2, the mass of seawater is a function of all the quantities involved in the weighing procedure:

$$m = m(\Delta R, d, M_{\mathrm{eq}}, \rho_{\mathrm{air}}, \rho_{\mathrm{std}})\ .$$

Therefore, the relative uncertainty in the estimation of seawater mass, $u(m)/m$, was calculated with the uncertainty propagation formula by

$$\frac{u(m)}{m} = \frac{1}{m}\left[\sigma^2(\Delta R) + \left(\frac{d}{\sqrt{6}}\right)^2 + u^2(M_{\mathrm{eq}}) + \left(\frac{\partial m}{\partial \rho_{\mathrm{air}}}\right)^2 u^2(\rho_{\mathrm{air}}) + \left(\frac{\partial m}{\partial \rho_{\mathrm{std}}}\right)^2 u^2(\rho_{\mathrm{std}})\right]^{\frac{1}{2}}\ , \tag{5}$$

where $\sigma(\Delta R)$ is the standard deviation of the the difference of readings, d is the digital resolution of the analytical balance as a triangular distribution (BIPM et al., 2008),

$u(M_{eq})$ is the uncertainty of the standard weights, provided by the calibration certificate. The uncertainties of the standard weights density, $u(\rho_{std})$, and air density, $u(\rho_{air})$, were negligible in the overall uncertainty. The sources of uncertainty affecting the mass measurement and associated relative magnitudes are listed in Table 1. The relative uncertainty of seawater mass is estimated to be 0.015%.

3.2. Contribution of the reference volume

According to Eq. 3, the uncertainty of the pycnometer reference volume, V_0, was obtained taking into account the contributions of the mass of the reference fluid ($\Delta M = M_{ref} - M_0$), the densities of the reference fluid, air of laboratory and standard weights, and the filling temperature and pressure:

$$V_0 = V_0(\Delta M, \rho_{ref}, \rho_{air}, \rho_{std}, T_0, p_0) \, . \tag{6}$$

Applying the uncertainty propagation to Eq. 3, the relative uncertainty, $u(V_0)/V_0$, is assessed by

$$\frac{u(V_0)}{V_0} = \frac{1}{V_0}\left[\left(\frac{\partial V_0}{\partial \Delta M}\right)^2 u^2(\Delta M) + \left(\frac{\partial V_0}{\partial \rho_{ref}}\right)^2 u^2\left(\rho_{ref}\right) + \left(\frac{\partial V_0}{\partial \rho_{air}}\right)^2 u^2\left(\rho_{air}\right) + \left(\frac{\partial V_0}{\partial \rho_{std}}\right)^2 u^2\left(\rho_{std}\right) + \left(\frac{\partial V_0}{\partial T_0}\right)^2 u^2(T_0) + \left(\frac{\partial V_0}{\partial p_0}\right)^2 u^2(p_0)\right]^{\frac{1}{2}} . \tag{7}$$

The uncertainty of the reference fluid mass, $u(\Delta M) = 0.002$ g, is given by the sum of the squares of the standard deviation of the readings difference, the balance resolution, and the standard weights uncertainty. As for the mass, the contributions of the uncertainties of the standard weights density, $u(\rho_{std})$, and the air density, $u(\rho_{air})$, resulted negligible in the overall uncertainty. As stated in Wagner and Pruss (2002), the uncertainty of IAPWS-95 for water density at 293.21 K and 50.8 MPa is $u(\rho_{ref}) = 0.003$ %. The uncertainty $u(T_0)$ of the temperature measurement is due to the calibration fit, the resolution of the instrument and the reading repeatability, and its value is within 0.01 K. The uncertainty of the pressure measurements $u(p_0)$ is due to the pressure transducer used and the measurement repeatability and it is 0.2 MPa.

The uncertainty of the pycnometer reference volume V_0 is lower than 0.01%; all the contributions considered and the associated relative magnitude are summarized in Table 1.

3.3. Volume uncertainty analysis

According to Eq. 4, the uncertainty of the pycnometer volume was determined considering the volume V as a function of the reference volume V_0, the thermal expansion coefficient α, the isothermal compressibility coefficient β, the temperature T and the pressure p:

$$V = V(V_0, \alpha, \beta, T, p) \, .$$

The volume relative uncertainty, $u(V)/V$, was estimated by using the standard formulation for the uncertainty propagation, as follows

$$\frac{u(V)}{V} = \frac{1}{V}\left[\left(\frac{\partial V}{\partial V_0}\right)^2 u^2(V_0) + \left(\frac{\partial V}{\partial \alpha}\right)^2 u^2(\alpha) + \left(\frac{\partial V}{\partial \beta}\right)^2 u^2(\beta) + \left(\frac{\partial V}{\partial T}\right)^2 u^2(T) + \left(\frac{\partial V}{\partial p}\right)^2 u^2(p)\right]^{\frac{1}{2}}, \quad (8)$$

where $u(V_0)$ is 0.002 cm^3. The uncertainties of the α and β coefficients, $u(\alpha)$ and $u(\beta)$, are due to the fitting process for their estimations; other sources of uncertainty are negligible.

The uncertainty on temperature, $u(T) = 0.01$ K, was calculated by the uncertainty of the calibration fit, the instrument resolution, the reading repeatability and the temperature gradient measured between the two thermometers. The uncertainty of the pressure transducer $u(p)$ is 0.01 MPa; this value includes the declared uncertainty of the instrument at the full-scale and the repeatability.

In Table 1, all contributions to the relative uncertainty of the volume along with their relative values are reported.

3.4. Density uncertainty analysis

From the perspective of the uncertainty calculation, because seawater was measured by the pseudo-isochoric method, density is a function of mass, volume, and absolute salinity

$$\rho = \rho(m, V, S_\mathrm{A})\,.$$

Applying the uncertainty propagation formula, the relative uncertainty of seawater density is expressed by

$$\frac{u(\rho)}{\rho} = \frac{1}{\rho}\left[\left(\frac{\partial \rho}{\partial m}\right)^2 u^2(m) + \left(\frac{\partial \rho}{\partial V}\right)^2 u^2(V) + \left(\frac{\partial \rho}{\partial S_\mathrm{A}}\right)^2 u^2\left(S_\mathrm{A}\right)\right]^{\frac{1}{2}}, \quad (9)$$

where $u(m)$ is the mass uncertainty and is 0.002 g, while $u(V)$ is the uncertainty of the volume at the measured temperature and pressure, whose value is 0.003 cm^3. Since the absolute salinity of the sample was not measured by the authors, its uncertainty, $u(S_\mathrm{A})$, was assumed starting from the value estimated by Le Menn (2011), combined with the value reported in McDougall et al. (2012). Table 1 summarizes all sources of uncertainty that play a role in the uncertainty budget of seawater density, and their relative magnitude.

The largest contribution to the uncertainty is due to the volume, as expected considering the many quantities involved in its measurement. The expanded relative uncertainty of seawater density is 0.05 % with a coverage factor $k = 2$, considering the worst case scenario.

Table 1: Uncertainty budget of standard seawater density (S_A = 35.158 g·kg^{-1})

Uncertainty source	Relative magnitude %
Mass	**0.015**
Reading standard deviation	0.015
Balance resolution	0.001
Standard weights mass	negligible
Air density	negligible
Standard weights density	negligible
Volume	**0.021**
Reference volume	0.014
Mass of the reference fluid	0.013
Reference water density	0.003
Air density	negligible
Standard weights density	negligible
Temperature	0.001
Pressure	0.002
Thermal expansion coefficient	0.008
Compressibility coefficient	0.015
Temperature	0.001
Pressure	0.001
Salinity	**<0.001**
COMBINED UNCERTAINTY ($k = 2$)	**0.05**

4. Results

The density measurements were carried out for a sample of standard seawater delivered by OSIL (Batch P160), with certified practical salinity $S_P = 34.993$, i.e., absolute salinity $S_A = 35.158$ g·kg^{-1}. Measurements were carried out at temperatures from about (261.15 to 313.15) K and in the pressure range between (21 to 110) MPa, for five samples of standard seawater of the same batch. All experimental densities along the constant-mass curves are listed in Table 2, where the values reported in italics identify metastable states.

Fig. 2 shows the pressure measurements as a function of temperature for each measuring cycle performed at constant mass. The measured thermodynamic states include also supercooled seawater region: the metastable equilibrium states. The plot of the densities as a function of temperature, along curves at constant mass, is reported in Fig. 3.

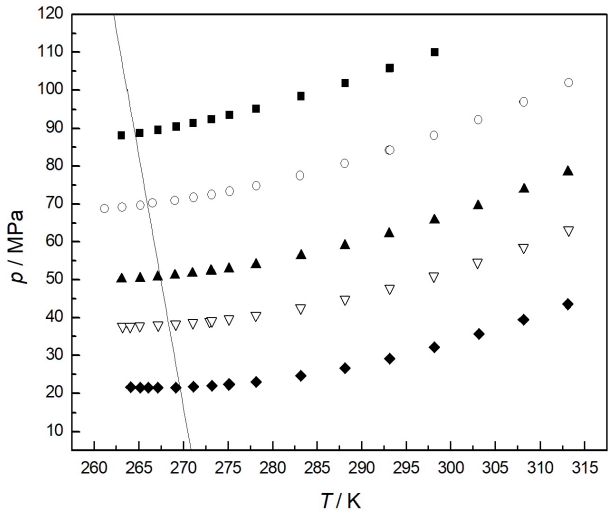

Figure 2: Pressure as a function of temperature at constant mass: ■, $m = 12.482$ g; ∘, $m = 12.371$ g; ▲, $m = 12.253$ g; ▽, $m = 12.174$ g; ◆, $m = 12.069$ g; —, melting curve.

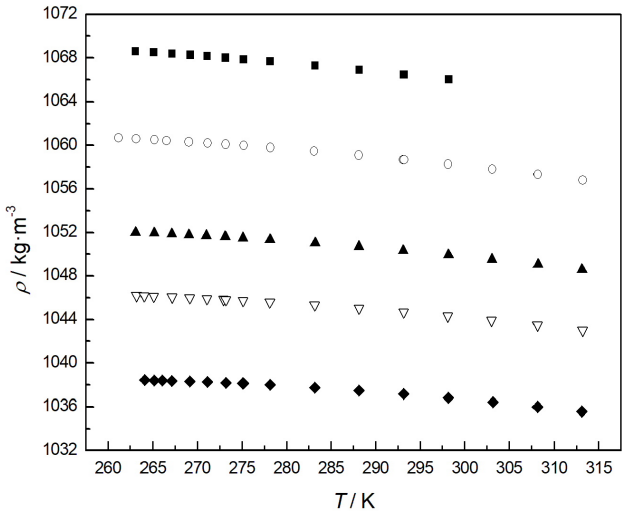

Figure 3: Density of standard seawater ($S_A = 35.158$ g·kg^{-1}) as a function of temperature at constant mass: ■, $m = 12.482$ g; ∘, $m = 12.371$ g; ▲, $m = 12.253$ g; ▽, $m = 12.174$ g; ◆, $m = 12.069$ g.

Table 2: Density ρ of standard seawater ($S_A = 35.158$ g·kg^{-1}) at temperature T and pressure p, for different masses m. The uncertainty associated with all values of density is 0.05 %. Entries in italics are the measurements carried out in metastable equilibrium.

T/ K	p / MPa	ρ / kg·m^{-3}	T/ K	p / MPa	ρ / kg·m^{-3}
		$m = 12.482$ g			
263.10	*88.10*	*1068.60*	275.18	93.55	1067.87
265.10	88.72	1068.50	278.18	95.16	1067.67
267.14	89.55	1068.39	283.20	98.43	1067.29
269.20	90.44	1068.26	288.17	101.82	1066.90
271.10	91.33	1068.15	293.13	105.71	1066.47
273.12	92.37	1068.02	293.21	105.84	1066.46
273.15	92.39	1068.01	298.23	109.96	1066.01
		$m = 12.371$ g			
261.20	*68.76*	*1060.68*	283.10	77.51	1059.46
263.17	*69.17*	*1060.60*	288.10	80.67	1059.09
265.16	*69.67*	*1060.52*	293.09	84.20	1058.70
266.55	70.26	1060.44	293.21	84.23	1058.69
269.05	70.94	1060.32	298.13	88.07	1058.27
271.15	71.73	1060.21	303.10	92.28	1057.82
273.17	72.47	1060.10	308.17	96.95	1057.33
275.20	73.36	1059.98	313.22	101.96	1056.81
278.18	74.79	1059.80			
		$m = 12.253$ g			
263.10	*50.17*	*1052.00*	278.15	54.00	1051.34
265.15	*50.37*	*1051.93*	283.21	56.37	1051.03
267.13	*50.71*	*1051.86*	288.16	59.02	1050.70
269.05	51.19	1051.77	293.10	62.14	1050.34
271.00	51.68	1051.69	298.20	65.73	1049.93
273.12	52.32	1051.59	303.09	69.52	1049.52
273.17	52.24	1051.59	308.21	73.90	1049.05
275.13	52.87	1051.50	313.14	78.48	1048.58
		$m = 12.174$ g			
263.22	*37.61*	*1046.18*	278.13	40.59	1045.59
264.02	*37.60*	*1046.16*	283.16	42.50	1045.32
265.12	*37.78*	*1046.12*	288.15	44.86	1045.02
267.15	*37.98*	*1046.06*	293.17	47.76	1044.67
269.14	38.25	1045.99	298.12	50.96	1044.30
271.07	38.62	1045.91	303.05	54.53	1043.91
272.95	38.94	1045.84	308.16	58.51	1043.48
273.20	39.11	1045.82	313.20	63.10	1043.00
275.14	39.61	1045.74			
		$m = 12.069$ g			
264.10	*21.57*	*1038.44*	278.15	23.05	1037.99
265.16	*21.54*	*1038.42*	283.18	24.64	1037.75

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266.05	*21.54*	*1038.39*	288.15	26.67	1037.48
267.14	*21.53*	*1038.37*	293.15	29.17	1037.16
269.15	*21.54*	*1038.32*	298.16	32.13	1036.82
271.13	21.71	1038.26	303.17	35.70	1036.42
273.21	21.98	1038.19	308.14	39.46	1036.01
275.05	22.34	1038.12	313.11	43.54	1035.58
275.16	22.34	1038.12			

The experimental densities of this work were compared to the density values provided by TEOS-10 formulation. Figs. 4 and 5 show the deviations of the measurements from TEOS-10 equation as a function of temperature and pressure, respectively. All the deviations are within ± 0.02 %, so considering the experimental uncertainty all measurements are in good agreement with TEOS-10. From Fig. 4, it is possible to note that most of the largest deviations correspond to the lowest temperature, and in particular to mestastable states. Also observing Fig. 5, it is clear that the largest deviations correspond to the lowest pressures, thus measurements carried out in the metastable region.

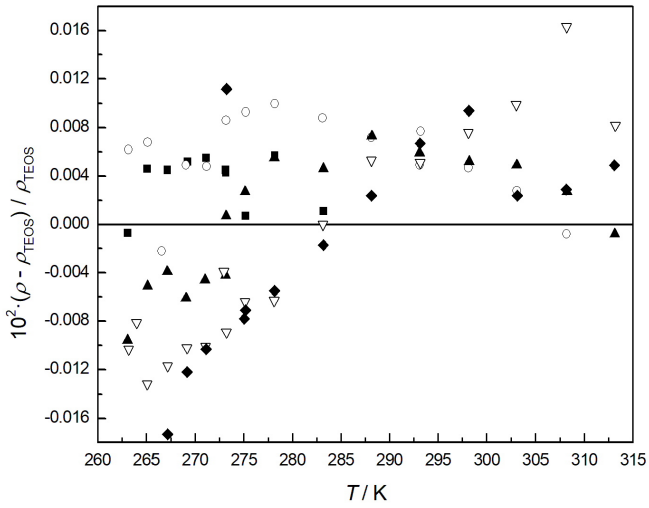

Figure 4: Deviations of experimental seawater density from the values of TEOS-10 (zero line) as a function of temperature: ■, m = 12.482 g; ∘, m = 12.371 g; ▲, m = 12.253 g; ▽, m = 12.174 g; ◆, m = 12.069 g.

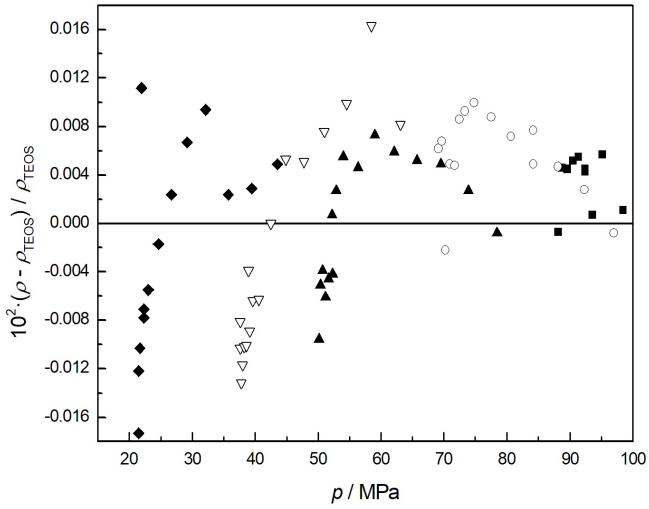

Figure 5: Deviations of experimental seawater density from the values of TEOS-10 (zero line) as a function of pressure: ■, m = 12.482 g; ∘, m = 12.371 g; ▲, m = 12.253 g; ▽, m = 12.174 g; ◆, m = 12.069 g.

Table 3: Coefficients for the interpolation function of density (Eq. 10) determined from the experimental densities, temperatures and pressures by means of the least squares method.

parameter	value	unit
a	0.182915	$m^3 \cdot kg^{-1} \cdot MPa$
b	$6.97805 \cdot 10^{-4}$	$m^3 \cdot kg^{-1}$
c	659.033	MPa
t_a	$-4.66555 \cdot 10^{-5}$	K^{-2}
t_b	8.82548	K^{-1}
t_c	$1.40672 \cdot 10^{-3}$	K^{-1}
t_d	$-6.07869 \cdot 10^{-5}$	K^{-2}
t_e	$-5.93252 \cdot 10^{-8}$	K^{-3}

5. Derived thermal properties

The measurements presented in this work, together with the experimental results of Romeo et al. (2019), carried out by means of a commercial vibrating tube densimeter at atmospheric pressure, were regressed to identify a model to calculate density. The model was chosen to be slender and handy, trying to balance the need for a very limited number of parameters and good accuracy. The model used is the following 8-parameters equation:

$$v(T,p) = \frac{a[1 + t_a(T - T_0)^2]}{p + c[1 + t_c(T - T_0) + t_d(T - T_0)^2 + t_e(T - T_0)^3]} + b[1 + t_b(T - T_0)], \quad (10)$$

where $v(T, p)$ is the specific volume and $a, b, c, t_a, t_b, t_c, t_d, t_e$ are parameters, whose values are shown in Tab. 3. Validity of Eq 10 was checked analyzing the residuals of the fit. In Figs. 6 and 7, relative difference between fit-predicted and experimental densities as a function of temperature and pressure, respectively, are shown. Residuals spread within $\pm 0.012\%$ and most of them within $\pm 0.007\%$, so widely less than the experimental uncertainty.

Equation 10 was used to calculate seawater density, isothermal compressibility and isobaric thermal expansion, in the temperature range between (263.15 to 313.15) K, with step of 10 K, and in the pressure range between (1 to 105) MPa. The set of density, isothermal compressibility and thermal expansitivity data is reported in Tab. 4. Fig. 8 shows the densities obtained by Eq. 10 as a function of pressure along isotherms. Comparison between the calculated densities and TEOS-10 values is reported in Fig. 9. The deviations scatter within ± 0.015 %. Based on these results, Eq. 10 can be used to calculate density within the fitted $T - p$ range with the same uncertainty value stated for the experimental density, i.e., 0.05 %.

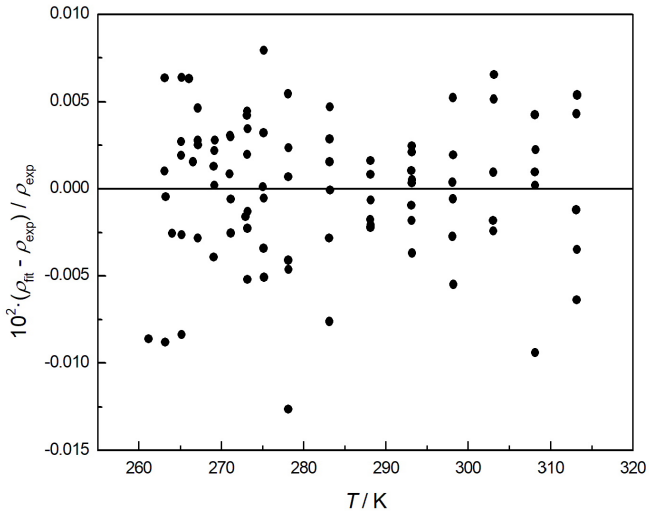

Figure 6: Percentage residuals of the fit (predicted density versus experimental density) as a function of temperature.

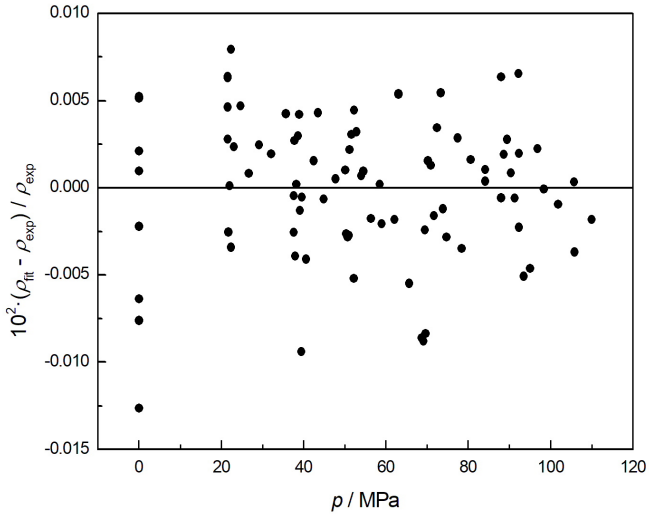

Figure 7: Percentage residuals of the fit (predicted density versus experimental density) as a function of pressure.

Table 4: Density ρ of standard seawater ($S_A = 35.158$ g·kg^{-1}) at temperature T and pressure p, calculated by using Eq.10 along with the isothermal compressibility κ and the isobaric thermal expansion α. Entries in italics refer to metastable states of liquid seawater.

p / MPa	ρ / kg·m^{-3}	κ/ GPa^{-1}	$10^4 \cdot \alpha$ / K^{-1}
	T = 263.15 K		
1.00	*1028.23*	*0.4969*	*-0.818*
15.00	*1035.27*	*0.4779*	*-0.321*
30.00	*1042.57*	*0.4587*	*0.178*
45.00	*1049.62*	*0.4407*	*0.645*
60.00	*1056.45*	*0.4237*	*1.083*
75.00	*1063.06*	*0.4077*	*1.493*
90.00	*1069.46*	*0.3926*	*1.879*
105.00	*1075.66*	*0.3926*	*2.241*
	T = 273.15 K		
1.00	1028.37	0.4655	0.500
15.00	1034.97	0.4484	0.861
30.00	1041.82	0.4310	1.226
45.00	1048.45	0.4147	1.568
60.00	1054.87	0.3993	1.891
75.00	1061.09	0.3848	2.195
90.00	1067.12	0.3710	2.481
105.00	1072.66	0.3580	2.752
	T = 283.15 K		
1.00	1027.29	0.4431	1.581
15.00	1033.56	0.4272	1.834
30.00	1040.08	0.4111	2.090
45.00	1046.39	0.3959	2.332
60.00	1052.51	0.3816	2.560
75.00	1058.44	0.3680	2.777
90.00	1064.20	0.3551	2.982
105.00	1069.78	0.3429	3.177
	T = 293.15 K		
1.00	1025.17	0.4280	2.517
15.00	1031.23	0.4129	2.677
30.00	1037.51	0.3976	2.840
45.00	1043.60	0.3831	2.995
60.00	1049.51	0.3694	3.143
75.00	1055.24	0.3564	3.284
90.00	1060.79	0.3441	3.419
105.00	1066.19	0.3324	3.548
	T = 303.15 K		
1.00	1022.15	0.4195	3.376
15.00	1028.07	0.4047	3.451

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30.00	1034.21	0.3897	3.528
45.00	1040.16	0.3756	3.604
60.00	1045.93	0.3622	3.677
75.00	1051.53	0.3495	3.749
90.00	1056.96	0.3374	3.818
105.00	1062.23	0.3260	3.886
	$T = 313.15$ K		
1.00	1018.28	0.4172	4.219
15.00	1024.14	0.4023	4.209
30.00	1030.22	0.3873	4.202
45.00	1036.11	0.3731	4.198
60.00	1041.82	0.3597	4.198
75.00	1047.36	0.3470	4.200
90.00	1052.73	0.3350	4.205
105.00	1057.94	0.3235	4.212

In Fig. 10 the derived isothermal compressibility as a function of pressure, along isotherms is shown. Compressibility results are compared to TEOS-10 values and shown in Fig. 11. Difference of isothermal compressibility are lower than 0.005 GPa^{-1} and, as expected, are higher for the isotherm of supercooled seawater. This latter is also the only isotherm for which the differences have an opposite trend compared to the others. Calculated isobaric thermal expansion as a function of pressure and represented along isotherms are reported in Fig. 12. Whereas in Fig. 13, expansitivities of this work and TEOS-10 are compared. Differences are lower than $0.24 \cdot 10^{-4}$ K^{-1}, and the two isotherms at the extreme temperatures show the highest differences, which are at the lowest pressure. Instead, for the intermediate temperatures, the differences are nearly constant.

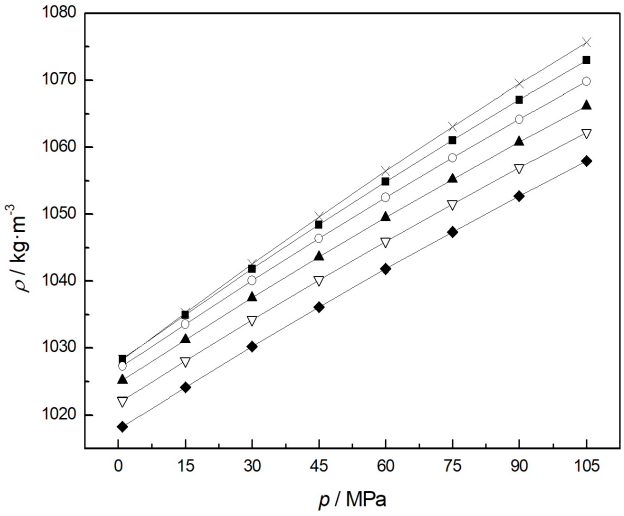

Figure 8: Density of seawater calculated by the fit (Eq. 10) as a function pressure, along isotherms: ×, $T = 263.15$ K; ■, $T = 273.15$ K; ∘, $T = 283.15$ K; ▲, $T = 293.15$ K; ▽, $T = 303.15$ K; ◆, $T = 313.15$ K.

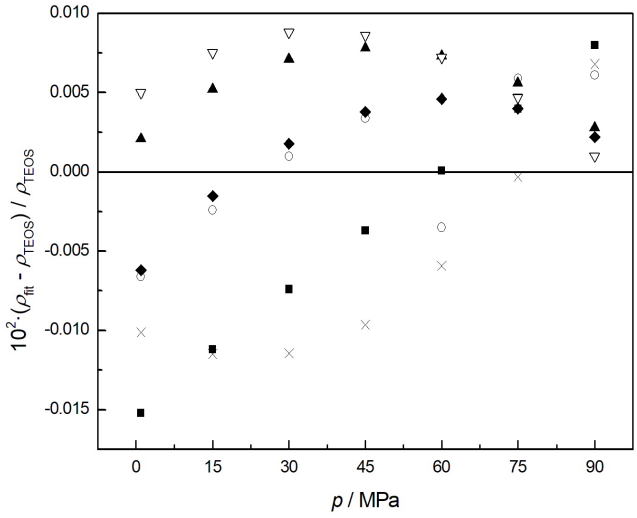

Figure 9: Percentage deviations of seawater densities calculated by the fit (Eq. 10) from the values of TEOS-10 (zero line) as a function pressure, along isotherms: ×, $T = 263.15$ K; ■, $T = 273.15$ K; ∘, $T = 283.15$ K; ▲, $T = 293.15$ K; ▽, $T = 303.15$ K; ◆, $T = 313.15$ K.

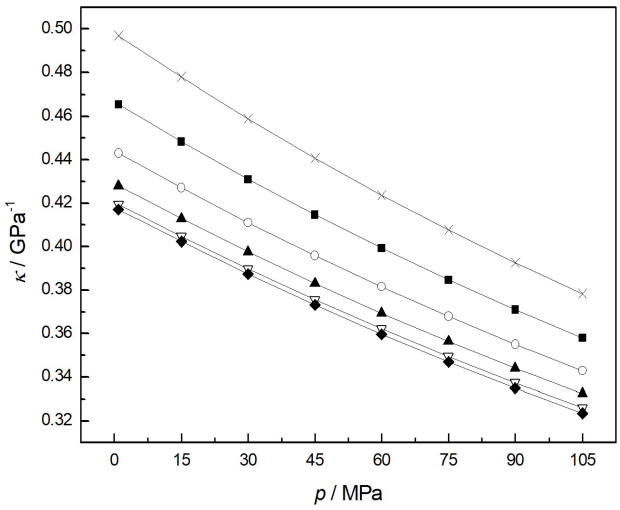

Figure 10: Isothermal compressibility of seawater as a function of pressure: ×, $T = 263.15$ K; ■, $T = 273.15$ K; ∘, $T = 283.15$ K; ▲, $T = 293.15$ K; ▽, $T = 303.15$ K; ◆, $T = 313.15$ K.

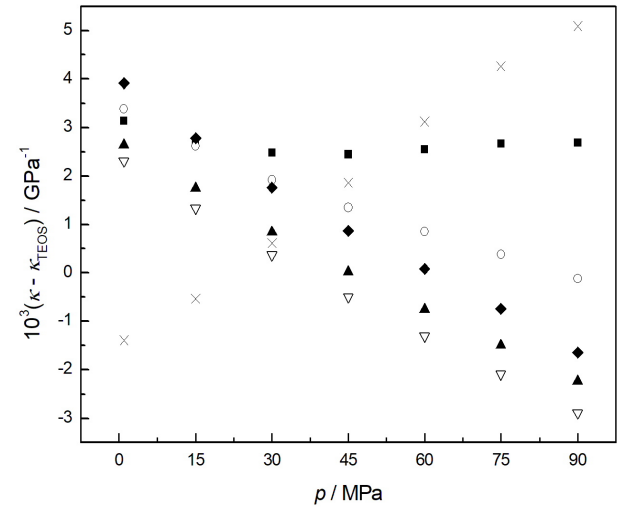

Figure 11: Deviations of isothermal compressibility derived in this work from data calculated by TEOS-10 as a function of pressure: ×, $T = 263.15$ K; ■, $T = 273.15$ K; ∘, $T = 283.15$ K; ▲, $T = 293.15$ K; ▽, $T = 303.15$ K; ◆, $T = 313.15$ K.

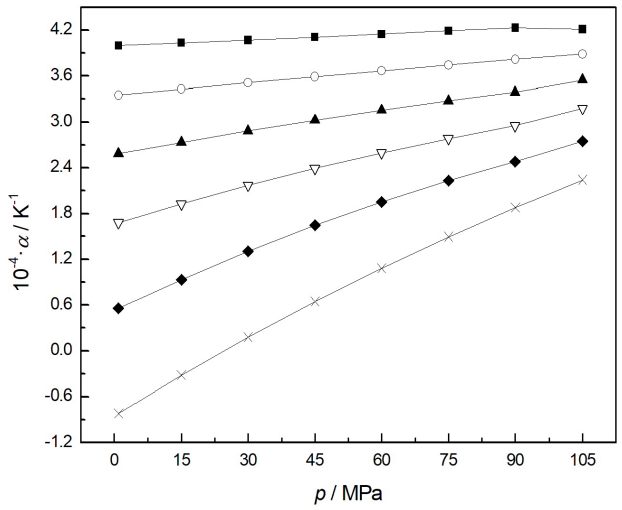

Figure 12: Isobaric thermal expansion of seawater as a function of pressure: ×, $T = 263.15$ K; ■, $T = 273.15$ K; ∘, $T = 283.15$ K; ▲, $T = 293.15$ K; ▽, $T = 303.15$ K; ◆, $T = 313.15$ K.

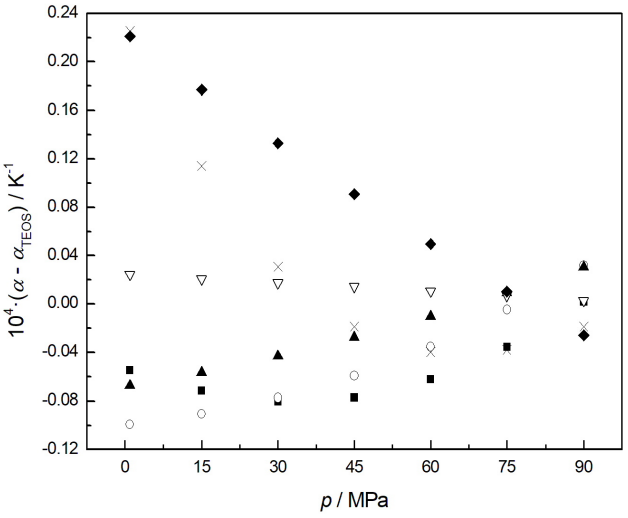

Figure 13: Deviations of isobaric thermal expansion derived in this work from data calculated by TEOS-10 as a function of pressure: ×, $T = 263.15$ K; ■, $T = 273.15$ K; ∘, $T = 283.15$ K; ▲, $T = 293.15$ K; ▽, $T = 303.15$ K; ◆, $T = 313.15$ K.

6. Conclusions

In this work, with the pseudo-isochoric method, density of standard seawater (S_A = 35.158 g·kg^{-1}) was measured. Measurements were carried out by means of a calibrated pycnometer of known volume as a function of temperature and pressure. The mass of seawater was determined by the gravimetric method. Seawater density was obtained for temperatures between (261.15 to 313.15) K and in the pressure range from about (21 to 110) MPa, thus partially covering the supercooled region, with an estimated expanded relative uncertainty of 0.05 %, with $k = 2$. The experimental values were compared to the equation of state of TEOS-10 (IOC et al., 2010). Considering the experimental uncertainty, all the measurements are in agreement with TEOS-10 data within ±0.02 %.

Starting from the high pressure experimental data, along with the measurements at atmospheric pressure of Romeo et al. (2019), a 8-parameters function of specific volume as a function of temperature and pressure was implemented. The function is able to determine seawater density from (263.15 to 313.15) K and from (1 to 105) MPa, with an uncertainty of 0.05 %. Additionally, from the calculated densities, the isothermal compressibilities and the isobaric thermal expansitivities were derived and compared with the values of TEOS-10, resulting within ±0.005 GPa^{-1} and ±0.24·10^{-4} K^{-1}, respectively.

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References

BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, OILM, 2008. Evaluation of measurement data – Guide to the expression of uncertainty in measurements, JMGM 100: 2008 GUM 1995 with minor corrections.

Davidson, S., Perkin, M., Buckley, M., 2004. The measurement of mass and weight. National Physical Laboratory.

Feistel, R., 2018. Thermodynamic properties of seawater, ice and humid air: TEOS-10, before and beyond. Ocean Sci. 14, 471-502.

Goodwin, A.R.H., Marsh, W.A., Wakeham, W.A., 2003. Measurement of the Thermodynamic Properties of Single Phases, Experimental Thermodynamics. Elsevier, Vol. VI.

Haumann, F.A., Moorman, R., Riser, S., Smedsrud, L.H., Maksym, T., Wong, A.P.S., Wilson, E.A., Drucker, R.,Talley, L.D., Johnson, K.S., Key, R.M., Sarmiento, J.L. 2020, Geophys. Res. Lett. 47, e2020GL090242.

Hoppmann, M., Richter, M.E., Smith, I.J., Jendersie, S., Langhorne, P.J., Thomas, D.N., Dieckmann, G.S., 2020. 1 (2020). Platelet ice, the Southern Ocean's hidden ice: a review. Ann. Glaciol., 1-28.

IOC, SCOR, IAPSO, 2010. The international thermodynamic equation of seawater – 2010: Calculation and use of thermodynamic properties. Intergovernmental oceanographic Commission, Manuals and Guides n. 56, UNESCO (English), 196.

Katlein, C., Mohrholz, V., Sheikin, I., Itkin, P., Divine, D.V., Stroeve, J., et al. 2020. Geophys. Res. Lett. 47, e2020GL088898 (2020).

Le Menn, M., 2011. About uncertainties in practical salinity calculations. Ocean Sci. 7, 651–659.

Lorefice, S., Romeo, R., Santiano, M., Capelli, A., 2014. Original pycnometers for volatile liquid density over wide ranges of temperature and pressure: practical example. Metrologia 51, 154-160.

McDougall, T.J., Jackett, D.R., Millero, F.J., Pawlowicz, R., Baker, P.M., 2012. A global algorithm for estimating Absolute Salinity. Ocean Sci. 8, 1123-1134.

OIML R111-1 (E), 2004. Weights of Classes E_1, E_2, F_1, F_2, M_1, M_{1-2}, M_{2-3} and M_3, Part 1: Metrological and technical requirements, International Organization of Legal Metrology.

Romeo, R., Giuliano Albo, P.A., Lago, S., 2019. Density of standard seawater by vibrating tube densimeter: Analysis of the method and results. Deep–Sea Res. I 154, 103157.

Romeo, R., Lago, S., Giuliano Albo, P.A., 2018. Experimental densities of subcooled deuterium oxide at pressures up to 160 MPa. J. Chem. Phys. 149, 154503.

Safarov, J., Berndt, S., Millero, F., Feistel, R., Heintz, A., Hassel, E., 2012. (p, ρ, T) properties of seawater: Extensions to high salinities. Deep-Sea Res. I 65, 146-156.

Safarov, J., Berndt, S., Millero, F.J., Feistel, R., Heintz, A., Hassel, E.P., 2013. (p, ρ, T) Properties of seawater at brackish salinities: Extensions to high temperatures and pressures. Deep-Sea Res. I 78, 95-101.

Safarov, J., Millero, F., Feistel, R., Heintz, A., Hassel, E., 2009. Thermodynamic properties of standard seawater: extensions to high temperatures and pressure. Ocean Sci. 5, 235-246.

Seitz, S., Feistel, R., Wright, D.G., Weinreben, S., Spitzer, P., De Bièvre, P., 2011. Metrological traceability of oceanographic salinity measurement results. Ocean Sci. 7, 45-62.

Wagner, W., Pruss, A., 2002. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. J. Phys. Chem. Ref. Data 31, 387-535.

Wright, D.G., Pawlowicz, R., McDougall, T.J., Feistel, R., Marion, G.M., 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.