

ISTITUTO NAZIONALE DI RICERCA METROLOGICA Repository Istituzionale

The absolute salinity of seawater and its measurands

This is the author's submitted version of the contribution published as: *Original* The absolute salinity of seawater and its measurands / Le Menn, M.; Giuliano Albo, P. A.; Lago, S.; Romeo, R.; Sparasci, F.. - In: METROLOGIA. - ISSN 0026-1394. - (2019).

Availability: This version is available at: 11696/59946 since: 2021-08-24T15:40:36Z

Publisher: IOP

Published DOI:

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright Institute of Physics Publishing Ltd (IOP) IOP Publishing Ltd is not responsible for any errors or omissions in this version of the manuscript or any version derived from it. The Version of Record is available online at DOI indicated above

1	1
2	
1	The absolute salinity of seawater and its measurands
2	Marc Le Menn ¹ , P. Alberto Giuliano Albo ² , S. Lago ² , R. Romeo ² and F. Sparasci ³
3 4	¹ Metrology and Chemical Oceanography Department, French Hydrographic and Oceanographic Service (Shom), Brest, France
5	² Istituto Nazionale di Ricerca Metrologica (INRiM), Turin, Italy
6	³ CNAM-INM, Laboratoire commun de métrologie, La Plaine Saint-Denis, France
7	Email address:
8	Marc.lemenn@shom.fr
9	¹ Corresponding author
10	

4

11

12 Abstract:

Salinity is an essential quantity to calculate many of physical properties of oceans, but it is also a quantity hardly definable considering the complexity of this material in its bio-geochemical composition and the imperfections of the existing measurement techniques. The TEOS-10 gives several definitions to the notion of absolute salinity, usable in function of the properties to study, but they are based on the concept of a constant elemental composition of seawater, so that, if its major inorganic components are well known, its real composition varies in time and space and its determination is still a challenge.

Most of salinity calculations are based on conductivity measurements. This publication reviews other techniques which are used or could be used to assess the absolute salinity of seawater, and question about the measurand of these techniques and the possibility to redefine the concept of salinity from physical properties.

24

25 Keywords: Seawater, Salinity, Conductivity, Density, Refractive index, Speed of sound

26

27 Introduction

In June 2009, the 25th Assembly of the International Oceanographic Commission adopted the description of the thermodynamic properties of seawater and of ice I_h, to replace the document EOS-80 (Equation of State of Seawater of 1980) [1] as the official description of seawater and ice properties in marine science. These properties are described in the document entitled the

32 Thermodynamic Equation Of SeaWater – 2010, or TEOS-10 [2].

33 So that the EOS-80 was based on the concept of practical salinity *S*_{*P*}, the TEOS-10 is based on the concept of Absolute salinity S_A . The practical salinity rests on the measurement of 34 conductivity ratio, temperature and pressure of seawater samples, and also, on the using of 35 empirical equations [1]. All the salinities stored in oceanographic databases are practical 36 salinities, and to keep the compatibility between the requirements of the TEOS-10 and the 37 databases contains, a concept of Reference salinity S_R has been defined. This Reference 38 salinity allows also the correction of bias between the definition of the practical salinity at 35 39 and a Reference-Composition Salinity (RCS) defined by Millero in 2008 [3], and the amount 40 of this correction is not negligible: 0.165 04 g kg⁻¹. 41

In order to approach the concept of Absolute salinity defined as the mass fraction of dissolved material in seawater, a salinity anomaly δS_A is added to the calculated S_R . δS_A can be determined by vibrating tube densimeter measurements and the inversion of the TEOS-10 equation for density to determine S_A . Before using the densimeter, seawater samples are filtrated with a 0.2 µm filter to eliminate suspended particles and, according to Millero and Pierrot [4], a material is defined as dissolved if it passes through a 0.2 µm filter. The practical

6

salinity of the sample being known, δS_A can be deducted. This method has been used in 2012 by McDougall *et al.* [5] to establish an algorithm based on the observed correlation between $S_A - S_R$, and the silicate concentration of seawater samples, the silicate concentration being estimated by interpolation of a global atlas.

Nowadays, the determination of S_A is therefore dependent on the RCS which can evolve in time according to the variations of the atmospheric CO₂ and its absorption by the oceans, and of two different measurement techniques: the conductivity cells associated with the Practical Salinity Scale of 1978 (PSS-78) formulation and the vibrating tube densimeter. That shows that it is not so easy to define the measurand when defining the salinity. That's as much true that the oceanic medium is chemically very complex as it will be shown below.

In the last years, advances have been realized in the adjustment of refractive index techniques 58 [6], [7], [8], [9], [10] or speed of sound measurements [11] to assess *in situ* salinity. These 59 developments press on to question again about the definition of the absolute salinity 60 measurand in the meaning developed in the International Vocabulary of Metrology (VIM) 2nd 61 edition: 'particular quantity subject to measurement'. The goal of this paper is to lead the way 62 to a new definition of the concept of absolute salinity, in accordance to the VIM 3rd edition 63 (JCGM 200:2012), where it is written: 'the specification of a measurand requires knowledge 64 of the kind of quantity, ..., body or substance carrying the quantity, including any relevant 65 component, and the chemical entities involved'. 66

67

68 1 – The actual definitions of the absolute salinity and the real composition of seawater

69 **1.1 – The actual definition of the absolute salinity**

Natural seawater is a complex material because oceans are sources of life and they are in chemical and physical interaction between the seabed and the atmosphere. Their salinity is a quantity recognized as a key climatological observable, object of a metrological challenge for measurements [12]. Until the approval of the TEOS-10 by the oceanographic community, it was largely admitted that the salinity of seawater can be defined by the mass fraction of its principal ionic constituents.

This ionic mass fraction has been assessed during several years by the notion of chlorinity. The chlorinity *Cl* was defined as the mass (in g) of halogens contained in a kilogram of seawater, the bromide and iodide ions being replaced by their equivalents in chloride. Its measure was made in laboratories on discrete samples of seawater. Actually it is defined as 0.3285234 times the ratio of the mass of pure silver required to precipitate all dissolved chloride, bromide and iodide in a sample of seawater to the mass of this sample [3].

With the perfecting of conductivity sensors in the '70s, it was possible to measure, *in situ*, a quantity which variations are proportional to chlorinity at constant temperature and pressure, and to obtain continue salinity profiles thanks to the calculation of a conductivity ratio and to the formulas of the PSS-78. But, seawater conductivity is strongly dependent on temperature

8

and pressure. An increase of temperature leads a decrease of the density of seawater and then a decrease in the number of ions per unit volumes and a decrease of the viscosity. Ions have then a higher mobility and the measured conductivity increases. At constant temperature, a pressure increase leads an increase of the volumetric concentration of ions. It improves also the dissociation of solutes and the conductivity increases in measurable proportions. Temperature and pressure change the stoichiometric composition of seawater but not its elemental composition.

As conductivity is strongly dependent on the effects of temperature and pressure on the ions concentrations, it is a good proxy of the entropy, the free energy and the enthalpy of the seawater. For example, a supply of solute modifies the free energy of the water according to the temperature of the middle. It increases also the entropy of the system.

But, according to Woosley et al. [13], trace and minor components of seawater such as 97 98 nutrients or inorganic carbon affect the evaluation of these properties. Conductivity measurements don't take into account the effects of the non-ionic components, and the non-99 ionic components have an effect on the density. Density variations are to the origin of the 100 thermohaline circulation and they are of a great importance in oceans numerical models. It is 101 why, the TEOS-10 manual defines (page 11) the notion of 'Density-salinity' or S_A^{dens} which is 102 the best estimate of *S*_A because it is measurable and traceable to the SI [14], and the notion of 103 104 salinity anomaly δS_A .

This manual tries also to define the notion of 'dissolved material' which is in the definition of 105 S_{A_2} and it takes the example of the CO_2 dissolution. This dissolution in water produces 106 amounts of CO₂, H₂CO₃, HCO₃⁻, CO₃⁻, H⁺, OH⁻ and H₂O according to the sensitivity of 107 dissociation constants to temperature, pressure and pH. That leads to define a 'Solution 108 Absolute Salinity' or S_A^{soln} as 'the mass fraction of dissolved non-H₂O material after a 109 seawater sample is brought to a constant temperature of 25 °C and a pressure of 101 325 Pa'. 110 This non-H₂O material includes non-ionic components. If their concentrations can be assessed 111 by laboratory measurements on discrete samples, no method exist to measure them in situ. 112

113 Other cases can be met where the composition of the seawater differs of the Reference-114 Composition defined by Millero [3]. For example, discharges of rivers or hydrothermal vents 115 into the ocean lead to define an 'Added-Mass Salinity' or S_A^{add} at a temperature of 25 °C and a 116 normal pressure.

Salinity is used also to trace seawater masses and to model ocean dynamics. This traceability 117 can be obtained by excluding the effects of the biogeochemical processes on S_A^{dens} , S_A^{soln} or 118 S_A^{add} to calculate a 'Preformed Absolute Salinity' called S*. These four definitions and 119 120 approach of the salinity are equivalent to S_R , only for samples of standard seawater. When the composition differs, a salinity anomaly δS_A must be calculated with the McDougall *et al.* 121 algorithm [5]. In order to form this algorithm, measurements of the density of 811 seawater 122 samples from most of the major basins of the world ocean, so that measurements of their 123 practical salinity, were made. Thereafter, using the samples reference salinities, reference 124 densities from the TEOS-10 equations were calculated and compared to the measured 125

densities. The difference $\delta \rho = \rho_{mes} - \rho(S_R, 25 \text{ °C}, 0 \text{ dbar})$ was used to estimate $\delta S_A = S_A^{dens} - S_R$ [3] knowing the empirical value of the partial derivative of density with respect to S_A :

$$\frac{\partial \rho}{\partial S_A}\Big|_{t=25^{\circ}C, p=0 dbar} \approx 0.7519$$
kg m⁻³/g kg⁻¹ (1)

128

Among various components of seawater (total alkalinity, total carbon dioxide or nitrates), silicate concentrations are best correlated with δS_A . According to McDougall *et al.* [5], that can be explained because it is correlated with the other variables responsible for errors in using S_P to determine S_A . It accounts for about 60 % of the variations of the above species and it has no significant effect on conductivity while it has a direct effect on density.

Since the density of seawater is rarely measured, a fit was then realized between Si(OH)₄ 134 concentrations and δS_A for the world oceans (with a standard error of 0.0054 g kg⁻¹) and for 135 the different basins to estimate δS_A from measurements of Si(OH)₄ concentrations and to 136 obtain values of $S_A(S_P, \phi, \lambda, p)$ where ϕ is the latitude, λ the longitude and p the sea pressure. 137 But, this assessment method rests on a simple correlation, and a relatively small number of 138 samples compared to the ocean's volume. Formulas to calculate δS_A are independent of 139 spatial-temporal evolutions, so that silicates were used during a long time as tracers of water 140 masses, and they are not appropriate to coastal areas, to the proximity of hydrothermal vent or 141 to polar countries. 142

143 δS_A can be estimated also from measurements of nitrate and silicate concentrations, and the 144 differences between the Total Alkalinity (*TA*) and Dissolved Inorganic Carbon (*DIC*) of the 145 sample, and the best estimate of *TA* and *DIC* in standard seawater (expressed in mol kg⁻¹). To 146 retrieve S_A^{dens} that gives:

147 $\delta S_A = (50.7 \text{ x } \Delta [S_i(OH_4)] + 38.9 \text{ x } \Delta [NO_3^-] + 4.7 \text{ x } (DIC - 2.080 \text{ x } S_p/35) + 55.6 \text{ x } (TA - 2.300 \text{ x } S_p/35)) / \text{mmol kg}^{-1}$ (2)

According to Wright *et al.* [15], the standard uncertainty of the model fit is 0.08 mg kg⁻¹ over the oceanic range, if all quantities are known precisely, and according to McDougall *et al.* [5], the difference between the two methods is less than 0.005 g kg⁻¹.

These methods using S_P are based on conductance measurements. Conductance depends on 152 the seawater conductivity, but also on the geometry of the measurement cell, on the frequency 153 154 of the applied signal and on the polarization effects at the electrode-solution interface, according to Pawlowics et al. [16]. Polarization effects arise as ions accumulate near the 155 electrodes, inducing an extra capacitance and this phenomenon can't be neglected at the 156 uncertainty level required in S_P calculations. S_P calculation is based on conductivity ratio, but, 157 because of polarization effects, Pawlowics *et al.* [16] underline that the ratio of two measured 158 conductances of two solutions differing in conductivity or composition is not necessarily 159 equivalent to the ratio of their conductivities. As much to say, for seawater conductance 160 161 measurements, the measurand is not only the seawater conductivity but it should include polarization effects also. 162

12

The TEOS-10 definitions of S_A rest on the concept of a Reference-Composition Salinity 163 (RCS). This RCS is based on the concept of constant mass ratio of the major inorganic 164 components of seawater, but the exact composition is not known in detail [3]. If changes in 165 the carbonate system or in the concentration of silicates, CaCO₃, CO₂ or nutrients occur, they 166 must be taken into account in δS_A , but it is not always possible to assess their values 167 completely. Furthermore, in polar countries, the sea ice cover contains concentrated brines 168 which are the site of *in situ* chemical and biological reactions [17]. Measurements made by 169 Butler *et al.* [17] have shown substantial divergence of S_P from S_A at very low temperatures, 170 creating inaccuracies and errors in the calculation of physical sea ice parameters, when S_P is 171 assumed to be equivalent to S_A . To model their observations they refined an S_P -T relationship 172 for sea ice brine to – 22.8 °C. 173

174

1.2 – Some other components of the complete composition

Considering difficulties in conductivity measurements, the concept of RCS excludes a given 175 number of components which concentrations are highly variable according to ocean places 176 and depths. Among these components there are the dissolved organic materials, which 177 concentration is assessed by CDOM (Colored Dissolved Organic Matter) measurements. The 178 CDOM is defined as one part of the organic matters which absorbs the light in the ultra-violet 179 and the blue parts of the spectrum and passes through a 0.2 µm filter according to Bricaud *et* 180 al. [18] and Kirk [19]. Therefore, according to Millero and Pierrot [4] it can be considered as 181 dissolved material. It comes from the degradation of the organic matter in coastal waters and 182 from the photosynthetic activity of macro-alga according to Carder *et al.* [20] or Hulatt *et al.* 183 [21]. It comes also from interactions between microbes, bacteria and phytoplankton [22], [23], 184 present in seawater. It is composed essentially of humic and fulvic acids, but its composition 185 is variable and stays relatively unknown. At the surface, the sun light breaks the big molecules 186 and the smaller are suppressed by microbes according to Miller and Moran [24]. The CDOM 187 can be found in all the oceans but with different concentrations. Organelli et al. [25] have 188 shown recently that, for example, the Black Sea was characterized by very high CDOM 189 contents, that the subtropical gyres (Atlantic and Pacific Oceans) have optical properties 190 consistent with previous bio-optical models and that high latitude (North Atlantic and 191 192 Southern oceans) and temperate (Mediterranean Sea) seas have optical properties which depart from existing bio-optical models. The North Atlantic subpolar gyre, observed in 193 wintertime, shows also high CDOM concentrations according to them. 194

CDOM plays an important role in the carbon cycle according to Blough and Del Vecchio 195 [26]. Consequently, it modifies the stoichiometric and elemental composition of the seawater 196 and its salinity. In 2011, Pawlowicz, Wright and Millero [27] have tried to assess the effect of 197 these biogeochemical processes on oceanic salinity or density relations by mathematical 198 analysis, the use of different salinity variables and haline contraction coefficients. This work 199 has led the definition of S_* which represents, according to them, 'the Standard Seawater 200 component of a real seawater to which biogeochemical processes add material'. But, in 2016 201 Pawlowicz et al. [16] recognized that 'the practical importance of the remaining organic 202 material is poorly understood'. To illustrate this sentence, Jessika Füssel et al. [27] have 203

14

shown that the poorly studied Nitrococcus bacterium is found in oceans worldwide. Nitrococcus, and other similar bacteria, replenish nitrate (NO_3^-) in the ocean through the oxidation of nitrite (NO_2^-) , and convert carbon dioxide (CO_2) at the same time. Nitrogen is needed for the making of proteins and nucleic acids, and its most abundant and stable form is nitrate.

More of these biogeochemical processes, a big number of molecules like Chlorofluorocarbons 209 (CFCs) or polycyclic aromatic hydrocarbons (PAHs), resulting of the anthropic activities can 210 be found in seawater to the state of traces. PAHs absorb also the light in the ultra-violet part 211 of the spectrum. They come from petrol combustion, mineral oils or fuels and are composed 212 of naphthalene, acenaphtene, phenanthrene, chrysene, pyrene or anthracene molecules. 213 According to the proximity of fooling sources, PAHs concentrations can vary from 0 to a few 214 215 ug l⁻¹ or mg l⁻¹. CFCs were used in refrigerants and aerosols. They cannot be broken down by seawaters, and they travel deeper over time, so that they can be used to date water masses in 216 the deep ocean. In the deep ocean and to the vicinity of natural hydro-thermal springs, 217 hydrogen sulfide distributions can be found in the same way. 218

Seawater contains also Suspended Particles Matter (SPM) measured by filtering a given 219 quantity of seawater and weighting the dried filter used. Measuring SPM indicates the 220 complete particles load of a sample. It is generally admitted that SPM concentrations can be 221 between 0.5 mg l⁻¹ and 4 mg l⁻¹ in the oceans fields, 4 mg l⁻¹ to 100 mg l⁻¹ in some coastal 222 waters and 100 mg l⁻¹ to several g l⁻¹ in estuaries. SPM contains organic (plankton and other 223 micro-organisms) and mineral particles placed in suspension by waves, storm [28] and carried 224 by the currents: alluvium, clay, inorganic matter, or aerosol particles, some of them passing 225 through a 0.2 µm filter. Bourin *et al.* [29] have shown, with measurements made in the Gulf 226 of Lion, that during storms all the water column can be impacted, with maximal 227 concentrations of 40 mg l^{-1} in this area. 228

The effect of low concentrations of suspended particulate matter on these measurements is 229 badly documented, but the theories developed to explain and predict the conductivity of 230 sediments show clearly that, under an electrical field, they interact with the ionic composition 231 of seawater [30]. Le Menn and Pacaud [31] have shown experimentally with sand, that for 232 low concentrations the effects on conductivity measurements are negligible, but they cannot 233 be neglected near some seabed or coastal areas. They have shown also that density 234 measurements are more sensible to SPM and the threshold to keep the uncertainty under 4 g 235 m⁻³ is close to the concentrations met in the open oceans. 236

SPM can also take the form of microplastics. By studying 17 salt brands originating from 8 different countries, Ali Karami *et al.* [32] have found recently that they contained microplastics-like particles larger than 149 μ m. According to them, 'out of the 72 extracted particles, 41.6% were plastic polymers, 23.6% were pigments, 5.50% were amorphous carbon, and 29.1% remained unidentified'. As a conclusion of this first part, the complexity of the seawater composition shows the difficulty in defining the measurand of the salinity, intended as quantity, and also the better way to assess it.

- 16
- 244

245 **2 – Problems in measuring the density of natural seawaters**

246

2.1 – Measurements with Vibrating Tube Densimeters

At this time, no instrument allows a direct measurement of density *in situ* and only a discrete 247 sampling can be made thanks to laboratory Vibrating Tube Densimeters (VTD). According to 248 249 Seitz et al. [33], the density measurements seem to be the best way to trace Standard Seawater (SSW) bottles to the SI. SSW is recognized by the International Association for the Physical 250 Sciences of the Ocean (IAPSO). These bottles are used to calibrate with the PSS-78 formulas, 251 reference laboratory salinometers like Autosal or Portasal from the Guildline company. They 252 contain seawater taken in the North Atlantic Ocean, filtrated and adjusted to obtain a salinity 253 close to 35. As SSW has a natural origin, the stability of its chemical composition cannot be 254 guaranteed, so that its traceability on a long-term to a stable and ubiquitous reference like the 255 SI. 256

In 2017, Schmidt et al. have therefore made measurements with VTD's on SSW at the 257 atmospheric pressure and under pressure, and they have determined relations linking the 258 density to the salinity, the temperature and the pressure for standard seawater [34]. When 259 salinity increases from 0 to 35 g kg⁻¹, density shows a small increase of only 3 %. Therefore, 260 density has to be measured with a relative uncertainty of 10⁻⁶ to follow salinity variations to 261 the level of 10⁻³ g kg⁻¹. That can be obtained with VTD only under hard experimental 262 conditions described by Schmidt *et al.* [35]. The substitution method they use needs 20 h per 263 sample on condition that the correction be unaffected by scattering. Consequently that 264 protocol cannot be applied for routine samples measurements, but in the case of SSW, on 265 absolute seawater densities they claim combined standard uncertainties of 2 g m⁻³ at 266 atmospheric pressure to 34 g m⁻³ up to 65 MPa. For relative densities, the uncertainty is 267 limited to 6 g m⁻³ up to 65 MPa [34] 268

VTD consists in measuring the oscillation period τ of a glass tube filled with the seawater. At atmospheric pressure, density ρ is obtained with an empirical relation:

$$\rho = A Q^2 - B \tag{3}$$

where *Q* is the quotient of τ by the oscillation period of a reference oscillator, *A* and *B* 272 constants depending on the characteristics of the cell, the temperature and the viscosity of the 273 fluid under test [36]. Therefore, they make relative density measurements thanks to a 274 calibration made with air and distilled water. In the range of seawater density variations, there 275 276 is no other pure substance which relation density – temperature is known with a sufficiently low uncertainty. Schmidt *et al.* [33] used volatile substances, *n*-nonane and 277 tetrachloroethylene, with a standard uncertainty of respectively 2.5 g m⁻³ (determined from 278 hydrostatic weighing) and 25 g m⁻³ (determined from measurements with a VTD DMA 279 5000M), to adjust their VTD used under high pressure. 280

18

In this instrument the measurand is the oscillation period from which the seawater density is deducted by a relation of calibration. But, since the fluid is vibrating, its viscosity, leading energy loss by rotational movement of the fluid called damping, introduces measurement errors [37]. A third term can be added to the relation (3) to correct the damping. Densities not corrected for this effect can be overestimated systematically. For seawater with $S_P = 35$, the correction can be close to 2 g m⁻³.

The damping effect leads to question about the effect of suspended particles on this correction and also on the homogeneity of the small quantity of seawater (≈ 1 ml for the DMA 5000M) introduced in the low diameter (2 mm) U-tube of the VTD when the sample is charged with particles of different sizes. The small diameter of the U-tube makes necessary the filtration of the seawater. As natural seawater must be filtrated before measurements it is difficult to determine its real density.

293 **2.2 – Measurements by pycnometry**

VTD are not the only laboratory instruments to measure density. Pycnometry can be an alternative method for density measurements, being usually less affected than VTD by the physical properties of the examined fluid, i.e. viscosity and surface tension.

Pycnometers are generally flasks of different shapes and materials (usually glass or metal for higher pressures), which volumes are known, filled with the liquid to be measured [38]. The measurement principle is based on the density definition, namely mass per unit volume of the substance. The measurement procedure consists of two steps: the determination of the pycnometer volume and the determination of the mass of the fluid contained in the pycnometer.

Commonly, because most of the pycnometers have irregular shape, the volume is obtained gravimetrically, at a reference pressure, p_0 , and temperature, T_0 , by weighting (for comparison with standards weights) the mass of the empty pycnometer, M_0 , and the mass of the pycnometer, M_{ref} , filled with a reference liquid of known density, ρ_{ref} :

307
$$V_0(T_0, p_0) = \frac{M_{\text{ref}} - M_0}{\rho_{\text{ref}}}$$
 (4)

Every mass value measured with an analytical balance is intended corrected for the buoyancy by the air density measured during the weighing process. Usually as reference fluid, pure water is used, having density known with an uncertainty of 0.0001% at ambient pressure and less than 0.003% for pressure up to 100 MPa [39].

To measure density over a wide (T, p) range, the reference volume of the pycnometer has to be corrected taking into account the deformation due to the effects of temperature and pressure. So the volume should be expressed as:

315
$$V(T,p) = V_0 [1 + \alpha (T - T_0) + \beta (p - p_0)]$$
 (5)

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

The pycnometer is filled with the fluid sample at a nominal temperature and compressed. The pressure is adjusted to the nominal value while the temperature is controlled. After reaching the thermodynamic equilibrium pressure and temperature are recorded. By the difference between the weight of the empty pycnometer, M_0 , and the pycnometer filled with the fluid, M, measured through an analytical balance, the mass of the sample, m, is determined. The density is calculated by

324
$$ho(T,p)$$

$$\rho(T,p) = \frac{(M-M_0)\rho_{\text{ref}}}{(M \,\text{i i$ ref} - M_0)[1+\alpha(T-T_0) + \beta(p-p_0)] = \frac{m}{V} \,\text{i}}.$$
(6)

Contrary to hydrostatic weighing, the use of pycnometers has the advantage that, since the 325 fluid sample is held in the cell, it is shielded during the entire measurement procedure from 326 the ambient or phenomena which may affect its composition, e.g. evaporation or 327 sedimentation. For these reasons, pycnometry would seem to be a suitable technique to 328 measure seawater density. However, the drawback in using a pycnometer to determine 329 seawater density is its associated relative uncertainty higher than 10⁻⁶ that is necessary for 330 salinity determination. In fact, nowadays the density uncertainty with the pycnometer is 331 usually in the order of 10⁻⁴ both at ambient pressure and high pressure. However, for 332 pycnometry, the estimation of the uncertainty is rather difficult and variable based on the 333 experimental apparatus and strongly dependent on the available instruments and the pressure 334 range of measurement. The main source of uncertainty is due to the volume determination, 335 which involves the uncertainty of reference water density and weighing procedure. 336 Considering only the water density as source of uncertainty, the IAPWS-95 formulation stated 337 an uncertainty of 0.0001 % at ambient pressure, while at higher pressure the uncertainty 338 increases from 0.001% to higher values (0.05%) [39]. Definitely at pressure higher than 339 atmospheric pressure, density uncertainty cannot be lower than present stated density 340 uncertainty of water. Considering measurements at ambient pressure the accuracy cannot be 341 better than 10⁻⁶ even if the overall uncertainty is strictly dependent on the balance resolution 342 and the ratio between the masses of the pycnometer and the sample inside it (the actual 343 measurand). 344

Nevertheless, an evaluation of the best possible accuracy that can be obtained with a pycnometer is demanding. First of all it is necessary to have an analytical balance with a fullscale and a resolution such that their ratio is lower than 10^{-6} in order to measure a volume and a mass with an uncertainty of the order of 10^{-6} . Consequently, the ratio between the balance resolution and the difference between the pycnometer and the amount of fluid inside, must be lower than 10^{-6} ; thus, the pycnometer must be designed according to this requirement.

However, up to now and to the best of authors' knowledge, only the hydrostatic weighing can achieve a density measurement resolution of 10^{-6} .

353 **2.3 - Hydrostatic weighing**

22

As said before, for many fluids, and in particular for liquids, the most accurate density 354 measurements are obtained using the method of the hydrostatic weighing. The measurement 355 principle is based on the possibility to weight a sinker, usually made of a chemically inactive 356 solid material with long term stability, both in air and when immersed in the testing fluid. In 357 these configurations, an analytical balance measures the sinker apparent-mass 358 $m * im - \rho V$, where *m* and *V* are the sinker mass and the sinker volume respectively while 359 *ρ* is the density of the fluid surrounding the sinker (air or testing fluid). Considering both 360 the weighing, the following system of equations can be obtained: 361

$$\begin{cases} m_{\rm air}^{i} = m - \rho_{\rm air} V\\ m^{i} = m - \rho V. \end{cases}$$
(7)

From which it is possible to eliminate *m* and calculate the density of the liquid ρ according to:

$$\rho(T,p) = m_{air}^{\iota} - \frac{m * \iota}{V(T,p)} + \rho_{air}(T,p,x) \iota$$
(8)

365

where x expresses the composition of the air accounting for molar fraction of carbon-dioxide and argon. Using this approach, the measurand is the apparent mass of the sinker.

It is quite common to have a certificate of the sinker mass and volume, measured at specified 368 temperature and pressure, in this way *m* is known, and its uncertainty includes the uncertainty 369 on air density determination. In this way, the first equation of (7) can be eliminated. For 370 density measurements, obtained in conditions different from those of the sinker certificate, 371 volume corrections are needed. This condition sets limits to the sinker materials since, when 372 requested uncertainty is in the order of few part per million, the isothermal compressibility 373 and the thermal expansion coefficients have to be known with the necessary level of 374 uncertainty. 375

When density measurements are requested as a function of pressure, hydrostatic weighing have to be significantly modified to weight the sinker when set into a pressure vessel. The widely used solution to this problem is to adopt a magnetic suspension capable to transmit the weight force through the top of the pressure vessel. However the magnetic suspension introduces new sources of uncertainty, for example the repeatability of the floating position and the force transmission error, so that these types of densimeters are affected by uncertainties that are sensibly higher than those obtained without a magnetic suspension.

Performances of hydrostatic weighing, used by national metrological institutes, are checked by sophisticated procedures of comparison named "key comparisons" regulated by the Bureau International des Poids et Mesures (BIPM). This approach is necessary since, despite a rigorous uncertainty analysis, it is possible that systematic errors may be hidden. According to the updated Calibration and Measurements Capabilities (CMC) [40], the best hydrostatic weighing, working at ambient pressure, are characterized by expanded uncertainties (k=2)

24

around 0.004 kg/m³ (~4 parts per million, ppm) for density values of approximately 1000 kg/m³. However these instruments are not equipped with magnetic suspensions and cannot operate at pressure different from ambient. When instruments are equipped with magnetic suspensions, uncertainty is around (15 or 20) ppm even when operating at ambient pressure. If measurements are carried out at higher pressure, uncertainty can only grow. Furthermore it has to be considered that, for obtaining results with such accuracy, only chemically stable fluids are adopted, usually *n*-nonane and water.

Hydrostatic weighing can of course be used to measure the density of seawater samples both
at ambient and higher pressure, but it has to expect that measurements will be affected by a
higher uncertainty since seawater is chemically active and not as stable as other reference
fluids.

400

3 – **Problems encountered with the refractive index measurements**

Another way to assess the seawater absolute salinity and density is to measure its refractive index *n*. The Lorentz – Lorenz formula gives a direct relation between *n* and ρ :

$$\frac{(n^2-1)}{(n^2+2)} = \frac{m_r \rho}{W}$$
(9)

 m_r being the molar refractivity and W the molecular weight of the species constituting the 405 fluid. For pure water, m_r depends strongly of the wavelength λ , and it varies slowly with 406 temperature *t* (no more than 1 % between ambient temperature and boiling point) and molar 407 density ρ [41]. Hence the molar refractivity of pure water behaves in the same way that other 408 elementary fluid, for a given wavelength. This can be explained theoretically and modelled by 409 an empirical relation function of ρ , t and λ [42]. Several authors attempted to establish 410 empirical relations between the seawater refractive index and its variations in wavelength, 411 temperature, salinity and pressure. In 1990, Millard and Seaver proposed a 27-terms algorithm 412 covering the range 500 - 700 nm in wavelength, 0 - 30 °C in temperature, 0 - 40 in practical 413 salinity and 0 - 11000 dbar in pressure, to compute the seawater refractive index [43]. By 414 measuring the refractive index and inverting this algorithm, salinity can be extracted with 415 accuracies close to oceanographic purposes at low pressure, but not at high pressure. 416

With techniques giving access to the phase of light waves, with several wavelengths it is theoretically possible to measure absolute refractive index values and then to retrieve the value of seawater salinity knowing the exact values of the wavelengths and by measuring the temperature and the pressure of the middle. In this case, the measurand is an optical property of the middle, its refractive index.

n is sensible to all the constituents of the fluid and is therefore a good proxy of the concept of salinity and techniques based on the measurement of *n* shows generally a good linearity versus the salinity. It can give access to an S_A or to a true δS_A by comparison to CTD values,

404

26

but Laser Gaussian beams are also sensible to turbidity. According to the wavelength and the 425 size of particles it leads diffraction phenomenon and that can be an obstacle to the using of 426 interferometric techniques in situ, so that they allow the achievement of the best resolutions. 427 But, as shown by Hou *et al.* [10], turbidity can also contribute to a light beam deviation more 428 than refractive index. This deviation is therefore a good proxy of the real density of the 429 middle but it leads errors in the measure of n and subsequently in the calculation of the 430 salinity with the Millard and Seaver algorithm for example. In the case of a refractometer, 431 Hou *et al.* have shown that theoretically the same beam can be used to measure the turbidity 432 and the refractive index, and *n* can be corrected. 433

Demonstrations have been made of the using of refractometers in situ [6], [9] but several 434 obstacles stay to make of them, instruments able to challenge conductivity cells in resolution 435 and precision. Like conductivity cells, they need a calibration with reference formulas linking 436 the measurand to salinity, temperature and pressure, the wavelength being a supplementary 437 quantity to determine. Another obstacle is the inaccuracy of Millard and Seaver relations with 438 pressure because of the low number of reference data used to fit the relations, or because of 439 the using of S_P instead of S_r or S_A in these relations, and the questionable real uncertainties of 440 all the reference data used to build the algorithm. 441

442

443 **4 – Problems encountered with the speed of sound measurements**

Speed of sound *w* is a thermodynamic quantity directly linked to the adiabatic compressibility 444 of the sample, namely $w^{-2} = (\partial \rho / \partial p)_s$ [44]. There are, mainly, two methods for measuring 445 speed of sound and they can be distinguished by the use of steady state waves or transient 446 waves. Steady states approach is very favorable when speed of sound is measured in gases, 447 but the method needs to use ultrasonic sources with almost flat frequency dependence. Such 448 transducers are usually not suitable to be used at high pressure, furthermore, the high acoustic 449 impedance of seawater makes this measurement method unsuitable, since the frequency 450 response of the resonant cavity does not show an evident frequency peak. On the contrary, 451 many of the oceanographic speed of sound sensors are based on a transient method, named 452 single path pulse-echo. This acoustic scheme uses an ultrasonic source to generate a wave-453 packet that spreads into the seawater and then it is reflected back to the source by a reflector. 454 The sensor measures the time *t* that signal needs to get back and, knowing the travelled 455 w=2L/t. These kind of distance 2L, it is possible to determine the speed of sound 456 oceanographic sensors are mechanically robust and can operate at pressure up to 90 MPa 457 (~9000 dbar) [45]. Since variations of temperature and pressure change the distance at which 458 the reflector has been set, speed of sound sensors have to be calibrated with a reference fluid 459 in suitable temperature and pressure ranges. The most used calibration fluid is pure water that 460 is one of the most studied. The equation of state for pure water [39] was realized considering 461 several sets of speed of sound measurements and recently Trusler [46] suggested to reduce the 462 estimated uncertainty of the equation of state to 0.03 % (now 0.1 %) for high pressure ranges. 463

28

For TEOS-10 [47], the equation of state of seawater, the uncertainty estimation is still debated [48], however it cannot be better than that one of pure water, reasonably. Equations of states, both for pure and seawater, are very important since their predictions are often used to calibrate oceanographic sensors. In this case, *in situ* speed of sound measurements are affected by an uncertainty that is, at least, that one of the equation but, typically it is even larger.

For speed of sound, the measurand is a time-of-flight that can usually be determined with a 470 resolution in the order of 10 ppm and a repeatability of 20 ppm, in laboratory conditions. 471 However, the main sources of uncertainty for speed of sound measurements are due to the 472 determination of the acoustic path-length, as a function of the temperature and pressure, and 473 the measurement of the absolute pressure. Once the speed of sound is measured, the salinity 474 475 can be estimated using empirical relations obtained in controlled laboratory conditions. As an example, Allen *et al.* [49] state that the use of speed of sound for calculating the salinity is 476 limited by the accuracy of the equations they found since they have uncertainty of 0.05 m/s. 477 Declared uncertainty corresponds to a relative uncertainty of 33 part per million when it is 478 calculated for pure water at ambient temperature and pressure. The same paper reports also 479 that there are commercial sensors able to reach the uncertainty of 0.02 m/s, or 13 part per 480 million in pure water, but it sounds strange since the best water speed of sound measurements, 481 obtained in controlled laboratory conditions, are affected by a relative uncertainty of 10 part 482 per million and the agreement with independent measurements is 30 part per million [50]. It is 483 possible that the authors fell in the common misunderstanding to use the *repeatability* of a 484 measurement to declare instrument uncertainty. To confirm this hypothesis, Von Rohden et 485 al. [45] calibrated a set of state-of-the-art commercial sensors using pure water for measuring 486 the speed of sound in North Atlantic seawater. They found a repeatability in the order of 20 487 ppm, but an agreement between different sensors is approximately 200 ppm that sounds more 488 realistic and representative of the typical measurement uncertainty, considering that all 489 measurements were obtained at ambient pressure. 490

For speed of sound sensors, based on transient method, the uncertainty budget is usually 491 dominated by the uncertainty associated to the determination of the travelled distance and the 492 pressure measurement. This means that for *in situ* measurements, the uncertainty can only 493 increase with respect to that one estimated in [45]. The calibration procedure is mainly 494 dedicated to the determination of the acoustic-path length at different temperatures and, 495 hopefully, pressure. Furthermore, in many cases, time-of flight measurements are not 496 corrected by diffraction effects since the necessary technical specifications (like source 497 diameter and source resonant frequency) are not declared and cannot be easily determined 498 during calibration. Diffraction corrections are in the order of 100 ppm and they strongly 499 depend on the measured speed of sound. For this reason, it is not rigorous to calibrate a sensor 500 in pure water and then measure seawater speed of sound, without correcting both the 501 calibration and the *in situ* measurement by diffraction effects. 502

Effects of pressure on the speed of sound uncertainty evaluation is twofold. Firstly, pressure changes the distance between the source and the reflector and, secondly, the uncertainty on

30

pressure measurement leads to a wrong association between the speed of sound measurement and the correspondent thermodynamics state. Usually, temperature acts on the same way of the pressure.

In an optimistic view, if the laboratory and *in situ* uncertainty was the same, speed of sound could be measured with a relative uncertainty of about 300 ppm up to high pressure. Considering the sensitivity coefficient that links salinity to speed of sound, the uncertainty associated to the salinity determination, starting from speed of sound, temperature and pressure measurement, should be in the order of 1 %.

513

514 **5 – Conclusion**

515 Salinity is an essential quantity to calculate many of physical properties of oceans, but it is 516 also a quantity hardly definable considering the complexity of the material in its bio-geo-517 chemical composition and the imperfections of the existing measurement techniques.

The TEOS-10 gives several definitions to the notion of absolute salinity, usable in function of 518 the properties to study. They are all based on conductivity or density measurements. 519 Conductivity measurements offer a precision suitable with the oceanographic requirements, 520 521 but they suffer of inaccuracies in relation with the amounts of non-ionic components present in seawater. The inaccuracies are also in relation with the defaults of the salinity scale 522 originally based on the Marcet principle of a constant elemental composition of seawater. To 523 complement the practical salinity measurements, the using of vibrating tube densimeters 524 developed in the last years. They allow the determination of salinity anomalies and the 525 approach of an absolute salinity, so that a better traceability of the standard seawater to the SI. 526 But they make relative density measurements with a calibration resting essentially on the air 527 and the pure water density relations. 528

Taking into account the volume and the dynamic variations of oceans, oceanographers need in 529 situ salinity or density profiles. Vibrating tube densimeters, pycnometric or hydrostatic 530 weighing methods are not usable in situ. For this reason two other techniques are under 531 development. The first one is based on refractive index measurements and the second one on 532 the speed of sound. The refractive index and the measurement techniques of Laser beam 533 deviations present the advantage to be sensible to all the components of the medium and they 534 could allow a new definition of the salinity based on a physical property of the seawater and 535 not on a chemical composition exhaustively unknown at this time and variable in time and 536 space. But, the perfecting of refractometers or interferometers insensible to the temperature 537 and pressure constraints of the medium is not easy and the oceanographic uncertainty 538 requirements on salinity are difficult to keep with this quantity, taking into account its 539 variation range and the necessary resolution. 540

The speed of sound measurements are challenging the refractometers because speed of sound profilers are still used in hydrography for several years to correct hydrographic multi or

32

543 mono-beam echo sounders. The more recent ones allow resolutions inferior to one centimeter 544 per second, but the uncertainty of their measurements is more close to 200 ppm at ambient 545 pressure and could be 300 ppm at high pressure. That corresponds to 0.35 for a salinity of 35 546 g/kg, which is not sufficient to reply to oceanographer's requirements described in references 547 [51] and [52].

In the seventieth, the perfecting of conductivity cells leaded to the abandon of chlorinity measurements and to the definition of the PSS-78. That definition with its imperfections, and the definitions of S_A described in the TEOS-10 manual, will stay probably as long as no other technology will have perfectly demonstrated its ability to retrieve in situ density or salinity profiles with a precision close to the precision of conductivity cells.

553

554 **References:**

[1] – UNESCO, 1981, 'The practical Salinity Scale 1978 and the International Equation of
State of Seawater 1980', UNESCO Technical papers in marine science 36, UNESCO, Paris.

557 [2] - IOC, SCOR and IAPSO, 2010, 'The international thermodynamic equation of seawater –

- 2010: Calculation and use of thermodynamic properties', Intergovernmental oceanographic
 Commission, *Manuals Guides* n° 56, UNESCO (English), 196 pp.
- [3] Millero F. J., Feistel R., Wright D. G., MacDougall T. J., 2008, 'The composition of
 standard seawater and the definition of the reference composition salinity scale', *Deep-Sea Res.* I, 55, 10-72.
- [4] Millero J. F., Pierrot D., 2002, 'Speciation of metals in natural seawaters', Chapter in *Chemistry of Marine Water and Sediments*, 193-220.
- 565 [5] McDougall T. J., Jackett D. R., Millero J. F., Pawlowicz R., Barker P. M., 2012, 'A
 566 global algorithm for estimating absolute salinity', *Ocean Sci.*, 8, 1123-1134.
- [6] Mahrt, K-H., Waldmann, C., 1988. Field proven high speed micro optical density
 profiler sampling 1000 times per second with 10⁻⁶ precision. <u>OCEANS '88, Proceedings</u>. 2,
 497-504.
- 570 [7] Alford M. H., D. W. Gerdt and C. M. Adkins, 2006, 'An Ocean Refractometer:
 571 Resolving Millimeter-Scale Turbulent Density Fluctuations via the Refractive Index', *J. of*572 *Atm. and Ocean. Techno.*, 23, 121-137.
- 573 [8] Grosso P., M. Le Menn, J.-L. de Bougrenet de la Tocnaye, ZY Wu, D. Malardé, 2010,
- 'Practical versus absolute salinity measurements, new advances in high performance seawater
 salinity sensors', *Deep-Sea Research I*, vol. 57, n°1, 151–156.

34

[9] – Le Menn M., de Bougrenet de la Tocnaye J. L., Grosso P., Delauney L., Podeur C.,
Brault P. and Guillerme O., 2011, 'Advances in measuring ocean salinity with an optical
sensor', *Meas. Sci. Technol.*, 22, (8pp).

[10] – Hou B., Grosso P., de Bougrenet de la Tocnaye J.L., Le Menn M., 2013, 'Principle and
implementations of a refracto-nephelo-turbidi-meter for seawater measurements', *Opt. Eng.*52 (4), 044402, doi: 10.1117/1.OE.52.4.044402.

[11] – Bewer P. G., Peltzer E. T., Ryan J., Kirkwood W. J. and Hofmann A. F., 2015, 'Ocean
chemistry and the speed of sound in seawater', *Marine Chemistry*, 117, 591-605.
DOI:10.1016/j.marchem.2015.09.009.

[12] – Feistel R., Wielgosz R., Bell S. A., Harvey A. H., Heinonen M., Hellmuth O.,
Kretzschmar H.-J., Lovell-Smith J. W., McDougall T. J., Pawlowicz R., Ridout P., Seitz S.,
Spitzer P. Stoica D, Wolf H., 2016, 'Metrological challenges for measurements of key
climatological observables: oceanic salinity and pH, and atmospheric humidity. Part 1:
overview', *Metrologia*, 53, R1-R11.

[13] – Woosley R. J., Huang F., Millero F. J., 2014, 'Estimating absolute salinity (*S_A*) in the
world's oceans using density and composition', *Deep-Sea Res.* I, 93, 14-20.

592 [14] - Seitz S., R. Feistel, D.G. Wright, S. Weinreben, P. Spitzer and P. de Bievre, 2011,
593 'Metrological traceability of oceanographic salinity measurement results', *Ocean Science* 7,
594 45-62, doi:10.5194/os-7-45-2011.

- [15] Wright D. G., Pawlowicz R., McDougall T. J., Feistel R., and 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.
- 598 [16] Pawlowicz R., Feistel R., McDougall T. J., Ridout P., Seitz S., Wolf H., 2016,
 599 'Metrological challenges for measurements of key climatological observables Part 2: oceanic
 600 salinity', *Metrologia*, 53, R12-R25.
- [17] Butler M. B., Stathys P., Kennedy H., 2016, 'The effect of mirabilite precipitation on
 the absolute and practical salinities of sea ice brine', *Marine Chemistry*, 184, 21-31.
- [18] Bricaud, A., Morel A., Prieur L., 1981, 'Absorption by dissolved organic matter of the
 sea (yellow substance) in the UV and visible domain', *Limnology and Oceanography*, 26: 43–
 53.
- [19] Kirk J. T. O., 1994, 'Light and photosynthesis in aquatic ecosystems', Second edition,
 Cambridge University Press, pp 12-15.
- [20] Carder K. L., Hawes S. K., Smith R. C., Steward R. G., Mitchell B. G., 1991,
 'Reflectance model for quantifying chlorophyll *a* in the presence of productivity degradation
 products', *Journal of Geophysical Research*, 9: 20599–20611.

36

[21] – Hulatt C. J., Thomas D. N., Bowers D. G., Norman L., Chi Zhang, 2009, 'Exudation
and Decomposition of Chromophoric Dissolved Organic Matter (CDOM) from some
Macroalgae', *Estuarine Coastal and Shelf Science*, doi:10.1016/j.ecss.2009.06.014.

[22] - Nelson N. B., Carlson C.A., Steinberg D.K., 2004, 'Production of chromophoric
dissolved organic matter by Sargasso Sea microbes', *Marine Chemistry* 89: 273-287.

[23] – Claustre H., Kerhervé P., Marty J. C., Prieur L., Videau C., Hecq J. H., 1994,
'Phytoplankton dynamics associated with a geostrophic front: ecological and biogeochemical
implications', *Journal of Marine Research*, 52, 711-742.

[24] - Miller W.L., Moran M.A., 1997, 'Interaction of photochemical and microbial processes
in the degradation of refractory dissolved organic matter from a coastal marine environment', *Limnology and Oceanography*, 42:1317-1324.

[25] – Organelli E., Claustre H., Bricaud A., Barbieux M., Uitz J., D'Ortenzion F., Dal'Olmo
G., 2017, 'Bio-optical anomalies in the world's oceans: An investigation on the diffuse
attenuation coefficients for downward irradiance derived from biogeochemical Argo float
measurements', *Journal of Geophysical Research*, DOI: 10.1002/2016JC012629.

[26] - Blough N. V., Del Vecchio R., 2002, 'Chromophoric DOM in the coastal environment',

In *Hansell, D. A. & C. A. Carlson* (ed), Biogeochemistry of marine dissolved organic matter, *Academic Press*, San Diego: 509–540.

[27] – Füssel J., Lücker S., Yilmaz P., Nowka B., A. H. J. van Kessel M., Bourceau P., Hach P.
F., Littman S., Berg J., Spieck E., Daims H., Kuypers M. M. M., Lam P., 2017, 'Adaptability
as the key to success for the ubiquitous marine nitrite oxidizer Nitrococcus', *Science Advances*, 3, 11. DOI: 10.1126/sciadv.1700807

[28] - Pawlowicz R., Wright D.G., Millero F., 2011, 'The effect of biogeochemical processes
on oceanic conductivity/salinity/density relationships and the characterization of real
seawater', *Ocean Science*, 7, 363-387.

[29] – Bourrin F., Many G., Durrieu de Madron X., Martín J., Puig P., Houpert L., Testor P.,
Kunesch S., Mahiouz K., Béguery L., 2015, 'Glider monitoring of shelf suspended particle
dynamics and transport during storm and flooding conditions', *Continental Shelf Research*109, 135–149.

[30] - Revil A., Glover P. W. J., 1997-I, 'Theory of ionic-surface electrical conduction in
porous media', *Physical Review* B, 55, 3, 1757-1773.

[31] - Le Menn M., Pacaud L., 2017, 'Effect of sediments on seawater conductivity and
density assessments', *Journal of Water Resources and Ocean Sciences*.

[32] – Karami A., Golieskardi A., Choo C. K., Larat V., S. Galloway T. & Salamatinia B.,
2017, 'The presence of microplastics in commercial salts from different countries', *Nature Scientific Reports*, 7:46173. DOI: 10.1038/srep46173.

- 647 [33] Seitz S., Feistel R., Wright D. G., Weinrenberg S., Spitzer P., de Bièvre P., 2011,
 648 'Metrological traceability of oceanographic salinity measurements results', *Ocean Science*, 7,
 649 45-62.
- 650 [34] Schmidt H., Seitz S., Hassel E., Wolf H., 2018, 'The density-salinity relation of 651 standard seawater', *Ocean Science*, 14, 15-40, 2018, https://doi.org/10.5194/os-14-15-2018
- [35] Schmidt H., Wolf H., Hassel E., 2016, 'A method to measure the density of seawater accurately to the level of 10^{-6'}, *Metrologia*, 53, 770-786.
- [36] Anton Paar, 2010, DMA 5000 M Instruction Manual.
- [37] Stabinger H., 1994, 'Density measurement using modern oscillating transducers', *South Yorkshire Trading Standards Unit*, Sheffield, 45-53.
- [38] Goodwin A., Marsh K., Wakeham W., 2003, 'Measurement of the thermodynamic
 properties of single phases', Elsevier.
- 659

660 [39] – 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*, 19, 2, 387–535.
- 663

666

664 [40] – Bureau International des Poids et Mesures web site,

- 665 https://kcdb.bipm.org/appendixC/country_list.asp?Sservice=M/Dens.2.2
- [41] Schiebener P., Straub J., Levelt Sengers J. M. H., Gallagher J. S., 1990, 'Refractive
 Index of Water and Steam as Function of Wavelength, Temperature and Density', *J. Phys.*
- 669 *Chem. Ref. Data*, 19, 3, 677-717.
- [42] Harvey A. H., Gallagher J. S., Levelt Sengers J. M. H., 1998, 'Revised Formulation for
 the Refractive Index of Water and Steam as a Function of Wavelength, Temperature and
 Density', J. Phys. Chem. Ref. Data, 27, 4, 761-774.
- [43] Millard R.C., Seaver G., 1990, 'An index of refraction algorithm for seawater over
 temperature, pressure, salinity, density and wavelength', *Deep-Sea Research*, 37, 12, 19091926.
- [44] Trusler J.P.M., 1991, 'Physical Acoustics and Metrology of Fluids, *The Adam Hilger Series on Measurement Science and Technology*, Bristol, Philadelphia and New York.
- [45] C. Von Rohden, F. Fehres, S. Rudtsch, 'Capability of pure water calibrated time-of-flight sensors for the determination of speed of sound in seawater', *JASA* 138 (2015).
- [46] Lin C.W. and Trusler J.P.M, 2012, 'The speed of sound and derived thermodynamic
- properties at temperature between (253 and 473) K and at pressure up to 400 MPa', *J. Chem. Phys.* 136.

40

686 [48] - R. Feistel, J. W. Lovell-Smith, P. Saunders and S. Seitz, 2016, 'Uncertainty of 687 empirical correlation equations', *Metrologia* 53(4).

- [49] J. T. Allen, P. W Keen, J. Gardiner, M. Quartley, C. Quartley, 2017, 'A new salinity
 equation for sound speed instruments', *Limnology and Oceanography Methods*, 15(9), pp.
 810-820
- [50] K. Fujii, R. Masui, 1993, 'Accurate measurements of speed of sound velocity in pure
 water by combining a coherent phase-detection technique and a variable path length
 interferometer', *JASA* 93(1), pp. 276-282.
- [51] WHPO Publication 90-1 Revision 2, 1991, WHP 91-1 : WOCE Operations Manual.
- [52] C. Wunsch, 2016, 'Global Ocean Integrals and Means, with Trend Implications', *An*.
- 696 *Rev. of Marine. Scie.* 8:1-33.