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Marc Le Menn, Paolo Alberto Giuliano Albo, Simona Lago, Raffaella Romeo,  
Fernando Sparasci

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PAPER

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# The absolute salinity of seawater and its measurands

Marc Le Menn<sup>1,4</sup>, Paolo Alberto Giuliano Albo<sup>2</sup>, Simona Lago<sup>2</sup>,  
Raffaella Romeo<sup>2</sup> and Fernando Sparasci<sup>3</sup>

<sup>1</sup> Metrology and Chemical Oceanography Department, French Hydrographic and Oceanographic Service (Shom), Brest, France

<sup>2</sup> Istituto Nazionale di Ricerca Metrologica (INRiM), Turin, Italy

<sup>3</sup> CNAM-INM, Laboratoire commun de métrologie, La Plaine Saint-Denis, France

E-mail: [Marc.lemenn@shom.fr](mailto:Marc.lemenn@shom.fr)

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## Abstract

Salinity is an essential quantity to calculate many of the physical properties of oceans, but it is also a quantity hard to define 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 the 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 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 questions the measurand of these techniques and the possibility to redefine the concept of salinity from physical properties.

Keywords: seawater, salinity, conductivity, density, refractive index, speed of sound

## 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 Thermodynamic Equation Of SeaWater—2010, or TEOS-10 [2].

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 conductivity ratio, temperature and pressure of seawater samples, and, on the use of empirical equations [1]. All the salinities stored in oceanographic databases are practical salinities, and to keep the compatibility between the requirements of the TEOS-10 and the databases contains, a concept of reference salinity  $S_R$  has been defined. This reference salinity

allows also for the correction of an inherited bias between the 1901 Knudsen salinity of  $35 \text{ g kg}^{-1}$ , from which the unitless numerical value of practical salinity of 35 had been borrowed in 1978 without updating it, and the related reference-composition salinity (RCS) defined by Millero *et al* in 2008 [3]. The amount of this correction is not negligible:  $0.16504 \text{ g kg}^{-1}$ .

In order to approach the concept of absolute salinity defined as the mass fraction of dissolved material in seawater, a salinity anomaly  $\delta S_A$  is added to the calculated  $S_R$ .  $\delta S_A$  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  $0.2 \mu\text{m}$  filter to eliminate suspended particles and, according to Millero and Pierrot [4], a material is defined as dissolved if it passes through a  $0.2 \mu\text{m}$  filter. The practical salinity of the sample being known,  $\delta S_A$  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.

<sup>4</sup> Author to whom any correspondence should be addressed.

The determination of  $S_A$  is therefore dependent on the RCS. As argued by Wright *et al* [6] ‘the RCS should remain unaltered to provide a stable representation of salinity for use with the TEOS-10 Gibbs function and in climate change detection studies’. The definition of the RCS of 2008 will remain unchanged, but the real composition can evolve slightly in time according to the variations of the atmospheric  $\text{CO}_2$  and its absorption by the oceans. These evolutions will affect salinity anomalies. The determination of  $S_A$  also depends on the conductivity cells associated with the Practical Salinity Scale of 1978 (PSS-78) formulation and on the vibrating tube densimeters. It shows that it is not so easy to define the measurand when defining the salinity. This highlights that the oceanic medium is chemically very complex as it will be shown below.

In recent years, advances have been realized in the adjustment of refractive index techniques [7–11] or speed of sound measurements [12] to assess *in situ* salinity. These developments press on to question again about the definition of the absolute salinity measurand in the meaning developed in the International Vocabulary of Metrology (VIM) 2nd edition: ‘particular quantity subject to measurement’. The goal of this paper is to lead the way to a new definition of the concept of absolute salinity, in accordance to the VIM 3rd edition (JCGM 200:2012), where it is written: ‘the specification of a measurand requires knowledge of the kind of quantity, ..., body or substance carrying the quantity, including any relevant component, and the chemical entities involved’.

## 1. The actual definitions of the absolute salinity and the real composition of seawater

### 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 a 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 [13]. 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 chlorinity.

Historically, 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 0.328 5234 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 1970s, it was possible to measure, *in situ*, a quantity the variations of which are proportional to chlorinity at constant temperature and pressure, and to obtain *in situ* continuous 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 and pressure. At a constant pressure, an increase or a decrease in temperature leads to a

variation on the density of seawater and on the dissociation constant. The number of ions per unit volume changes, so that the viscosity. Ions have therefore a different mobility and the measured conductivity varies. At a constant temperature, a pressure increase leads to an increase of the volumetric concentration of ions. It also improves 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 probably a good proxy of the entropy, the free energy and the enthalpy of the seawater.

But, according to Woosley *et al* [14], trace and minor components of seawater such as nutrients or inorganic carbon affect the evaluation of these properties. Conductivity measurements do not consider the effects of the non-ionic components, and the non-ionic components have an effect on the density. Density variations are to the origin of the thermohaline circulation and they are of a great importance in oceans numerical models. It is why, the TEOS-10 manual defines (page 11) the notion of ‘density-salinity’ or  $S_A^{\text{dens}}$  which is the best estimate of  $S_A$  because it is measurable and traceable to the SI [15], and the notion of salinity anomaly  $\delta S_A$ .

This manual tries also to define the notion of ‘dissolved material’ which is in the definition of  $S_A$ , and it takes the example of the  $\text{CO}_2$  dissolution. This dissolution in water produces amounts of  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}^+$ ,  $\text{OH}^-$  and  $\text{H}_2\text{O}$  according to the sensitivity of dissociation constants to temperature, pressure and pH. That leads to define a ‘solution absolute salinity’ or  $S_A^{\text{soln}}$  as ‘the mass fraction of dissolved non- $\text{H}_2\text{O}$  material after a seawater sample is brought to a constant temperature of 25 °C and a pressure of 101 325 Pa’. This non- $\text{H}_2\text{O}$  material includes non-ionic components. If their concentrations can be assessed by laboratory measurements on discrete samples, no method exists to measure them *in situ*.

Other cases can be met where the composition of the seawater differs to the reference-composition defined by Millero [3]. For example, discharges of rivers or hydrothermal vents into the ocean lead to define an ‘added-mass salinity’ or  $S_A^{\text{add}}$  at a temperature of 25 °C and a normal pressure.

Salinity is also used to trace seawater masses and to model ocean dynamics. This traceability can be obtained by excluding the effects of the biogeochemical processes on  $S_A^{\text{dens}}$ ,  $S_A^{\text{soln}}$  or  $S_A^{\text{add}}$  to calculate a ‘preformed absolute salinity’ called  $S_*$ . These four definitions and approaches to salinity are equivalent to  $S_R$ , only for samples of standard seawater. When the composition differs, a salinity anomaly  $\delta S_A$  may be calculated with the McDougall *et al* algorithm [5]. In order to form this algorithm, measurements of the density of 811 seawater samples were taken from most of the major basins of Earth’s oceans, so that measurements of their practical salinity, were made. Thereafter, using the samples reference salinities, reference densities from the TEOS-10 equations were calculated and compared to the measured densities. The difference  $\delta\rho = \rho_{\text{mes}} - \rho(S_R, 25\text{ °C}, 0\text{ dbar})$  was used to estimate  $\delta S_A = S_A^{\text{dens}} - S_R$  [3] knowing the empirical value of the partial derivative of density with respect to  $S_A$ :

$$\left. \frac{\partial \rho}{\partial S_A} \right|_{t=25^\circ\text{C}, p=0 \text{ dbar}} \approx 0.7519 \text{ kg m}^{-3} / \text{g kg}^{-1}. \quad (1)$$

Among various components of seawater (total alkalinity, total carbon dioxide or nitrates), silicate concentrations are best correlated with  $\delta S_A$ , in the open ocean. 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  $\text{Si}(\text{OH})_4$  concentrations and  $\delta S_A$  for the world oceans (with a standard error of  $0.0054 \text{ g kg}^{-1}$ ) and for the different basins to estimate  $\delta S_A$  from measurements of  $\text{Si}(\text{OH})_4$  concentrations and to obtain values of  $S_A(S_P, \phi, \lambda, p)$  where  $\phi$  is the latitude,  $\lambda$  the longitude and  $p$  the sea pressure. But, this assessment method rests on a simple correlation, and a relatively small number of samples compared to the ocean's volume. Formulas to calculate  $\delta S_A$  are independent of spatial-temporal evolutions, so that silicates were used during a long time as tracers of water masses, and they are not appropriate to coastal areas, to the proximity of hydrothermal vent or to polar countries.

In the open ocean,  $\delta S_A$  can be estimated also from measurements of nitrate and silicate concentrations, and the differences between the total alkalinity (TA) and dissolved inorganic carbon (DIC) of the sample, and the best estimate of TA and DIC in standard seawater (expressed in  $\text{mol kg}^{-1}$ ). To retrieve  $S_A^{\text{dens}}$  that gives:

$$\delta S_A = (50.7 \times \Delta [\text{Si}(\text{OH})_4] + 38.9 \times \Delta [\text{NO}_3^-] + 4.7 \times (\text{DIC} - 2.080 \times S_P/35) + 55.6 \times (\text{TA} - 2.300 \times S_P/35)) / \text{mmol kg}^{-1}. \quad (2)$$

According to Wright *et al* [6], the standard uncertainty of the model fit is  $0.08 \text{ mg kg}^{-1}$  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  $0.005 \text{ g kg}^{-1}$ .

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

The TEOS-10 definitions of  $S_A$  rest on the concept of a reference-composition salinity (RCS). This RCS is based on the concept of constant mass ratio of the major inorganic components of seawater, but the exact composition is not

known in detail [3]. If changes in the carbonate system or in the concentration of silicates,  $\text{CaCO}_3$ ,  $\text{CO}_2$  or nutrients occur, they must be taken into account in  $\delta S_A$ , but it is not always possible to assess their values completely. Furthermore, in polar countries, the sea ice cover contains concentrated brines which are the site of *in situ* chemical and biological reactions [17]. Measurements made by Butler *et al* [17] have shown that at very low temperatures,  $S_A$  is only poorly represented by  $S_P$  values which therefore may create inaccuracies and errors in the calculation of physical sea ice parameters. To model their observations, they refined an  $S_P - T$  relationship for sea ice brine to  $-22.8^\circ\text{C}$ . We also note that in 2009, Marion *et al* [18] used the geochemical model (FREZCHEM) to quantify the  $S_A - T$  boundaries at  $P = 0.1 \text{ MPa}$  and the range of these boundaries for future atmospheric  $\text{CO}_2$  increases.

## 1.2. Some other components of the complete composition

Considering difficulties in conductivity measurements, the concept of RCS excludes a given number of components which concentrations are highly variable according to ocean places and depths. Among these components there are the dissolved organic materials, which concentration is assessed by colored dissolved organic matter (CDOM) measurements. The CDOM is defined as one part of the organic matters which absorbs the light in the ultra-violet and the blue parts of the spectrum and passes through a  $0.2 \mu\text{m}$  filter according to Bricaud *et al* [19] and Kirk [20]. Therefore, according to Millero and Pierrot [4] it can be considered as dissolved material. It comes from the degradation of the organic matter in coastal waters and from the photosynthetic activity of macro-alga according to Carder *et al* [21] or Hulatt *et al* [22]. It also comes from interactions between microbes, bacteria and phytoplankton [23, 24], present in seawater. It is composed essentially of humic and fulvic acids, but its composition is variable and stays relatively unknown. At the surface, the sun light breaks the big molecules and the smaller are suppressed by microbes according to Miller and Moran [25]. The CDOM can be found in all the oceans but with different concentrations. Organelli *et al* [26] have shown recently that, for example, the Black Sea was characterized by very high CDOM contents ( $2$  to  $6.6 \text{ mg l}^{-1}$ ), that the subtropical gyres (Atlantic and Pacific Oceans) have optical properties consistent with previous bio-optical models and that high latitude (North Atlantic and Southern Oceans) and temperate (Mediterranean Sea) seas have optical properties which depart from existing bio-optical models. The North Atlantic subpolar gyre, observed in wintertime, shows also high CDOM concentrations according to them ( $1.4$  to  $2.5 \text{ mg l}^{-1}$ ).

CDOM plays an important role in carbon cycle according to Blough and Del Vecchio [27]. Consequently, it modifies the stoichiometric and elemental composition of the seawater and its salinity. In 2011, Pawlowicz, Wright and Millero [28] tried to assess the effect of these biogeochemical processes on oceanic salinity or density relations by mathematical analysis, the use of different salinity variables and haline contraction coefficients. This work led to the definition of  $S_*$  which represents, according to them, 'the Standard Seawater component

of a real seawater to which biogeochemical processes add material'. But, in 2016 Pawłowicz *et al* [16] recognized that 'the practical importance of the remaining organic material is poorly understood'. To illustrate this sentence, Jessika Füssel *et al* [29] showed that the poorly studied *Nitrococcus* bacterium is found in oceans worldwide. *Nitrococcus*, and other similar bacteria, replenish nitrate ( $\text{NO}_3^-$ ) in the ocean through the oxidation of nitrite ( $\text{NO}_2^-$ ), and convert carbon dioxide ( $\text{CO}_2$ ) at the same time. Nitrogen is needed to make proteins and nucleic acids, and its most abundant and stable form is nitrate. The concentration of bacteria is a function of oxygen concentrations.

More of these biogeochemical processes, a large number of molecules like Chlorofluorocarbons (CFCs) or polycyclic aromatic hydrocarbons (PAHs), resulting in the anthropic activities can be found in seawater to the state of traces. PAHs also absorb the light in the ultra-violet part of the spectrum. They come from petrol combustion, mineral oils or fuels and are composed of naphthalene, acenaphthene, phenanthrene, chrysene, pyrene or anthracene molecules. According to the proximity of fouling sources, PAHs concentrations can vary from 0 to a few  $\mu\text{g l}^{-1}$  or  $\text{mg l}^{-1}$ . 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 the deep ocean. In the deep ocean and to the vicinity of natural hydro-thermal springs, hydrogen sulfide distributions can be found in the same way.

Seawater also contains suspended particles matter (SPM) measured by filtering a given quantity of seawater and weighing the dried filter used. Measuring SPM indicates the complete particle load of a sample. It is generally admitted that SPM concentrations can be between  $0.5 \text{ mg l}^{-1}$  and  $4 \text{ mg l}^{-1}$  in the oceans fields,  $4 \text{ mg l}^{-1}$  to  $100 \text{ mg l}^{-1}$  in some coastal waters and  $100 \text{ mg l}^{-1}$  to several  $\text{g l}^{-1}$  in estuaries. SPM contains organic (plankton and other micro-organisms) and mineral particles placed in suspension by waves and storms [30] and carried by the currents: alluvium, clay, inorganic matter, or aerosol particles, some of them passing through a  $0.2 \mu\text{m}$  filter. Bourin *et al* [30] showed, with measurements made in the Gulf of Lion, that during storms all of the water column can be impacted, with maximal concentrations of  $40 \text{ mg l}^{-1}$  in this area.

The effect of low concentrations of suspended particulate matter on these measurements is badly documented, but the theories developed to explain and predict the conductivity of sediments show clearly that, under an electrical field, they interact with the ionic composition of seawater [31]. Le Menn and Pacaud [32] experimented with sand, to show that that for low concentrations the effects on conductivity measurements are negligible, but they cannot be neglected near some seabed or coastal areas. They also outlined that density measurements are more sensible to SPM and the threshold to keep the uncertainty under  $4 \text{ g m}^{-3}$  is close to the concentrations met in the open oceans.

SPM can also take the form of microplastics. By studying 17 salt brands originating from 8 different countries, Ali Karami *et al* [33] found recently that they contained microplastic-like particles larger than  $149 \mu\text{m}$ . 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'.

If all these other components can be found to maximum concentrations of a few  $\text{mg l}^{-1}$  in different ocean places, their effect on salinity measurement accuracy is difficult to assess. It is the function of their densities and of their ability to be dissolved or not under ionic forms. Non-ionic components will not be detected by conductivity sensors, so that they will increase or decrease the measured densities (except when their densities are equivalent to seawater densities). In the case of sedimentary SPM, Le Menn and Pacaud [32] both showed that they decrease the measured conductivity and they increase the measured density, increasing in this way, the systematic error between  $S_P$  and  $S_A$  even at low concentrations.

Seawater also contains dissolved gases which do not appear in the RCS. All of the atmospheric gases are found in solution in sea water so that rare gases like ammonia, argon, helium, neon and hydrogen sulphide near hydrothermal vent fields. Their concentrations depend on the temperature, the salinity and the pressure. Cold water and seawaters with low salinity hold more gas than high salinity or high temperature waters. They cannot be detected by conductivity sensors but they have an effect on density measurements. Harvey *et al* [34] have showed that density measurements of distilled water must be corrected by  $-2.5 \cdot 10^{-6} \text{ g cm}^{-3}$  at  $20 \text{ }^\circ\text{C}$  if it was air saturated. As deep waters hold more gas than shallow waters, it causes the problem of lab measurements of the density when samples are collected at great depth, given that they degas when lifted up.

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 a better way to assess it.

## 2. Problems in measuring the density of natural seawaters

### 2.1. Measurements with vibrating tube densimeters

At this time, no instrument allows a direct measurement of density *in situ* under pressure and only a discrete sampling can be made thanks to laboratory vibrating tube densimeters (VTD). According to Seitz *et al* [15], 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 Sciences of the Ocean (IAPSO). These bottles are used to calibrate with the PSS-78 formulas, reference laboratory salinometers like Autosal or Portasal from the Guildline company. They contain seawater taken in the North Atlantic Ocean, filtrated and adjusted to obtain a salinity close to 35. As SSW has a natural origin, the stability of its chemical composition cannot be guaranteed, just as its traceability on a long-term to a stable and ubiquitous reference like the SI [34].

In 2017, Schmidt *et al* have therefore made measurements with VTD's on SSW at the atmospheric pressure and under pressure, and they have determined relations linking the density to the salinity, the temperature and the pressure for standard

seawater [35]. When salinity increases from 0 to 35 g kg<sup>-1</sup>, the density shows a small increase of only 3%. Therefore, the density has to be measured with a relative uncertainty of 10<sup>-6</sup> to follow salinity variations to the level of 10<sup>-3</sup> g kg<sup>-1</sup>. That can be obtained with VTD only under hard experimental conditions described by Schmidt *et al* [36]. The substitution method they use needs 20h per sample on condition that the correction be unaffected by scattering. Consequently, that protocol cannot be applied for routine samples measurements, but in the case of SSW, on absolute seawater densities they claim combined standard uncertainties of 2 g m<sup>-3</sup> at atmospheric pressure to 34 g m<sup>-3</sup> up to 65 MPa. For relative densities, the uncertainty is limited to 6 g m<sup>-3</sup> up to 65 MPa [35].

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

$$\rho = A Q^2 - B \quad (3)$$

where  $Q$  is the quotient of  $\tau$  by the oscillation period of a reference oscillator,  $A$  and  $B$  constants depending on the characteristics of the cell, the temperature and the viscosity of the fluid under test [37]. Therefore, they make relative density measurements thanks to a calibration made with air and distilled water. In the range of seawater density variations, there is no other pure fluid which relation density—temperature is known with a sufficiently low uncertainty. Schmidt *et al* [35] used volatile substances, *n*-nonane and tetrachloroethylene, with a standard uncertainty of respectively 2.5 g m<sup>-3</sup> (determined from hydrostatic weighing) and 25 g m<sup>-3</sup> (determined from measurements with a VTD DMA 5000M), to adjust their VTD used under high pressure.

In this instrument the measurand is the oscillation period from which the seawater density is deduced 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 [38]. 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<sup>-3</sup>.

The damping effect leads to a question about the effect of suspended particles on this correction and also on the homogeneity of the small quantity of seawater ( $\approx 1$  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.

## 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), whose volumes are known, filled with the liquid to be measured [39]. 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 an irregular shape, the volume is obtained gravimetrically, at a reference pressure,  $p_0$ , and temperature,  $T_0$ , by weighing (for comparison with standards weights) the mass of the empty pycnometer,  $M_0$ , and the mass of the pycnometer,  $M_{\text{ref}}$ , filled with a reference liquid of known density,  $\rho_{\text{ref}}$ :

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

Every mass value measured with an analytical balance is intended to be corrected for the buoyancy by the air density measured during the weighing process. Usually as a reference fluid, pure water is used, having a known density with an uncertainty of 0.0001% at ambient pressure and less than 0.003% for pressure up to 100 MPa [40].

To measure the 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:

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

where  $\alpha$  and  $\beta$  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

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

Contrary to hydrostatic weighing, the use of pycnometers has the advantage that, since the fluid sample is held in the cell, it is shielded during the entire measurement procedure from the ambient or phenomena which may affect its composition, e.g. evaporation or sedimentation. For these reasons, pycnometry would seem to be a suitable technique to measure seawater density. However, the drawback in using a pycnometer to determine seawater density is its associated relative uncertainty higher than 10<sup>-6</sup> that is necessary for salinity determination. In fact, nowadays the density uncertainty with the pycnometer is usually in the order of 10<sup>-4</sup> both at ambient pressure and high pressure. However, for pycnometry, the estimation of the uncertainty is rather difficult, and variable based

on the experimental apparatus and strongly dependent on the available instruments and the pressure range of measurement. The main source of uncertainty is due to the volume determination, which involves the uncertainty of the reference water density and weighing procedure. Considering only the water density as a source of uncertainty, the IAPWS-95 formulation stated an uncertainty of 0.0001% at ambient pressure, while at a higher pressure the uncertainty increases from 0.001% to higher values (0.05%) [40]. At pressures higher than atmospheric pressure, density uncertainty cannot be lower than present stated density uncertainty of water. Considering measurements at an ambient pressure the accuracy cannot be better than  $10^{-6}$  even if the overall uncertainty is strictly dependent on the balance resolution and the ratio between the masses of the pycnometer and the sample inside it (the actual measurand).

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

### 2.3. Hydrostatic weighing

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

$$\begin{cases} m_{\text{air}}^* = m - \rho_{\text{air}} V \\ m^* = m - \rho V \end{cases} \quad (7)$$

From which it is possible to eliminate  $m$  and calculate the density of the liquid  $\rho$  according to:

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

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 a specified temperature and pressure, in this way  $m$  is known, and its uncertainty includes the

uncertainty on air density determination. In this way, the first equation of (8) can be eliminated. For density measurements, obtained in conditions different from those of the sinker certificate, volume corrections are needed. This condition sets limits to the sinker materials since, when requested uncertainty is in the order of few part per million, the isothermal compressibility and the thermal expansion coefficients have to be known with the necessary level of uncertainty.

When density measurements are requested as a function of pressure, hydrostatic weighing have to be significantly modified to weigh 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) [41], the best hydrostatic weighing, working at ambient pressure, are characterized by expanded uncertainties ( $k = 2$ ) around  $0.004 \text{ kg m}^{-3}$  (~4 parts per million, ppm) for density values of approximately  $1000 \text{ kg m}^{-3}$ . However, these instruments are not equipped with magnetic suspensions and cannot operate at a 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 one has to expect that the measurements will be affected by a higher uncertainty since seawater is chemically active and not as stable as other reference fluids.

### 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  $\rho$ :

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

$m_r$  being the molar refractivity and  $W$  the molecular weight of the species constituting the fluid. For pure water,  $m_r$  depends strongly of the wavelength  $\lambda$ , and it varies slowly with

temperature  $t$  (no more than 1% between ambient temperature and boiling point) and molar density  $\rho$  [42]. Hence the molar refractivity of pure water behaves in the same way that other elementary fluids behave, for a given wavelength. This can be explained theoretically and modelled by an empirical relation function of  $\rho$ ,  $t$  and  $\lambda$  [43]. Several authors have attempted to establish empirical relations between the seawater refractive index and its variations in wavelength, temperature, salinity and pressure. In 1990, Millard and Seaver proposed a 27-terms algorithm covering the range 500–700 nm in wavelength, 0 °C–30 °C in temperature, 0–40 in practical salinity and 0–11 000 dbar in pressure, to compute the seawater refractive index [44]. By measuring the refractive index and inverting this algorithm, salinity can be extracted with accuracies close to oceanographic purposes at low pressure, but not at high pressure.

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 medium. In this case, the measurand is an optical property of the medium, 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  $\delta S_A$  by comparison to CTD values, but laser Gaussian beams are also sensible to turbidity. According to the wavelength and the size of particles it leads diffraction phenomenon and that can be an obstacle to the using of interferometric techniques *in situ*, so that they allow the achievement of the best resolutions. But, as shown by Hou *et al* [11], turbidity can also contribute to a light beam deviation more than the refractive index. This deviation is therefore a good proxy of the real density of the medium but it leads to errors in the measure of  $n$  and subsequently in the calculation of the salinity with the Millard and Seaver algorithm for example. In the case of a refractometer, Hou *et al* have shown that theoretically the same beam can be used to measure the turbidity and the refractive index, and  $n$  can be corrected.

Demonstrations have been made of the use of refractometers *in situ* [7, 10] but several obstacles stay to make of them instruments able to challenge conductivity cells in resolution and precision. Like conductivity cells, they need a calibration with reference formulas linking the measurand to salinity, temperature and pressure, the wavelength being a supplementary quantity to determine. Another obstacle is the inaccuracy of Millard and Seaver relations with pressure (and dissolved gas [34]) because of the low number of reference data used to fit the relations, or because of the using of  $S_P$  instead of  $S_r$  or  $S_A$  in these relations, and the questionable real uncertainties of all the reference data used to build the algorithm.

#### 4. Problems encountered with the speed of sound measurements

Speed of sound  $w$  is a thermodynamic quantity directly linked to the adiabatic compressibility of the sample, namely

$w^{-2} = (\partial\rho/\partial p)_S$  [45]. There are, two main methods for measuring the speed of sound and they can be distinguished by the use of steady state waves or transient waves. The steady states approach is very favorable when the speed of sound is measured in gases, but the method needs to use ultrasonic sources with almost flat frequency dependence. Such transducers are usually not suitable to be used at high pressure, furthermore, the high acoustic impedance of seawater makes this measurement method unsuitable, since the frequency response of the resonant cavity does not show an evident frequency peak. On the contrary, many of the oceanographic speed of sound sensors are based on a transient method, named single path pulse-echo. This acoustic scheme uses an ultrasonic source to generate a wave-packet that spreads into the seawater and then it is reflected back to the source by a reflector. The sensor measures the time  $t$  that signal needs to get back and, knowing the travelled distance  $2L$ , it is possible to determine the speed of sound  $w = 2L/t$ . These kinds of oceanographic sensors are mechanically robust and can operate at pressure up to 90 MPa (~9000 dbar) [46]. Since variations of temperature and pressure change the distance at which the reflector has been set, speed of sound sensors have to be calibrated with a reference fluid in suitable temperature and pressure ranges. The most used calibration fluid is pure water that is one of the most studied. The equation of state for pure water [40] was realized considering several sets of speed of sound measurements and recently Trusler [47] suggested to reduce the estimated uncertainty of the equation of state to 0.03% (now 0.1%) for high pressure ranges. For TEOS-10 [2], the equation of state of seawater, the uncertainty estimation is still debated [48], however it cannot be better than the one for 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 resolution in the order of 10 ppm and a repeatability of 20 ppm, in laboratory conditions. However, the main sources of uncertainty for speed of sound measurements are due to the determination of the acoustic path-length, as a function of the temperature and pressure, and the measurement of the absolute pressure. Once the speed of sound is measured, the salinity 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 limited by the accuracy of the equations they found since they have uncertainty of  $0.05 \text{ m s}^{-1}$ . Declared uncertainty corresponds to a relative uncertainty of 33 part per million when it is calculated for pure water at an ambient temperature and pressure. The same paper reports also that there are commercial sensors able to reach the uncertainty of  $0.02 \text{ m s}^{-1}$ , or 13 part per million in pure water, but it sounds strange since the best water speed of sound measurements, obtained in controlled laboratory conditions, are affected by a relative uncertainty of 10 part per million and the agreement with independent measurements is

30 part per million [50]. It is possible that the authors fell into the common misunderstanding to use the *repeatability* of a measurement to declare instrument *uncertainty*. To confirm this hypothesis, Von Rohden *et al* [46] calibrated a set of state-of-the-art commercial sensors using pure water for measuring the speed of sound in North Atlantic seawater. They found a repeatability in the order of 20 ppm, but an agreement between different sensors is approximately 200 ppm that sounds more realistic and representative of the typical measurement uncertainty, considering that all measurements were obtained at ambient pressure.

For speed of sound sensors, based on the transient method, the uncertainty budget is usually dominated by the uncertainty associated to the determination of the travelled distance and the pressure measurement. This means that for *in situ* measurements, the uncertainty can only increase with respect to that one estimated in [46]. The calibration procedure is mainly dedicated to the determination of the acoustic-path length at different temperatures and, hopefully, pressure. Furthermore, in many cases, time-of flight measurements are not corrected by diffraction effects since the necessary technical specifications (like source diameter and source resonant frequency) are not declared and cannot be easily determined during calibration. Diffraction corrections are in the order of 100 ppm and they strongly depend on the measured speed of sound. For this reason, it is not rigorous to calibrate a sensor in pure water and then measure the seawater speed of sound, without correcting both the calibration and the *in situ* measurement by diffraction effects.

The 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 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, the 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%.

## 5. Conclusion

Salinity is an essential quantity to calculate many of the physical properties of oceans, but it is also a quantity hard to define considering the complexity of the 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 the function of the properties to study. They are all based on conductivity or density measurements. Conductivity measurements offer a precision suitable with the oceanographic requirements, but they suffer

inaccuracies in relation to the amounts of non-ionic components present in seawater. The inaccuracies are also in relation to the defaults of the salinity scale originally based on the Marcet principle of a constant elemental composition of seawater. To complement the practical salinity measurements, the using of vibrating tube densimeters has been developed in recent years. They allow for the determination of salinity anomalies through the approach of an absolute salinity, so that there is a better traceability of the standard seawater to the SI. But they make relative density measurements with a calibration resting essentially on the air and the pure water density relations.

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

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 mono-beam echo sounders. The more recent ones allow for resolutions inferior to  $1 \text{ cm s}^{-1}$ , but the uncertainty of their measurements is closer to 200 ppm at ambient pressure and could be 300 ppm at high pressure. That corresponds to 0.35 for a salinity of  $35 \text{ g kg}^{-1}$ , which is not sufficient to reply to the oceanographer's requirements described in [51, 52].

In the 1970s, the perfecting of conductivity cells led scientists to abandon chlorinity measurements and led 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 remain as long as no other technology perfectly demonstrates its ability to retrieve *in situ* density or salinity profiles with a precision close to the precision of conductivity cells.

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## ORCID iDs

Marc Le Menn  <https://orcid.org/0000-0001-9367-4458>

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