IMPROVING THE UNCERTAINTY OF SEAWATER DENSITY -ABSOLUTE SALINITY RELATIONSHIPS

Introduction

The density of seawater ρ is the most important thermodynamic property for modelling ocean circulation or water level anomalies. Its measurement is also a means of determining the **absolute salinity S_A** of seawater, which is the quantity chosen by the authors of TEOS-10 (Thermodynamic Equation Of Seawater of 2010) to the detriment of the **practical salinity S_P**, which remains the only quantity (without unit) that can be measured in situ.

In order to be able to follow the variations linked to climate change, oceanographers have a very low tolerance on the measurement of ρ: 0.0015 kg/m³ or 1.5 ppm. This tolerance is very close to the best measurements made in metrology laboratories at atmospheric pressure. The current uncertainties in the relationships between S_A, temperature t and pressure p range from 0.007% to 0.012% at best, and do not meet the needs of oceanographers. **They are also an obstacle to the development and calibration of instruments for in situ measurements.**

Practical salinity – Absolute salinity - Density

TEOS-10 recommends to calculate S_A with the relation: $S_A = S_R + \delta S_A$ where δS_A is the absolute salinity anomaly and S_R is the reference composition salinity obtained from a measurement of S_P and the relation: $S_R(g/kg) \approx \frac{35.16504}{35} S_P$

Examples of CTD instruments.

S_P is calculated from conductivity C, t and pressure p measurements made with CTD instruments.

S_A, t and p are used in the TEOS-10 equation that gives the specific volume (inverse of ρ). It is a 72 coefficient equation and the uncertainty in the resulting values is poorly established (Feistel *et al.*, 2016)

Improved databases to establish the relationship $\rho = f(S_A, t, p)$ would provide a better estimate of the uncertainties in the TEOS-10 calculation relationships.

Silicates are the better documented elements that create salinity anomalies and change the density of seawater without changing its conductivity, however, there are still many other contributing elements to the density that are poorly documented and/or poorly understood. They can't be detected by conductivity cells and they introduce conductivity measurements errors that are difficult to assess.

Even though the established electrical techniques are well-suited for in-situ measurements of S_P in the oceans, optical or acoustical techniques remain options to explore in order to progress on similar capabilities for S_A and ρ. In the last years, important advances have been made in optical instruments. They are based on measurements of the refractive index (R. I.) of seawater.

Laboratory measurements of density

When the salinity increases from 0 to 40 g kg⁻¹, the density shows a small increase of just 3 %. Therefore, density has to be measured with a relative uncertainty better than 10⁻⁶ to follow salinity variations to the required level of 10⁻³ g kg⁻¹. This is the major problem of seawater density measurement for Absolute Salinity estimation and **just a few laboratory techniques allow to achieve this performances**:

- **vibrating-tube densimeters** with the substitution technique described by Schmidt *et al.* in 2016. It needs 20 h for processing a sample on condition that the correction is unaffected by scattering. That makes it unsuitable for the routine measurement of seawater samples. Standard uncertainties of 0.001 kg m⁻³ at atmospheric pressure, 0.01 kg m⁻³ up to 10 MPa and 0.02 kg m⁻³ up to 65 MPa are claimed by the authors in the 5 – 35 °C temperature range and for salt contents of up to 35 g kg⁻¹.

Vibrating-tube densimeter Anton-Paar DMA 5000 M.

- **The method of hydrostatic weighting** developed by Fujii *et al*. in 2001, where the mass of a 1 kg sphere was compared to that of the prototype kilogram through a secondary standard and the volume of the sphere was measured by optical interferometry. They claim to have obtained a relative combined standard uncertainty of 1 x 10⁻⁷ for the absolute density measurement.


Density testing facility of the Federal Office of Metrology and Suveying, Austria (From Buchner, Imeko 20ᵗʰ TC3, 2007).

When measurements are made under pressure, the sinker is generally equipped with a magnetic suspension assembly capable of transmitting the weight force through the top of the pressure vessel. In order to eliminate the uncertainty caused by magnetic forces acting on the fluids, Kayukawa *et al. (*2012) used dual sinkers and control of the magnetic coupling's levitation height. **The approach was reported as being accurate to approximately 100 ppm in density, with a measurement precision better than 1 ppm.**

Density, absolute salinity and refractive index

The most advanced in situ measurement instruments for S_A are based on measurements of the R.I. of seawater n.
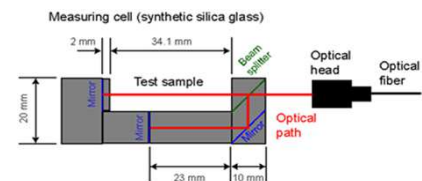
Example of instruments developped to measure n and to retrieve S_A or ρ. On the left, a refractometer called NOSS already tested on profiling floats at 2000 m. Above, a diagram of the device developed in Japan and tested at a depth of over 6000 m (from Ushida *et al*., 2019).

n **is in relation with density and composition** by a relationship found independently by H. Lorentz and L. Lorenz. In contrast to conductivity, n is sensitive to all dissolved constituents in seawater. **It is therefore an ideal candidate for measuring S_A, δS_A or ρ.**

The Lorentz-Lorenz relationship has been used to quantify the scattering properties of water from its derivative with density but also to establish empirical relationships between n, S and p.

For Seawater, several empirical relationships exist. They are useful to calibrate instruments in R.I. and S. The more complete is a 27-term algorithm for computing seawater R.I. covering the ranges of 500 - 700 nm in wavelength, 0 - 30 °C in temperature, 0 - 40 in Practical Salinity and 0 - 11000 dbar in pressure (Millard & Seaver, 1990).

The associated standard uncertainty is estimated to vary from 0.4 ppm for pure water at atmospheric pressure to 80 ppm for seawater at high pressures. By measuring the R.I. and inverting this algorithm, the salinity can be extracted with uncertainties close to those needed for oceanographic use at low pressure, but not at high pressure.

At high pressures, this formula is based on only 20 experimental measurement points and **an effort would be needed to increase this number of points and their measurement uncertainty**.

Conclusion

In order to meet the needs of oceanographers, much progress is therefore needed to improve the uncertainties in the fundamental relationships between ρ, S_A, t, p and n, in particular when p is different from atmospheric pressure.

Considering the required uncertainty level and the importance of density/salinity measurements in ocean physics and climate change, it is a key technical challenge for metrology over the next decade.

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