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Practical versus absolute salinity measurements: New advances in high performance seawater salinity sensors

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Optical salinity sensors described here measure directly the seawater refractive index and thus enable a measurement of the seawater density and composition variation. We detail the measurement dependence to environmental parameters (in particular temperature and pressure) compared to conductivity sensors, and demonstrate that it may be advantageous to directly measure refractive index rather than electrical conductivity and so obtain a more direct route to density and absolute salinity.

1. Introduction

A recent publication of Millero et al. (2008a) has revived the debate on the difference between the practical salinity, as measured today with conductivity cells, and the absolute salinity, which is a key parameter in accessing the thermodynamic properties of the ocean. This difference is emphasized when the medium composition is far from that of standard seawater. This point highlights the present need, for models of ocean interaction with the atmosphere (through the evaporation and precipitation of freshwater), to measure salinity with the highest possible accuracy (Jackett et al., 2006). If conductivity sensors can be calibrated with a small uncertainty, the accuracy of these calibrations is relative because of the low correlation between conductivity and salinity, exacerbated by the strong dependence of conductivity on temperature, resulting in several concerns. Even if in practice there are several ways to measure the salinity, the accuracy depends on the application. Among them, refractometry is the most direct. Based on seawater refractive index measurements (SCOR/IAPSO, 2007.), the refractive index is directly related to the medium density (ρ) and thus provides a more accurate assessment of the absolute salinity, whatever the medium. Actually, all the seawater physical properties are derived from salinity (S), temperature (T) and pressure (p). This applies to the density with the equation of International State of Seawater

(TEOS-10), where $\rho=f(S, T, p)$. Even if it is clear that refractive index depends on temperature, the dependence is ten times smaller than for conductivity. The choice for conductivity sensors was mainly motivated by the fact that refractometers were not accurate enough (Millero 1996). Recent advances on high-resolution detection devices such as, for instance, position sensor devices (PSD), have changed the situation, making possible the measurement of very small deviation angles provided by refractometers.

2. Practical and absolute salinity

Absolute salinity (S_a) is the mass fraction of total dissolved solids per kilogram of seawater. In practice, this mass is difficult to determine. A protocol was adopted in 1902 by an international commission to approach the value of the dissolved substance mass. The salinity becomes the mass of solids contained in one kilogram of seawater, carbonates being transformed into oxides, bromide and iodide being replaced by the equivalent of chloride, and organic matter being oxidized. This is always the definition of the absolute salinity expressed in g kg^{-1} . This definition is impossible to use for routine measures, and the international community adopted a method of measurement based on chloride, defined as the mass (g) of halogen contained in one kilogram of seawater, bromide and iodide ions being replaced by their equivalent amount of chloride. From 1902 to 1962, the following definition was used: $S=0.03+1.8050 \times \text{Cl}$ (in ‰), where Cl=chlorinity. From 1962 to 1969, the formula used was

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$S = 1.80655 \times Cl$, by using works on chlorinity, conductivity, salinity and density. From 1969 to 1978, the following formula was used: $S = 1.80655 \times 0.3285234 \times Ag$ (in %) to eliminate the chlorine variations linked to progress in the knowledge of atomic weights of Cl and Ag. Finally, a new definition was adopted in 1978, based on the measurement of a conductivity ratio, because during this time, as mentioned above, other measurement means were not accurate enough. Because a conductivity sensor does not measure the absolute salinity (S_a) as defined above, one introduced salinities calculated with the 'Practical Salinity Scale' of 1978 (PSS 78) (Perkin and Lewis, 1980). The practical salinity (symbol S) of a seawater sample is defined according to the ratio K_{15} between electrical conductivity (expressed in Siemens per meter, $S m^{-1}$) of a seawater sample at $15^\circ C$ and normal atmospheric pressure and the conductivity of a KCl solution in which the mass fraction is 0.0324356 at the same temperature and pressure. A value of K_{15} equal to 1 is, by definition, a practical salinity equal to 35 (1):

$$S = 0.0080 - 0.1692K_{15}^{1/2} + 25.38531K_{15} + 14.0941K_{15}^{3/2} - 7.0261K_{15}^2 + 2.7081K_{15}^{5/2} \quad (1)$$

S depends on conductivity, temperature and pressure. Algorithms to compute S involve 6 equations with 24 coefficients (see Appendix A). This definition raises some issues: first, seawaters that have the same conductivity have the same salinity, even if their composition and chlorinity are different. Non-electrolytes, such as $Si(OH)_4$, NO_3 or CO_2 , are not detected by the conductivity sensors, but they impact seawater physical properties. Jackett et al., (2006) estimated from studies of Millero and Leung (1976) and Fofonoff (1992) that

$$S_a = (1.0045 \pm 0.0005) S \quad (2)$$

The difference of $0.45 \pm 0.05\%$ results in an uncertainty of 0.16 ppt at $S=35$ so that it is possible to calibrate conductivity sensors to hold an uncertainty on S equal to 0.003. But, in the absolute, what is the meaning of this uncertainty? Moreover, the correlation between electrical conductivity and temperature is more than 80% (Lueck, 1990). This dependence added to the thermal anomaly of conductivity cells creates artifacts in the salinity computing, because it is difficult to align the response time of temperature and conductivity sensors. The order of magnitude of salinity errors increases to 0.017 in strong temperature gradients for Sea-Bird Electronics SBE 9, after application of a correction relation and suitable empirical coefficients to the measured conductivity, as shown recently (Mensah et al., 2009). To reduce the errors mentioned above, it is better to measure the refractive index of seawater. This property is directly related to density through the Lorentz-Lorenz relation (1881) and therefore to the absolute salinity. In 1990, Millard and Seaver (1990) showed that density calculations using refractive index measurements were four to five times more accurate than those based on conductivity. On the basis of recent experiments and developments (Malardé et al., 2009), we discuss how to optimize a refractometer implementation, taking advantage of recent technical advances in position sensors, and we compare its performance and dependence on environmental parameters with those of conductivity sensors.

3. Design of a PSD refractometer for practical salinity ranges

Refractive index n_m of a medium is the ratio between the speed of light in a vacuum (c) to its value (v) in the considered medium $n_m = c/v$. There are different approaches to measure the refractive index, such as fibre Bragg grating (Joseph Espejo and Dyer, 2007) or Brillouin effect (Nikes et al., 1996), surface plasmon sensor

(Matsubara et al., 1990), refractometer (Minato et al., 1989), or interferometer (Le Menn and Lotrian, 2001). Among these, the refractometer is the simplest and the most straightforward. Its accuracy depends on the ability to detect small beam deviations. It is intrinsically the natural device to measure refractive index (Fig. 1). The voltage supplied by the position sensor (PSD) is directly related to the seawater refractive index (n_{sea}) by the Snell-Descartes law (3), because the incidence angle (i) is fixed and the glass refractive index (n_{glass}) is known if one knows pressure and temperature

$$n_{glass} \times \sin(i) = n_{sea} \times \sin(r) \quad (3)$$

Other methods mentioned above are either too bulky (interferometer), not accurate enough (Brillouin, plasmon), or too sensitive to the environment (Bragg grating) to be used in-situ. For seawater, refractive index depends on salinity (S), temperature (T), pressure (p) and wavelength (λ). The difficulty is due to the fact that refractive index variation (δn_{sea}) is only 0.8% (Fig. 2) in the full range of ocean salinity from $S=0$ to $40 g kg^{-1}$. This means that to measure salinities with an accuracy of $10^{-3} g kg^{-1}$, it is required to measure the refractive index with an accuracy of 2×10^{-7} .

Such an accuracy was impossible to reach until the emergence in the early 2000s of the high-resolution 1D-Position Sensitive Device (PSD) [15], for which the ratio (Nb) of the sensor size (l_{PSD}) over the minimum detectable displacement (δP) is

$$Nb = \frac{l_{PSD}}{\delta P} \quad (4)$$

For example, the newly available PSD S3932 is 12 mm long with $0.3 \mu m$ position accuracy, providing an intrinsic resolution $Nb=40,000$. Dividing the index range variation (8×10^{-3}) by 40,000 samples provides an intrinsic refractive index accuracy of 2×10^{-7} , opening new ways for designing refractometers. As the full salinity range is about $40 g kg^{-1}$, the intrinsic resolution is $10^{-3} g kg^{-1} (40/40,000)$. With such a resolution, it is possible to create a new database two orders of magnitude better than the one used by Millard and Seaver to upgrade their algorithm. Furthermore, one should keep in mind that 40,000 sampling points are available. This enables a salinity resolution of $10^{-3} g kg^{-1}$ in the full salinity range. But in practice, in oceanographic applications, where the required range of salinity is two times lower, the measurement resolution can be $5 \times 10^{-4} g kg^{-1}$. This point becomes critical for a refractometer design. In practice, the salinity range (SR) should cover the sensor length. This new

Fig. 1. Refractive index sensor principle.

Fig. 2. Variation of refractive index versus salinity.

Fig. 3. Preferred embodiment.

condition allows one to define, for refractometers, an Absolute Salinity Resolution (ASR), which can be expressed as follows:

$$ASR = \frac{SR}{Nb} \quad (5)$$

In contrast to Fig. 1, refractometers are preferably made up of a dual glass–seawater–glass interface (Fig. 3). According to the Snell–Descartes laws (3), when the incidence angle (i) increases the refraction angle (r_1) increases, until the limit of total reflection.

It is thus desirable to design a sensor with the largest incidence angle to take advantage of the largest refractive angle variation (δr) for the smallest refractive index variation (δn_{sea}). The relationship relating δn_{sea} and δr is

$$\delta n_{sea} = \frac{n_{glass} \cos(r_1)}{\sin(2\theta)} \sqrt{1 - \left(\frac{n_{sea}}{n_{glass}} \cos(r_1)\right)^2} \delta r \quad (6)$$

Another free parameter is the propagation distance L . However, for compactness reasons (even if the optical beam can be folded), this length is constrained. For instance, to meet the required salinity range, the sensor should be located at distance L as short as possible. This results in a preferred embodiment for a refractometer, given in Fig. 3 with $i \approx 62^\circ$ (maximum incident angle for $n_{glass} \approx 1.5$) and L adjusted according to the required resolution δn_{sea} . The angular resolution can be written as

$$\delta r \approx \frac{\delta P}{L} \quad (7)$$

From Eqs. (6) and (7), refractive index resolution (δn_{sea}) can be written as

$$\delta n_{sea} = \frac{n_{glass} \cos(r_1)}{\sin(2\theta)} \sqrt{1 - \left(\frac{n_{sea}}{n_{glass}} \cos(r_1)\right)^2} \frac{\delta P}{L} \quad (8)$$

In practice δP is fixed and L can be adjusted. For example, with $\delta n_{sea} = 2 \times 10^{-7}$ (required accuracy), $\delta P = 0.3 \mu m$ (PSD accuracy), $n_{sea} = 1.335$, $n_{glass} = 1.51$ and $i = 62^\circ$. From Eqs. (6) and (7), $\delta r = 3 \times 10^{-6}$ rad (0.6 arcsec) and $L = 100$ mm. At this distance, the laser beam moves 12 mm, covering the full range of salinity (0–40 g kg⁻¹). In conclusion, the design depends mainly on the salinity required, accuracy and sensor resolution. As we noted at the beginning of this section, the required salinity range does not necessarily cover 40 g kg⁻¹. Depending on the considered range, we should find a trade-off between the sensor length and its resolution. From Eqs. (4), (5) and (7), we can derive the fundamental angular resolution

$$\delta r = \frac{l_{PSD} \times ASR}{SR \times L} \quad (9)$$

$$OSA = \sqrt{ASR^2 + \left(\frac{\partial S}{\partial n_{glass}} \times \frac{\partial n_{glass}}{\partial T} \delta T\right)^2 + \left(\frac{\partial S}{\partial \lambda} \times \frac{\partial \lambda}{\partial T} \delta T\right)^2 + \left(\frac{\partial S}{\partial L} \times \frac{\partial L}{\partial T} \delta T\right)^2 + \left(\frac{\partial S}{\partial n_{glass}} \times \frac{\partial n_{glass}}{\partial P} \delta P\right)^2} \quad (10)$$

For example, to improve the salinity accuracy, if the required salinity range (SR) is two times lower, we have several possibilities: either double the prism path L (not interesting),

Table 1
Refractometer design improvement for three salinity ranges.

Salinity range (g kg ⁻¹)	Prism path (mm)	PSD size (mm) and (Nb)	Salinity resolution (g kg ⁻¹)
20	55	3 (30,000)	7×10^{-4}
30	66	6 (30,000)	10^{-3}
40	100	12 (40,000)	10^{-3}

use a PSD two times smaller, or use a PSD four times smaller with a prism path two times smaller. For three salinity ranges (20, 30 and 40 g kg⁻¹), Table 1 shows the optimized possible solutions, i.e. with available PSD, $L \leq 100$ mm and salinity resolution $\leq 10^{-3}$ g kg⁻¹.

If we now consider the refractometer behaving in real oceanic environments, the critical point is the impact of temperature (–2 to 40 °C) and pressure (0–600 bar) changes over the physical and geometrical parameters of the refractometer: glass refractive index (dn/dT and dn/dp), optical path length (dL/dT) and laser wavelength drift ($d\lambda/dT$). To minimize the impact of these parameters it is required to assess the dependence of the amplitude of their variations on the optical design as a function of wavelength, temperature and pressure. Temperature changes impact three opto-geometrical quantities: glass refractive index, laser diode wavelength and path length. Concerning dn/dT a solution consists in using the prism made of two half-prisms whose thermo-optical coefficients have the same value but opposite signs (for example, Schott glass K7 and NFK-51). This allows a reduction of the overall thermo-optical coefficient of the refractometer from 3×10^{-7} to 4×10^{-8} K⁻¹. Simulations performed with the optical software ZEMAX have shown that over the temperature range –2 to 40 °C, the sensor positioning error is about 0.03 μm (for a PSD), resulting in a salinity uncertainty of 10^{-4} g kg⁻¹. Temperature also causes the wavelength to drift. If the laser diode used in the sensor emits at 635 nm with a typical coefficient $d\lambda/dT = 0.2$ nm/°C, which corresponds to 8 nm drift over the required temperature range, simulations show a positioning error $\delta P_\lambda = 6 \mu m$. This error can be made electronically negligible (0.03 μm) if we know the temperature with an accuracy of 0.2 °C. Finally, temperature impacts the path length L . For an expansion coefficient equal to 12×10^{-6} K⁻¹ for the glass used, results in, for $L = 100$ mm, a positioning error $\delta P_L = 6 \mu m$. This means that, as for wavelength, corrections can be made electronically, and the error will be negligible if the temperature is known to 0.2 °C.

Pressure changes impact the refractive index with a coefficient $dn/dP = 4 \times 10^{-8}$ /dbar (Mahrt and Waldmann, 1988). If the pressure is known with an accuracy of 1 dbar, the added uncertainty on salinity is 2×10^{-4} . Therefore, conditions required to make the environment impact negligible are summarized in Table 2 with temperature range 0–40 °C, salinity range 0–40 g kg⁻¹, pressure range 0–6000 dbar, and $L = 100$ mm.

The final uncertainty (10) on the salinity measured by the sensor can be assessed by the quadratic sum of its intrinsic resolution and related uncertainties with respect to the environmental parameters summarized in Table 1 and given by the Overall Sensor Accuracy (OSA)

In this equation the critical term is related to pressure, since the accuracy of pressure sensors, in the range 0–6000 dbar, cannot be reduced much below 1 dbar. In our case $OSA = 1.02 \times 10^{-3}$ g

Table 2
Pressure and temperature required neglecting environment impact.

Variable parameters	Uncertainty on refractive index	Uncertainty on salinity (g kg^{-1})	Temperature required accuracy (available) ($^{\circ}\text{C}$)	Pressure required accuracy (available) (dbar)
$n_{\text{glass}}(f(T))$	2×10^{-8}	10^{-4}	Nothing (dual-prism)	
$\lambda(f(T))$	$< 10^{-9}$	$< 10^{-5}$	0.2 (0.003)	
$L(f(T))$		$< 10^{-5}$	0.2 (0.003)	
$n_{\text{glass}}(f(p))$	4×10^{-8}	2×10^{-5}		1 (1)

Fig. 4. Sensitivity to temperature of conductivity (dashed curve) and refractive index (solid curve) and its impact on salinity.

kg^{-1} . Our sensor's highly accurate refractive index values yield highly accurate salinity values. The obtained values can be directly introduced in the algorithm for computing the seawater absolute salinity. Therefore, it is useful to compare the intrinsic environmental dependence of this technique with conductivity sensors.

4. Conductivity and refractive index sensor behavior in-situ

Conductivity and refractive index sensors provide, after temperature and pressure corrections, respectively, the exact conductivity and refractive index values of the seawater sample. These values are the first inputs for salinity algorithms. To calculate salinity, additional data are required: temperature and pressure for conductivity and temperature, pressure and wavelength for refractive index. Concerning the environment dependence, we notice that wavelength dependence concerns only the refractometer but can be neglected if temperature is known to within 0.2°C . The most critical parameter is the temperature dependence of both sensors. Fig. 4 shows the dependence of these sensors to this parameter. Algorithms used are the PSS 78 (1) for conductivity and Seaver and Millard (Millard and Seaver, 1990) one for the refractive index (see Appendix B). Around the average salinity and temperature of the open ocean (34.78 g kg^{-1} and 4°C) Fig. 4 shows clearly that conductivity is ten times more sensitive to temperature than to refractive index. Whatever the requested accuracy of salinity, the conductivity sensor must be combined with a temperature sensor about an order of magnitude more accurate than needed for the refractometer. For example, if the required precision on salinity is $10^{-3} \text{ g kg}^{-1}$, it is necessary to know the temperature to $2 \times 10^{-2}^{\circ}\text{C}$ for the refractive index sensor and to $2 \times 10^{-3}^{\circ}\text{C}$ for the conductivity sensor.

Fig. 5. Sensitivity to pressure of conductivity (dashed curve) and refractive index (solid curve) and its impact on salinity.

Table 3
Refractive index and conductivity sensors: performance comparison for the same measured salinity.

Parameters	Sensor	
	Refractive index	Conductivity
Kind of measured salinity	Absolute	practical
Measurement uncertainty	0.0013	0.0030
Measurement accuracy	0.0023	0.0068
Correction on absolute salinity	No	0.16 g kg^{-1}
Requirement on temperature ($^{\circ}\text{C}$) for $S = 10^{-3} \text{ g kg}^{-1}$	2×10^{-2}	2×10^{-3}
Requirement on pressure (dbar) for $S = 10^{-3} \text{ g kg}^{-1}$	1.7	2
Protection against fouling	Chloride device	TBT device or paint

Concerning the pressure dependence (Fig. 5), refractive index sensor and conductivity sensor have almost identical sensitivities to pressure. To resolve salinity to $10^{-3} \text{ g kg}^{-1}$ pressure must be known to 1.8 dbar for the refractive index sensor and to 2 dbar for conductivity sensor.

In conclusion, refractive index sensors have several advantages over conductivity sensors. If we consider that the sensor set-up in salinity probes is provided with a thermometer accurate to 0.003°C and a pressure gauge accurate to 1 dbar, we can derive Table 3. We can also add that conductivity sensors need anti-fouling device or paints to be protected against shifts of their specifications caused by bio-fouling. The glass surfaces of the refractometer can be protected by other techniques like chloride devices, which are less toxic.

5. Conclusions

Until 1978, salinity measurements were performed mainly by chemists. With the PSS-78 it became the business of the electronics specialists. Would it now become the business of an optical scientist? Until now the lack of high-performance sensors for in-situ measurements of refractive indices limited the interest in such approaches. Emergence of high-resolution position sensors, such as PSD, makes such approaches possible, and recent results (Malardé et al. 2009) have been achieved approaching the performance of conductivity sensors in terms of measurement uncertainty, making it dependent only on the sensor being accessible to spatial resolution, this latter being limited only by

the accuracy needed mainly for pressure sensors ($\delta r < 0.1$ arcsec required 0.3 dbar and $3 \times 10^{-3} ^\circ\text{C}$). The substantial advantage of a high-resolution refractometer ($\delta r < 1$ arcsec), like the one we present here, is the index measurement directly related to the absolute salinity of the medium, which is the parameter that enters, or should enter, into oceanic models. The question that arises then is: how would it be possible to convert conductivity measurements into measurements of index, at the databases level and how would it be possible to relate the salinities measured by a refractometer to the salinities measured by conductivity sensors.

Appendix A

PSS 78 algorithm

p is expressed in dbar, T in $^\circ\text{C}$ and C in S/m

$$A1 = 0.0080, A2 = -0.1692, A3 = 25.3851, A4 = 14.0941, A5 = -7.0261, A6 = 2.7081B1 = 0.0005, B2 = -0.0056, B3 = -0.0066, B4 = -0.0375, B5 = 0.0636, B6 = -0.0144C1 = 0.676697, C2 = 2.00564E - 2, C3 = 1.104259E - 4, C4 = -6.9698E - 7, C5 = 1.0031E - 9D1 = 3.426E - 2, D2 = 4.464E - 4, D3 = 0.4215, D4 = -3.107E - 3E1 = 2.070E - 5, E2 = -6.370E - 10, E3 = 3.989E - 15$$

Probe:

$$R = \frac{C}{4.2914} R1 = C1 + (C2 + (C3 + (C4 + C5 \times T) \times T) \times T) \times T$$

$$RP = \frac{1 + ((E1 + (E2 + E3 \times p) \times p) \times p)}{(1 + (D1 + D2 \times T) \times T + (D3 + D4 \times T) \times R)} RT = \frac{R/R1}{RP}$$

Salinometer:

$$SRT = SQR(RT)B = B1 + (B2 + (B4 + B6 \times RT) \times RT) \times SRT + (B3 + B5 \times RT) \times RT$$

$$DS = B \times (T - 15) / (0.757 + 0.0162 \times T)$$

$$S = A1 + (A2 + (A4 + A6 \times RT) \times RT) \times SRT + (A3 + A5 \times RT) \times RT + DS$$

Appendix B

Seaver and Millard algorithm

p is expressed in dbar, T in $^\circ\text{C}$ and λ in μm .

$$N(T, p, S, \lambda) = N_I(T, \lambda) + N_{II}(T, \lambda, S) + N_{III}(p, T, \lambda) + N_{IV}(S, p, T)$$

$$N_I(T, \lambda) = 1.32807 - 5.28839E - 6 \times T - 3.07383E - 6 \times T^2 + 3.01247E - 8 \times T^3 - 2.08832E - 10 \times T^4$$

$$+ 2.80263E - 6 / \lambda^6 + 7.50197E - 6 / \lambda^4 - 0.00254717 / \lambda^2 + 0.0000105086 \times T \times \lambda$$

$$+ 2.12822E - 7 \times T^2 \times \lambda - 1.70588E - 9 \times T^3 \times \lambda - 0.00455368 \times \lambda^2 (S.D. = 1.2 \times 10^{-7})$$

$$N_{II}(T, \lambda, S) = 0.000190291 \times S - 7.39603E - 7 \times S \times T + 8.98185E - 9 \times S \times T^2 + 1.2788E - 10 \times S \times T^3$$

$$+ 2.42396E - 6 \times S / \lambda^2 - 3.58949E - 7 \times S \times T \times \lambda (S.D. = 4.6 \times 10^{-6})$$

$$N_{III}(p, T, \lambda) = 1.58684E - 6 \times p - 1.57407E - 11 \times p^2 - 9.48345E - 9 \times p \times T + 1.01003E - 10 \times p \times T^2$$

$$+ 5.80852E - 15 \times p \times T^2 + 1.07121E - 8 \times p / \lambda^2 (S.D. = 2.65 \times 10^{-5})$$

$$N_{IV}(S, p, T) = -1.11775E - 9 \times p \times S + 5.73113E - 11 \times p \times S \times T - 1.54605E - 12 \times p \times S \times T^2$$

$$(S.D. = 1.97 \times 10^{-5})$$

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