

Appendix E:

Algorithm for calculating Practical Salinity

E.1 Calculation of Practical Salinity in terms of K_{15}

Practical salinity S_p is defined on the Practical Salinity Scale of 1978 (Unesco (1981, 1983)) in terms of the conductivity ratio K_{15} which is the electrical conductivity of the sample at temperature $t_{68} = 15^\circ\text{C}$ and pressure equal to one standard atmosphere ($p = 0$ dbar and absolute pressure P equal to 101 325 Pa), divided by the conductivity of a standard potassium chloride (KCl) solution at the same temperature and pressure. The mass fraction of KCl in the standard solution is 32.4356×10^{-3} (mass of KCl per mass of solution). When $K_{15} = 1$, the Practical Salinity S_p is by definition 35. Note that Practical Salinity is a unit-less quantity. Though sometimes convenient, it is technically incorrect to quote Practical Salinity in “psu”; rather it should be quoted as a certain Practical Salinity “on the Practical Salinity Scale PSS-78”. When K_{15} is not unity, S_p and K_{15} are related by (Unesco, 1981, 1983) the PSS-78 equation

$$S_p = \sum_{i=0}^5 a_i (K_{15})^{i/2} \quad \text{where} \quad K_{15} = \frac{C(S_p, t_{68} = 15^\circ\text{C}, 0)}{C(35, t_{68} = 15^\circ\text{C}, 0)}, \quad (\text{E.1.1})$$

and the coefficients a_i are given in the following table. Note that the sum of the six a_i coefficients is precisely 35, while the sum of the six b_i coefficients is precisely zero. Equation (E.1.1) is valid in the range $2 < S_p < 42$.

i	a_i	b_i	c_i	d_i	e_i
0	0.0080	0.0005	6.766097×10^{-1}		
1	- 0.1692	- 0.0056	2.00564×10^{-2}	3.426×10^{-2}	2.070×10^{-5}
2	25.3851	- 0.0066	1.104259×10^{-4}	4.464×10^{-4}	$- 6.370 \times 10^{-10}$
3	14.0941	- 0.0375	$- 6.9698 \times 10^{-7}$	4.215×10^{-1}	3.989×10^{-15}
4	- 7.0261	0.0636	1.0031×10^{-9}	$- 3.107 \times 10^{-3}$	
5	2.7081	- 0.0144			

E.2 Calculation of Practical Salinity at oceanographic temperature and pressure

The following formulae from Unesco (1983) are valid over the range $-2^\circ\text{C} \leq t \leq 35^\circ\text{C}$ and $0 \leq p \leq 10\,000$ dbar. Measurements of salinity in the field generally measure the conductivity ratio R

$$R = \frac{C(S_p, t_{68}, p)}{C(35, t_{68} = 15^\circ\text{C}, 0)} = \frac{C(S_p, t_{68}, p)}{C(S_p, t_{68}, 0)} \frac{C(S_p, t_{68}, 0)}{C(35, t_{68}, 0)} \frac{C(35, t_{68}, 0)}{C(35, t_{68} = 15^\circ\text{C}, 0)} \quad (\text{E.2.1})$$

which has been expressed in (E.2.1) as the product of three factors, which are labeled R_p , R_t and r_t as follows

$$R = \frac{C(S_p, t_{68}, p)}{C(35, t_{68} = 15^\circ\text{C}, 0)} = R_p R_t r_t. \quad (\text{E.2.2})$$

The last factor r_t has been fitted to experimental data as the polynomial in temperature (t_{68})

$$r_t = \sum_{i=0}^4 c_i (t_{68} / ^\circ\text{C})^i \quad (\text{E.2.3})$$

and the factor R_p has been fitted to experimental data as a function of p , t_{68} and R as

$$R_p = 1 + \frac{\sum_{i=1}^3 e_i p^i}{1 + d_1 (t_{68} / ^\circ\text{C}) + d_2 (t_{68} / ^\circ\text{C})^2 + R [d_3 + d_4 (t_{68} / ^\circ\text{C})]} \quad (\text{E.2.4})$$

Thus for any sample measurement of R it is possible to evaluate r_t and R_p and hence calculate

$$R_t = \frac{R}{R_p r_t} \quad (\text{E.2.5})$$

At a temperature of $t_{68}=15^\circ\text{C}$, R_t is simply K_{15} and Practical Salinity S_p can be determined from (E.1.1). For temperatures other than $t_{68}=15^\circ\text{C}$, Practical Salinity S_p is given by the following function of R_t with $k = 0.0162$,

$$S_p = \sum_{i=0}^5 a_i (R_t)^{i/2} + \frac{(t_{68} / ^\circ\text{C} - 15)}{[1 + k (t_{68} / ^\circ\text{C} - 15)]} \sum_{i=0}^5 b_i (R_t)^{i/2} \quad (\text{E.2.6})$$

Equations (E.1.1) and (E.2.6) are valid only in the range $2 < S_p < 42$. Outside this range S_p can be determined by dilution with pure water or evaporation of a seawater sample. Practical Salinity S_p can also be estimated from the extensions of the Practical Salinity Scale proposed by Hill *et al.* (1986) for $0 < S_p < 2$ and by Poisson and Gadhoumi (1993) for $42 < S_p < 50$. The values of Practical Salinity S_p estimated in this manner may then be used in Eqn. (2.4.1), namely $S_R \approx u_{PS} S_p$ to estimate Reference Salinity S_R .

The temperatures in Eqns. (E.2.1) to (E.2.6) are all on the IPTS-68 scale. The functions and coefficients have not been refitted to ITS-90 temperatures. Therefore in order to calculate Practical Salinity from conductivity ratio at a measured pressure and t_{90} temperature, it is necessary first to convert the temperature to t_{68} using $t_{68} = 1.00024 t_{90}$ as described Eqn. (A.1.3) of appendix A.1. This is done as the first line of the computer code described in the GSW software library (appendix N). Further remarks on the implications of the different temperature scales on the definition and calculation of Practical Salinity can be found in appendix E.4 below.

E.3 Calculation of conductivity ratio R for a given Practical Salinity

When Practical Salinity is known and one wants to deduce the conductivity ratio R associated with this value of Practical Salinity at a given temperature, a Newton-Raphson iterative inversion of Eqn. (E.2.6) is first performed to evaluate R_t . Because r_t is a function only of temperature, at this stage both R_t and r_t are known so that Eqn. (E.2.4) can be written as a quadratic in R with known coefficients which is solved to yield R . This procedure is outlined in more detail in Unesco (1983) and is also available in the GSW algorithm library as the function `gsw_cndr_from_SP`. Note that this iterative inverse procedure is done in terms of t_{68} ; the code accepts t_{90} as the input and immediately converts this to a t_{68} temperature before performing the above iterative procedure. The iteration is stopped when the Practical Salinity corresponding the output conductivity ratio differs from the input Practical Salinity by less than 10^{-10} .

E.4 Evaluating Practical Salinity using ITS-90 temperatures

We first consider the consequence of the change from IPTS-68 to ITS-90 for the definition of Practical Salinity as a function of K_{15} and the defining mass fraction of KCl. Suppose Practical Salinity S_p were to be evaluated using the polynomial (E.1.1) but using K_{15-90} instead of K_{15} , where K_{15-90} is defined

$$K_{15-90} = \frac{C(S_p, t_{90} = 15^\circ\text{C}, 0)}{C(35, t_{90} = 15^\circ\text{C}, 0)}. \quad (\text{E.4.1})$$

The magnitude of the difference $K_{15-90} - K_{15}$ can be calculated and is found to be less than 6.8×10^{-7} everywhere in the range $2 < S_p < 42$. Further calculation shows that $\partial S_p / \partial K_{15} < 41$ everywhere in the valid range of Practical Salinity, so that the consequence of using K_{15-90} in (E.1.1) instead of K_{15} incurs a change in Practical Salinity of less than 3×10^{-5} . This is nearly two orders of magnitude below the measurement accuracy of a sample, and an order of magnitude smaller than the error caused by the uncertainty in the definition of the mass fraction of KCl. If all the original measurements that form the basis of the Practical Salinity Scale were converted to ITS-90, and the analysis repeated to determine the appropriate mass fraction to give the required conductivity at $t_{90} = 15^\circ\text{C}$, the same mass fraction 32.4356×10^{-3} would be derived.

Notwithstanding the insensitivity of this conductivity ratio to such a small temperature difference, following Millero *et al.* (2008a) the definition of Practical Salinity can be restated with reference to the ITS-90 scale by noting that the K_{15} ratio in Eqn. (E.1.1) can equivalently refer to a ratio of conductivities at $t_{90} = 14.996^\circ\text{C}$.

The fact that the conductivity ratio R_t is rather weakly dependent on the temperature at which the ratio is determined is important for the practical use of bench salinometers. It is important that samples and seawater standards should be run at the same temperature, stable at order 1 mK. This is achieved by the use of a large water bath in the instrument. However, it is not critical to know the stable bath temperature to any better than 10 or 20 mK.

The ratios R_p , R_t and r_t that underlie the temperature-dependent expression (E.2.6) for Practical Salinity are more sensitive to the difference between IPTS-68 and ITS-90 temperatures and this is the reason why we recommend retaining the original computer algorithms for these ratios, and to simply convert the input temperature (which these days is on the ITS-90 temperature scale) in to the corresponding IPTS-68 temperature using $t_{68} = 1.00024 t_{90}$ as the first operation in the software. Thereafter the software proceeds according to (E.2.1) – (E.2.6).

E.5 Towards SI-traceability of the measurement procedure for Practical Salinity and Absolute Salinity

The observation of climate change taking place in the world ocean on a global scale over decades or centuries requires measurement techniques that permit the highest accuracy currently available, long-term stability and world-wide comparability of the measured values. The highest reliability for this purpose can be ensured only by traceability of these measurement results to the primary standards of the International System of Units (SI), supported by the National Metrological Institutes such as the NIST (National Institute of Standards and Technology) in the US, the NPL (National Physical Laboratory) in the UK, or the PTB (Physikalisch-Technische Bundesanstalt) in Germany.

In order to compute the thermodynamic properties of a seawater sample with standard composition, three independent parameters must be measured. Since the introduction of the Practical Salinity Scale of 1978 as an international standard for oceanography, these three properties have been electrolytic conductivity, temperature and

pressure, from which salinity, density and other properties are computed in turn by standard algorithms. The traceability of temperature and pressure measurement results, for example by CTD sensors, is ensured due to established calibration procedures carried out by the manufacturer or other laboratories and will not be considered here any further.

The observation of the ocean's salinity is a more complicated task (Millero *et al.* (2008a)). Even though over the last century different and permanently improved methods were developed and introduced in oceanography, traceability of salinity measurement results to SI units has not yet been achieved (Seitz *et al.* 2008 and Seitz *et al.* (2010b)). This implies the risk that readings taken today may possess an enlarged uncertainty when being compared with observations taken a hundred years from now, a circumstance that will reduce the accuracy of long-term trend analyses performed in the future.

A quantity, quite generally, is a "property of a phenomenon, body or substance, where the property has a magnitude that can be expressed as a number" (ISO/IEC, 2007). The process to obtain this number is called measurement. The value of the indicated number (the quantity value) is determined by a calibration of the measuring system with a reference having a known quantity value of the same kind. In turn, the quantity value of the reference is assigned in a superior measurement procedure, which is likewise calibrated with a reference and so on. This calibration hierarchy ends in a primary reference procedure used to assign a quantity value and a unit to a primary standard for that kind of quantity. Thus, the unit of a measured quantity value expresses its link (its metrological traceability) to the quantity value of the corresponding primary standard. Obviously, quantity values measured at different times or locations, by different persons with different devices or methods can be compared with each other only if they are linked to the same reference standard, whose corresponding quantity value must be reproducible with a high degree of reliability.

Concerning comparability of measured quantity values a second aspect is of importance. The quantity value of a primary standard can only be realised with an inevitable uncertainty. The same holds for every measurement and calibration. A measurement result therefore always has to indicate the measured quantity value and its uncertainty. Obviously, the latter increases with every calibration step down the calibration hierarchy. Measured quantity values can evidently only be assumed equivalent if their difference is smaller than their measurement uncertainty (compatibility). On the other hand they can only be assumed reliably different, if the difference is larger than the uncertainty.

To ensure comparability in practice, the International System of Units (SI) was established. National Metrological Institutes (NMIs) have developed primary reference procedures to realise the SI units in the form of primary standards. Extensive (ongoing) efforts are made to link these units to fundamental and physical constants in order to achieve the highest degree of reproducibility. Moreover, the NMIs periodically conduct international comparison measurements under the umbrella of the International Bureau of Weights and Measures, in order to ensure the compatibility of the quantity values of national standards.

PSS-78, and similarly the new Reference-Composition Salinity Scale (Millero *et al.* (2008a)), compute the salinity value from a measured conductivity ratio with respect to the K_{15} conductivity ratio of IAPSO Standard Seawater (SSW, Culkin and Ridout (1998) and Bacon *et al.* (2007)), which plays the role of a primary standard. The production procedure of IAPSO Standard Seawater, and in particular the adjustment of its conductivity to that of a potassium chloride (KCl) solution of definite purity and the corresponding assignment of the K_{15} ratio, can be seen as a primary reference procedure. However both of these solutions are artefacts lying outside the SI system; they are not subject to regular international inter-comparisons; their sufficiently precise replicability by arbitrary

independent laboratories is neither known nor even granted. A slow drift of artefact properties cannot rigorously be excluded, similar in principle to the “evaporation” of mass from the kilogram prototype stored in Paris. It is impossible to foresee effects that might affect the conductivity of SSW solution one day. Thus, with respect to decadal or century time scales, there is an uncertainty of its K_{15} ratio, which a priori can not be quantified and puts long term comparability of salinity measurement results at risk.

This fundamental problem, which is related to any artificial reference standard, can, at least in principle, be avoided if the conductivity of seawater is measured traceable to primary SI standards (“absolute” conductivity) rather than relying on a conductivity ratio. Unfortunately the related uncertainty of absolute conductivity measurements with present-day state-of-the-art technology is one order of magnitude larger than that of the relative measurements presently used for the ocean observation system (Seitz *et al.* (2008)).

A way out of this practical dilemma is the measurement of a different seawater quantity that is traceable to SI standards and possesses the demanded small uncertainty, and from which the salinity can be computed via an empirical relation that is very precisely known (Seitz *et al.* (2010b)). Among the potential candidates for this purpose are the sound speed, the refractive index, chemical analysis (e.g. by mass spectroscopy) of the sea-salt constituents, in particular chlorine, and direct density measurements. The latter has three important advantages, i) SI-traceable density measurements of seawater can be carried out with a relative uncertainty of 1 ppm (Wolf (2008)), which perfectly meets the needs of ocean observation, ii) a relation exists between density and the Absolute Salinity of seawater is available with a relative uncertainty of 4 ppm in the form of the TEOS-10 Gibbs function, iii) the measurand, density, is of immediate relevance for oceanography, in contrast to other options.

It is important to note that the actual measuring procedure for a quantity value is irrelevant for its traceability. To measure the weight of a person, a mass balance can be used, a spring or a magnetic coil; it is the quantity value that is traceable, not the method to achieve this value. The method in use is not intrinsically important except in so far as it is responsible for the uncertainty of the quantity value. Hence, we may measure the density of seawater with a CTD conductivity sensor, provided this sensor is properly calibrated with respect to an SI-traceable density reference standard. In practice, this will mean that the sensor calibration in oceanographic labs must be done with standard seawater samples of certified density rather than certified Practical Salinity. The density value returned from the CTD reading at sea is then converted into an Absolute Salinity value by means of the equation of state of seawater, and eventually into a Practical Salinity number for storage in data centres. The latter step may include some modification regarding local sea salt composition anomalies. Storing a salinity value rather than the related density reading has the advantage of conservativity with respect to dilution or changes of temperature or pressure.

This conceptual proposal of WG127 is still immature and needs to be worked out in more detail in the following years. Although it may imply only minor changes in the practical use of a CTD or similar devices, the new concept is very promising regarding the long-term reliability of observations made in the near future for climatic trend analyses to be performed by the coming generations. An immediate consequence of this proposal is to have the density (at a given temperature and pressure) of several samples of each batch of IAPSO Standard Seawater measured when they are produced and have these densities made available as reference values for each batch.