

The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale

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Abstract

Fundamental determinations of the physical properties of seawater have previously been made for Atlantic surface waters, referred to as “Standard Seawater”. In this paper a Reference Composition consisting of the major components of Atlantic surface seawater is determined using these earlier analytical measurements. The stoichiometry of sea salt introduced here is thus based on the most accurate prior determination of the composition, adjusted to achieve charge balance and making use of the 2005 atomic weights. Reference Seawater is defined as any seawater that has the Reference Composition and a new Reference-Composition Salinity S_R is defined to provide the best available estimate of the Absolute Salinity of both Reference Seawater and the Standard Seawater that was used in the measurements of the physical properties. From a practical point of view, the value of S_R can be related to the Practical Salinity S by $S_R = (35.16504/35) \text{ g kg}^{-1} \times S$. Reference Seawater that has been “normalized” to a Practical Salinity of 35 has a Reference-Composition Salinity of exactly $S_R = 35.16504 \text{ g kg}^{-1}$.

The new independent salinity variable S_R is intended to be used as the concentration variable for future thermodynamic functions of seawater, as an SI-based extension of Practical Salinity, as a reference for natural seawater composition anomalies, as the currently best estimate for Absolute Salinity of IAPSO Standard Seawater, and as a theoretical model for the electrolyte mixture “seawater”.

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1. Introduction

The idea that the chemical compositions of seawater samples from different parts of the world

ocean are very similar dates back to about 1820 when Alexander Marcet made suggestions of this nature based on rather limited observations and rather inaccurate analysis by today’s standards. Subsequent work supported this idea and resulted in the introduction of the concept of salinity. This concept has had a major impact on oceanographic measurements since many ocean properties can be

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represented as a function of just the salinity, temperature and pressure of a seawater sample. Although the Marcet principle is a good approximation, it is only an approximation and this fact has led to different and sometimes inconsistent approaches and concepts for the practical and theoretical description of seawater properties. In rather simplified pictures, we briefly discuss the evolution of related scales and standards to explain the reasoning and the aim of this paper.

Defining arbitrarily as the “Standard Seawater” certain samples taken from the North Atlantic surface water in a specific region, as proposed first by Martin Knudsen at the international conference for the exploration of the sea held in Stockholm 1899 (Knudsen, 1903), it can be assumed that the chemical composition of all these samples is practically identical, even though the composition is not known in detail. By laboratory experiments, various properties of these samples were studied quantitatively in the form of accurate “fundamental determinations”, carried out mainly in the 1960s and 1970s. In particular, among these properties were chlorinity, Cl ; electrical conductivity, C ; density, ρ (mentioned here as a representative for all thermodynamic properties like heat capacity, sound speed, etc.), and the concentrations of the major sea salt constituents in the form of their mass fractions, w , in grams of solute per kilogram of solution. At a given temperature t and pressure p , relations between seawater properties could be derived from these data and presented in the form of tables or empirical functions, like the equations of state $\rho(Cl, t, p)$ or $\rho(C, t, p)$, Fig. 1.

A special role has been played by the Absolute Salinity S_A defined as the mass fraction of dissolved material in seawater. A precise direct experimental determination of S_A is practically impossible. However, the principle of constant relative proportions in combination with mass conservation of the chemical constituents guarantees that the Absolute Salinity of Standard Seawater is a multiple of the chlorinity (Cl) of Standard Seawater, $S_A = \alpha \times Cl$, where chlorinity is proportional to the mass fraction of chlorine (Cl) as discussed in Section 3, and the factor α is just a constant number, independent of temperature, pressure and chlorinity. An important distinction between salinity and chlorinity is that chlorinity can be accurately measured using standard analytical techniques while even today this is not true for salinity. Marcet’s principle together with chlorinity measurements thus provided a

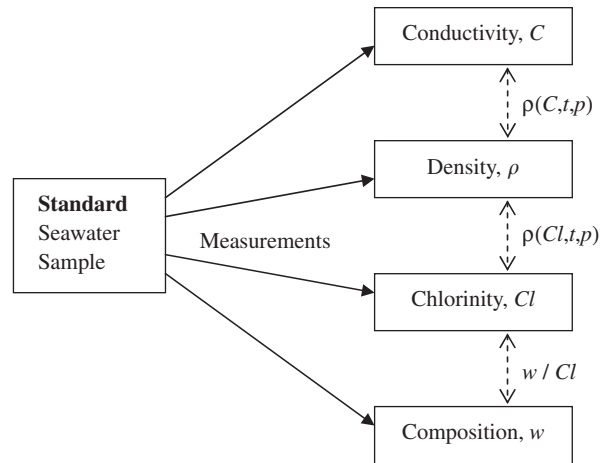


Fig. 1. Properties derived experimentally from Standard Seawater samples allowed the mathematical construction of quantitative relations between the properties such as the equation of state of seawater.

relatively simple determination of salinity for more than a century. One may say that S_A expresses the same information as Cl for Standard Seawater, although in terms of a different “concentration unit”.

Historically, the factor α has been specified to ensure consistency at $S = 35$ with the Knudsen equation for salinity, which was based on salinity estimates obtained via the evaporation of seawater. This approach has ignored a known significant systematic error in Knudsen’s equation, in order to ensure continuity of the tables and standards. Regardless of this questionable rationale, some official standards were formulated in terms of “salinity” rather than chlorinity, with the consequence that a confusing variety of salinity notions arose, like “Absolute Salinity”, “evaporation salinity”, “conductivity salinity”, “Practical Salinity”, etc. Absolute Salinity is in fact the most relevant concentration measure for most purposes but it demands a proper definition and reconsideration of the value of α used to convert between chlorinity and Absolute Salinity for Standard Seawater. In this paper, we propose a new value of this constant (see Eq. (6.3)) together with another representation of salinity, the “Reference-Composition Salinity”, as the best current approximation for the Absolute Salinity of Standard Seawater.

Chlorinity is not the only quantity that has been used as a ‘standard’ measure of salinity; conductivity has also served this purpose. The two approaches are essentially equivalent for Standard Seawater

(Millero et al., 1977), but the resulting values for derived quantities such as densities are not precisely consistent when composition anomalies are present, as for example in the Baltic Sea (Millero and Kremling, 1976). Thus, prior to 1978, two incompatible definitions of salinity were in use, one based on the chlorinity, the other one on the conductivity of seawater (Unesco, 1981a). This fact complicated the history of salinity measurements and caused severe problems in the international cooperation of oceanographers and the comparability of their results, Fig. 2.

As stated by the joint panel on oceanographic tables and standards (JPOTS) at its meeting in September 1980 in Sidney, Canada, a new, single salinity definition had become necessary to resolve the existing ambiguity associated with the chlorinity–salinity–conductivity relationships and to supersede both the predecessor scales. This resulted in the introduction in 1978 of the Practical Salinity Scale, PSS-78, which is based on a carefully determined salinity–conductivity relationship. Subsequently, chlorinity has been regarded as a separate, independent variable in describing the properties of seawater (Unesco, 1981a,b), Fig. 3.

In the formulation of PSS-78, “the Practical Salinity, symbol S , of a sample of seawater, is defined in terms of the ratio K_{15} of the electrical conductivity of the seawater sample at the temperature of 15 °C and the pressure of one standard atmosphere, to that of a potassium chloride (KCl) solution, in which the mass fraction is 32.4356×10^{-3} , at the same temperature and pressure. The K_{15} value exactly equal to 1 corresponds,

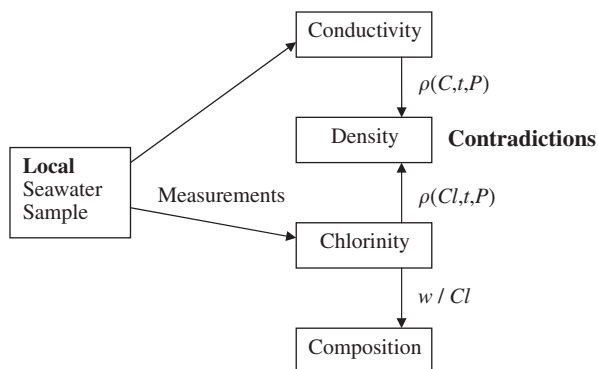


Fig. 2. Before 1978, the densities of local seawater samples determined from either conductivity or chlorinity, calculated from the equation of state of Standard Seawater, could produce inconsistent results when the local seawater properties deviated from those of Standard Seawater.

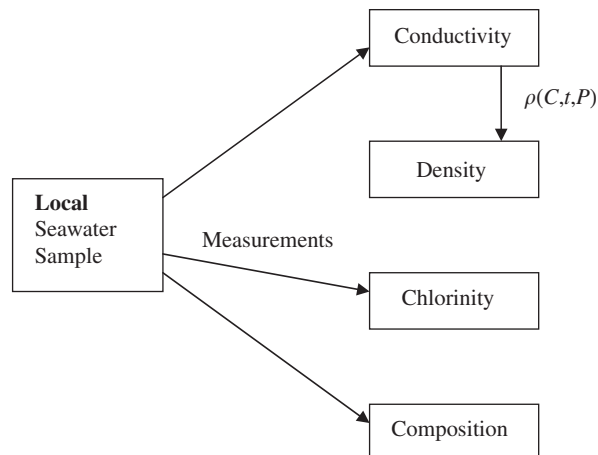


Fig. 3. Since the definition of PSS-78, conductivity is the single standard property used to estimate thermodynamic properties (such as density) of seawater samples taken from arbitrary locations. Chlorinity is regarded as an independent property of lower significance, this way resolving the conflict in Fig. 2.

by definition, to a Practical Salinity exactly equal to 35” (Unesco 1981a,b). Seawater with a Practical Salinity of 35 has provided a benchmark in past discussions of salinity and we use it here in order to maintain consistency with this generally accepted oceanographic standard. It is thus useful to introduce a term that can be used to conveniently refer to this benchmark.

Definition 1. The term *KCl-normalized seawater* is used to describe any seawater sample that has the same specific electric conductivity as a solution of potassium chloride (KCl) in pure water with the KCl mass fraction of $32.4356 \text{ g kg}^{-1}$ when both are at the ITS-90 temperature $t = 14.996 \text{ °C}$ and one standard atmosphere pressure, $P = 101\,325 \text{ Pa}$. KCl refers to the normal isotopic abundances of potassium and chlorine as described by the International Union of Pure and Applied Chemistry (IUPAC, 2005). Pure water is taken here as Vienna Standard Mean Ocean Water (VSMOW), as described in the 2001 Guideline of the International Association for the Properties of Water and Steam (IAPWS, 2001).

Note that ‘KCl-normalized seawater’ (or ‘normalized seawater’ for short) does not describe any particular type or chemical composition of seawater. Rather, it provides a convenient way to refer to any seawater sample that has a Practical Salinity of 35. Any sample of regional seawater, whether it is of standard composition or anomalous, can in

principle be ‘normalized’ with respect to the KCl conductivity reference by adding or removing pure water and adjusting its temperature and pressure to the conditions given in Definition 1, provided that these adjustments can be conducted without any further exchange of matter like precipitation or degassing from the solution.

The temperature 14.996 °C on the ITS-90 scale that appears in Definition 1 corresponds to 15 °C on the IPTS-68 scale, and is rounded to integer millikelvins. At this temperature, the conductivity ratio between a seawater sample and the KCl standard is rather insensitive to temperature changes so that even the use of $t = 15$ °C rather than $t = 14.996$ °C would result in a change in salinity that is well within experimental uncertainty (Brian King, personal communications).

The concentration of the potassium chloride solution used in the definition of Practical Salinity (and in the definition of normalized seawater) was determined such that at 15 °C on the IPTS-68 temperature scale the conductivity ratio is unity with respect to North Atlantic surface seawater with a salinity of 35‰ on the old chlorinity-based salinity scale. This choice ensured continuity of that salinity with the previous scale. The temperature of 15 °C in this definition refers to the International Practical Temperature Scale of 1968, IPTS-68, corresponding to 14.996 °C in the currently valid International Temperature Scale of 1990, ITS-90 (Rusby, 1991). One standard atmosphere is 101 325 Pa in current SI units (ISO, 1993a). Practical Salinity is specified as a dimensionless quantity omitting units or a designator—a decision which triggered a controversial discussion from the beginning (Unesco, 1986) that continues to this day. The number S enters as an independent variable into various subsequent formulas for the computation of thermodynamic seawater properties, such as the 1980 International Equation of State of Seawater, EOS-80 (Millero et al., 1980; Millero and Poisson, 1981; Fofonoff and Millard, 1983), or the recent Gibbs function formulation (Feistel, 2003).

Practical Salinity must be clearly distinguished from Absolute Salinity, symbol S_A , which is defined as the ratio of the mass of dissolved material in seawater to the total mass of seawater (Unesco, 1985). In practice, this quantity cannot be measured directly and a Practical Salinity is defined for reporting oceanographic observations (Unesco, 1981a, b). This definition leaves open the question of what exactly “dissolved material” is. If for

example CO_2 is dissolved in water, a chemical equilibrium between the different compounds H_2O , CO_2 , H_2CO_3 and HCO_3^- will establish in the solution, depending on temperature and pressure. “Dissolved material”, however, is thought of as being a conservative amount of substance, independent of temperature and pressure, and distinct from the solvent. The salinity definition by an International Commission in 1902 was more specific in this respect, but too impractical for a regular application (Forch et al., 1902; Sverdrup et al., 1942; Lyman, 1969).

The primary aim of this paper is to define a new salinity variable, S_R , called the Reference-Composition Salinity or Reference Salinity for short. This Reference Salinity provides the means to more accurately estimate the Absolute Salinity S_A of a local seawater sample. The relationship between the Reference Salinity and other properties of seawater (such as Practical Salinity and chlorinity) will be derived for surface Atlantic seawater which was used to determine the Practical Salinity and the physical chemical properties of Standard Seawater. The exact chemical composition of real seawater is unknown at the present time, but it is possible to determine the stoichiometry of the reference sea salt using the latest atomic weights and best estimates of the major components. This approach results in the definition of a Reference Composition for seawater. If a seawater sample actually has this Reference Composition then its Reference Salinity is the best current estimate of its Absolute Salinity. For a more general local sample whose composition differs from the Reference Composition, its Reference Salinity can still be calculated as an estimate of its Absolute Salinity, but it may be desirable to determine an additional salinity correction to provide a better estimate of S_A . The largest such corrections would be based on measurements of changes in the carbonate system and the addition of CaCO_3 , CO_2 and nutrients from the oxidation of plant material. In this paper we concentrate on the derivation of the Reference Composition and Reference Salinity. The possibility of determining a correction for the Absolute Salinity is discussed conceptually in Section 7 but any practical suggestions for calculating the salinity and density corrections to account for variations in composition are beyond the scope of this paper.

An operational or practical definition of Reference Salinity is illustrated in the upper right-hand two boxes of Fig. 4. The Practical Salinity S is first

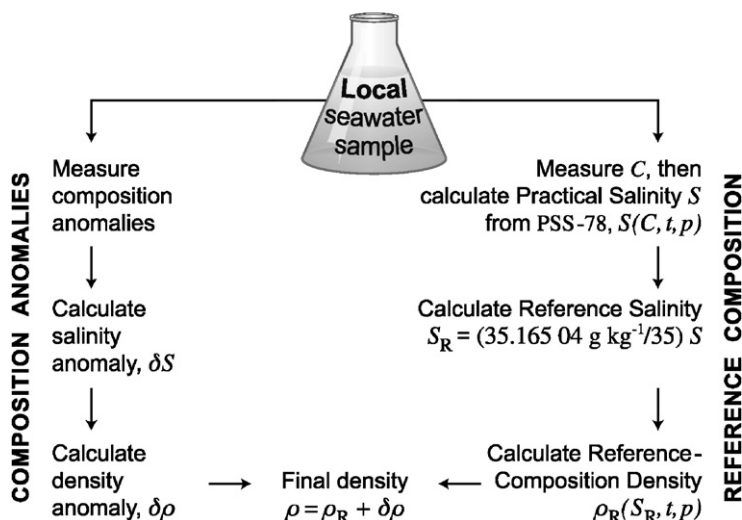


Fig. 4. The right-hand part of this diagram summarizes a *practical* version of the definition of the Reference Salinity and thereby the Reference Composition density $\rho_R(S_R, t, p)$. The calculations on the right-hand side treat the local sample as though it has Reference Composition. If supplementary measurements exist from which the deviation of the dissolved components from the Reference Composition can be estimated, the left-hand side of the diagram can be used to refine the estimate of the density of the local seawater sample.

calculated from the *in situ* temperature, pressure and conductivity of the seawater parcel. The practical definition of the Reference Salinity of the local seawater sample is then determined from the Practical Salinity according to the simple formula $S_R = (35.16504/35) \text{ g kg}^{-1} \times S$. This practical definition will suffice for most purposes, but we note that it is only defined over the salinity range where the Practical Salinity is defined. This shortcoming will be avoided in the strict definition given in Section 5.

The value of S_R can be used in theoretical and chemical models or experiments with artificial seawater. The main reasons for introducing S_R are:

- (1) The definition of Practical Salinity S on the PSS-78 scale is separate from the system of SI units (BIPM, 2006). Reference Salinity can be expressed in the unit (g kg^{-1}) , as a measure of Absolute Salinity. This approach could terminate the ongoing controversies in the oceanographic literature about the use of “psu” or “pss” and make research papers more readable to the outside scientific community and consistent with SI.
- (2) The freshwater mass fraction of seawater is not $(1-0.001S)$. Rather, it is $(1-0.001S_A/(\text{g kg}^{-1}))$, where S_A is the Absolute Salinity, defined as the mass fraction of dissolved material in seawater. The values of $S_A/(\text{g kg}^{-1})$ and S are known to differ by about 0.5%. There seems to be no good

reason for continuing to ignore this known difference, e.g., in ocean models.

- (3) PSS-78 is limited to the salinity range 2–42. For a smooth crossover on one side to pure water, and on the other side to concentrated brines up to saturation, as e.g., encountered in sea ice at very low temperatures, salinities beyond these limits need to be defined. While this poses a challenge for S , it is trivial for S_R .
- (4) The theoretical Debye–Hückel limiting laws of seawater behavior at low salinities, used for example in the determination of the Gibbs function of seawater, can only be computed from a chemical composition model, which is available for S_R but not for S .
- (5) For artificial seawater of Reference Composition, S_R has a fixed relation to chlorinity, independent of conductivity, salinity, temperature, or pressure.
- (6) The next largest improvement in the equation of state of seawater will come from incorporating the variation in the composition of seawater. Stoichiometric anomalies can be specified accurately relative to Reference Salinity with its known salt composition, but only uncertainly with respect to IAPSO Standard Seawater with unknown composition.

Regarding point number 2, Practical Salinity S is a dimensionless number of the order of 35 in the

open ocean; no units or their multiples are permitted. There is however more freedom in choosing the representation of “Absolute Salinity” S_A since it is defined as “the mass fraction of dissolved material in seawater”. For example, all the following quantities are equal (see ISO, 1993a; BIPM, 2006):

$$\begin{aligned} 35 \text{ g/kg} &= 35 \text{ mg/g} = 0.035 \text{ kg/kg} = 0.035 = 3.5\% \\ &= 35\,000 \text{ ppm} = 35\,000 \text{ mg/kg}. \end{aligned}$$

In particular, it is strictly correct to write the freshwater fraction of seawater as either $(1 - 0.001S_A/(\text{g kg}^{-1}))$ or as $(1 - S_A)$ but it would be incorrect to write it as $(1 - 0.001S_A)$. Clearly it is essential to consider the units used for Absolute Salinity in any particular application. If this is done, there should be no danger of confusion, but to maintain the numerical value of “Absolute Salinity” close to that of Practical Salinity S we adopt the first option above, namely g kg^{-1} as the preferred unit for S_A (as in $S_A = 35 \text{ g kg}^{-1}$). The Reference Salinity, S_R , is defined to have the same units and follows the same conventions as S_A .

Regarding point number 6, the ratios of major constituents of seawater are nearly constant throughout the world oceans but this is not true for the minor components like nutrients and carbonate. The changes in the composition of these minor components of seawater affect S_A and the Practical Salinity S in different ways (Millero, 2000). This makes it difficult to examine the physical properties of ocean waters. In particular, S does not respond to changes in the composition of electrically neutral solutes that do influence S_A and related properties such as density. The introduction of Reference Salinity that equals Absolute Salinity for seawater of Reference Composition will simplify consideration of the influence on Absolute Salinity of changes in the composition due to addition of nutrients and carbonates in ocean waters at the present time and in the future. Since the influences on many physical properties, including density, of the addition of small amounts of solutes to seawater are well represented by accounting for changes in Absolute Salinity without accounting for changes in composition (Millero, 2000), the value of S_A can be useful in accounting for the effect on the physical properties of ocean waters. Before the composition of this reference water is defined, the history of the concept of the salinity of seawater is discussed in the next section.

In many marine databases, so-called GF3 codes are used as identifiers for the measured quantities

(IOC, 1987; ICES, 2005). The most relevant salinity codes are SSAL for pre-1978 salinities and PSAL for Practical Salinities. Here we suggest the GF3 code “RSAL” to be used in the future for values of Reference Salinity in g kg^{-1} .

2. The concept and determination of salinity

The first extensive investigations of the major inorganic components of seawater were made by Forchhammer in 1865. He determined the concentrations of Cl^- , SO_4^{2-} , Mg^{2+} , Ca^{2+} and K^+ directly and Na^+ by difference. He made these measurements on several hundred surface water samples from all parts of the world. Based on these analyses, he determined that the ratio of major salts in samples of seawater from various locations was almost constant, consistent with earlier speculation by Marcet (1819), who wrote “... all the specimens of sea water which I have examined, however different in their strength, contain the same ingredients all over the world, these bearing very nearly the same proportions to each other; so that they differ only as to the total amount of their saline contents” (p. 194). The statement about near-constant ratios of seawater constituents is variously known as Forchhammer’s Principle, the Principle of Constant Proportions or Marcet’s principle. Forchhammer’s results have been criticized on the grounds that he used only surface samples and that his analytical methods were inaccurate but he is often credited with introducing the concept of salinity. In particular, he established the fact that total salt content could be reasonably estimated from knowledge of chlorosity (equal to the chlorinity of the sample times its density at 20°C) alone.

In 1884 Dittmar reported analyses on 77 seawater samples collected at various depths for the major oceans during the 1873–1876 cruise of the H.M.S. Challenger. His results agreed fairly well with the work of Forchhammer although he did find small variations in the relative amounts of Mg^{2+} , K^+ , SO_4^{2-} , Ca^{2+} and Na^+ that were larger than the experimental error. In particular, the values of Ca^{2+} for deep waters were found to be 0.3% higher than surface waters. This is due to the dissolution of CaCO_3 in deep waters and has been confirmed in more recent studies (Millero, 2006). The results of Dittmar were recalculated by Lyman and Fleming (1940) using modern atomic weights. Dittmar’s determination of the bromine–chlorine mass ratio of $\text{Br/Cl} = 3.40\%$ was confirmed for North Atlantic

seawater by Berglund (1885) and used later by Sørensen for the bromine correction of evaporation salinity (Forch et al., 1902).

In 1900, seawater samples were collected from different parts of the world oceans for a comparative study of density, done by Martin Knudsen, as well as chlorinity, $Cl(\text{‰})$, and salinity, $S(\text{‰})$, done by Søren Peter Lauritz Sørensen (Forch et al., 1902). For nine of those samples both $Cl(\text{‰})$ and $S(\text{‰})$ were determined, one from the Red Sea, one from the North Atlantic, one from the North Sea and six from the Baltic Sea, including the Kattegat. From these results, Knudsen (1901) developed an approximate relation between $S(\text{‰})$ of seawater and $Cl(\text{‰})$, that has since come to be known as Knudsen's formula:

$$S(\text{‰}) = 0.03 + 1.805 Cl(\text{‰}). \quad (2.1)$$

We consciously use here the symbols $S(\text{‰})$ and $Cl(\text{‰})$ to distinguish these historical quantities from those after the definition of Practical Salinity. The values of $S(\text{‰})$ were determined by evaporating the seawater over 5 days at temperatures up to 480 °C, and the $Cl(\text{‰})$ of seawater was determined by titration of the sample with AgNO_3 precipitating the halides Cl, Br and I. Note that although the iodine content of seawater is negligible, the bromine content is sufficient to result in a significant difference between chlorinity and the mass of chlorine in grams contained in 1 kg of seawater and this distinction is important. This correction was carefully done in Sørensen's experiments. The constant offset in Knudsen's formula was caused by the influence of Baltic Sea water on the samples analyzed by Sørensen and is not necessarily valid for seawater from other parts of the world. Decades later, this Baltic Sea composition anomaly was described by Buch (1945), Rohde (1966), Nehring and Rohde (1967) and Millero and Kremling (1976). Although (2.1) is known to provide a somewhat inaccurate measure of Absolute Salinity, it continues to influence measures of salinity to this day.

For his calculation of the chlorine mass from silver precipitation, Sørensen had used the atomic weights of $107.938 \text{ g mol}^{-1}$ for Ag and $35.453 \text{ g mol}^{-1}$ for Cl. Since estimates of atomic weights change over time, the original chlorinity definition of 1902 turned out to be inappropriate, and in 1937 the chlorinity in per mille of seawater was redefined as the mass in grams of pure silver necessary to precipitate the halogens in 328.5234 g of seawater (Jacobsen and Knudsen, 1940). The value 328.5233 frequently found in the

literature (Sverdrup et al., 1942; Lyman, 1969) is a misprint (Andrew Dickson, priv. comm.) This definition gives

$$Cl(\text{‰}) = 0.3285234 Ag(\text{‰}). \quad (2.2)$$

The $Ag(\text{‰})$ is the mass in grams of Ag necessary to precipitate the halogens in 1 kg of seawater (Jacobsen and Knudsen, 1940). Thus the definition of chlorinity is independent of any updates in atomic weight estimates and is simply related to the mass of silver used in a titration of seawater through the proportionality constant 0.3285234. In the 1937 standard (Jacobsen and Knudsen, 1940), the term salinity was completely omitted and chlorinity was the only variable describing the salt concentration in seawater.

We note that the 2005 atomic weights A from Wieser (2006) given in Table 1 yield $A_{\text{Cl}}/A_{\text{Ag}} = 35.453/107.8682 = 0.3286696$. Thus, the present best estimate of “true chlorinity” or “true chlorinity equivalent” is equal to $0.3286696/0.3285234 = 1.000445$ times the official definition of chlorinity. The definition of chlorinity used here will maintain consistency with the historical definition (2.2). We emphasize that this definition of formal chlorinity is not equal to the mass fraction of chlorine in seawater. There are three reasons for this: (i) the coefficient of proportionality has deliberately not been updated from the value determined by the ratio of 1902 atomic weight estimates, (ii) silver precipitates not only silver chloride but also silver bromide (and negligible amounts of silver iodide) and (iii) the bromine–chlorine ratio (0.3477% in Table 3) in a given sample of seawater may not be the same as in Knudsen's “Standard-Water No. VI” of 1900, given as 0.340%.

For a number of years the IAPSO Standard Seawater Service prepared seawater collected from surface waters in the North Atlantic with a known, measured chlorinity. These samples were supplied to oceanographers to standardize the AgNO_3 solutions used to determine chlorinity. The salinity was then determined from the Knudsen equation (2.1).

Cox et al. (1967) examined the conductivity ratio R_{15} of open ocean seawater at 15 °C and 1 standard atmosphere pressure to standards of known $Cl(\text{‰})$. The results were used to determine the fitted equation:

$$S(\text{‰}) = -0.08996 + 28.29720 R_{15} + 12.80832 R_{15}^2 - 10.67869 R_{15}^3 + 5.98624 R_{15}^4 - 1.32311 R_{15}^5. \quad (2.3)$$

Table 1
Atomic weights of the elements 2005 (Wieser, 2005)

Symbol	Atomic weight A (g/mol)	Name
H	1.007 94(7)	Hydrogen
B	10.811(7)	Boron
C	12.010 7(8)	Carbon
N	14.006 7(2)	Nitrogen
O	15.999 4(3)	Oxygen
F	18.998 403 2(5)	Fluorine
Na	22.989 769 28(2)	Sodium
Mg	24.305 0(6)	Magnesium
Si	28.085 5(3)	Silicon
S	32.065(5)	Sulfur
Cl	35.453(2)	Chlorine
K	39.098 3(1)	Potassium
Ca	40.078(4)	Calcium
Br	79.904(1)	Bromine
Sr	87.62(1)	Strontium
Ag	107.868 2(2)	Silver
I	126.904 47(3)	Iodine
H ₂ O	18.015 268(2)	
OH	17.007 33(7)	
CO ₂	44.009 5(9)	
CO ₃	60.008 9(10)	
HCO ₃	61.016 84(96)	
B(OH) ₃	61.833 0(70)	
B(OH) ₄	78.840 4(70)	
SO ₄	96.062 6(50)	

A number in parentheses indicates the uncertainty in the last digit(s) of the atomic weight (ISO 1993b). The molecular weights of compounds are computed from the sums of their constituents without accounting for valence electron masses or binding energies, except for H₂O which is taken from IAPWS (2001), and which corresponds to water with the isotopic composition of VSMOW. OH is computed from H₂O.

They converted their expression for chlorinity to salinity using

$$S(\text{‰}) = 1.80655 Cl(\text{‰}), \quad (2.4)$$

where the factor 1.80655 was determined from the value of S/Cl given by Knudsen's equation (2.1) at $S = 35.000$ (Lyman, 1969). This relationship was accepted by the international oceanographic committees (Wooster et al., 1969). Unfortunately the relationship between S and R_{15} was referred to as a new definition of salinity while in fact this polynomial merely expresses $Cl(\text{‰})$ in terms of R_{15} , with a conversion to salinity based on a rather crude approximation. Eq. (2.2) can also be combined with (2.4) to eliminate chlorinity, giving

$$S(\text{‰}) = 1.80655 \times 0.3285234 Ag(\text{‰}). \quad (2.2')$$

In 1969, as relation (2.3) was accepted by international oceanographic committees, *in situ* salin-

ometers became commercially available. Since the so-called new definition applied only for temperatures above 10 °C it became necessary to use extrapolation equations to analyze the conductivity ratio at low temperatures. In addition, measurements of the conductivity of Standard Seawater relative to a particular batch (P64-1973) were made for samples bottled from 1926 to 1975. The results showed differences in relative conductivity corresponding to differences of up to 0.008 in $S(\text{‰})$. Similarly, the measured densities of seawater samples of similar $Cl(\text{‰})$, or similar conductivity salinities using (2.4), had $u_c(\rho) = 0.002 \text{ kg m}^{-3}$ (Millero et al., 1977), where the symbol u_c expresses the combined standard uncertainty (ISO, 1993b). This work and similar studies pointed out that Standard Seawater provided only an approximate conductivity standard for ocean studies.

In 1975 a Joint Panel on Oceanographic Tables and Standards (JPOTS) committee was formed to examine the equation of state of seawater and the salinity. This committee recommended that the Practical Salinity Scale of 1978 should be used to determine the salinity of seawater (Lewis and Perkin, 1978). This broke the $S(\text{‰})$ – $Cl(\text{‰})$ relationship in favor of a salinity–conductivity ratio relationship. All waters with the same conductivity have the same Practical Salinity even though the composition and chlorinity may differ. This was thought to be the best method to determine seawater properties. Unfortunately this is not always the case since non-electrolytes like SiO₂ are not detected by conductivity, but do change the physical properties of seawater.

As noted in Section 1, the Practical Salinity S of seawater is defined to be equal to 35.000 when the conductivity ratio is 1.0000 at 15 °C (on the IPTS-68 temperature scale) and one standard atmosphere with a solution containing a mass of 32.4356 g of KCl in 1 kg of solution. This mass of KCl was determined to give a conductivity ratio of 1 with Standard Seawater with $Cl(\text{‰}) = 35/1.80655$. The total spread of the three independent laboratory estimates averaged to determine this quantity is equivalent to only 6×10^{-7} in S (Dauphinee, 1980), making this a negligible source of uncertainty. The salinity dependence on the conductivity ratio was determined by measuring the conductivity ratio of $S = 35.000$ seawater that was either diluted with pure water or carefully evaporated to remove the desired weight of pure water (referred to as weight-evaporated in the definition of Practical Salinity).

We emphasize that the value of salinity assigned to the seawater used in these conductivity studies was determined from the known values of $Cl(\text{‰})$ using the relation $S = 1.80655 Cl(\text{‰})$ (Lewis, 1980), in which the coefficient of proportionality is determined from Knudsen's equation at $S = 35$. Consequently, the Practical Salinity Scale was essentially established by determining the relationship between chlorinity and conductivity ratio for Standard Seawater and then converting to salinity using $S = 1.80655 Cl(\text{‰})$. The constant of proportionality between Practical Salinity and the chlorinity of Standard Seawater is thus fundamental to the definition of Practical Salinity. Since the determination of Practical Salinity was originally derived from chlorinity, since the method of determining chlorinity has been stable for over 100 years, and since chlorinity is exactly conservative on mixing whereas Practical Salinity, defined by an empirical polynomial function, only approximately satisfies this strict condition, we take the definition of chlorinity (i.e., (2.2) or equivalently (3.1) below) to be more fundamental than the definition of Practical Salinity in terms of conductivity ratio.

We now comment on two distinct aspects of the PSS-78 definition of Practical Salinity. First there is the choice of the exact mass ratio of KCl ($32.4356 \text{ g kg}^{-1}$) which, at the specified temperature and pressure, has the same conductivity as Standard Seawater that is assigned the Practical Salinity 35. We do not envisage that this part of PSS-78 will ever need to be revised since it represents the definition of the value 35 for Practical Salinity and this should never be altered. The other aspect of the PSS-78 definition of Practical Salinity is the polynomial relating Cl (and correspondingly, S through $S = 1.80655 Cl(\text{‰})$) to the conductivity ratio. In principle, this polynomial could be revised at some future time to obtain a new Practical Salinity that would be more conservative than the PSS-78 definition of S . Such an update to the polynomial relating Cl to conductivity ratio could arise if more accurate laboratory measurements on Standard Seawater of the conductivity ratio were found to not be consistent with the PSS-78 polynomial. (Such changes in S would not influence our definition of Reference-Composition Salinity except to provide a corresponding improvement in the practical estimate of S_R that can be derived from S .) Currently PSS-78 fits the most accurate relevant measurements made on Standard Seawater within the

experimental uncertainty, so there is no indication that a revision is needed.

In the introduction to the Practical Salinity Scale 1978 and the International Equation of State of Seawater 1980, [Unesco \(1981a,b\)](#) state that the Practical Salinity $S = 35$ is equivalent to a chlorinity of 19.3740‰ . This is correct within the stated uncertainty of 0.002 in salinity, but in the strict sense it is inconsistent with the basic conversion between Practical Salinity and chlorinity. For consistency with the common definition of the standard ocean state, given by $S = 35$ (exact) and the basic conversion between chlorinity and Practical Salinity that was used as a foundation of the Practical Salinity Scale, $S = 1.80655 Cl(\text{‰})$, we have to regard the chlorinity of the standard ocean as a derived quantity, i.e., $Cl(\text{‰}) = 35/1.80655 \approx 19.373945$ for the standard ocean ([Culkin and Smith, 1981](#)). It should be noted that the relationship $S = 1.80655 Cl(\text{‰})$ is not an exact relationship even for Standard Seawater because Practical Salinity is precisely defined in terms of a particular polynomial in K_{15} and chlorinity is precisely defined by Eq. (2.2); this relationship could thus be negated by more accurate silver nitrate titrations and more accurate measurements of conductivity than are currently available for Standard Seawater. Indeed, the chlorinity of normalized ($S = 35$) Standard Seawater cannot even be precisely determined from laboratory measurements due to the variability that exists between the different water samples referred to as “Standard Seawater”. For example, the variations of conductivity S and the values calculated from Eq. (2.4) for Standard Seawater (Batches P91–P113) differ on the average by 0.0015 with a maximum difference of 0.005. We note in passing that the chlorinity value $Cl(\text{‰}) = 19.3740$ of [Unesco \(1981a,b\)](#) actually belongs to the salinity 35.0001 ([Poisson, 1980](#)). This chlorinity difference is less than the variations in chlorinity known to exist between different batches of Standard Seawater and it is not relevant with regard to the present accuracy of most experiments. However, it is relevant for the definition of the new Reference Salinity Scale, in order to consistently link the traditional chlorinity definition to the 1978 Practical Salinity definition via the Reference Composition model, which in turn is derived from different, independent experiments.

Finally, we emphasize that although the chlorinity is connected to a conductivity standard, the Practical Salinity is still related to the evaporation

salinity not the true total salts in the standard. Thus there is a systematic discrepancy between Practical Salinity and the Absolute Salinity that is of broadest interest. This well-known discrepancy is eliminated in the definition of Reference Salinity introduced here.

3. Updated estimates of seawater composition

Modern studies of the major components of Standard Seawater were carried out by Cox, Culkin and Riley (Cox et al., 1967; Culkin, 1965; Culkin and Cox, 1966; Morris and Riley, 1966; Riley and Tongudai, 1967) as part of an international study of the salinity of seawater. Measurements of Carpenter and Manella (1973) of Mg showed that the measurements of earlier workers were incorrect. Warner (1971) made reliable estimates of the $F/Cl(\%)$ and Uppström (1974) determined the $B/Cl(\%)$ for seawater samples. The current best estimates of the major constituents relative to the chlorinity are given in Table 2. Here, we have used the fact that chlorinity can be defined as a mass fraction to express it in g kg^{-1} .

Note that the value of r_{Cl} (w_{Cl}/Cl) where w_{Cl} is the mass fraction of chlorine in solution) reported in Table 2 is not unity. The chlorine content r_{Cl} of standard seawater can be computed from the stoichiometric balance, $r_{\text{Ag}}/A_{\text{Ag}} = r_{\text{Cl}}/A_{\text{Cl}} + r_{\text{Br}}/A_{\text{Br}}$, using the definition of chlorinity, Eq. (3.1), $r_{\text{Ag}} = 1/0.3285234$, and the bromine content, $r_{\text{Br}} = 0.003473$, Table 2. This gives the value $r_{\text{Cl}} = 0.9989041$ listed in Table 2.

Definition 2. The *chlorinity* is defined as 0.3285234 times the ratio of the mass of pure silver (g) required to precipitate all dissolved chloride, bromide and iodide in seawater to the mass of seawater (kg). That is

$$Cl/(\text{g kg}^{-1}) = 0.3285234 Ag/(\text{g kg}^{-1}). \quad (3.1)$$

Pure silver means normal isotopic abundance as described by the International Union of Pure and Applied Chemistry (IUPAC, 2005).

Chlorinity has the formula symbol Cl if not otherwise specified in the respective context. Note that since chlorinity has been defined as a mass fraction, it has the unit g kg^{-1} , or equivalent units, consistent with the unit conversion rules of SI. This definition of chlorinity maintains consistency with (2.2) and hence also with the relation $S = 1.80655 \times Cl/(\text{g kg}^{-1})$ (Cox et al., 1967; Lewis

Table 2

The composition of Standard Seawater represented by r , the measured values of the mass ratio of the major components of seawater relative to the chlorinity, Cl

Solute	r	Reference
Mg^{2+}	0.06626	Carpenter and Manella (1973)
	0.06692	Culkin and Cox (1966)
	0.06667	Riley and Tongudai (1967)
Ca^{2+}	0.02126	Culkin and Cox (1966)
	0.02128	Riley and Tongudai (1967)
K^{+}	0.0206	Culkin and Cox (1966)
	0.0206	Riley and Tongudai (1967)
Sr^{2+}	0.00040	Culkin and Cox (1966)
	0.00042	Riley and Tongudai (1967)
Cl^{-}	0.9989041	Computed from the definition of chlorinity ^a
SO_4^{2-}	0.1400	Morris and Riley (1966)
Br^{-}	0.003473	Morris and Riley (1966)
F^{-}	0.000067	Warner (1971)
B	0.000232	Uppström (1974)

Both the mass ratios and Cl are given in g kg^{-1} so that r has units of $(\text{g kg}^{-1})/(\text{g kg}^{-1})$ or simply 1.

^aThe value of r_{Cl} is given by $r_{\text{Cl}} = [1/(0.3285234 A_{\text{Ag}}) - r_{\text{Br}}/A_{\text{Br}}] \times A_{\text{Cl}}$. The commonly found value of 0.99891 (e.g., Millero, 1982) reflects the use of an older atomic weight for silver.

and Perkin, 1981) that provided a foundation for the definition of Practical Salinity. It is thus essentially unchanged from the previous definition but restated here as a mass fraction, maintaining numerical consistency with the obsolete ‘parts per thousand’ and its original 1902 definition as a measure of chlorine content.

To examine the carbonate and borate components of seawater one needs to know the pH and total alkalinity ($TA \equiv [\text{HCO}_3^-]_{\text{T}} + 2[\text{CO}_3^{2-}]_{\text{T}} + [\text{B}(\text{OH})_4^-]_{\text{T}} + [\text{OH}^-]_{\text{T}}$) of the waters. In the recent work (Millero, 2006) this was done by assuming that the $pH = 8.1$ and $TA = 2300 \mu\text{mol kg}^{-1}$. Since the fugacity of CO_2 and the total alkalinity and chlorinity at the time of the physical chemical measurements around 1976 are known ($f\text{CO}_2 = 33.74 \text{ Pa} = 333 \mu\text{atm}$, $TA = 2300 \mu\text{mol kg}^{-1}$, $Cl = 19.374 \text{ g kg}^{-1}$; Millero et al., 1993), we have re-determined the components of the carbonate and borate system using the CO_2sys Quick Basic program of Lewis and Wallace (1998). The program uses the $pK_1^* = 5.837$, $pK_2^* = 8.955$ for carbonic acid (Mehrbach et al., 1973, as reformulated by Dickson and Millero, 1987), $pK_{\text{HB}}^* = 8.588$ for boric acid (Dickson, 1990), $pK_0^* = 1.547$ (Weiss,

1974) and $pK_w^* = 13.211$ for the dissociation of water (Millero, 1995) all on the seawater pH scale ($[H^+]_{sws} = [H^+] + [HSO_4^-] + [HF]$). The resulting concentrations for the carbonate and borate species are given in Table 3.

For the condition of electro-neutrality, the charge-weighted sum of the various concentrations ($= Z \times \text{moles}$, where Z is the charge), must vanish. That is

$$\sum_k Z_k r_k Cl / A_k = 0. \quad (3.2)$$

This equation has been used to estimate the Na^+ concentration (mol kg^{-1}) from the values of all remaining solutes given in Table 3, to yield

$$Z_{Na} r_{Na} Cl / A_{Na} = -\sum_a - \sum_c = 0.4689677 \text{ mol kg}^{-1}. \quad (3.3)$$

Here, $\sum_a = -0.6055548 \text{ mol kg}^{-1}$ is the sum of the charge-weighted anion concentrations, and $\sum_c = 0.1365871 \text{ mol kg}^{-1}$ is the sum of the charge-

weighted concentrations for Mg^{2+} , Ca^{2+} , K^+ and Sr^{2+} . This value for Na^+ was used to determine the mass ratio, r_{Na} , for sodium using the atomic weight A_{Na} of Na^+ given in Table 1. The sum of the r values of the ionic and the two neutral solutes ($B(OH)_3$ and CO_2) gives a value of 1.8150682, etc. which gives a best-estimate value of the Absolute Salinity $S_A \approx 35.00000 \text{ g kg}^{-1} \times 1.8150682 / 1.80655 \approx 35.165031 \text{ g kg}^{-1}$. This is the best estimate that can be determined from existing laboratory data on the stoichiometry of seawater and its estimated standard uncertainty, based on the uncertainties in the measured major components, is $u_c(S_A) = 0.007 \text{ g kg}^{-1}$. This uncertainty is largely related to the error (0.0002) in the value of r_{SO_4} (Morris and Riley, 1966). This leads to an uncertainty in S_A of 0.006 g kg^{-1} . Note that the uncertainty in this estimate is approximately 24 (i.e., $0.165/0.007$) times smaller than the error involved in using S as an estimate for the Absolute

Table 3

The relative contributions of all the major components for seawater with S and t equal to 35 and 25°C , respectively, derived using $fCO_2 = 33.74 \text{ Pa} = 333 \mu\text{atm}$ and $TA = 2300 \mu\text{mol kg}^{-1}$

Solute i	r_i	$A_i/(\text{g mol}^{-1})$	$(r_i/A_i)/(\text{mol kg}^{-1})$	$10^7 X_i$	$10^7 X_i$ (rounded)	$10^7 X_i Z_i$ (rounded X_i)
Na^+	0.5564924	22.98976928	24.2060889	4 188 071.5	4 188 071	4 188 071
Mg^{2+}	0.0662600	24.30500000	2.7261880	471 677.6	471 678	943 356
Ca^{2+}	0.0212700	40.07800000	0.5307151	91 822.9	91 823	183 646
K^+	0.0206000	39.09830000	0.5268771	91 158.8	91 159	91 159
Sr^{2+}	0.0004100	87.62000000	0.0046793	809.6	810	1620
Cl^-	0.9989041	35.45300000	28.1754464	4 874 838.9	4 874 839	-4 874 839
SO_4^{2-}	0.1400000	96.06260000	1.4573830	252 152.4	252 152	-504 304
HCO_3^-	0.0054100	61.01684000	0.0886640	15 340.4	15 340	-15 340
Br^-	0.0034730	79.90400000	0.0434647	7520.1	7520	-7520
CO_3^{2-}	0.0007400	60.00890000	0.0123315	2133.6	2134	-4268
$B(OH)_4^-$	0.0004100	78.84036000	0.0052004	899.8	900	-900
F^-	0.0000670	18.99840320	0.0035266	610.2	610	-610
OH^-	0.0000070	17.00734000	0.0004116	71.2	71	-71
$B(OH)_3$	0.0010030	61.83302000	0.0162211	2806.5	2807	0
CO_2	0.0000220	44.00950000	0.0004999	86.5	86	0
Sum	1.8150685		57.7976977	10 000 000.0	10 000 000	0

The derivation of these results begins with the values of r_i given in Table 2 plus the additional considerations discussed in the text of Section 3. The columns are,

r_i —(g/kg of solution)/ Cl from the observed stoichiometry of sea salt, with Na^+ adjusted within the uncertainty to satisfy (4.1) and (4.2).
 A_i —atomic weight (g/mol).

r_i/A_i —(mol/kg of chlorine equivalent) from the adjusted observed stoichiometry.

$10^7 X_i$ — 10^7 times the mole fractions from the observed stoichiometry of sea salt, using the slightly adjusted values for Na^+ and CO_2 .

$10^7 X_i$ (rounded)— 10^7 times the mole fractions of the Reference Composition.

$10^7 X_i Z_i$ — 10^7 times the charge-weighted mole fractions of the Reference Composition, Z —charge.

The columns r/A and $10^7 X$ were computed from columns two and three of r and A , respectively, using 8-byte floating point numbers while the following column is rounded so that each mole fraction, X_i , when multiplied by 10^7 , is an integer. The last column also contains integers. The adjustment to the “observed” r_i value of Na^+ (from 0.5564927 to 0.5564924) was chosen to exactly achieve the sums of 10 000 000 and 0 in the last two columns. The highlighted column, $10^7 X_i$ (rounded), is the definition of the mole fractions of the Reference Composition of sea salt. This column is an essential element of this paper.

Salinity. This composition of seawater can be used to examine the effect of composition on the physical chemical properties of seawater.

The above procedure gave values for the mass fraction of sodium relative to chlorinity of $r_{\text{Na}} = w_{\text{Na}}/\text{Cl} = 0.5564927$. In the following section we define a Reference Composition of Standard Seawater and in so doing we will slightly change this ratio to $r_{\text{Na}} = 0.5564924$, as appears in Table 3 and as described below. This change results in a small modification of our best estimate of the Absolute Salinity of Standard Seawater, and hence also in our definition of Reference Salinity.

4. Reference Composition and Reference Seawater

Recall that Reference Salinity is introduced to provide an estimate of the Absolute Salinity S_A of “Standard Seawater”. Here, we define a Reference Composition by determining the stoichiometry of the reference sea salt using the best estimates of seawater composition and atomic weights presently available. Reference Seawater is then defined as seawater with the Reference Composition and in the next section, the Reference Salinity is defined to give the best possible estimate of the Absolute Salinity of Reference Seawater.

The matter dissolved in seawater is referred to as sea salt. For a proper definition of the Reference Composition we use mole fractions X_i of the major components of sea salt, rounded to 7 digits after the decimal point. This accuracy was chosen for consistency with that of the chlorinity definition, Eq. (3.1). Note that the upper case letters X_i and W_i are used in Tables 1–4 for quantities expressed as fractions of total salt content. Minor adjustments are performed in such a way that the integer numbers $10^7 \times X_i$ exactly obey the conditions of normalization:

$$\sum_i 10^7 \times X_i = 10^7 \quad (4.1)$$

and of electro-neutrality

$$\sum_i 10^7 \times X_i \times Z_i = 0. \quad (4.2)$$

The mass fractions W_i of the Reference Composition are computed from the mole fractions and the atomic weights by the formula

$$W_i = \frac{X_i A_i}{\sum_k X_k A_k}, \quad (4.3)$$

where the summation extends over all solutes, k .

Dividing each side of (4.3) by A_i and summing over k gives $(\sum X_k A_k)^{-1} = \sum W_k / A_k$. Substituting this in (4.3) and using $r_i = w_i/\text{Cl} = S_R W_i/\text{Cl}$ (with S_R/Cl the same for all components) gives the formula

$$X_i = \frac{r_i / A_i}{\sum_k r_k / A_k}. \quad (4.4)$$

We choose to define the Reference Composition in terms of the mole fractions X_i and we note that although the mass fractions W_i of the Reference Composition may change in the future for consistency with future changes in standard atomic weights, the mole fractions will not be influenced by such updates. Using mole fractions for the definition thus avoids the need for future revisions of the Reference Composition which otherwise may be required to exactly obey conditions (4.1) and (4.2).

In a first step, we computed the mole fractions from the relative mass fractions r_i reported in the second column of Table 3, but with the value of r_{Na} still equal to the experimentally estimated value of 0.5564927. The mole fractions obeyed both $\sum_i X_i = 1$ and $\sum_i X_i Z_i = 0$ to double precision (8 byte) machine accuracy, since the values of X_i and r_{Na} were obtained from (4.4) and (3.2), respectively. However, when the mole fractions X_i were rounded they did not exactly satisfy either (4.1) or the electro-neutrality criterion (4.2). Although this is of little consequence for most applications, for theoretical studies we require values of X_i that exactly fulfill these two criteria. Thus, we made a small adjustment to achieve these results, namely a slight reduction in r_{Na} (determined to satisfy the neutrality condition (4.2), which also resulted in (4.1) being satisfied) from the experimentally estimated value 0.5564927 to 0.5564924. This small change is within experimental uncertainty and is sufficient to exactly fulfill (4.1) and (4.2) using the rounded values of X_i .

Since the rounded mole fractions that define our Reference Composition results are an essential element of this paper, we explain in detail how each column of Table 3 was calculated. The second column of Table 3 displays the (slightly) adjusted relative mass fractions of the components of sea salt and all of the columns of this table are derived from this adjusted column. The third column lists the atomic weights (repeated from Table 1). The fourth column r_i/A_i is simply the ratio of the two prior

columns, converted from mol g^{-1} to mol kg^{-1} by the factor of 1000. The fifth column evaluates X_i from (4.4) for each solute, where the denominator, $\sum_k r_k/A_k$ is the sum of column 4, namely 57.7977... mol kg^{-1} . The sixth and seventh columns are the values of $10^7 X_i$ and $10^7 X_i Z_i$, respectively, for the rounded values of X_i . The fact that these two columns of integers sum to 10,000,000 and 0 indicates that (4.1) and (4.2) are exactly satisfied. The rounded mass fractions in column six of Table 3 (and repeated in column two of Table 4) are an essential result of this paper, as they serve to define the Reference Composition of seawater of standard composition.

When a salt mixture is dissolved in water, usually some of its compounds dissociate into ions until their concentrations obey the mass action laws governed by their respective dissociation constants. Some of the ions may also associate again into neutral compounds which were originally not present among the salt species prior to their dissolution. Some may react with the solvent to form further new compounds or ions. The quantitative ratios between the concentrations of the ions, their associates and electrically neutral compounds represent the particular unique thermodynamic equilibrium state, which depends on temperature,

Table 4

The ionic stoichiometry used in the determination of the Reference Composition, expressed in mole fractions, weight fractions and as fractions of chlorinity

Solute, i	$10^7 X_i$ (Definition)	$X_i A_i$	W_i	w_i (g kg^{-1})	r_i	r_i/A_i (mol kg^{-1})	x_i (mol kg^{-1})	m_i (mol kg^{-1})
Properties of sea salt of Reference Composition				Properties of KCl-normalized Reference Seawater				
Na^+	4188071	9.6282786	0.3065958	10.78145	0.556492	24.2060869	0.4689674	0.4860597
Mg^{2+}	471678	1.1464134	0.0365055	1.28372	0.066260	2.7261903	0.0528171	0.0547421
Ca^{2+}	91823	0.3680082	0.0117186	0.41208	0.021270	0.5307158	0.0102821	0.0106568
K^+	91159	0.3564162	0.0113495	0.39910	0.020600	0.5268780	0.0102077	0.0105797
Sr^{2+}	810	0.0070972	0.0002260	0.00795	0.000410	0.0046816	0.0000907	0.0000940
Cl^-	4874839	17.2827667	0.5503396	19.35271	0.998904	28.1754480	0.5458696	0.5657647
SO_4^{2-}	252152	2.4222377	0.0771319	2.71235	0.140000	1.4573806	0.0282352	0.0292643
HCO_3^-	15340	0.0935998	0.0029805	0.10481	0.005410	0.0886617	0.0017177	0.0017803
Br^-	7520	0.0600878	0.0019134	0.06728	0.003473	0.0434639	0.0008421	0.0008728
CO_3^{2-}	2134	0.0128059	0.0004078	0.01434	0.000740	0.0123340	0.0002390	0.0002477
$\text{B}(\text{OH})_4^-$	900	0.0070956	0.0002259	0.00795	0.000410	0.0052018	0.0001008	0.0001045
F^-	610	0.0011589	0.0000369	0.00130	0.000067	0.0035257	0.0000683	0.0000708
OH^-	71	0.0001208	0.0000038	0.00014	0.000007	0.0004104	0.0000080	0.0000082
$\text{B}(\text{OH})_3$	2807	0.0173565	0.0005527	0.01944	0.001003	0.0162238	0.0003143	0.0003258
CO_2	86	0.0003785	0.0000121	0.00042	0.000022	0.0004971	0.0000096	0.0000100
Sum	10000000	31.4038218	1.0000000	35.16504	1.815069	57.7976995	1.1197694	1.1605813
H_2O				964.83496	49.800646	2764.3577452	53.5565144	55.5084720
Sum				1000.00000	51.615714		54.6762838	56.6690534

$10^7 X_i$ (Definition)— 10^7 times the mole fractions of the Reference Composition (from Table 3).

$X_i A_i$ —the atomic weight of each component weighted by its mole fraction. Note the sum of this column is the average atomic weight of sea salt, $\langle A \rangle$, 31.4038218... g mol^{-1} .

W_i —mass fractions of sea salt (grams of a particular solute/grams of total solute).

w_i —mass fraction of the solution (grams of a particular solute/kg of solution). The sum of this column is the special Reference Salinity corresponding to $S = 35$, S_R^{35} , which is exactly 35.16504 g kg^{-1} .

$r_i = w_i/CI^{35}$ (g/kg of solution)/ CI^{35} . The sum of this column is $S_R/CI = S_R^{35}/CI^{35} \approx 1.815069$.

r_i/A_i —(mol/kg of chlorine equivalent).

$x_i = w_i/A_i = CI \times r_i/A_i$ (mol/kg of solution).

$m_i = X_i m$ (molality, mol/kg of solvent, from Eq. (5.10b). The molality of H_2O is $1/A_{\text{H}_2\text{O}}$.

The first column of the table is a repeat from Table 3 and is the exact definition of Reference Composition. The numbers in the other columns of this table are all derived from this definition, together with the atomic weights and the exact value $S_R^{35} = 35.16504 \text{ g kg}^{-1}$ which was derived from Eq. (5.5) (to seven significant figures). The numbers for r_i and r_i/A_i differ from those in Table 3. Those in Table 3 are adjusted to satisfy (4.1) and (4.2) but are not yet influenced by the rounding introduced in the sixth column of that table. Also, the sum of the r_i values in Table 4 is slightly smaller than the sum of the experimentally based values in Table 3, as is required for consistency with our value of S_R^{35} .

pressure and the concentrations of all components. This equilibrium exactly conserves the original masses of chemical elements (and stable compounds) of the dissolved components and is independent of the way their atoms were originally assembled into neutral molecules.

Thus, the composition of seawater has two aspects, the elemental composition which is subject to the mass conservation law, and the stoichiometric composition of the various compounds and ions which are subject to the thermodynamic equilibrium. Here we use the term elemental composition to indicate the composition in terms of the basic elements present, irrespective of the specific forms that they are present in. If two solutions possess the same elemental composition, they will have the same pairwise stoichiometric ratios of their ions, atoms and molecules when both solutions are in equilibrium at a common temperature and pressure. A change in temperature or pressure will result in a change in stoichiometric composition, but the elemental composition is unchanged provided there is no gain or loss of material from the solution. The idea of an elemental composition is used to define the Reference Composition of sea salt while consideration of the stoichiometric composition is required for a definition of Reference Seawater.

Definition 3. The *Reference Composition* of the substance dissolved in seawater, called *sea salt*, is defined by the list of solutes and their mole fractions, X_i , as given in columns 1 and 2 of Table 4. Any aqueous solution with an elemental solute composition consistent with Table 4 has the Reference Composition, irrespective of its detailed stoichiometry at a particular temperature and pressure.

Note that nothing is specified about the solution's chlorinity, conductivity, temperature or pressure.

The value of $pH = 8.1$ assumed for the composition of standard seawater on the seawater pH scale ($[H^+]_{\text{SWS}} = [H^+] + [HSO_4^-] + [HF]$) implies a small concentration of H^+ ions to be present. These ions are not a part of the Reference Composition of sea salt, rather, they are considered a part of the solvent. In the limiting case of vanishing salinity, the solution does no longer contain any sea salt but still H^+ ions as described by the ionization constant of water. The total concentration of hydroxyl ions, $[OH^-]$, in seawater is therefore slightly higher than given by the Reference Composition of sea salt,

namely by the amount of $\Delta[OH^-] = [H^+]$ due to the dissociation of H_2O solvent molecules. The dissociation constant of pure water as a function of temperature and pressure is available from IAPWS (2007) and has the value $pK_W = 13.995$ at 25°C and 101325 Pa .

The second aspect of seawater composition enters the definition of Reference Seawater, used to describe seawater of Reference Composition.

Definition 4. *Reference Seawater* is defined as seawater with Reference Composition solute dissolved in pure water as the solvent, and adjusted to its thermodynamic equilibrium state.

Reference Seawater at any particular (t, p, Cl) combination will equilibrate to Reference Seawater at any other (t, p, Cl) combination that can be reached by dilution with pure water or evaporation without removing any sea salt from the solution, even though the combination of ions and compounds may be different.

For some purposes such as theoretical models of seawater composition (Pierrot and Millero, 2000; Marion et al., 1999; Feistel, 2003), it is necessary to define a Reference Composition in terms of a detailed specification of ions and compounds such as those given in Table 4. The elemental composition can be more precisely realized but it is less rigorous than a specified combination of ions and compounds. Realization of the latter is complicated by the fact that the stoichiometry of dissolved substance depends on the chemical equilibria between the different solute constituents and the solvent, so the detailed ionic composition of seawater will vary with t, p and Cl . Thus, for any particular (t, p, Cl) combination, a stable equilibrium of Reference Composition seawater exists with a combination of ions and compounds that is similar to rather than exactly equal to those specified in Table 4. Note however, that at the special point given by $t = 25^\circ\text{C}$ and $p = 1\text{ atm}$, KCl-normalized Reference Seawater will match the elemental composition exactly and the detailed composition of ions and compounds listed in Table 4 within the experimental uncertainty of the chemical analysis of Standard Seawater.

In Definition 4, we specify one particular type of Reference Seawater that can be precisely defined. This is all that we require for the present discussion. Other possibilities are less precisely defined but may be more useful in particular situations. Below, we

list some of these possibilities and assign names for easy reference.

- (i) Type I Reference Seawater: This is the theoretical seawater type defined in Definition 4 that is simply referred to as “Reference Seawater” here. It has Reference Composition as its exact elemental composition but its ionic stoichiometry and conductivity is determined by the thermodynamic equilibria at any particular temperature, pressure and chlorinity and is not exactly known. At $t = 25^\circ\text{C}$, $p = 1\text{ atm}$ and KCl-normalized concentration, its ionic stoichiometry agrees with that of Table 4 within the experimental uncertainty of the chemical analysis of Standard Seawater and the thermodynamic equilibrium constants.
- (ii) Type II Reference Seawater: A theoretical model of seawater with Reference Composition that has exactly the ionic stoichiometry given in Table 4 at $t = 25^\circ\text{C}$, $p = 1\text{ atm}$ and KCl-normalized concentration (or equivalently, $Cl = 19.374\text{ g kg}^{-1}$, within present uncertainties) and stoichiometries at other conditions determined by the respective chemical equilibrium constants. Although the stoichiometry of the equilibrium state of a solution created in a laboratory at $t = 25^\circ\text{C}$, $p = 1\text{ atm}$ and $Cl = 19.374\text{ g kg}^{-1}$ will not agree *exactly* with that given by Table 4, this is currently the best theoretical estimate of the thermodynamic equilibrium states of Reference Seawater. This type of model has been used for running Pitzer models of seawater (Pierrot and Millero, 2000; Millero and Pierrot, 2005; Feistel and Marion, 2007).
- (iii) Type III Reference Seawater: A theoretical model of seawater that has exactly the ionic stoichiometry as given in Table 4 for all values of temperature, pressure and chlorinity. This is the simplest, invariant estimate to the thermodynamic equilibrium states of Reference Seawater (Definition 4). It ignores small variations in the equilibrium state with temperature, pressure and chlorinity but is useful for the computation of limiting laws for the Gibbs function of seawater (Feistel, 2003).
- (iv) Type IV Reference Seawater: An artificial seawater solution that has the Reference Composition within the uncertainty of the related chemical laboratory synthesis technologies. Its ion stoichiometries are close to those of

the above theoretical models; variability with t , p and Cl will be best represented by Type II Reference Seawater. It may be used in future lab experiments to quantitatively determine the thermodynamic equilibrium properties and the conductivity of Reference Seawater at representative combinations of t , p and Cl .

- (v) Finally, we note that, within small uncertainties, IAPSO Standard Seawater has the elemental Reference Composition and the ionic stoichiometry of Reference Seawater at any t , p and Cl .

5. Reference-Composition Salinity

Reference-Composition Salinity (or Reference Salinity for short) is defined to give the best current estimate of the Absolute Salinity of seawater of Reference Composition. To ensure conservativity, it is defined (a) as not being influenced by changes of pressure and temperature of a fixed mass of seawater and (b) in terms of a mixture of two seawater samples with specified Reference Salinities.

Definition 5. Reference-Composition Salinity, S_R .

- (a) The *Reference-Composition Salinity of pure water* is defined to be zero. Pure water is meant here as Vienna Standard Mean Ocean Water, VSMOW, as described in the 2001 Guideline of the International Association for the Properties of Water and Steam (IAPWS, 2001).
- (b) The *Reference-Composition Salinity of normalized Reference Seawater* is defined to be exactly $35.16504\text{ g kg}^{-1}$.
- (c) The *Reference-Composition Salinity* is defined to be conservative during mixing. If a seawater sample of mass m_1 and Reference-Composition Salinity S_{R1} is mixed with another seawater sample of mass m_2 and Reference-Composition Salinity S_{R2} , the final Reference-Composition Salinity S_{R12} of this sample is

$$S_{R12} = \frac{m_1 S_{R1} + m_2 S_{R2}}{m_1 + m_2}. \quad (5.1)$$

Negative values of m_1 and m_2 corresponding to the removal of seawater with the appropriate salinity are permitted, so long as $m_1(1-S_{R1}) + m_2(1-S_{R2}) > 0$. In particular, if $S_{R2} = 0$ (pure water) and m_2 is chosen to normalize the seawater sample, then $S_{R12} = 35.16504\text{ g kg}^{-1}$ and the original Reference-Composition Salinity

of sample 1 is given by $S_{R1} = [1 + (m_2/m_1)] \times 35.16504 \text{ g kg}^{-1}$.

- (d) The *Reference-Composition Salinity of a seawater sample at given temperature and pressure* is equal to the Reference-Composition Salinity of the same sample at another temperature and pressure when the transition process is conducted without exchange of matter, in particular, without evaporation, precipitation or degassing of substance from the solution.

Regarding conditions 5(a) and (b), VSMOW is consistent with the currently most accurate thermodynamic description of air-free fluid water, IAPWS-95 (IAPWS, 1996) and $35.16504 \text{ g kg}^{-1}$ is currently the best estimate of the Absolute Salinity of normalized ($S = 35$) seawater with the composition of Standard Seawater or the Reference Composition. The determination of this value is discussed below.

Condition 5(c) envisages that one takes a local sample of seawater and then either dilutes the sample with pure water or evaporates water from the sample until the conductivity ratio exactly matches that of condition 5(b). At this point the diluted (or evaporated) sample has a Reference Salinity exactly equal to $35.16504 \text{ g kg}^{-1}$. The original Reference Salinity of the sample is then determined by accounting for the addition or removal of pure water during the normalization process. This approach is sketched in

the upper two boxes of the right-hand side of Fig. 5; R represents $(1 + m_2/m_1)$ where m_1 is the original mass of the seawater sample and $|m_2|$ is the mass of pure water added or removed in the normalization process. The condition $m_1(1 - S_{R1}) + m_2(1 - S_{R2}) > 0$ must be obeyed to ensure that some solvent remains in the final solution. E.g., if m_2 is negative and corresponds to removal of pure water, then $|m_2| < m_1(1 - S_{R1})$ is obviously required.

The algorithm for the definition of Reference Salinity is sketched in the upper two boxes of the right-hand side of Fig. 5.

The value $35.16504 \text{ g kg}^{-1}$ used in Definition 5 is currently the best estimate of the Absolute Salinity of normalized ($S = 35$) seawater with the composition of Standard Seawater or the Reference Composition. To determine this estimate, we first make use of the definition of chlorinity as expressed by Eq. (3.1), which can be written as

$$Cl = 0.3285234 A_{Ag} \times (W_{Cl}/A_{Cl} + W_{Br}/A_{Br} + W_I/A_I) \times S_A. \quad (5.2)$$

From Eq. (4.3) we see that $W_i/A_i = X_i/\langle A \rangle$, where $\langle A \rangle = \sum_k X_k A_k = 31.4038218 \dots \text{ g mol}^{-1}$ (5.3)

is the mole-weighted average atomic weight of the elements in sea salt, determined from Table 4.

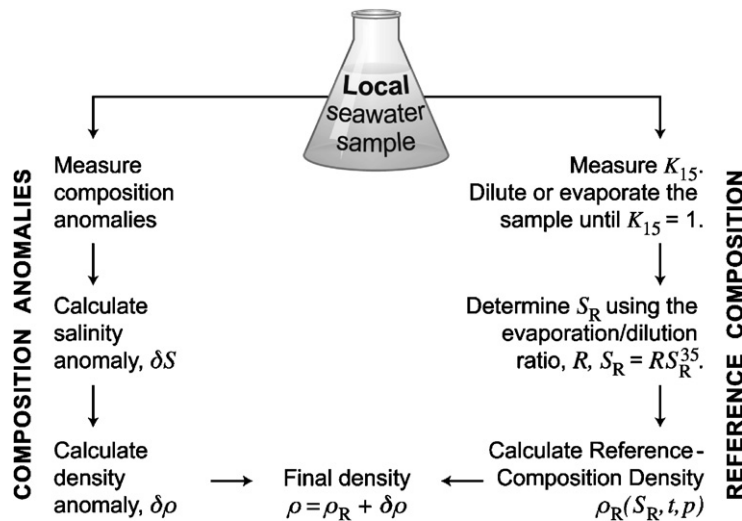


Fig. 5. The right-hand part of this diagram summarizes the theoretical definition of the Reference-Composition Salinity S_R and thereby the Reference-Composition density $\rho_R(S_R, t, p)$. The calculations on the right-hand side treat the local sample as though it has Reference Composition. If supplementary measurements exist from which the deviation of the dissolved components from the Reference Composition can be estimated, the left-hand part of the diagram can be used to refine the estimate of the density of the local seawater sample. K_{15} is the conductivity ratio to the KCl standard and S_R^{35} is the Reference Salinity of normalized seawater, $35.16504 \text{ g kg}^{-1}$.

Eq. (5.2) can therefore be expressed as

$$Cl = 0.3285234 \times (A_{Ag}/\langle A \rangle) \times (X_{Cl} + X_{Br} + X_I) \times S_A \quad (5.4)$$

for Reference Seawater. Thus, the Absolute Salinity of normalized ($S = 35$) Reference Seawater with $X_I = 0$ is precisely

$$S_A^{35} = \frac{(35/SonCl)}{0.3285234 \times (X_{Cl} + X_{Br})} \times \frac{\langle A \rangle}{A_{Ag}}, \quad (5.5)$$

where *SonCl* is the ratio of Practical Salinity to chlorinity for Reference Seawater. With the atomic weights from Table 1, the mole fractions from Table 4 and *SonCl* set equal to $1.80655 \text{ (g kg}^{-1}\text{)}^{-1}$, Eq. (5.5) gives $S_A^{35} = 35.16504 \text{ g kg}^{-1}$ to seven significant figures. We have used this value in condition 5(b) of our definition of Reference Salinity. Below we refer to this value as S_R^{35} .

Ideally, we would like S_R^{35} to be precisely equal to the Absolute Salinity of normalized Reference Seawater. While our chosen value of S_R^{35} provides a greatly improved estimate of Absolute Salinity in comparison to the estimate provided by Practical Salinity, there are two remaining sources of uncertainty that prevent us from determining the desired exact value of the Absolute Salinity. First, from Eq. (5.5) we see that the determination of Absolute Salinity depends on the ratio of atomic weights, $A_{Ag}/\langle A \rangle$, which cannot be precisely prescribed due to the uncertainties indicated in Table 1. Second, in order to maintain a direct connection between Reference Salinity and Practical Salinity, we have chosen S_R^{35} to correspond to a specific value of conductivity ratio rather than to a particular value of chlorinity. This introduces the factor *SonCl* which is not precisely known for Reference Seawater. Nevertheless, each of the associated uncertainties is relatively small.

The uncertainty associated with the atomic weight estimates is easily determined. From (5.5), the relative uncertainty $u_c^a(S_A^{35})/S_A^{35}$, associated only with the uncertainties in the atomic weights of the individual elements, satisfies the relation

$$\left[\frac{u_c^a(S_A)}{S_A} \right]^2 = \left[\frac{u_c(\langle A \rangle)}{\langle A \rangle} \right]^2 + \left[\frac{u_c(A_{Ag})}{A_{Ag}} \right]^2, \quad (5.6)$$

where $u_c(\langle A \rangle)$ and $u_c(A_{Ag})$ represent the uncertainties in $\langle A \rangle$ and A_{Ag} , respectively. From the uncertainties given in Table 1, it is easily shown that the uncertainty in the average atomic weight is strongly dominated by the uncertainty in the atomic weight of chlorine. As well, the uncertainty asso-

ciated with the atomic weight of silver in Eq. (5.6) is small compared to the first term, so we obtain as our final estimate

$$\frac{u_c^a(S_A)}{S_A} \approx \frac{X_{Cl}}{\langle A \rangle} \times u_c(A_{Cl}) = W_{Cl} \times \frac{u_c(A_{Cl})}{A_{Cl}}. \quad (5.7)$$

Using $u_c(A_{Cl})/A_{Cl} \approx 5.6 \times 10^{-5}$ from Table 1, $W_{Cl} \approx 0.55$ from Table 4 and $S_A \approx 35 \text{ g kg}^{-1}$, we find that the estimated standard uncertainty in the value of S_A , associated with the uncertainties in atomic weights, is $u_c^a(S_A) = 0.001 \text{ g kg}^{-1}$ for $S_A = 35 \text{ g kg}^{-1}$. Since Reference Salinity is defined in terms of a mixture of $S = 0$ and 35 seawater, the standard uncertainty in the Reference Salinity varies in proportion to the salinity.

The uncertainty associated with the factor *SonCl* for the Reference Composition is more difficult to estimate with confidence. Although we cannot yet provide a definitive conversion factor between Practical Salinity and chlorinity, there is good reason to expect that it will be very close to the value of $1.80655 \text{ (g kg}^{-1}\text{)}^{-1}$ that was used in PSS-78 to relate Practical Salinity to chlorinity. A quantitative estimate of the uncertainty in *SonCl* can be obtained by noting that the difference between S_R^{35} and S_A^{35} for Reference Seawater is expected to be no larger than 0.007 g kg^{-1} , the combined uncertainty remaining in the direct experimental determination of the Absolute Salinity of Standard Seawater. Since our Reference Salinity based on *SonCl* = $1.80655 \text{ (g kg}^{-1}\text{)}^{-1}$ agrees precisely with the observational estimate (obtained as explained following (3.3) but using the value of r_{Na} given in Table 3, the relative error in our choice of *SonCl* is expected to be of the same order as the relative uncertainty in S_A . Thus, we estimate the uncertainty in *SonCl* as $0.007 \times 1.80655/35 = 0.00036$.

Note that although S_R^{35} is specified as a fixed number that depends on current estimates of the atomic weights and *SonCl*, the influence of updates of these quantities on Absolute Salinity estimates is trivially determined from Eq. (5.5). Allowing for the possibility of future updates, the best estimate of the Absolute Salinity for Reference Seawater is

$$\begin{aligned} S_A &= \frac{1.80655}{SonCl} \times \frac{A_{Ag}^{2005}}{\langle A \rangle^{2005}} \times \frac{\langle A \rangle}{A_{Ag}} \times S_R \\ &= 6.2052732872 \dots \times \frac{1}{SonCl} \times \frac{\langle A \rangle}{A_{Ag}} \times S_R. \end{aligned} \quad (5.8)$$

Of course, using the best currently available information this gives simply $S_A = S_R$.

Finally, we discuss some additional results derived from the mole fractions X_i of the Reference Composition as given in the sixth column of Table 3 and reproduced in the second column of Table 4. The third column of Table 4 gives the atomic weight of each element from Table 1 weighted by its mole fraction. The mass fractions of a particular solute as a fraction of the total mass of sea salt W_i appear in the fourth column of Table 4 and are determined to 7 significant figures via Eq. (4.3) using the third column. The mass fraction of a particular solute of normalized Reference Seawater as a fraction of the total mass of solution w_i is simply $S_R^{35} W_i$ and is shown in the fifth column of Table 4; the sum of this column is S_R^{35} . The elements of the sixth column of Table 4, $r_i = w_i / C\bar{l}^{35}$, are the values from the previous column divided by $C\bar{l}^{35} = 35 / 1.80655 \text{ g kg}^{-1}$. The seventh column of Table 4, r_i / A_i in $\text{mol (kg Cl equiv)}^{-1}$, is the previous column divided by the atomic weights from Table 1 and converted using $1000 \text{ g} = 1 \text{ kg}$. The sixth and seventh columns of Table 4 are preferred over columns 2 and 4 of Table 3 since they include the influence of the rounding introduced in the sixth column of Table 3 and also because the sum of column six of Table 4 is consistent with the determination of Absolute Salinity in terms of chlorinity, Eq. (5.2) or (5.4). The eighth and ninth columns of Table 4 are the moles of solute per kg of solution and the moles of solute per kg of solvent (molality), respectively.

An additional quantity that is useful for theoretical models is the valence factor $\langle Z^2 \rangle$ of sea salt which can be obtained from the last two columns of Table 3:

$$\langle Z^2 \rangle = \sum_k X_k Z_k^2 = 1.2452898. \quad (5.9)$$

In theoretical electrolyte models, the salt concentration is often expressed in terms of the molality, m , giving the moles of salt per kg of water (as opposed to the moles of salt per kg of solution), or the ionic strength, I . The molality is given by

$$m = \frac{1}{\langle A \rangle} \frac{S_A}{(1 - S_A)} \quad (5.10a)$$

$$\approx (1000.0/31.4038218) \text{ mol kg}^{-1} \times \frac{S_R}{(1 - S_R)}, \quad (5.10b)$$

where the second line follows upon approximating Absolute Salinity with the Reference Salinity and

using the mole fractions given in Table 4 together with the atomic weights given in Table 1 to determine $\langle A \rangle$. The inverse relations corresponding to (5.10a) and (5.10b) are:

$$S_A = \frac{m}{m + 1/\langle A \rangle}, \quad (5.11a)$$

$$S_R \approx \frac{m}{m + (1000.0/31.4038218) \text{ mol kg}^{-1}}. \quad (5.11b)$$

The ionic strength is computed from Eqs. (5.9) and (5.10b), as

$$\begin{aligned} I &= \frac{1}{2} m \langle Z^2 \rangle = 0.6226449 \times m \\ &\approx (622.6449/31.4038218) \text{ mol kg}^{-1} \times \frac{S_R}{(1 - S_R)}. \end{aligned} \quad (5.12)$$

We note that, consistent with the discussions following Eq. (2.2) and preceding Definition 2, the mass fraction of chlorine relative to chlorinity reported in Table 4 is $r_{\text{Cl}} = 0.998904$, etc. and not 1.0000000 as a literal interpretation of the name chlorinity seems to suggest. Chlorinity was originally defined in 1902 as “the total amount of chlorine, bromine and iodine in grams contained in one kilogram of seawater, assuming that the bromine and the iodine had been replaced by chlorine” (Forch et al., 1902; Sverdrup et al., 1942). Here, we have neglected the very small influence of iodine on Standard Seawater. Therefore in Table 4, after substituting all bromine by chlorine, the historical chlorinity notion (from 1902, involving a ratio of atomic weights) compared to the modern definition (from 1937, with the atomic weight ratio replaced by a fixed number) corresponds to the quantity $r_{\text{Cl}} + (r_{\text{Br}}/A_{\text{Br}}) \times A_{\text{Cl}} = 1.000445$. The deviation of this value from unity by 0.0445% is essentially due to changes in atomic weight estimates during the last century (a value of 0.0485% was calculated by Jacobsen and Knudsen, 1940). While the formal chlorinity value determined for a particular seawater sample remained unchanged over this period of time, the ‘apparent’ chlorine fraction has changed over time with changes in the respective atomic weight estimates. We note that such changes have no impact at all on empirically determined formulae such as the equation of state that depend on S , t , p or Cl .

6. Approximate conversions between practical salinity, chlorinity and reference salinity

The conventional quantities used to quantitatively describe the salt content of natural seawater are chlorinity, Cl ; Practical Salinity, S ; and Absolute Salinity S_A . Chlorinity, as calculated from silver nitrate titrations according to Eq. (2.2), or equivalently Eq. (3.1) of Definition 1, was used for almost all fundamental laboratory determinations of thermodynamic seawater properties which support the 1980 International Equation of State of Seawater, and also for the recent 2003 formulation of thermodynamic properties in terms of a Gibbs function of seawater, even though both are formally written with Practical Salinity S as the independent variable. Practical Salinity is presently applied worldwide in collecting and archiving oceanographic salinity observations. Here we derive the relationship between the new Reference Salinity S_R and both chlorinity and Practical Salinity. The relationship with Practical Salinity leads to a practical method for the routine estimation of the Reference Salinity S_R of a local fluid parcel.

To determine these relations, we first note that both Reference Salinity and chlorinity satisfy the mixing condition given as condition 5(c) of Definition 5 and both vanish for pure water. Thus Reference Salinity is exactly proportional to Chlorinity for Reference Seawater. Within experimental uncertainty, Practical Salinity is related to chlorinity for Standard Seawater (and hence also for Reference Seawater) by $S = 1.80655 Cl / (g\ kg^{-1})$, so Reference Salinity is also proportional to Practical Salinity to the accuracy and over the range that Practical Salinity is determined ($2 < S < 42$). Consequently, the following may be used as a Practical Definition of Reference Salinity that maintains consistency with the accepted definition of Practical Salinity.

Within the range where Practical Salinity S is defined by PSS-78 and within the uncertainty with which S is determined, Reference Salinity S_R is approximately given by

$$S_R \approx (35.16504/35) g\ kg^{-1} \times S \quad (6.1)$$

with the corresponding inverse formula being

$$S \approx (35/35.16504) \times S_R / (g\ kg^{-1}). \quad (6.2)$$

These relations are exact at $S = 35$ and deviate away from $S = 35$ only due to the slight non-conservativity of S due to its definition in terms a

fitted polynomial in K_{15} . Note from (6.1) that $S_R \approx 1.004715 g\ kg^{-1} \times S$ so that Reference Salinity is approximately 0.47% larger than Practical Salinity. Eq. (6.1) is recommended as a method for estimating the Reference Salinity S_R of a local seawater sample within the range where S is defined $2 < S < 42$. Reference Salinities outside this range can be determined by dilution with pure water or evaporation of a seawater sample. They can also be estimated from the extensions of the Practical Salinity Scale proposed by Hill et al. (1986) for $0 < S < 2$ and by Poisson and Gadhoumi, 1993 for $42 < S < 50$.

We can also give the following approximate relation between Reference Salinity and chlorinity for Reference Seawater:

$$S_R \approx (35.16504/35) \times 1.80655 Cl \approx 1.815069 Cl \quad (6.3)$$

with the corresponding inverse formula being

$$Cl \approx (35/35.16504) \times S_R / 1.80655 \approx 0.5509433 S_R. \quad (6.4)$$

Note that while (6.1) and (6.2) are excellent approximations for any seawater sample, the validity of (6.3) and (6.4) requires that $S \approx 1.80655 Cl / (g\ kg^{-1})$ for the seawater sample of interest. This may not be a good approximation in the presence of composition anomalies.

7. Local anomalies of seawater composition

As the equation of state for Standard Seawater is refined, the variations in composition of local seawater samples become more and more important in terms of their relative contributions to density and other seawater property errors. Variations in composition have a maximum impact on density of about $24 g\ m^{-3}$ in the open ocean (Millero et al., 1978) and about $130 g\ m^{-3}$ in the Baltic Sea estuary (Millero and Kremling, 1976). This is now the major remaining source of error in the equation of state (Jackett et al., 2006).

Standard salinometer measurements of Practical Salinity provide one example of the inconsistencies that can be caused by composition anomalies. If for example the Practical Salinity of a seawater sample from the surface waters of the Baltic Sea is estimated (using, for example, an Autosol salinometer) at a temperature of $15^\circ C$ while at sea and again at a temperature of $25^\circ C$ in the laboratory the values may differ due to the presence of anomalies.

Although Practical Salinity is strictly defined such that it is independent of the particular temperature of the sample, such differences in salinity estimates can be caused by the algorithms used to estimate Practical Salinity from measurements at arbitrary values of temperature and pressure. These algorithms were determined from measurements on Standard Seawater and are not guaranteed to be reliable for seawater that includes composition anomalies; a caution regarding this limitation is included on the final page of [Unesco \(1981b\)](#).

One approach to correcting for errors associated with composition anomalies would be to develop a conversion table (or a function of longitude, latitude and depth that fits the data in such a table) applicable to present-day conditions. S_R can be determined from S as discussed in the previous section. If we then determine geographical variations in the absolute salinity, S_X , of local seawater by $\delta S_A = S_X - S_R$ to account for geographical variations in composition, we can eliminate most of the remaining density errors. Use of this correction of S_R will also result in substantial improvement in other thermodynamic properties (e.g., entropy, heat capacity, enthalpy, freezing points) making determination of such a correction for S_R particularly useful. How can we do this?

The density ρ of a local seawater sample, X , computed from its conductivity-based Reference Salinity, S_R , by means of the equation of state of seawater, $\rho(S_R, t, p)$, can be compared with the density ρ^X determined for the same sample by direct methods. Local density anomalies are considered significant if local solute anomalies are such that the deviation $|\rho - \rho^X|$ exceeds 10 g m^{-3} (roughly 1 part in 100 000).

Since deviations from the Reference Salinity are generally small, it is easy to determine a meaningful correction. Define $\delta S_A = S_X - S_R$, where S_X is the local value of Absolute Salinity. The salinity correction δS_A is obtained from the density difference by solving the equation

$$\rho^X = \rho(S_R + \delta S_A, t, p) \approx \rho(S_R, t, p) + \left(\frac{\partial \rho}{\partial S_R} \right)_{t,p} \delta S_A, \quad (7.1)$$

i.e.,

$$\delta S_A = \frac{1}{\beta(S_R, t, p)} \left[\frac{\rho^X}{\rho(S_R, t, p)} - 1 \right], \quad (7.2)$$

where β is the isothermal haline contraction coefficient.

Once δS_A (and hence S_X) is known, corrected thermodynamic properties are computed from the standard formulas using S_X as the local Absolute Salinity variable in place of the Reference Salinity, S_R .

The above approach could provide useful large-scale corrections to global seawater properties provided solute anomalies are small and remain close to present-day conditions. To include the influence of solute anomalies on thermodynamic properties in the case where anomalies deviate significantly from present-day values as, for example, in climate change models, a different approach will be needed. If a modelling study is carried out in which carbon and nutrients are included as state variables, then one possibility is to write $S_X = S_R + \delta S_A$ (carbon, nutrients) and determine a functional relationship for δS_A . For example, [Millero \(2000\)](#) uses observations from the Pacific to obtain the empirical relation:

$$\delta S_A / (\text{g kg}^{-1}) = [37.9(\text{NTA}-2295) + 72.8\text{SiO}_2 + 47.7\text{NO}_2 + 3]/756 \quad (7.3)$$

and it may be possible to determine similar relations that are more broadly applicable. This approach warrants further investigation.

8. Conclusion

A new measure of salinity has been defined that has several advantages over the Practical Salinity Scale. This Reference Salinity S_R is defined to accurately represent the Absolute Salinity S_A of an artificial seawater solution with a Reference Composition that has stoichiometry in molar fractions ([Tables 3 and 4](#)) based on the most accurate determinations of the IAPSO Standard Seawater constituents, and the 2005 atomic weights of IUPAC ([Table 1](#)). An approximate relation to Practical Salinity S is determined which is suitable for practical applications while maintaining a direct connection with the currently most widely accepted measure of salinity. Reference Salinity S_R is intended to be used as the new independent salinity variable for future thermodynamic functions of seawater, as an SI-based extension of Practical Salinity, as a reference for natural seawater composition anomalies, as the currently best estimate for Absolute Salinity of IAPSO Standard Seawater, and as a theoretical model for the electrolyte “seawater”. Reference Salinity is the mass fraction of

salt in IAPSO Standard Seawater with an estimated combined standard uncertainty of 0.007 g kg^{-1} .

It is important to note that while there is a simple linear relation from which Reference Salinity can be quite accurately determined from Practical Salinity, Reference Salinity breaks with the historical convention of remaining consistent with Knudsen's formula for the standard ocean ($S = 35$, $t = 0^\circ\text{C}$) in favour of being the most accurate representation of Absolute Salinity possible. Seawater of Reference Composition and Practical Salinity $S = 35$ (i.e., normalized Reference Seawater) has a Reference Salinity of exactly $35.16504 \text{ g kg}^{-1}$, hence its numerical value in g kg^{-1} is greater than its Practical Salinity by approximately 0.47%. This difference is approximately 24 times the uncertainty in Reference Salinity as a representation of the Absolute Salinity of Standard Seawater.

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Glossary of Terms

Absolute Salinity, S_A : The ratio of mass of dissolved material in seawater to the total mass of seawater (Unesco, 1985).

Average Atomic weight of sea salt, $\langle A \rangle = \sum_k X_k A_k$: The mole-weighted average of the atomic weights of the dissolved components included in the definition of Reference Composition.

Chlorinity, Cl : Defined as 0.3285234 times the ratio of the mass of pure silver required to precipitate all dissolved chloride, bromide and iodide in seawater to the mass of seawater. Over the past century, a simple scaling of chlorinity has provided a stable and reliable measure of the amount of salt in seawater.

Conductivity ratio, K_{15} : The symbol used to represent the conductivity ratio used in the definition of Practical Salinity. It is the ratio of the electrical conductivity of a seawater sample at a temperature of 15 °C (IPTS-68) and a pressure of one standard atmosphere, to that of a potassium chloride (KCl) solution at the same temperature and pressure, in which the mass fraction (g of KCl per gram of solution) is 32.4356×10^{-3} (R_{15} is used to designate the corresponding ratio with respect to Standard Seawater that has been adjusted to a Practical Salinity of 35).

Density Anomaly, $\delta\rho$: The difference between the actual density of a seawater sample and the Reference Composition density.

Normalized seawater: Any seawater sample that has been adjusted to have a Practical Salinity of 35.

Practical Salinity, S : The globally accepted standard for reporting the salinity of seawater since approximately 1978. Practical Salinity is defined in terms of the ratio of the electrical conductivity of a seawater sample relative to a particular concentration of KCl solution at specified temperature and pressure and is easily measured at sea using a salinometer. Practical Salinity has no units.

PSS-78: The scale introduced in 1978 on which the Practical Salinity is given.

Reference Composition: A precisely defined mixture of artificial seawater designed to provide the most accurate possible representation of the composition of Standard Seawater. The mole fractions of this mixture are given in Table 4.

Reference Seawater: Seawater with the Reference Composition.

Reference-Composition density, ρ_R : The estimate of density based on an equation of state using the Reference Salinity as a measure of dissolved material in a seawater sample.

Reference-Composition Salinity, S_R : The Reference-Composition Salinity of a local seawater sample is defined exactly by the theoretical Definition 5 (see also Fig. 5). A practical approximate version of Reference-Composition Salinity is given in Eq. (6.1) (see also Fig. 4). If the seawater sample has Reference Composition, then its Reference-Composition Salinity is the best available estimate of its Absolute Salinity.

Reference Salinity, S_R : The name ‘Reference Salinity’ is used as a short form for ‘Reference-Composition Salinity’.

Standard Seawater: Certain samples of surface water taken from a specific region in the North Atlantic. The composition of these samples is very nearly constant and has been used as a measurement standard.