Review

Metrological challenges for measurements of key climatological observables Part 2: Oceanic salinity

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Abstract

Salinity is a key variable in the modelling and observation of ocean circulation and ocean-atmosphere fluxes of heat and water. In this paper, we examine the climatological relevance of ocean salinity, noting fundamental deficiencies in the definition of this key observable, and its lack of a secure foundation in the International System of Units, the SI. The metrological history of salinity is reviewed, problems with its current definitions and measurement practices are analysed, and options for future improvements are discussed in conjunction with the recent seawater standard TEOS-10.

(Some figures may appear in colour only in the online journal)

1. Introduction

This is part 2 of a series of companion papers (Feistel *et al* 2016, Dickson *et al* 2016, Lovell-Smith *et al* 2016) examining metrological challenges for measurements of key climatological observables; in this paper we examine seawater salinity. Salinity is a term used to quantify the total mass of inorganic substance dissolved in pure water to form a given mass of seawater. During the last century, only two methods of measuring this total mass were successfully exploited to establish salinity scales that were officially adopted by oceanography, namely by drying a sample and weighing the residue (Forch *et al* 1902), or by carrying out a complete chemical analysis of the sample's composition and adding up the constituent masses (Millero *et al* 2008). Neither method is appropriate for the frequent and regular measurements required in oceanographic studies. In addition, the two methods are also known

to result in numerically different values for the same seawater (Millero *et al* 2008), partly because of insufficient knowledge of chemical changes that occur during drying at high temperatures over several days.

Despite the problems of measuring the dissolved content directly, salinity as a conserved seawater property (IOC *et al* 2010), now classified as an 'Essential Climate Variable' (GCOS 2010), is a key variable for ocean modelling and observation. In practice, salinity has therefore been officially defined until recently by specific measurement techniques applied to a proxy property. Since 1978 this proxy has been the electrical conductivity, and the technique has been a measurement of electrical conductance relative to that of a bottled standard reference material called IAPSO Standard Seawater (SSW), which is officially approved for this purpose by the International Association for the Physical Sciences of the Oceans (IAPSO). SSW in turn is calibrated relative to the

conductance of a potassium chloride (KCl) solution of specified concentration. A relative conductance measurement using the same instrument for the comparison is necessary because it provides a significantly lower uncertainty than (absolute) conductivity measurements. An uncertainty level of $0.002\,\mathrm{g}$ kg^{-1} in dissolved mass fraction (i.e., a relative uncertainty of 6×10^{-5} for typical seawater with a dissolved mass fraction of about $35\,\mathrm{g\,kg}^{-1}$) is required for routine research and monitoring purposes (SUN 1985, King *et al* 2001, Seitz *et al* 2011). On the other hand, the tabulated KCl conductivity standard (Pratt *et al* 2001), which provides an electrical conductivity value traceable to the International System of Units (SI), has a larger relative uncertainty of 2×10^{-4}. One problem with this operational definition is that the relative chemical composition of seawater changes slightly from place to place in the ocean, and such changes, which can measurably affect other physical properties of seawater, cannot be determined with knowledge of the proxy only.

Significant efforts have been made to ensure consistency of salinity measurements over the past century by both the use of SSW and the development of standard protocols. Unfortunately, no robust link has yet been established between any of the salinity definitions and the International System of Units (SI), despite the fact that *Practical Salinity* defined by the 1978 Practical Salinity Scale (Unesco 1981a) was recommended for oceanography in the context of SI units (SUN 1985, Siedler 1998). Thus there are potential problems with the long-term stability and intercomparability of salinity measurements. Here we discuss the history of oceanic salinity measurements, technical details of current practices and their deficiencies, and a suggested plan for remedying them. We begin by briefly outlining the climatological relevance of ocean salinity.

2. Climatological relevance

The concentration of dissolved substances, that is, seawater salinity, varies from place to place, and from time to time at specific places in the ocean. Salinity changes occur as a result of mixing processes in the water column and, more dramatically, by precipitation and evaporation at the surface, by freezing and melting of sea ice, and by freshwater discharge from rivers and glaciers. Much smaller changes also occur due to biogeochemical processes in the ocean related to the uptake of inorganic matter into living organisms near the surface, and its remineralization from sinking detritus at depth (Pawlowicz *et al* 2011). Oceanic composition and salinity changes may also result from increased atmospheric CO_2 (Bender 2013, see also Dickson *et al* 2016, Part 3 of this issue).

The oceans play an important role in redistributing heat and water over the Earth. Most of the Earth's free water (97%) is stored in the oceans, and 75 to 90% of the Earth's surface freshwater fluxes occur at the ocean-atmosphere interface (Durack *et al* 2013). The oceans also export 50 to 90% of absorbed solar energy to the atmosphere in the form of latent heat associated with evaporation of water (Josey *et al* 1999, 2013, Emery *et al* 2006, Pierrehumbert 2010, Feistel and Ebeling 2011,

Wells 2012). The related global hydrological cycle is reflected in the distribution of sea-surface salinities. Arid regions in the trade-wind belts show higher, and humid regions at the equator and at mid-latitudes lower salinities than the global average. While observations of latent heat fluxes are technically demanding and subject to large uncertainties, on the order of 20% or $30\,\mathrm{W\,m}^{-2}$ (Katsaros 2001, Josey *et al* 2013, Lovell-Smith *et al* 2016, part 4 of this issue), local long-term trends in salinity are precisely measureable indicators for climatic changes in the terrestrial water cycle and its sensitivity to global warming (Durack and Wijffels 2010, Durack *et al* 2012, 2013, Pierce *et al* 2012). However, surface salinity is also affected by various processes other than evaporation or precipitation (Josey *et al* 2013).

Ocean currents also transport vast amounts of heat polewards within the ocean. Oceanic heat is most usefully quantified in thermodynamic terms defined by the Thermodynamic Equation of Seawater 2010 (TEOS-10, see McDougall 2003, IOC *et al* 2010, McDougall *et al* 2013, Feistel *et al* 2016, Part 1 of this issue). As an illustration, the Gulf Stream alone carries about 1.3 PW to the North Atlantic across a zonal section along 26 °N (Bryden and Imawaki 2001), which corresponds to about 1% of the global solar irradiation, or to roughly 100 times the total human power consumption of 14 TW (Lu *et al* 2009). While surface currents are mostly wind-driven, advection at depths below 100 m or so is almost entirely caused by pressure gradients resulting from differences in sea level and water density, and is deflected by the Coriolis force and topographic obstacles. Salinity has a strong effect on density, which is particularly relevant in cold high-latitude and deep ocean regions, and hence salinity deviations can modify heat transports. An important scientific use of measured salinity values is to estimate the density of seawater (in conjunction with the measured temperature and pressure), using an equation of state. Seawater equations of state are empirical correlations determined from careful laboratory measurements on SSW.

Typically, an increase of $0.01\,\mathrm{g\,kg}^{-1}$ in Absolute Salinity, S_A (see section 4 for a precise definition), leads to a relative increase of 8×10^{-6} in density, ρ, as a result of the haline contraction coefficient,

$$\frac{1}{\rho}\left(\frac{\partial \rho}{\partial S_A}\right)_{T,p} \approx 0.8\,\mathrm{kg\,kg}^{-1}, \qquad (1)$$

which varies in the range between 0.66 at great depths and 0.83 at the surface. A relative uncertainty in the range of 1×10^{-6} to 4×10^{-6} is at the resolution limit of today's oceanographic density measurements, see section 5.

3. Brief history

It has long been known that common salt (sodium chloride, NaCl) is the predominant solute in seawater. The concentration of halides; principally chloride, but also including bromide and iodide, can be measured by determining the mass of the precipitate or of the silver required in titration with a silver nitrate ($AgNO_3$) solution. The chlorine equivalent of

this result is termed chlorinity (*Cl*). Early chemical analysis (Marcet 1819, Forchhammer 1865, Dittmar 1884) revealed that the ratios to *Cl* of the mass fractions of the remaining major seawater solutes are, to a good approximation, the same in all oceans and at all depths, suggesting measurements of *Cl* could be scaled to estimate total solute. In order to do this, the Danish chemist S P L Sørensen dried nine seawater samples of known chlorinity and weighed the residue (Forch *et al* 1902). Six of the samples came from the Baltic Sea, and one each from the North Sea, North Atlantic, and Red Sea; none came from the South Atlantic, Indian and Pacific Oceans. The correlation derived from those results,

$$S_K = 0.03 \text{ g kg}^{-1} + 1.805 \times Cl, \qquad (2)$$

became known as the equation that defined Knudsen Salinity, S_K, expressed as the mass fraction of precipitable salt in seawater. This definition was in practical use at least until 1969 even though it was already discouraged in a 1937 standard, when chlorinity was officially chosen to be the only variable to be used in describing the salt concentration in seawater.

In this 1937 oceographic standard (Jacobsen and Knudsen 1940, Millero *et al* 2008), the chlorinity was formally defined by the equation,

$$Cl = 0.328\,5234 \times Ag, \qquad (3)$$

where *Ag* is the ratio of the mass of pure silver necessary to precipitate the halogens in seawater, to the mass of the seawater sample. The italicized symbols *Cl* and *Ag* for mass fractions were defined in earlier oceanographic standards and are not to be confused with the chemical symbols of the elements, Cl and Ag. For historical and chemical reasons, the value of *Cl* resulting from equation (3) does not exactly match the mass fraction of chloride in seawater, which is $0.998\,9041 \times Cl$ (Millero *et al* 2008). The numerical conversion factor in equation (3) was fixed in the 1937 standard in order to eliminate from the calculation of *Cl* any effects resulting from gradual improvements in published values for atomic weights, which had by then already caused relative changes of 5×10^{-4} (Reeburgh 1966), and to ensure long-term comparability of the measurement results. Chlorinity can be measured with an uncertainty of 0.0004 g kg^{-1} by the Volhard titration method, and of 0.0002 g kg^{-1} by direct silver-mass comparison (Carritt 1963), although routine measurements typically have an uncertainty of around 0.01 g kg^{-1} (Lewis and Perkin 1978).

Routine titrations were standardized using SSW, which was distributed in sealed glass ampoules labelled with a batch number and the batch chlorinity. This reference material, originally proposed by Knudsen (Knudsen 1903) was produced in Copenhagen under the direction of F Nansen from 1902 to 1908, and then by Knudsen until 1948, all under the auspices of the International Council for the Exploration of the Seas (ICES). In 1948, the Association International d'Oceanographie Physique (now IAPSO) took over the responsibility for SSW, with H. Thomsen in charge of administration, and F. Hermann (who began as Knudsen's assistant in 1941) in charge of preparation and calibration. Hermann subsequently took over all responsibility in 1960. When Hermann retired in 1974, the responsibility and equipment for producing SSW was transferred to F

Culkin at the Institute of Oceanographic Sciences, Wormley, UK, who had collaborated with Hermann on chlorinity calibrations for some years (Culkin and Smed 1979). In 1989, responsibility was transferred to a private company, Ocean Scientific International Ltd, Havant, UK, under the direction of Ridout (who began as Culkin's assistant). Since 2000, SSW has been distributed in crimp-sealed borosilicate bottles.

The salinity offset in equation (2), which implies that Knudsen Salinity values are not conserved when mixing with pure water, is caused by the fact that six of the nine samples analysed by Sørensen were taken from the Baltic Sea, into which additional dissolved salts (primarily lime) are discharged by rivers (Millero and Kremling 1976, Feistel *et al* 2010a). For the open ocean this awkward feature was eventually corrected by introducing the Cox Salinity S_C,

$$S_C = 1.80\,655 \times Cl, \qquad (4)$$

which coincides with equation (2) at the standard-ocean salinity of $S_C = S_K = 35 \text{ g kg}^{-1}$ (Wooster *et al* 1969, Lyman 1969), i.e. for seawater with a chlorinity of $Cl = 19.373\,94 \text{ g kg}^{-1}$.

Traditionally, the mass fraction unit g kg^{-1} was expressed as ‰ (originally by Knudsen 1901), or as ppt (meaning *part per thousand*), and the use of these symbols is often taken to imply that they result from a chlorinity titration. While ppt or ‰ represent the same unit as g kg^{-1}, the SI brochure (BIPM 2006) discourages the use of these symbols in new publications (e.g., for confusion with *part per trillion*). Different quantities should generally be distinguished by their symbols, not their units. According to this rule, the latest salinity definition (IOC *et al* 2010) does not require a specific unit to be used exclusively.

Beginning in the 1950s, electrical conductivity measurements with sufficient accuracy were increasingly used to characterise the dissolved ionic content of seawater, in order to replace the less convenient silver titration procedure (although the earliest recorded usage of conductance measurements for this purpose dates to the 1920s, Wenner *et al* 1930). Conductance ratio measurements were eventually established officially as the Practical Salinity Scale 1978 (PSS-78, Unesco 1981a), which is still the world-wide reference for salinity measurements, expressed in values of Practical Salinity, S_P.

Although oceanographers typically use the term 'conductivity' (and/or 'conductivity ratio') for their measurements, some careful distinctions should be made. *Conductivity* is a property of seawater substance, depending on its chemical composition, temperature, and pressure, but is independent of the mass, shape, or surface properties of a given seawater sample. It is constant for applied signal frequencies up to the MHz range, where ion–ion interactions begin to be important. In contrast, *conductance* (the inverse of electrical resistance) is a measurement value obtained from a particular instrument, which also depends on the geometry of the measurement cell and, due to polarization effects at the electrode-solution interface, on the frequency of the applied measurement signal. These polarization effects, which typically dominate at applied signal frequencies under a few kHz (Schwan 1968, Ishai *et al* 2013), arise mainly as ions accumulate near the

electrodes, inducing an extra capacitance. Considering these effects even at higher frequencies is necessary at the uncertainty levels required in oceanographic research.

Conductivity can be calculated from a measured conductance value once the cell constant of the measurement cell has been determined for a particular measurement signal, which scales the measured conductance to the conductivity, and polarization effects eliminated. Typically, cells are calibrated using a measurement standard of known conductivity (Spitzer and Seitz 2011). The calibrated measurement is then sometimes called the *specific conductance* instead of the conductivity, although, confusingly, limnologists usually use the term 'specific conductance' to refer to a calibrated measurement only after it is also temperature-corrected to a reference temperature of 25 °C. This temperature correction is usually about 2% per °C (Wetzel 2001).

In metrological laboratories, the conductivity of a primary measurement standard (e.g., of a KCl solution), traceable to the SI, is determined using a cell in which the geometry is carefully determined by dimensional measurements which are used to calculate the cell constant from first principles. In addition, polarization effects on the measurement are avoided by using impedance spectroscropy. This involves making measurements with alternating current (AC) signals of different frequencies, typically of a few kHz for conductivities typical for seawater, identifying surface polarization effects by their spectral behaviour, and correcting for them by extrapolating to infinite frequency (Pratt *et al* 2001).

Since impedance spectroscopy is not carried out in oceanographic instruments, and they are not calibrated using a traceable standard, it is more correct to say that they measure conductance ratios. It must be emphasized that the ratio of measured conductances between two solutions differing in conductivity or composition is not necessarily equivalent to the ratio of their conductivities because of the effects of polarization. This deviation can be minimized if the two solutions are at least similar in composition.

SSW, originally produced to standardize chlorinity titration, was then adapted to standardize the electrical conductance measurements required by PSS-78. There have been many investigations of the reliability of SSW for this purpose (Culkin and Ridout 1998, Bacon *et al* 2000, 2007), and of apparent differences that occur in batch-to-batch comparisons (Park 1964, Mantyla 1980 1987, Aoyama *et al* 2002, Kawano *et al* 2006). For the SSW samples used to develop PSS-78, chlorinity was correlated with the dimensionless conductivity ratio K_{15} between SSW and a KCl solution with a solute mass fraction of 32.4356 g kg^{-1}. This ratio was determined at 15 °C on the International Practical Temperature Scale of 1968 (IPTS-68) or 14.996 °C on the current International Temperature Scale of 1990 (ITS-90), and a pressure of one standard atmosphere. At the resulting values of K_{15}, chlorinity was converted to Practical Salinity, $S_P(K_{15})$, by means of the formula (4) from which the unit ppt (or ‰) was then omitted to denote the conductivity-ratio measurement in contrast to chlorinity titration (a source of much confusion to non-specialists, who often append the officially discouraged descriptor 'PSU' for 'Practical Salinity Units' to unit-less numerical values of

S_P). A major reason for this decision was that 'the numerical values of practical salinity would be similar to the numerical values of previous salinity data, when expressed in ‰' (Unesco 1981b), that is, similar to Cox Salinity (equation (4)).

Since it was known as early as 1937 that S_K (and hence also S_C) numerically underestimate the real mass fraction of dissolved matter in seawater by about 0.5%, the new formal salinity variable S_P was no longer considered to express a mass fraction (Unesco 1981b), although in practice it has often been used that way. For uniformity and comparability of measurement results, the use of chlorinity was discouraged in favour of S_P because the stoichiometric relations that were used to derive equation (4) are violated for real ocean water, which often contains minor deviations in its chemical composition relative to that of SSW. The primary and most demanding purpose of oceanographic salinity measurements is the calculation of seawater density to estimate significant ocean currents driven by sometimes tiny horizontal pressure gradients. In real ocean waters, densities calculated using a correlation from S_P turned out to be mostly closer to their true values than densities calculated from S_C because changes in conductivity partially account for the effects of these minor deviations, which rarely include any halogens that would also affect chlorinity (Lewis and Perkin 1978).

Remaining errors in density calculations were considered to be mostly within the limits of accuracies thought to be attainable at the time in salinity determinations (± 0.01‰). However, within a few years an uncertainty of ± 0.002 was specified for open-ocean Practical Salinity measurements in the World Ocean Circulation Experiment (King *et al* 2001); modern measurements are then at least an order of magnitude less uncertain than estimates of thermodynamic properties like density which are derived using Practical Salinities in an equation of state (Pawlowicz *et al* 2012).

More recently, the recognition that conceptual problems with the existing Equation of State 1980 (EOS-80, Unesco 1981a) prevented the use of common thermodynamic quantities such as entropy and enthalpy in studies of oceanic heat transport led to the development of TEOS-10 (IOC *et al* 2010). In addition to providing a better description of 'heat' (see Feistel *et al* 2016, Part 1 of this issue), TEOS-10 also addressed a number of metrological and scientific issues with the existing PSS-78 definition of salinity, which will now be described in more detail.

4. Current definition and measurement practice

It has been and will remain established oceanographic practice to derive the Practical Salinity (PSS-78) of seawater from parallel *in situ* measurements of electrical conductance, temperature and pressure, converting these measurements to Practical Salinity by the procedures and correlation formula provided by PSS-78 (or its future update). Although the PSS-78 Practical Salinity is no longer an official definition of seawater salinity, it does represent a temperature and pressure-corrected conductance measurement which should continue to be reported and stored in national databases.

Table 1. Reference Composition of sea salt (Millero *et al* 2008). The given mole fractions are exact by definition. Derived mass fractions are rounded to seven digits to the right of the period and may be subject to future updates of molar masses. Enclosed in brackets are uncertainties derived from the uncertainties of the 2005 IUPAC atomic masses (Wieser 2006) that were used for the 2008 definition of sea salt. The sodium fraction is adjusted to satisfy the condition of electroneutrality.

Solute	Electric charge	Mole fraction	Mass fraction	Molar mass g mol^{-1}
Na^+	+1	0.418 8071	0.306 5958	22.989 769 28(2)
Mg^{2+}	+2	0.047 1678	0.036 5055	24.305 0(6)
Ca^{2+}	+2	0.009 1823	0.011 7186	40.078(4)
K^+	+1	0.009 1159	0.011 3495	39.098 3(1)
Sr^{2+}	+2	0.000 0810	0.000 2260	87.62(1)
Cl^-	−1	0.487 4839	0.550 3396	35.453(2)
SO_4^{2-}	−2	0.025 2152	0.077 1319	96.062 6(50)
HCO_3^-	−1	0.001 5340	0.002 9805	61.016 84(96)
Br^-	−1	0.000 7520	0.001 9134	79.904(1)
CO_3^{2-}	−2	0.000 2134	0.000 4078	60.008 9(10)
$B(OH)_4^-$	−1	0.000 0900	0.000 2259	78.840 4(70)
F^-	−1	0.000 0610	0.000 0369	18.998 403 2(5)
OH^-	−1	0.000 0071	0.000 0038	17.007 33(7)
$B(OH)_3$	0	0.000 2807	0.000 5527	61.833 0(70)
CO_2	0	0.000 0086	0.000 0121	44.009 5(9)
Sea salt	0	1.000 0000	1.000 0000	31.404(2)

Conductance sensors are calibrated with respect to SSW samples of certified conductance ratio K_{15}. PSS-78 is formally valid only when used with the temperature scale of 1968 (IPTS-68) over a temperature range of −2 °C to 35 °C, and it is only valid for seawater that has Practical Salinity between 2 and 42. A correction to take into account the numerical differences between IPTS-68 temperatures and current ITS-90 temperatures, which are usually less than 0.01 °C under oceanographic conditions, is implemented in TEOS-10.

The correlations provided by PSS-78 are purely empirical and were determined by statistically fitting equations to laboratory measurements over the stated range. Further corrections are known for precise measurements in more dilute seawater (Hill *et al* 1986) and at slightly higher concentrations (Poisson and Gadhoumi 1993). The reduced accuracy of PSS-78 correlations when extrapolated to much higher temperatures and salinities has recently been investigated by Pawlowicz, (2012).

SSW is used as a reference substance in practice rather than KCl solutions because the variations of conductivity with temperature and, less significantly, with pressure are different between the two solutions, and to minimize biases from polarization effects. SSW is currently produced by a commercial organisation (Ocean Scientific International Ltd., UK, or OSIL), under the endorsement of the International Association for the Physical Sciences of the Oceans (IAPSO), and hence is also known more formally as IAPSO SSW. This IAPSO SSW consists of near-surface water that is obtained from time to time from a particular part of the North Atlantic, filtered, diluted with de-ionised water and UV-treated to remove organic material and particulate, and then bottled in airtight crimp-sealed borosilicate glassware (Bacon *et al* 2007). It is labelled with a batch number (which has now reached P158, since numbering began in 1906). Since 1980 (batch P91), the K_{15} and the Practical Salinity of the batch is also indicated on the label.

The labelled K_{15} and Practical Salinity of IAPSO SSW is obtained by a series of conductance measurements at OSIL relative to KCl standard solutions, prepared using precise weights of Merck Suprapur® (or equivalent) KCl crystals, with the conductance ratio assumed to be equivalent to a conductivity ratio (Bacon *et al* 2007). IAPSO SSW prepared by OSIL is the primary reference material to which all worldwide PSS-78 salinity measurement results are traceable (Seitz *et al* 2011), although attempts have been made to produce a second SSW product, called Chinese Primary Standard Seawater, from independently created KCl solutions (Ma and Tian 2004, JCOMM 2014).

Although SSW is carefully manufactured to be a reference solution for PSS-78, it is metrologically problematic to have the definition of salinity rely on a particular measurement technique applied to a physical artefact that is derived from a natural source, changes with age, and depends on subtle details of the production process. Instead, it is more useful to separate the definition of a quantity from the set of instructions ('mise en pratique', see BIPM 2006) that in practice allows its measurement at the lowest level of uncertainty. Recently, as part of the development of TEOS-10, a first step was taken to move towards this separation. Instead of basing a salinity definition on a physical artefact, the best available stoichiometric data for the composition of SSW was used to define a fixed Reference Composition for seawater (given in table 1). SSW is now considered to be a physical realization of this tabulated Reference Composition, and the correlations of PSS-78 the best available estimate of the electrical properties of Reference-Composition seawater.

This redefinition in turn permitted the recalculation of the factor relating chlorinity, and in turn also Practical Salinity, to the solute mass fraction (Millero *et al* 2008). The resulting salinity measure, obtained by adding up the mass of solutes in Reference-Composition seawater, was termed Reference-Composition Salinity, or abbreviated for convenience, Reference Salinity, S_R. In SSW it can be estimated from a PSS-78 conductance measurement using:

$$S_R/(\text{g kg}^{-1}) = (35.165\,04\,/\,35) \times S_P. \tag{5}$$

Given the specified composition, the largest uncertainty in the relation (5) results from the uncertainty of the molar mass of naturally-occurring chlorine (Millero *et al* 2008).

The exact mole fractions of the Reference Composition shown in table 1 are defined to provide the best estimate currently available for the stoichiometric composition of SSW; as a part of the TEOS-10 standard, it is the first officially endorsed chemical sea-salt model in the history of oceanography. Earlier seawater composition models differed slightly from it and from each other (Forchhammer 1865, Millero and Leung 1976, Millero 1982, Feistel 2003). As the name suggests, it is intended as a fixed reference stoichiometry relative to which deviations found in real seawater can be described as small perturbations (Pawlowicz 2010, Feistel *et al* 2010b, Pawlowicz *et al* 2011). In fact the composition of bottled SSW is also suspected to vary slightly from batch to batch (Goyet *et al* 1985), and both ocean waters and SSW contain many trace constituents (Kennish 2001) not included in the Reference Composition. However, although future work may result in more exact knowledge of the composition of SSW (of any vintage), this will not affect the definition of the TEOS-10 Reference Composition (Wright *et al* 2011).

Consistent with table 1 and PSS-78, as expressed by equation (5), the Reference-Composition Salinity Scale (Millero *et al* 2008) assigns a salinity of $35.165\,04$ g kg^{-1} to so-called KCl-normalised seawater. The latter term is used to describe any seawater sample (e.g., one whose chemical composition may differ from the Reference Composition) that has the same electric conductivity as a solution of potassium chloride (KCl) in pure water with the KCl mass fraction of 32.4356 g kg^{-1} when both are at the ITS-90 temperature $t = 14.996$ °C and standard atmosphere pressure, $p = 101\,325$ Pa. Thus by definition, the Reference Salinity of a given sample remains unaltered if the pressure or temperature of the sample is changed, and is scaled by the mass fractions if pure water (assumed to have zero salinity) is added or removed. Pure water is understood to have the isotopic composition of Vienna Standard Mean Ocean Water, VSMOW (IAPWS 2001, BIPM 2006).

In order to link current practice to this definition, measured Practical Salinity values can be converted to Reference Salinity by means of equation (5). However, for seawater whose composition is slightly different from Reference Composition, the Reference Salinity thus determined will not necessarily represent the solute mass fraction accurately, nor will it always give best results for other properties of seawater (such as density) when the TEOS-10 correlations are used. Thus as far as necessary and available, corrections for sea-salt composition anomalies, denoted δS_A, must be obtained by using additional information. The final (corrected) salinity value, on the Reference-Composition Salinity Scale, is called Absolute Salinity S_A:

$$S_A = S_R + \delta S_A \tag{6}$$

and S_A is then the salinity argument to be used in TEOS-10 correlations for other properties of seawater.

At present there are several possible methods for determining δS_A. First, the anomalies can be ignored, and this may be sufficient if the required accuracy is low. Since δS_A in the open ocean is generally less than 0.03 g kg^{-1} this would be true in many situations when the salinity is required only to determine chemical equilibrium constants through additional correlation equations. This may also be true for certain measurements in the coastal ocean where salinity variations can be large, such as for hydrophysical monitoring of the Baltic Sea (HELCOM 2014), although coastal corrections are possible, and may be an order of magnitude larger than in the open ocean (Pawlowicz 2015). Second, under the assumption that the spatial fields of oceanic salinity, carbonate system and macro-nutrients are relatively stable, this anomaly can be extracted from values tabulated for that location and depth in a global atlas following the algorithm of McDougall *et al* (2012). This is probably sufficient for observations taken over large areas in the open ocean. Third, the correction can be obtained by comparisons with direct density measurements performed in the laboratory (Millero *et al* 2008, Wright *et al* 2011). This procedure is useful for laboratory studies or in situations where water can be obtained from sampling bottles retrieved from certain depths. Finally, the anomaly can be estimated from an additional correlation equation if chemical measurements of the most variable seawater constituents in the open ocean (carbonate system and macro-nutrients) are also available (Pawlowicz *et al* 2011).

In determining the correction, another subtle point arises concerning the precise definition of Absolute Salinity. This involves the ultimate use of the variable. As derived densities are considered to be the most important application at highest precision, the Absolute Salinity is actually defined to be the value that will result in the most accurate density when the correlations specified in TEOS-10 for calculating density are used (Wright *et al* 2011). This is not necessarily the actual solute mass fraction, as different chemical constituents in seawater have different effects on conductivity and density (Pawlowicz *et al* 2011). However, corrections are also available to produce the best estimate of solute mass fraction, if this is desired. In this way, TEOS-10 is the first oceanographic standard that supports systematic consideration of natural seawater composition variations.

5. Problems and deficiencies

Although TEOS-10 has many improvements over previous salinity definitions, there still remain two fundamental problems with the current definition and measurement technology of seawater salinity: (i) a lack of traceability of salinity measurement results to the SI, and (ii) an incomplete knowledge of methods to handle small deviations in the chemical composition of the dissolved salts from the Reference Composition, which regionally occur in the oceans and marginal seas and may have relevant effects on seawater properties.

5.1. Lack of traceability to the SI

At present, the electrical conductivity of seawater can be determined in an SI-traceable way to within an uncertainty

of about 0.03% (Seitz *et al* 2010), equivalent to a salinity standard uncertainty of $0.01\,g\,kg^{-1}$ for a typical seawater of salinity $35\,g\,kg^{-1}$. This is comparable to the stated uncertainty of 0.02% in the tabulated SI-traceable conductivity of KCl standard solutions that are often used to calibrate conductivity measurement cells in other scientific fields (Pratt *et al* 2001). However, individual salinity-measuring instruments, known as salinometers, commercially available and in widespread oceanographic use, can demonstrate measurements with stability and reproducibility about one order of magnitude better than this. By careful calibration with SSW, different workers can routinely measure Practical Salinity with a reproducibility of better than 0.002 (0.006%), traceable to SSW, if the time elapsed between the measurements does not exceed the expiry time of SSW; and differences on this scale are found to have meaning within the limits of known ocean behaviour.

A possible concern for the future is that this reproducibility is usually observed when all parties are using the same model of salinometer. Other precision salinometers are now being developed, but as yet no systematic intercomparisons between different salinometer designs have been carried out.

Not only might instrument differences affect intercomparisons of field measurements, but the electrode-solution interaction of the KCl reference solution defined by PSS-78 differs from that of SSW. This means that two different types of measurement device may, at the very low uncertainty levels of concern here, measure a different ratio of conductances between the same KCl solution and SSW sample at the same temperature. This could affect the label values of SSW. The use of SI-traceable calibrations allow for the identification and correction of such measurement biases, but since this is not possible at present an additional uncertainty remains.

Bottled SSW ages for poorly understood reasons, and present recommendations as written on bottle labels since batch P151 are that it should be used within 3 years of calibration (OSIL 2012). Samples are archived by OSIL and their characteristics retested after storage, with little long-term variation found in Practical Salinity (Bacon *et al* 2007). However, batch-to-batch tests carried out independently by other workers have found systematic differences between batches, and correcting for these systematic differences can sometimes improve comparisons between field measurements of ocean water bodies (Bacon *et al* 2000, Kawano *et al* 2006, Pang 2015). These apparent systematic differences were as large as 0.002 in S_P. Recent improvements may be due to the change from soda glass ampoules to borosilicate bottles in 2000 (Bacon *et al* 2007). Whether or not these apparent differences are inherent to SSW, or arise from handling effects as SSW is stored and shipped globally, or are statistical artefacts is as yet unresolved. Also unresolved is the question of how properties of SSW batches other than Practical Salinity may undergo systematic drifts or random changes over time.

IAPSO Standard Seawater and the KCl solution specified by PSS-78 are metrological artefacts. The stability of their properties, in particular their composition and conductivity, must be considered as uncertain at the level of uncertainty required in oceanography and climatology, in particular with respect to the multi-decadal time scales relevant for current and future oceanographic observation. Consequently, on these long time scales the comparability of measurement results for Practical Salinity cannot be guaranteed by the current traceability practice. Traceability of ocean salinity measurement results to stable SI standards is therefore highly desirable.

5.2. Composition variability

Two aspects of chemical composition require further work. These are, first, the composition of SSW, and second, the practical determination of deviations from the composition of SSW in real seawaters, and the determination of any corrections that arise from these deviations.

The best verification of the agreement of the composition given in table 1 with that of SSW would require the preparation of artificial seawater with the given solutes and pure water whose isotopic composition is specified by VSMOW. The prepared solution is expected to be consistent with SSW in density within a relative uncertainty of about 4×10^{-6} and in Practical Salinity within 0.007 (Millero *et al* 2008). The fact that as yet no successful experiment of this type is known from the literature indicates that the composition analysis of SSW needs to be improved in the future to determine the deviations from the Reference Composition, using the most advanced chemical analysis techniques. In fact, the accuracy of measurements of seawater salinity is mainly limited at present by the uncertainty of the underlying metrological reference (e.g. uncertainty in composition, molar masses and certified SSW samples) rather than by that of the practical measurement procedures (e.g. stability and repeatability of electronic sensor readings).

The composition of real seawater varies with location and with time. It may contain significantly more or less pure water than certified samples of SSW, and the relative amounts of different solutes may also vary slightly. As previously noted, the mass fraction of dissolved solute on the Reference-Composition Salinity Scale is termed Absolute Salinity, S_A, (IOC *et al* 2010, Wright *et al* 2011). Reference Salinity S_R based on a measurement of electrical conductance using equation (5), is currently the best estimate for the Absolute Salinity of IAPSO Standard Seawater. However, the relationship between solute mass and the electrical conductivity of real seawater may differ because of these composition differences, and hence the Absolute Salinity and the Reference Salinity calculated using equation (5) may also differ. The deviation between the two salinity values, δS_A, defined by equation (6) is denoted the Absolute Salinity Anomaly and serves as a measure for the solute-composition anomaly of a given sample with respect to the Reference Composition.

However, the concept of salinity has many subtle details, both in terms of its conceptual definition and in its practical determination. Defining 'dissolved inorganic solute' in seawater is not entirely straightforward (Millero *et al* 2008, Pawlowicz *et al* 2011, Wright *et al* 2011). Also, although salinity definitions usually include only inorganic constituents, at present the practical importance of the remaining organic material (e.g. for density or other thermodynamic properties) is poorly understood (Millero *et al* 2010).

The first issue in defining salinity involves the choice of constituents to include. Although practically every chemical element known is contained in seawater at some concentration, many of these occur at such low concentrations (such as some nutrients or trace elements) that they have little effect on a gross 'salinity'. Traditionally, constituents that occur in concentrations of less than about $0.001\,g\,kg^{-1}$ are neglected in definitions of salinity. However, there are several exceptions. The first is that some dissolved gases (primarily oxygen O_2 and nitrogen N_2) are present at somewhat higher levels, but are neglected nevertheless because they have little practical effect on seawater densities and conductivities. On the other hand, carbon dioxide (CO_2) gas and the hydroxide (OH^-) ion are included even though they are present at lower levels, because they are required for a simple description of the marine carbonate system that may significantly affect electrical conductivity. Finally, macro-nutrients such as nitrate and silicic acid are usually not included, although the latter can be present in concentrations of up to $0.02\,g\,kg^{-1}$ in the deep North Pacific.

The second issue in defining salinity is that the chemical equilibria involved in the carbonate system, which includes CO_2, HCO_3^-, CO_3^{2-}, $B(OH)_4$, $B(OH)_3^-$, and OH^- (and is significantly affected by seawater pH, see Dickson *et al* Part 3 of this issue) are particularly problematic. At any given conditions, the equilibrium composition of these components may deviate from the Reference Composition as a result of chemical solute-solute and solute-solvent reactions, which are concentration, temperature and pressure-dependent. On the other hand, one of the most important requirements of any salinity definition is conservation with respect to dilution, warming and compression of the seawater sample. Thus, a conservative salinity measure cannot be easily defined in terms of the total mass of a varying solute (Millero *et al* 2008, Wright *et al* 2011, Pawlowicz *et al* 2011). The problem becomes even more complex when additional constituents (e.g. macro-nutrients) are introduced by biogeochemical processes.

A related problem is a proper definition of seawater molality since reactions between the solute components and with solvent as well as ionic association will change the total number of dissolved particles. This is additionally complicated by the fact that any distinction between 'associated' and 'dissociated' pairs of ions is subject to arbitrary physical convention (Bjerrum 1926, Falkenhagen and Ebeling 1971, Ebeling and Grigo 1982, Justice 1991). This essential point is only infrequently mentioned as a severe problem in the literature on electrolytic solutions; it is relevant also for the physically rigorous definition of pH (as discussed in Dickson *et al* 2016, part 3 of this issue). The crossover between bound and free ions in a solution is smooth rather than stepwise as the associated/dissociated classification suggests (Robinson and Stokes 1970). An important metrological consequence is that properties of free ions in a partly dissociated solute cannot be measured directly but only derived from theoretical relations (such as Pitzer equations or mass-action laws) which implement the particular threshold assumed. Measurable quantities should not depend on that arbitrary definition.

The definition of the Reference Composition includes neutral molecules and free ions. The molality of seawater depends on this convention and cannot be measured unambiguously without it. However, this convention is not necessarily consistent with other conventions such as those used to define ionic association constants. For example, as a result of ionic association, 2-2 electrolytes like $MgSO_4$ are known to begin deviating at extremely small concentrations from the limiting laws that imply full dissociation (Falkenhagen *et al* 1971). In contrast, all Mg^{2+} and SO_4^{2-} is counted as as if they were free ions in the Reference Composition, even at the much higher concentrations that are typical for ocean waters.

In the definition of the Reference Salinity, the problem of chemical reactions in the solution was conceptually circumvented by first moving the seawater sample to a reference temperature and pressure, and then adding or removing pure water until the Practical Salinity equals 35.000 within these significant digits, counting the particles and their masses in just the way they are listed in table 1, and then correcting by the dilution factor. For real seawaters a similar invariant reference condition cannot be so easily defined because the relative composition (and conductivity) is different. Instead, the problem is dealt with in TEOS-10 by considering Reference-Composition Seawater of the same density as that of the sample (at specified reference conditions). An alternative future approach might be that only the atoms different from hydrogen and oxygen are counted as elemental salt constituents, i.e., a measure that is rigorously invariant with respect to any chemical reactions.

Finally, it is important to keep in mind that the precision of currently available measurement technology and research needs imply that uncertainties of Practical Salinity estimates may be an order of magnitude less than those of the derived estimates of thermodynamic properties (Pawlowicz *et al* 2012), because of composition changes. Oceanographic standards prior to TEOS-10 provided no means for discussing and compensating for seawater composition anomalies. Now, in the context of TEOS-10, the increasing demands of ocean modeling and climate research have highlighted the issue of composition variations and their effects on seawater properties.

In general, theoretical considerations make it plain that a single concentration variable is insufficient to describe all the properties of a varying multi-component solution, but complete chemical analysis of seawater samples on a routine basis is impractical. In several cases it turns out that secondary measurements of a different physical property or composition variable can be used to estimate first-order corrections if the primary salinity variable is conventional Practical Salinity (Feistel *et al* 2010b, Pawlowicz *et al* 2011, McDougall *et al* 2012). Several methods based on different choices for secondary measurands, such as density or carbon/nutrient concentrations, have been developed. However, since these definitions have all been developed relatively recently, there is little practical experience in judging the strengths and weaknesses of each for different applications.

6. Suggested tasks

Carrying out a full chemical analysis for the major constituents of seawater to an accuracy resolving as many as 6 significant
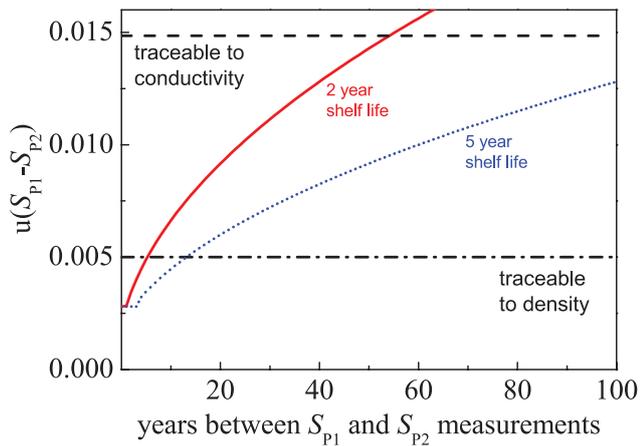
Figure 1. Uncertainty of the difference of two independent salinity measurements, S_{P1} and S_{P2}, versus the time elapsed between the measurements. The uncertainty increases for results traceable to the conductance ratio of SSW, depending on the assumed shelf life of SSW: the *solid red line* to 2 years (Culkin and Ridout 1998), the *dotted blue line* to 5 years (Bacon *et al* 2007). In contrast, the uncertainties do not increase with time if the results are traceable to the SI. The *dash-dotted line* refers to results traceable to density which would provide a better bound on uncertainty after about a decade, the *dashed line* to SI conductivity standards, which would not provide a useful bound until measurements were separated by many decades.

digits is far too complicated a procedure to be used for regular salinity measurements at sea (or even in the laboratory). It has been and will remain common practice to use a suitable sea-water property as a surrogate measurand, with salinity calculated from this measurement result by means of a correlation equation between salinity and this property. Consequently, the specified property correlation must be a part of the standard measurement procedure for salinity. Traceability of measurements of this property to the SI is desirable because this enables a reliable comparison of measurement results with stated uncertainties, independent of the elapsed time between the measurements.

Currently, an electrical conductance ratio with SSW is used as the measurand, and the correlation equations given by PSS-78 are incorporated into TEOS-10. As discussed in section 5, conductivity measurements are traceable to the SI but only with an uncertainty that is somewhat larger than is needed for scientific investigations of ocean general circulation. For the time being, it appears to be technically infeasible to reduce this uncertainty to a level that would satisfy oceanographic and climatological demands. Instead, today's precision measurements are traceable to metrological artefacts (SSW and ultimately KCl solutions) with finite useful lifetimes. Although these artefacts are compared with their predecessors in a chain through time (Bacon *et al* 2007), each comparison in the chain will increase the uncertainty. Hence, the uncertainty in comparisons between salinities traceable to these artefacts will also increase as these salinities are determined at more widely spaced times.

Figure 1 shows an estimation of the corresponding uncertainties between two salinities measured some time apart under current practices. The uncertainty of the difference between results traceable to the conductance ratio of SSW

is $\sqrt{2} \times 0.002$ if those are measured within the expiry time of a particular batch of SSW. Although comparison between batches is complicated by the details of the purity of different KCl batches and other technical details (Bacon *et al* 2007), we can crudely estimate that the uncertainty will increase as $\sqrt{2 \times N/N_{sl} + 1} \times 0.002$ (Seitz *et al* 2011), where N is the number of years and N_{sl} is the assumed shelf life of SSW (somewhere between 2 and 5 years). The uncertainty will increase even beyond that of results traceable to SI conductivity standards (about $\sqrt{2} \times 0.01$) after several decades.

To provide a smaller upper limit on the uncertainty, another property must be considered. Among the potential candidates for the representative measurand such as chlorinity, density, sound speed, refractive index or microwave emissivity (Klemas 2011), the density of seawater appears to be the most suitable for several reasons (Seitz *et al* 2011, Wright *et al* 2011). With the commercial availability of vibrating-tube densimeters (Kremling 1971), measurements of the deviation of seawater density from that of pure water are possible outside specialised facilities and may become a practical alternative to conductance ratio for highly accurate salinity measurements in the laboratory.

One aim of a recent European research project (EMRP 2010) was to reduce the relative uncertainty of routine density measurements with vibrating-tube densimeters to less than 2×10^{-6}. This goal was achieved by optimising a substitution method (Wolf 2008, Feistel *et al* 2010a). A relationship between density and salinity was determined in a salinity range between $2\,\mathrm{g\,kg^{-1}}$ and $35\,\mathrm{g\,kg^{-1}}$ and at temperatures between 5 °C and 35 °C with a maximum relative uncertainty in density of less than 2×10^{-6} at the lower temperatures and increasing to 2.6×10^{-6} at 35 °C. By such a method the density of seawater is traceable to the density of pure water (figure 2), which acts in this case as a reference liquid with SI-traceable density values known with a relative uncertainty of about 1×10^{-6} from the CIPM-2001 or IAPWS-95 formulations (Tanaka *et al* 2001, Harvey *et al* 2009), which are consistent with TEOS-10. The maximum combined relative standard uncertainty of a density measurement is then about $\sqrt{(2.5 \times 10^{-6})^2 + (1 \times 10^{-6})^2} \approx 2.8 \times 10^{-6}$. Consequently, the uncertainty of the difference between two density measurements is $\sqrt{2} \times 2.8 \times 10^{-6} \approx 4 \times 10^{-6}$. For liquids, no routine density measurement techniques with smaller uncertainties are currently available.

Although the relative uncertainty of density measurements is much smaller than that of conductivity measurements, density changes resulting from changes in dissolved salt content are small relative to a large base value given by the density of pure water. Whereas conductivity changes by a factor of more than 16 when increasing the salinity from 2 to $42\,\mathrm{g\,kg^{-1}}$, density is changed only by about 3%. Therefore, the advantage of a very small uncertainty in density, which is indeed about two orders in magnitude smaller than that in conductivity, must be qualified. A relative uncertainty of 4×10^{-6} in seawater density is equivalent to an uncertainty in salinity of about $0.005\,\mathrm{g\,kg^{-1}}$. At this level of uncertainty, density still cannot replace conductance ratio as a basis for comparison of measurement
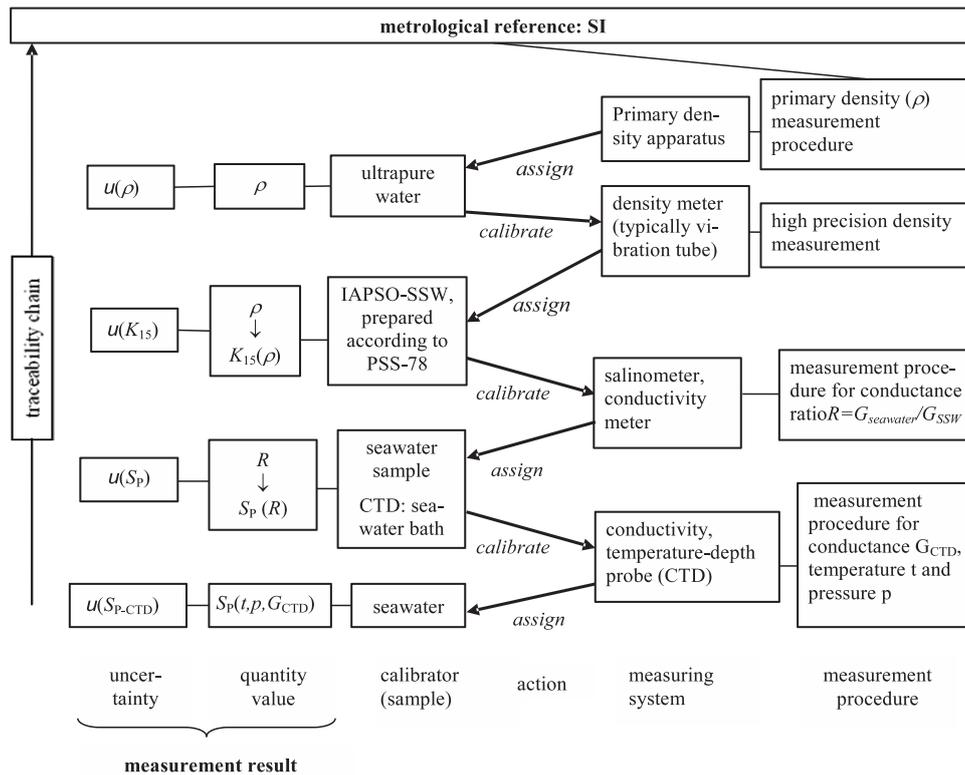
Figure 2. Metrological traceability chain for measurement results of Absolute Salinity, referenced to the SI density standard.

results at very short time scales, but because it is traceable to the SI its uncertainty will not increase with time (figure 1), and it can therefore provide superior results over time scales longer than about a decade.

A suggested new concept that takes advantage of currently available density measurement technology and at the same time leaves established oceanographic practice largely unaffected is a combination of conductance ratio and density measurement (Seitz et al 2011). In this concept, the salinity of SSW samples can be additionally certified (or at least checked) by density measurements in combination with the TEOS-10 equation of state. At a given reference temperature and pressure, the density of an SSW sample corresponding to a specified salinity is measured by the sample's producer and its Practical Salinity value is calculated via the equation of state and the Reference Salinity, equation (5). This value can be compared directly with the value achieved according to the PSS-78 procedures, which will reveal possible longer-term changes in SSW properties. Recent investigations supported the validity of this procedure (EMRP 2010). However, many practical aspects must still be investigated before it would be feasible to transition to obtaining salinity from density instead of from conductance ratio.

The use of density for routine salinity measurements has other advantages. Although, as for conductivity, absolute measurements are possible, it is usually easier to make measurements relative to a reference liquid. Certified reference liquids for density are usually measured by a validated density measurement apparatus (often a hydrostatic weighing apparatus) and are delivered with a certificate giving the density value together with its uncertainty and guaranteeing the

traceability to SI. However, ultra-pure water, which is routinely produced in many laboratories, and has characteristics that are well known, can also be used as a reference liquid for density measurements.

Ultrapure water can be produced in a highly reproducible way by commercial apparatuses, such as by reverse osmosis or double distillation. The purity of this water can be checked by chemical analysis. An easy verification is a conductivity measurement that is implemented in many pure-water producing devices working with reverse osmosis, since the electrical conductivity will be sensitive to the presence of ions that result from the dissolution of salts or of gases such as CO_2 (Zhang et al 2014). However, electrical conductivity measurements cannot account for all possible impurities. The presence of non-ionic elements must be checked using other techniques. The dissolution of non-conductive silicate in particular may be important if glass bottles are used for storage.

One problem may be caused by a varying content of dissolved air. The air content of ultra-pure water depends on the handling of the sample as well as on ambient air pressure and temperature; its influence on density is about 0.002 to $0.003\,\mathrm{kg\,m^{-3}}$ at laboratory conditions (Harvey et al 2005). To avoid this problem it is strongly recommended that airless or de-gassed water, which can be produced by boiling and subsequently avoiding any open contact to air, is used. If this is impossible, an air correction can be carried out as described by Tanaka et al (2001) or by Harvey et al (2005).

Density is also sensitive to the isotopic composition of the water. The CIPM formulation of liquid water density is based on Vienna Standard Mean Ocean Water, VSMOW (IAPWS 2001, BIPM 2006) which possesses a well-defined isotopic

composition with regard to deuterium and ^{18}O. The isotopic composition of pure water is known to vary geographically (Jasechko *et al* 2013). Although this has to be checked at least once for a given location, the temporal variation is often found to be negligible. If the influence of the isotopic composition on density is on the order of $3\,\mathrm{g\,m^{-3}}$ or larger, it should be handled as a correction to the water density table based on VSMOW. The recommended procedure is described by Tanaka *et al* (2001).

With these conditions accounted for, ultra-pure water can be used worldwide as a reference liquid, avoiding the need to make absolute density measurements routinely. The density of this water is easily available from standard tables or formulations for water density, and its traceability to the SI is guaranteed by these values. Although the suggested dual conductance ratio/density certification does not necessarily require the end user of SSW to make density measurements, the capability of doing so will allow for investigations into the quality of SSW after shipping and storage, which may account for some of the discrepancies found in different analyses of salinity determination procedures (Kawano *et al* 2006, Bacon *et al* 2007).

Once these technical issues are resolved, then official adoption of a density traceability in SSW would require the cooperation of organizations like the International Bureau of Weights and Measures (BIPM), the intergovernmental organization through which Member States act together on matters related to measurement science and measurement standards (including the SI), the International Association for the Properties of Water and Steam (IAPWS), which maintain the standards underlying TEOS-10, and the International Association for the Physical Sciences of the Oceans (IAPSO) which endorses SSW. Modifications to TEOS-10, if required, would also involve the Intergovernmental Oceanographic Commission (IOC), to communicate these modifications to international ocean programs and member countries, and to observational practitioners.

The issue of variations in relative chemical composition has received attention, and TEOS-10 procedures (see section 4) include results of that work. However, there are still many unknowns, and the sensitivity of seawater density and conductivity to changes in the chemical composition of both SSW and real seawater requires further investigation. These changes may cause changes in the temperature and pressure dependencies of measured values, which could lead to problems when laboratory measurements are used to characterise *in situ* properties. Measurements of Baltic seawater samples (Feistel *et al* 2010a) and numerical calculations (Pawlowicz *et al* 2011, Wright *et al* 2011) suggest that composition variations typical of those in nature can sometimes lead to significant errors and increased uncertainty of properties derived from conductivity measurements when using equations developed for SSW. In addition, the effect of composition variations on the density of SSW as it ages and is distributed is unknown, although preliminary results suggest that silicic acid levels may increase by dissolution from glass bottles, which will affect density but not conductivity. Marine chemists are well aware of silicate dissolution from glass bottles (Knudsen 1903, Culkin and Smed 1979, Yan *et al* 2015), even though this process is often only indirectly mentioned in standard handbooks of marine chemistry such as Grasshoff *et al* (1983).

A related issue is that the types and spatial variability of relative composition changes in the real ocean are known only imperfectly. The effects of carbon and nutrient changes explain most of the available density errors observed in the open ocean if composition variations are ignored (Pawlowicz *et al* 2011), but there have only been limited investigations of density errors and composition changes near continental shelves, near and above hydrothermal vent fields, and in regions of significant ice formation, which may involve different chemical processes. Relevant data would become more readily available in the future if direct density measurements on seawater samples become more routine, and this should be encouraged.

Finally, although more routine density measurements can be carried out on water samples, electronic *in situ* instrumentation would greatly increase their viability. However, electronic sensors for oceanographic *in situ* density measurements are not yet available, although this seems to be a solvable, mainly technical and financial, problem. There has been no widespread demand for such a sensor because density could be easily and accurately computed from salinity by standard correlation equations (although as discussed above the actual accuracy of the results was less than generally thought because the effect of composition variations was ignored before TEOS-10). A correlation equation to be used for the salinity calculation from density is formulated as an IAPWS Release (IAPWS 2008) and is part of TEOS-10. However, due to its widespread use and field-tested acceptance, conductance ratio will remain the salinity measure of choice for the foreseeable future.

7. Conclusion

The most recent definition of *seawater salinity* is related directly to the mass fraction of solute in seawater at specified temperature and pressure, independent of specific operational procedures. This allows for more flexibility in operational procedures to determine this mass fraction. Unhappily, the current traceability practice using PSS-78 procedures cannot be entirely replaced at the desired uncertainty level with another technique of similar accuracy that is traceable to the SI. Practical Salinity, or the corresponding conductance ratio, must still be labelled on the SSW bottles. This does have the advantage that the calibration and measurement practice of practitioners should not be affected in the immediate future.

Nevertheless, implementing a degree of traceability to the SI will significantly improve the reliability of long-term comparisons of observational data. The most promising, SI-traceable surrogate measurand is seawater density at specified temperature and pressure, converted to salinity using the TEOS-10 equation of state. The basic conceptual problems of this approach are mostly solved. However, substantial technical and institutional problems remain to be addressed before new practical implementations can be recommended to the international oceanographic community.

Finally, determining the effect of composition variations on seawater properties to some extent relies on knowing what these composition variations might be in the real ocean. Although this problem is probably solved for most of the open ocean, more observations need to be taken, especially in areas at the edges of the 'open ocean', to better understand composition variations that might occur there. Encouraging the routine measurement of high-precision density (through promulgation of methods and development of equipment) will help achieve this goal.

Acknowledgments

References

Aoyama M, Joyce T M, Kawano T and Takatsuki Y 2002 Standard seawater comparison up to P129 *Deep Sea Res. I* **49** 1103–14

Bacon S, Culkin F, Higgs N and Ridout P 2007 IAPSO standard seawater: definition of the uncertainty in the calibration procedure, and stability of recent batches *J. Atmos. Ocean. Technol.* **24** 1785–99

Bacon S, Snaith H M and Yelland M J 2000 An evaluation of some recent batches of IAPSO standard seawater *J. Atmos. Ocean. Technol.* **17** 854–61

Bender M L 2013 *Paleoclimate* (Princeton & Oxford: Princeton University Press)

BIPM 2006 *The International System of Units (SI)* 8th edn Organisation Intergouvernementale de la Convention du Mètre (Sevres: Bureau International des Poids et Mesures www.bipm.org/en/si/si_brochure/

Bjerrum N 1926 Ionic association. I. Influence of ionic association on the activity of ion at moderate degree of association *Det Kongelige Danske Videnskabernes Selskabs Skrifter* **7** 1–48

Bryden H L and Imawaki S 2001 Ocean heat transport *Ocean Circulation and Climate* ed G Siedler *et al* (San Diego: Academic) pp 455–74

Carritt D E 1963 Chemical instrumentation *The Sea, Volume 2, The Composition of Sea-Water, Comparative and Descriptive Oceanography* ed M N Hill (New York: Wiley) pp 109–23

Culkin F and Ridout P S 1998 Stability of IAPSO standard seawater *J. Atmos. Ocean. Technol.* **15** 1072–5

Culkin F and Smed J 1979 The history of standard seawater *Oceanol. Acta* **2** 355–64

Dickson J, Camões M F, Spitzer P, Fisicaro P, Stoica D, Pawlowicz R and Feistel R 2016 Metrological challenges for measurements of key climatological observables. Part 3: Seawater pH *Metrologia* **53** R26–R39

Dittmar W 1884 Report on researches into the composition of ocean-water, collected by H.M.S. Challenger, during the years 1873–1876. The Voyage of H.M.S. Challenger *Phys. Chem.* **1** 1–257 http://escholarship.org/uc/item/38p2q583

Durack P J and Wijffels S E 2010 Fifty-year trends in global ocean salinities and their relationship to broad-scale warming *J. Clim.* **23** 4342–62

Durack P J, Wijffels S E and Boyer T P 2013 Long-term salinity changes and implications for the global water cycle *Ocean Circulation and Climate. A 21st Century Perspective* ed G Siedler *et al* (Amsterdam: Elsevier) pp 727–57

Durack P J, Wijffels S E and Matear R J 2012 Ocean salinities reveal strong global water cycle intensification during 1950 to 2000 *Science* **336** 455–8

Ebeling W and Grigo M 1982 Mean spherical approximation-mass action law theory of equilibrium and conductance in ionic solutions *J. Solution Chem.* **11** 151–67

Emery W J, Talley L D and Pickard G L 2006 *Descriptive Physical Oceanography* (Amsterdam: Elsevier)

EMRP 2010 Metrology for ocean salinity and acidity ENV05 OCEAN. European Metrology Research Programme www.ptb.de/emrp/705.html

Falkenhagen H and Ebeling W 1971 Equilibrium properties of ionized dilute electrolytes *Ionic Interactions* ed S Petrucci vol 1 (New York: Academic) pp 1–59

Falkenhagen H, Ebeling W and Hertz H G 1971 *Theorie der Elektrolyte* (Leipzig: S. Hirzel Verlag)

Feistel R 2003 A new extended Gibbs thermodynamic potential of seawater *Prog. Oceanogr.* **58** 43–115

Feistel R and Ebeling W 2011 *Physics of Self-Organization and Evolution* (Weinheim: Wiley)

Feistel R *et al* 2016 Metrological challenges for measurements of key climatological observables: Oceanic salinity and pH, and atmospheric humidity. Part 1: overview *Metrologia* **53** R1–R11

Feistel R, Marion G M, Pawlowicz R and Wright D G 2010b Thermophysical property anomalies of Baltic seawater *Ocean Sci.* **6** 949–81 www.ocean-sci.net/6/949/2010/

Feistel R, Weinreben S, Wolf H, Seitz S, Spitzer P, Adel B, Nausch G, Schneider B and Wright D G 2010a Density and absolute salinity of the Baltic sea 2006–2009 *Ocean Sci.* **6** 3–24 www.ocean-sci.net/6/3/2010/

Forch C, Knudsen M and Sørensen S P L 1902 Berichte über die konstantenbestimmungen zur aufstellung der hydrographischen tabellen *Det Kongelige Danske videnskabernes selskabs skrifter* 6. Raekke, Naturvidenskabelige og Mathematiske Afdeling XII, 1. 151

Forchhammer G 1865 On the composition of sea-water in the different parts of the ocean *Phil. Trans. R. Soc.* **155** 203–62 www.jstor.org/stable/108888

GCOS 2010: *Implementation Plan for the Global Observing System for Climate in support of the UNFCCC (2010 Update)* (Geneva: World Meteorological Organization) WMO-TD/ No. 1532 (GCOS-138) p 180 www.wmo.int/pages/prog/gcos/Publications/gcos-138.pdf

Goyet C, Poisson A, Brunet C and Culkin F 1985 IAPSO standard seawater as a reference standard for alkalinity determinations *Deep-Sea Res.* **32** 1437–43

Grasshoff K, Ehrhardt M and Kremling K 1983 *Methods of Seawater Analysis* (Weinheim: Verlag Chemie)

Harvey A H, Kaplan S G and Burnett J H 2005 Effect of dissolved air on the density and refractive index of water *Int. J. Thermophys.* **26** 1495–514

Harvey A H, Span R, Fujii K, Tanaka M and Davis R S 2009 Density of water: roles of the CIPM and IAPWS standards *Metrologia* **46** 196–8

HELCOM 2014 Manual for marine monitoring in the COMBINE programme of HELCOM. Technical Annex I: Temperature and salinity measurements of seawater. Cooperative Monitoring in the Baltic Marine Environment—COMBINE, Helsinki Commission (HELCOM). Last updated: 17 January 2014. helcom.fi/action-areas/monitoring-and-assessment/manuals-and-guidelines/combine-manual

Hill K D, Dauphinee T M and Woods D J 1986 The extension of the Practical Salinity Scale 1978 to low salinities *IEEE J. Ocean. Eng.* **OE-11** 109–12

IAPWS 2001 *Guideline on the use of fundamental physical constants and basic constants of water.* The International Association for the Properties of Water and Steam, Revision 2012. www.iapws.org

IAPWS 2008 *Release on the IAPWS formulation 2008 for the thermodynamic properties of seawater.* The International Association for the Properties of Water and Steam www.iapws.org

IOC, SCOR, IAPSO 2010 *The International Thermodynamic Equation of Seawater—2010: Calculation and Use of Thermodynamic Properties.* Intergovernmental Oceanographic Commission, Manuals and Guides No. 56, UNESCO (English), p 196, Paris. www.TEOS-10.org

Ishai P B, Talary M S, Caduff A, Levy E and Feldman Y 2013 Electrode polarization in dielectric measurements: a review *Meas. Sci. Technol.* **24** 102001

Jacobsen J P and Knudsen M 1940 *Urnormal 1937 or Primary Standard Sea-Water 1937.* International Association of Physical Oceanography, Publication scientifique No. 7, Secrétariat de l'Association, Liverpool University, 38 pp

Jasechko S, Sharp Z D, Gibson J J, Birks S J, Yi Y and Fawcett P J 2013 Terrestrial water fluxes dominated by transpiration *Nature* **496** 347–50

JCOMM 2014 *Fourth JCOMM Marine Instrument Workshop for the Asia-Pacific Region* (Weihai, China, 21–23 October 2014). *JCOMM Meeting Report No. 118*, World Meteorological Organization, Geneva www.jcomm.info/RMICAP-4

Josey S A, Gulev S and Yu L 2013 Exchanges through the ocean surface *Ocean Circulation and Climate. A 21st Century Perspective* ed G Siedler *et al* (Amsterdam: Elsevier) pp 115–40

Josey S A, Kent E C and Taylor P K 1999 New insights into the ocean heat budget closure problem from analysis of the SOC air–sea flux climatology *J. Clim.* **12** 2856–80

Justice J-C 1991 Ionic interactions in solution: VI. The activity expansion and the association concept *J. Solution Chem.* **20** 1017–29

Katsaros K 2001 Evaporation and humidity *Encyclopedia of Ocean Sciences* ed J H Steele, vol 2 (Oxford: Academic) pp 870–7

Kawano T, Aoyama M, Joyce T, Uchida H, Takatsuki Y and Fukasawa M 2006 The latest batch-to-batch difference table of standard seawater and its application to the WOCE onetime sections *J. Oceanogr.* **62** 777–92

Kennish M J 2001 *Practical Handbook of Marine Science* (Boca Raton, FL: CRC Press)

King B A, Firing E and Joyce T M 2001 Shipboard observations during WOCE *Ocean Circulation and Climate, International Geophysics Series* vol 77 p 715 (San Diego: Academic)

Klemas V 2011 Remote sensing of sea surface salinity: an overview with case studies *J. Coast. Res.* **27** 830–8

Knudsen M 1901 *Hydrographische Tabellen* (Copenhagen and Hamburg: G.E.C.GAD and L Friedrichsen & Co)

Knudsen M 1903 On the standard-water used in the hydrographical research until July 1903. *J. Cons. Int. Explor. Mer* **s1** 3–9

Kremling K 1971 New method for measuring density of seawater *Nature* **229** 109–10

Lewis E L and Perkin R G 1978 Salinity: its definition and calculation *J. Geophys. Res.* **83** 466–78

Lovell-Smith J W, Feistel R, Harvey A H, Hellmuth O, Bell S A, Heinonen M and Cooper J R 2016 Metrological challenges for measurements of key climatological observables. Part 4: atmospheric relative humidity *Metrologia* **53** R40–R59

Lu X, McElroy M B and Kiviluoma J 2009 Global potential for wind-generated electricity *Proc. Natl Acad. Sci. USA* **106** 10933–8 www.pnas.org/content/106/27/10933

Lyman J 1969 Redefinition of salinity and chlorinity *Limnol. Oceanogr.* **14** 928–9

Ma C and Tian R 2004 Study on the preparation technique of chinese primary standard seawater *Ocean Technol.* **23** 1–8 (in Chinese)

Mantyla A W 1980 Electrical conductivity comparisons of standard seawater batches P29 to P84 *Deep Sea Res.* A **27** 837–46

Mantyla A W 1987 Standard seawater comparisons updated *J. Phys. Oceanogr.* **17** 543–8

Marcet A 1819 On the specific gravity, and temperature of sea water, in different parts of the ocean, and in particular seas; with some account of their saline contents *Phil. Trans. R. Soc.* **109** 161–208

McDougall T J 2003 Potential enthalpy: a conservative oceanic variable for evaluating heat content and heat fluxes *J. Phys. Oceanogr.* **33** 945–63

McDougall T J, Feistel R and Pawlowicz R 2013 Thermodynamics of seawater *Ocean Circulation and Climate. A 21st Century Perspective* ed G Siedler *et al* (Amsterdam: Elsevier) pp 141–58

McDougall T J, Jackett D R, Millero F J, Pawlowicz R and Barker P M 2012 A global algorithm for estimating absolute salinity *Ocean Sci.* **8** 1123–34 www.ocean-sci.net/8/1123/2012/os-8-1123-2012.pdf. Computer software available from www.TEOS-10.org

Millero F J 1982 The thermodynamics of seawater. Part I. The PVT properties *Ocean Sci. Eng.* **7** 403–60

Millero F J, Feistel R, Wright D G and McDougall T J 2008 The composition of standard seawater and the definition of the reference-composition salinity scale *Deep-Sea Res. I* **55** 50–72

Millero F J, Huang F, Woosley R J, Letscher R T and Hansell D A 2010 Effect of dissolved organic carbon and alkalinity on the density of arctic ocean waters *Aquatic Geochem.* **17** 311–26

Millero F J and Kremling K 1976 The densities of Baltic waters *Deep-Sea Res.* **23** 1129–38

Millero F J and Leung W H 1976 The thermodynamics of seawater at one atmosphere *Am. J. Sci.* **276** 1035–77

OSIL 2012 Using IAPSO Standard Seawater www.osil.co.uk/Resources/SeawaterTechnicalPapers/tabid/104/articleType/ArticleView/articleId/216/Using-IAPSO-Standard-Seawater.aspx

Pang Y 2015 *Final Report. JCOMM Inter-Comparison Project for Seawater Salinity Measurements January 2013–December 2014.* National Center of Ocean Standard and Metrology (NCOSM), Taijin, China

Park K 1964 Reliability of standard sea water as a conductivity standard *Deep Sea Res.* **11** 85–7

Pawlowicz R 2010 A model for predicting changes in the electrical conductivity, practical salinity, and absolute salinity of

seawater due to variations in relative chemical composition *Ocean Sci.* **6** 361–78

Pawlowicz R 2012 The electrical conductivity of seawater at high temperatures and salinities *Desalination* **300** 32–9

Pawlowicz R 2015 The absolute salinity of seawater diluted by riverwater *Deep Sea Res I* **101** 71–9

Pawlowicz R, McDougall T, Feistel R and Tailleux R 2012 An historical perspective on the development of the thermodynamic equation of seawater—2010 *Ocean Sci.* **8** 161–74 www.ocean-sci.net/8/161/2012/

Pawlowicz R, Wright D G and Millero F J 2011 The effects of biogeochemical processes on oceanic conductivity/salinity/density relationships and the characterization of real seawater *Ocean Sci.* **7** 363–87

Pierce D W, Gleckler P J, Barnett T P, Santer B D and Durack P J 2012 The fingerprint of human-induced changes in the ocean's salinity and temperature fields *Geophys. Res. Lett.* **39** L21704

Pierrehumbert R T 2010 *Principles of Planetary Climate* (Cambridge: Cambridge University Press)

Poisson A and Gadhoumi M H 1993 An extension of the practical salinity scale 1978 and the equation of state 1980 to high salinities *Deep-Sea Res.* **40** 1689–98

Pratt K W, Koch W F, Wu Y C and Berezansky P A 2001 Molality-based primary standards of electrolytic conductivity (IUPAC Technical Report) *Pure Appl. Chem.* **73** 1783–93

Reeburgh W S 1966 Some implications of the 1940 redefinition of chlorinity *Deep-Sea Res.* **13** 975–6

Robinson R A and Stokes R H 1970 *Electrolyte Solutions* 2nd revised edn (London: Butterworth and Co)

Schwan H P 1968 Electrode polarization impedance and measurements in biological materials *Ann. New York Acad. Sci.* **148** 191–209

Seitz S, Feistel R, Wright D G, Weinreben S, Spitzer P and de Bievre P 2011 Metrological traceability of oceanographic salinity measurement results *Ocean Sci.* **7** 45–62 www.ocean-sci.net/7/45/2011/

Seitz S, Spitzer P and Brown R J C 2010 CCQM-P111 study on traceable determination of practical salinity and mass fraction of major seawater components *Accreditation Qual. Assur.* **15** 9–17

Siedler G 1998 SI units in oceanography. Berichte aus dem Institut für Mereskunde an der Christian-Albrechts-Universität Kiel, Nr. 101

Spitzer P and Seitz S 2011 Electrolytic conductivity *Handbook of Metrology and Testing* 2nd edn ed H Czichos *et al* (New York: Springer) chapter 9.3

SUN 1985 *The International System of Units (SI) in Oceanography Report of IAPSO Working Group on Symbols, Units and Nomenclature in Physical Oceanography (SUN).* Unesco technical papers in marine science 45, p 124

Tanaka M, Girard G, Davis R, Peuto A and Bignell N 2001 Recommended table for the density of water between 0 °C and 40 °C based on recent experimental reports *Metrologia* **38** 301–9

Unesco 1981a The Practical Salinity Scale 1978 and the International Equation of State of Seawater 1980. Unesco technical papers in marine science 36, Unesco, Paris

Unesco 1981b *Tenth report of the joint panel on oceanographic tables and standards (Sidney, B.C., Canada, 1–5 September 1980).* Unesco technical papers in marine science 36, Unesco, Paris

Wells N C 2012 *The Atmosphere and Ocean* (Oxford: Wiley)

Wenner F, Smith E H and Soule F M 1930 Apparatus for the determination aboard ship of the salinity of sea water by the electrical conductivity method, bureau of standards *J. Res. Natl. Bur. Stand.* **5** 711–32

Wetzel R G 2001 *Limnology* (San Diego, CA: Academic)

Wieser M E 2006 Atomic weights of the elements 2005 (IUPAC technical report) *Pure Appl. Chem.* **78** 2051–66 available at: www.iupac.org/publications/pac/78/11/2051/

Wolf H 2008 Determination of water density: limitations at the uncertainty level of 1×10^{-6} *Accreditation Qual. Assur.* **13** 587–91

Wooster W S, Lee A J and Dietrich G 1969 Redefinition of salinity *Limnol. Oceanogr.* **14** 437–8

Wright D G, Pawlowicz R, McDougall T J, Feistel R and Marion G M 2011 Absolute salinity, 'density salinity' and the reference-composition salinity scale: present and future use in the seawater standard TEOS-10 *Ocean Sci.* **7** 1–26

Yan X K, White D R, Hao X M, Yu Z J, Edgar H and Duan Y N 2015 Assessing impurities in triple-point-of-water cells using a capacitance conductivity test *Int. J. Thermophys.* **36** 240–51

Zhang B, Lin Z, Zhang X and Wang X 2014 Absolute measurement system for low electrolytic conductivity of aqueous solutions based on van der Pauw's theory using a flow-through cell *Accreditation Qual. Assur.* **19** 433–8