Ocean Sci., 7, 45–62, 2011
www.ocean-sci.net/7/45/2011/
doi:10.5194/os-7-45-2011
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Metrological traceability of oceanographic salinity measurement results

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Received: 28 May 2010 – Published in Ocean Sci. Discuss.: 22 July 2010
Revised: 13 December 2010 – Accepted: 18 December 2010 – Published: 19 January 2011

Abstract. Consistency of observed oceanographic salinity data is discussed with respect to contemporary metrological concepts. The claimed small uncertainty of salinity measurement results traceable to the conductivity ratio of a certified IAPSO Standard Seawater reference is not metrologically justified if results are compared on climatic time scales. This applies in particular to Practical Salinity \(S_P\), Reference Salinity \(S_R\), and the latest estimates of Absolute Salinity using the TEOS-10 formalism. On climate time scales an additional contribution to the uncertainty that is related to unknown property changes of the reference material must be accounted for. Moreover, when any of these measured or calculated quantity values is used to estimate Absolute Salinity of a seawater sample under investigation, another uncertainty contribution is required to quantify the accuracy of the equations relating the actually measured quantity to the Absolute Salinity. Without accounting for these additional uncertainties, such results cannot be used to estimate Absolute Salinity with respect to the International System of Units (SI), i.e. to the unit chosen for the mass fraction of dissolved material in the sample, which is \("\text{g kg}^{-1}\)". From a metrological point of view, such deficiencies in the calculations involving other quantities will produce SI-incompatible results. We outline how these problems can be overcome by linking salinity to primary SI measurement standards.

1 Introduction

Absolute Salinity \(S_A\) is defined as the mass fraction of dissolved material in seawater at equilibrium for \(t = 25 ^\circ C\) and \(P = 101325 \text{ Pa}\) (Millero et al., 2008). From a practical point of view, frequent routine mass fraction measurements of all relevant seawater constituents are impossible to achieve. For seawater samples with a given chemical composition of the dissolved material but variable amounts of water, the measurement of a single independent property of the solution in addition to temperature and pressure is sufficient to obtain a measure of salinity. The halide mass fraction (providing the “Chlorinity” in \("\text{g kg}^{-1}\)"), the electrolytic conductivity (providing the “Practical Salinity” \(S_P\) on a “unitless” scale, i.e. with unit 1) or the refractive index, which is not in regular practical use (Malardé et al., 2009), are appropriate quantities that can serve this purpose. An equation estimating Absolute Salinity of IAPSO¹ Standard Seawater (SSW) from either Practical Salinity or Chlorinity at a specified reference point of temperature, pressure and concentration was proposed by Millero et al. (2008); it returns the Reference-Composition Salinity \(S_R\) in \("\text{g kg}^{-1}\)". For the stability and robustness of its in-situ sensors (SeaBird, 1989) under the harsh conditions experienced at sea, conductivity has been the unrivalled, most successful and reliable quantity for in-situ observation of salinity since the introduction of the Practical Salinity Scale 1978 (PSS-78).

Particularly in oceanography, many measurements are undertaken at different times by various persons using diverse devices at numerous locations all over the world oceans. Such measurement results are stored in databases of global
observation systems and are used for oceanographic and climate change research. It is therefore of fundamental importance that inconsistencies be avoided and that the measured quantity values be linked to a common, time-stable reference in order to permit unrestricted comparison of the measurement results from different times, locations and observers (referred to as “metrological comparability” (comparability) of measurement results (VIM, 2008)). SSW currently serves as a common reference for Practical Salinity measurement results. It was already introduced by Knudsen in 1899, carefully chosen for exactly the purpose of realizing metrological comparability of measurement results. SSW is produced commercially by the IAPSO Standard Sea-Water Service (OSIL, 2010) from North Atlantic seawater according to the specification given in the background papers of PSS-78 (UNESCO, 1981).

In the present paper the concept of “metrological traceability” (traceability) (VIM, 2008) is outlined in Sect. 2, which is an approach used to realise the comparability of measurement results by linking them to a common, stable reference (De Bièvre, 2008; De Bièvre et al., 2010). In Sects. 3 and 4 measurement results for Practical Salinity are evaluated with respect to this concept. It is shown that Practical Salinity results are currently not traceable to metrological references consistent with the International System of Units (SI) and that this has an important consequence: the current reference of Practical Salinity measurement results to the $K_{15}$ conductivity ratio of SSW puts their long-term metrological comparability at risk. Since the stability of SSW is estimated to be around two to five years (Bacon et al., 2000; Culkin and Ridout, 1998) and its replicability cannot be guaranteed on climatologically timescales, the small uncertainty that is commonly attributed to Practical Salinity data applies only over a relatively short time scale.

Moreover, this small uncertainty does not indicate the uncertainty in the estimate of how many grams of material are actually dissolved in a kg of a measured seawater sample. Thus, estimates of Absolute Salinity based on Practical Salinity measurements, when used in calculations together with other measured quantities that are linked to SI references, have to account for this additional uncertainty contribution. Otherwise the estimates of Absolute Salinity will be inconsistent with the SI. This issue will be stressed in Sect. 5 against the historical background of estimating Absolute Salinity.

Finally, in Sect. 6 we will demonstrate how Practical Salinity measurement results can be linked to SI references without effectively changing the established measurement and calibration procedures of oceanographic laboratories.

2 Metrological traceability

Metrological traceability addresses the origin and the reliability of any quantity value that a measuring system yields. The concept of linking a measurement result to a commonly accepted reference by calibration is as plausible as it is old. However, people are often not aware of the metrological demand on the measurement results, which allows or rejects comparison of data and their respective simultaneous implementation in further calculations within the SI. Therefore, before we discuss the reliability of salinity data from a metrological point of view, it is necessary to summarize the metrological traceability concept and some of its implications.

A “quantity”, quite generally, is a “property of a phenomenon, body or substance, where the property has a magnitude that can be expressed as a number”, the “quantity value” (VIM, 2008). A measuring system indicating the quantity value should have been calibrated by means of a stable “measurement standard” (VIM, 2008) immediately before the measurement. This measurement standard has a known quantity value of the same kind. The expression “known” means that the quantity value of the measurement standard together with its uncertainty has been assigned using a sophisticated measurement procedure, which is likewise calibrated by means of a measurement standard and so on. This “calibration hierarchy” (VIM, 2008) is often ended in a “primary reference measurement procedure” (VIM, 2008) that is used to assign a quantity value and a unit to the “primary measurement standard” (primary standard) (VIM, 2008) for that kind of quantity. Note that such a procedure can nevertheless consist of measurements of other quantities, which are used to calculate the quantity value of the primary standard and which, of course, have to be traceable likewise to their primary measurement standards. For example, the conductivity value of a primary conductivity standard is calculated from temperature, resistance and length measurements, which are traceable to the corresponding primary temperature, resistance and length standards (Brinkmann et al., 2003). Moreover, the unit of a measured quantity value also expresses its metrological traceability to the corresponding primary standard of that kind of quantity. For instance, a balance reading can be given in “kilograms” only if the actual balance in use is calibrated with a measurement standard (i.e. a weight), the quantity value of which (its “mass value”) is traceable to the SI primary measurement standard “kilogram”, currently still realised as the reference platinum/iridium body stored in Paris. Obviously, quantity values measured at different times or locations, by various persons with diverse measurement systems or procedures, can be compared with each other only if they are traceable to the same reference (providing metrological comparability of measurement results).

Concerning comparability of measured quantity values a second aspect is of importance. The quantity value of any measurement standard can only be assigned with

\textsuperscript{2}The important metrological expressions introduced here are defined in the International Vocabulary of Metrology. The definitions can also be found in the annex of this article.
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is the electrolytic conductivity of a seawater sample and depends on the temperature of the sample and the pressure experienced by it during the measurement. In metrological terms an “output quantity” (Practical Salinity) is calculated from a measured “input quantity” (conductivity ratio) using a “measurement function” or, more general, a “measurement model” (VIM, 2008). The coefficients of the polynomial are “influence quantities”, which affect the indicated Practical Salinity value, although they do not affect the actual measured input quantity. They are based on measurement results (Perkin and Lewis, 1980), which therefore have a measurement uncertainty. This will be of importance in Sect. 5, where we discuss under what conditions this uncertainty contribution to a Practical Salinity result has to be considered.

The equations of PSS-78 include algorithms to determine $R$ and Practical Salinity at 14.996 °C and standard atmospheric pressure (0.101325 MPa) from measurements at other values of temperature and pressure. However, for clarity we express all quantities, including $\kappa_s$, in terms of conditions evaluated at 14.996 °C and standard atmospheric pressure. Note that 14.996 °C on today’s temperature scale ITS-90 is equivalent to 15 °C on the previous scale IPTS-68 on which PSS-78 was defined. In particular PSS-78 and the KCl solution is defined such that the Practical Salinity value is 35 if $\kappa_s = \kappa_{\text{KCl}}$ (Culkin and Smith, 1980; Dauphinee et al., 1980; Poisson, 1980), each evaluated at 14.996 °C.

A measuring device for Practical Salinity, such as a salinometer or a conductivity-temperature-depth probe (CTD), measures the conductance $G$ of a sample filled into the measuring cell. For calibration of a salinometer IAPSO Standard Seawater (SSW) is used. SSW is prepared from seawater, collected from the North Atlantic by ships of opportunity and sold in bottles. The conductivity of such a sample is adjusted by the manufacturer, typically by dilution, to the conductivity of the KCl sample defined in PSS-78 (Bacon et al., 2007). To this end its conductance $G_{\text{SSW}}^m$ is accurately measured and adjusted until it is near that of the KCl solution $G_{\text{KCl}}^m$. Since it is impossible to prepare the defined KCl solution with the desired accuracy, solutions with slightly higher and lower concentrations are prepared and $G_{\text{KCl}}^m$ is derived by an interpolation (Bacon et al., 2007). The superscript $m$ indicates a group of measurements performed by the manufacturer using exactly the same device and procedures. This is considered to be crucial to guarantee the metrological equivalence of the adjusted conductivities. From $G_{\text{SSW}}^m$ and $G_{\text{KCl}}^m$ the so-called $K_{15}$ ratio is calculated and inscribed on the labels of the SSW bottles

$$K_{15} = \frac{G_{\text{SSW}}^m}{G_{\text{KCl}}^m} .$$

The conductance ratio of a seawater sample, which is indicated by an SSW-calibrated salinometer, is finally calculated from

$$R = \frac{G_{s}^u}{G_{\text{SSW}}^u} K_{15} .$$

3There is no primary measurement standard for the base unit “mole”, but since1996 evaluations of equivalence of primary measurement standards for amount-of-substance measurements are slowly added.
$G_s$ is the measured conductance of the sample, $G_{SSW}^u$ is the measured conductance of the SSW sample used for calibration. Here the superscript $u$ indicates measurements performed with a user’s salinometer (using exactly the same device). Note that in general the measured conductance $G$ of a solution is correlated to the conductivity $\kappa$ of the solution by the cell constant $K$ of the specific measuring cell in use (not to be confused with $K_{15}$):

$$G = \frac{\kappa}{K} .$$  \hspace{1cm} (4)

Hence, assuming that the cell constant of the measuring cell is indeed stable and independent of the solution, $K_{15}$ is equivalent to the conductivity ratio of SSW and the KCl-solution, since the cell constants cancel in Eq. (2) and (3). Likewise Eq. (1) is equivalent to Eq. (3), i.e. the conductance ratio indicated by a SSW calibrated salinometer represents the conductivity ratio of the seawater sample and the KCl-solution defined in PSS-78. It should be noted that in practice $K_{15}$ of SSW is determined by measurements of conductivity ratios using a salinometer (Bacon et al., 2007). However, the ratio of the measured conductivity ratios is equivalent to the conductance ratio in Eq. (2) for the reasons mentioned.

Figure 1 illustrates the traceability chain for Practical Salinity and conductivity ratio measurement results, respectively. It visualises how the numerical values of a measurement result are linked to its reference by an unbroken chain of calibrations according to IUPAC recommendations (De Bièvre et al., 2010). The right hand side specifies the measurement procedures and systems used to assign a numerical value and its uncertainty to the solution property “conductivity ratio”. The left hand side shows the solutions which then embody the (quantified) property “conductivity ratio” and which are used to calibrate a measurement system in the next deeper level of the calibration hierarchy. In this hierarchy IAPSO SSW acts as a primary measurement standard for conductivity ratio measurement results, i.e. it represents the highest level embodiment of the property “conductivity ratio”. The realisation of the $K_{15}$ ratio, which comprises the preparation of SSW and the KCl solutions and the corresponding measurements, is the primary reference measurement procedure. The specification of the $K_{15}$ ratio within the PSS-78 documentation (UNESCO, 1981) acts as the metrological reference for the traceability of conductivity ratio measurement results and consequently for Practical Salinity results, which are derived from them. Note that the metrological reference for traceability of a measurement result usually corresponds rather to a normative document than a measurement standard (De Bièvre et al., 2010). Figure 1 also includes CTD measurements, which will be discussed further below.

As outlined in Sect. 2 the indicated quantity value in a measurement result is inextricably linked with its uncertainty in order to make it useful for comparisons. Following the “Guide to the expression of uncertainty in measurement” (GUM, 2008) the combined uncertainty of $R$ is calculated from the input quantities of Eq. (3) as

$$u(R)^2 = \left( \frac{K_{15}}{G_{SSW}^u} u(G_s^u) \right)^2 + \left( \frac{G_s^u K_{15}}{G_{SSW}^u} u(G_{SSW}^u) \right)^2 + \left( \frac{G_s^u}{G_{SSW}^u} u(K_{15}) \right)^2 - 2 \frac{K_{15} G_s^u}{G_{SSW}^u} u(G_s^u) r(G_s^u, G_{SSW}^u) .$$  \hspace{1cm} (5a)

whereas the uncertainty of $K_{15}$ is calculated from Eq. (2)

$$u(K_{15})^2 = \left( \frac{1}{G_{KCI}^m} u(G_{SSW}^m) \right)^2 + \left( \frac{G_{SSW}^m}{G_{KCI}^m} u(G_{KCI}^m) \right)^2 - \frac{G_{SSW}^m}{(G_{KCI}^m)^3} u(G_{SSW}^m) r(G_{SSW}^m, G_{KCI}^m) ,$$  \hspace{1cm} (5b)

The terms on the right hand side of Eqs. (5a) and (5b) account for a possible correlation of the conductances, whereas $r(u(G_s^u), u(G_{SSW}^u))$ and $r(G_{SSW}^m, G_{KCI}^m)$, respectively, are the corresponding correlation coefficients. Measurement uncertainties are typically stated as “standard uncertainties” (GUM, 2008), which for normally distributed results correspond to a level of confidence of about 68%. Multiples of the standard uncertainty (“expanded uncertainties” (GUM, 2008)) can be used in the end measurement result if an increased level of confidence is desired. Here a “coverage factor” (GUM, 2008) of two is typical. Equations (5) express the general dependence of $u(R)$ from the uncertainties of the measured input quantities, which on their part may depend on a variety of influences. A more detailed discussion is beyond the scope of this paper. However, Eq. (5b) particularly summarizes uncertainties in the measured conductances due to the preparation procedure of SSW and the KCl solutions, the “stability” and “sensitivity” (VIM, 2008) of the salinometer in use, the interpolation calculation, and “measurement reproducibility” (using different devices, different operators, different locations, etc.) (VIM, 2008). Bacon et al. (2007) have calculated the standard uncertainty $u_{15}(K_{15})$ to be $5 \times 10^{-4}$ at the time of manufacture, based on an analysis of the SSW production. In Eq. (5a) $u(G_{SSW}^u)$ and $u(G_s^u)$ account for the “measurement repeatability” (VIM, 2008). Their values can be statistically determined by conductance measurements of SSW and the seawater sample under “repeatability conditions” (using the same device, operator, locations, etc.). The overall relative uncertainty of a measured conductivity ratio using a Guildline 8400B salinometer is stated to be smaller than $10^{-4}$ at a conductivity ratio of one and the “24-h accuracy” of Practical Salinity results is given as “better than $+/-0.002$” at a Practical Salinity of 35 (Guildline, 2004). No information is given whether this value is a standard or an expanded uncertainty. Most recently Le Menn (2009) has calculated an expanded uncertainty of
0.0022 at a Practical Salinity of 35 for a Guideline Portasal salinometer.

It must be emphasized that the absolute conductivity values corresponding to Eqs. (1) to (3) are not measured in current practice, i.e. they are not measured traceable to the SI (in units of Ω⁻¹ m⁻¹), even though the conductance meter of the devices are typically calibrated using resistors, which are calibrated with respect to the SI. This is because the solution electrode interaction in the measuring cell causes the measured conductance to deviate from the actual solution conductance. Only if the cell constant is calibrated using an SI traceable conductivity standard of assigned conductivity \( \kappa_{\text{ref}} \) (Brinkmann et al., 2003), which is not current practice, can the absolute conductivity of a solution be calculated from the measured conductance. If two measurement results are individually not traceable to the SI, then their ratio is not traceable to the SI either. Hence, the metrological reference for \( K_{15} \) is the SSW preparation procedure defined in PSS-78 only, but the link of \( K_{15} \) to the SI is missing. Consequently, conductivity ratio measurement results from Eq. (3) are not traceable to the SI either. Note that the absolute conductivity measurements performed by Poisson (1980) and Culkin and Smith (1980) cannot serve to link Practical Salinity measurement results to the SI. Firstly, just as any measurement device or standard has to be routinely calibrated, the absolute conductivity of every new batch of SSW and the corresponding KCl solution, respectively, would need to be measured routinely in order to guarantee the SI link of Practical Salinity results on the long term run. Secondly, in practice the uncertainties of conductivity ratio measurement results do not include the uncertainty of absolute conductivity measurements, which will be discussed in the following.

The crucial difference in metrological reference of \( K_{15} \) becomes obvious in the uncertainty contributions of \( K_{15} \). In case \( K_{15} \) is referred to the SI, its uncertainty needs to consider the uncertainties of \( G_{\text{SSW}}^{\text{m}} \) and \( G_{\text{KCl}}^{\text{m}} \) with respect to SI-traceable values of measurement standards. The uncertainties of a conductance measurement result traceable to the SI is calculated from Eq. (4). The uncertainties of \( G_{\text{SSW}}^{\text{m}} \) and \( G_{\text{KCl}}^{\text{m}} \) are then given by

\[
\begin{align*}
 u(G_{\text{KCl}}^{\text{m}})^2 &= \left( \frac{1}{K^{\text{m}}} u(K^{\text{m}}) \right)^2 + \left( \frac{\kappa_{\text{KCl}}}{(K^{\text{m}})^2} u(K^{\text{m}}) \right)^2, \quad (6a) \\
 u(G_{\text{SSW}}^{\text{m}})^2 &= \left( \frac{1}{K^{\text{m}}} u(K^{\text{m}}) \right)^2 + \left( \frac{\kappa_{\text{SSW}}}{(K^{\text{m}})^2} u(K^{\text{m}}) \right)^2. \quad (6b)
\end{align*}
\]

The uncertainty of the cell constant \( u(K^{\text{m}}) \) is also calculated from Eq. (4) (solved for \( K^{\text{m}} \))

\[
 u^2(K^{\text{m}}) = \left( \frac{1}{G_{\text{ref}}^{\text{m}}} u(K_{\text{ref}}) \right)^2 + \left( \frac{\kappa_{\text{ref}}}{G_{\text{ref}}^{\text{m}}} u(G_{\text{ref}}) \right)^2. \quad (6c)
\]

\( G_{\text{ref}} \) is the measured conductance of a solution of known absolute conductivity \( \kappa_{\text{ref}} \) and known uncertainty \( u(K_{\text{ref}}) \). \( u(G_{\text{ref}}) \), \( u(\kappa_{\text{KCl}})/K^{\text{m}} \) and \( u(\kappa_{\text{SSW}})/K^{\text{m}} \) account for sensitivity and stability of the measuring device during the conductance measurements of the reference solution, SSW and the KCl-solutions, respectively. The uncertainty attributed to stability can be statistically determined by measurements under repeatability conditions. That attributed to sensitivity is usually calculated from the resolution of the indication unit. The uncertainty of \( K_{15} \) is then calculated from Eq. (5b). Note that here the specific uncertainties of the SSW production procedure do not enter into the uncertainty of \( K_{15} \). The uncertainty of Practical Salinity results which are determined from SI traceable conductivity measurements are found to be about five time larger compared to results traceable to \( K_{15} \) (Seitz et al., 2010). This is the obvious reason why the specification of \( K_{15} \) according to the PSS-78 definitions is the metrological reference of choice for the traceability of Practical Salinity results rather than the SI. In the next section, we will discuss the consequences of the missing SI link.

Finally, a peculiarity concerning the traceability of conductivity ratio results measured with CTD probes should be mentioned. Habitually CTDs are inserted into a stirred and temperature-stabilized seawater bath for calibration. Conductances are measured at various temperatures and, depending on the intended application, at one or more salinities. The salinities are represented by Practical Salinity measurements using a SSW-calibrated salinometer. Calibration is done at atmospheric pressure. Afterwards a sensor-specific calibration curve is numerically fitted to the data in order to correlate the CTD conductance signal to a conductivity, calculated from the Practical Salinity and the temperature by inverting the Practical Salinity relations.

Additionally to the laboratory calibration in situ calibrations during cruises are frequently done. Here, simultaneously to the CTD measurements, separate temperature measurements by a standard thermometer and collection of water samples are carried out in a well-mixed layer. The Practical Salinity of the samples is measured by a salinometer (calibrated with SSW). The conductance signal of the CTD is corrected (if necessary) by comparison to a conductivity obtained by inverting the PSS-78. The input quantities are the Practical Salinity of the sample, the temperature of the calibrated standard thermometer and the data of the pressure sensor. Uncertainties of Practical Salinity results using CTDs were recently investigated in detail (Le Menn, 2009) and are not discussed here. But it must be mentioned that due to the above procedure a CTD measurement of Practical Salinity includes an additional level within the calibration hierarchy.
Fig. 1. Illustration of the current traceability of a measured conductivity ratio \( R \) and the derived Practical Salinity result \( S_p \) respectively to the \( K_{15} \) ratio of Standard Seawater (SSW). Starting from the top of the figure and working towards the bottom, it indicates (i) the metrological reference for conductivity ratio measurements, which is the (standardizing) documentation of PSS-78 (UNESCO, 1981), in particular the definition of the conductivity ratio. This also describes (ii) the procedure how to realize (embody) the (iii) \( K_{15} \) ratio in IAPSO-SSW. In turn, SSW is used for the calibration of a salinometer. (iv) According to a measurement procedure that is described by the manufacturer, such a calibrated salinometer can then be used to measure the (v) conductivity ratio of a seawater sample, which is finally used to calculate Practical Salinity. Concerning a CTD probe (vi) a procedure is defined to prepare a seawater bath and measure its \( R \) value using a calibrated salinometer. This (vii) bath is then used to calibrate a CTD for (ix) Practical Salinity measurements according to (viii) a defined measurement procedure. Each of these steps relies on the previous as part of the calibration hierarchy (far left column) and represents an element of the metrological traceability chain in the reversed order (next to leftmost column). The leftmost column of boxes indicates the typical uncertainties associated with recently calibrated salinometers and CTDs. Note that no uncertainty is attributed to the \( K_{15} \) value of SSW, however, the uncertainty associated with a salinometer measurement, also accounts for the instability of SSW. The second column of boxes from the left shows typically measured quantity values to which these uncertainties apply, both giving the measurement result. The third column of boxes indicates the sample under consideration for each step in the calibration hierarchy. The column of arrows indicates specific connections in terms of quantity values passed between the levels. An arrow from the right to the left hand side indicates that a measurement procedure (rightmost column of boxes) and measuring systems (next to rightmost column) are used to assign a quantity value (conductivity ratio or Practical Salinity) to a sample. An arrow from the left to the right hand side indicates that a quantity value, which is embodied in a solution, is used to calibrate a measurement system.
(see Fig. 1), which necessarily results in an additional contribution to the total uncertainty. Major contributions that are relevant for the comparability of CTD measurement results result from the lack of harmonisation of a salinometer bath set temperature and the uncertainty in timing from the moment when a salinity sample was taken until that sample was measured. Hence, the uncertainties associated with Practical Salinity results obtained from CTD measurements are inevitably larger than those obtained from salinometer measurements.

4 Consequences of conductivity ratio traceability to only $K_{15}$

The traceability of conductivity ratio measurement results to the $K_{15}$ value of SSW, but currently missing SI traceability, entails two important consequences, which have to be accounted for when Practical Salinity results are compared for oceanographic monitoring purposes or when used in ocean model validation. These will be discussed in this section.

4.1 Verification of SSW replicability

In contrast to fundamental physical phenomena, such as the atomic microwave transition in the caesium-133 that serves to define the “second” in SI, human-made measurement standards such as SSW are inevitably subject to variations over time or between independent realisations. Raw materials, production procedures, equipment, experimental skill, technical personnel, North Atlantic seawater variability and even the company producing SSW can and will change, at least on longer time scales, sometimes in unpredictable ways or for unknown reasons. It is obvious that a variation in the physico-chemical properties of SSW influences Practical Salinity measurement results. The uncertainty of a Practical Salinity measurement result therefore has to include a contribution that in particular accounts for stability and replicability of SSW. To that effect, Bacon et al. (2007) presented an uncertainty budget for the comparability of various batches are measured with respect to the $K_{15}$ ratio of a single batch (Aoyama et al., 2002; Culkin and Ridout, 1998; Mantyla, 1980, 1987). Of course such a comparison can reasonably be performed only with batches that have not exceeded the expiry time of a few years. Culkin and Ridout (1998) state an expire time of about two years, while Bacon et al. (2007) found no significant changes within a five year period. If a SSW batch was measured in two such comparisons it can be used as a link between the investigations. Hence, the results of one investigation can be corrected relative to another by the difference of the results of the linking key batch. By looking for such linking key batches in various investigations, where it is fresh in one investigation and old in the other, the verification of SSW replicability can be extended to much longer periods (Aoyama et al., 2002; Bacon et al., 2000; Mantyla, 1980). However, with every step back in time, with width given by the expiry time, the uncertainty of the corrected values increases. This can be roughly estimated, using the uncertainty value 0.002 of a Practical Salinity measurement, stated for a Guildline Autosal salinometer. This uncertainty refers to the SSW batch that has actually been used for the calibration. Comparing two results $S_{P1}$ and $S_{P2}$ of a linking key batch, where $S_{P1}$ has been measured in one investigation and $S_{P2}$ in another, older investigation, gives a combined uncertainty (GUM, 2008) of $u^2(S_{P2} - S_{P1}) = 0.002^2 + 0.002^2$ for the difference of the values. Using this difference to correct for a possible offset results in the older investigation, then the combined uncertainty of the corrected values is $u^2_{corr} = 3 \times 0.002^2$. This procedure can be continued. Going $N$ steps back in time therefore results in a combined uncertainty of $u^2_N = (2 \times N + 1) \times 0.002^2$, or $u_N = \sqrt{2 \times N + 1} \times 0.002$, respectively, for the corrected values. Thus, assuming an expiry time of two years, the Practical Salinity value of a 50-year-old SSW batch has an uncertainty of around 0.014, if it is referred to a recently collected SSW batch by the described comparison method. Assuming a five year expiry time, it has an uncertainty of around 0.009. In case another uncertainty value is taken as a basis instead of 0.002, e.g. (Le Menn, 2009), the calculation can easily be adapted accordingly. In any case the uncertainty will increase with increasing time between the compared batches.

To summarize the results of this section, the small uncertainty of 0.002 for Practical Salinity data traceable to the $K_{15}$ ratio of SSW (relative uncertainty of $6 \times 10^{-5}$ at $S_P = 35$) is only justified for the comparison of results that have been measured within a few years time period. Regarding longer time periods an increasing uncertainty contribution must be added to account for the limited replicability of SSW. Today, the actual replicability of SSW might be better than the uncertainty estimated above suggests. However, unless the $K_{15}$ ratio of SSW is linked to a stable reference, this remains an assumption without metrological support. In particular, any
small but systematic drift of North Atlantic seawater properties would probably remain unnoticed unless alternative independent measurement procedures are developed to reveal the change.

4.2 Inconsistency of salinity measurement results with the SI

Besides comparability, metrological traceability of measurement results to a coherent system of units guarantees that measurement results of different quantities can be used consistently with the equations correlating these quantities. Complex systems of equations such as the equations used to determine the thermodynamic properties of seawater typically depend on several quantities, the measurement results of which in turn often depend on several other measured quantities. Furthermore, the traceability of these results usually involves measurements of additional quantities. Contradictions that arise from traceability to inconsistent measurement standards are therefore very difficult to reveal. Such an investigation of Practical Salinity data has not yet been performed. Nevertheless, due to its importance, this aspect of metrological traceability will be illustrated below using a much simpler illustrative example.

Imagine the task of measuring the distance \( \Delta s \) that light travels in a time \( \Delta t \). \( \Delta s \) and \( \Delta t \) are related by the speed of light

\[
c_o = \frac{\Delta s}{\Delta t}.
\]

\( c_o \) is defined as a fixed value, while the quantity value of \( \Delta t \) is linked to the microwave transition of caesium (Quinn, 1995). Thus an independent reference for the measurement of \( \Delta s \) would violate Eq. (7), except in the unlikely event that its corresponding quantity value matches by accident. For this reason the unit “meter” is defined in a way that its reference is linked to the microwave transition of caesium (Quinn, 1995). An independent reference for the measurement of \( \Delta s \) would violate Eq. (7), except in the unlikely event that its corresponding quantity value matches by accident. For this reason the unit “meter” is defined in a way that its reference is linked to the microwave transition of caesium (Quinn, 1995). An independent reference for the measurement of \( \Delta s \) would violate Eq. (7), except in the unlikely event that its corresponding quantity value matches by accident. 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5 Estimates of Absolute Salinity

Absolute Salinity is defined as the mass fraction of dissolved material in a given mass of seawater, i.e., \((\text{mass of dissolved material})/(\text{mass of solution})\). From a practical point of view it is unrealistic to perform routine mass measurements of all relevant seawater constituents. Under the assumption of constant mass fractions in seawater, it is sufficient to measure a single quantity of a seawater sample that is sensitive to the mass of dissolved material in order to derive an estimate for its Absolute Salinity. Throughout much of this section we restrict attention to solutions of Standard Seawater composition. However, at the end of the section we discuss two measurement models that allow for composition anomalies relative to Standard Seawater.

Since Absolute Salinity is defined in terms of masses, it is obvious that any estimate of Absolute Salinity should be traceable to the SI unit “kg”. In the history of salinity measurements different measures have been established, including Chlorinity, Practical Salinity and the recently defined Reference Composition Salinity, from which estimates for Absolute Salinity can be calculated. In this section we discuss traceability of such estimates to the SI unit “kg”. Since the different estimates are closely related to each other, first it is necessary to briefly recall their historical development, both before and after the introduction of PSS-78 (Lewis, 1980), in order to clarify the corresponding routes of traceability.

Chlorinity is (up to correction factors resulting from updates of the atomic weights since 1900, (Jacobsen and Knudsen, 1940) the mass of chlorine with the same amount as the amount of halides present in the seawater sample, derived from the mass of pure silver needed to precipitate them. Via the Knudsen formula (Millero et al., 2008) the Chlorinity is linked to Absolute Salinity (“Knudsen Salinity”), which had originally been estimated as the mass of dry substance that remained after evaporating all water from a sample (Forch et al., 1902). Unfortunately the uncertainties of the underlying early mass-fraction measurements were recognized to be relatively large compared to the measurement uncertainty associated with measuring Chlorinity. Because of this, the concept of Absolute Salinity was completely abandoned in 1937 (Jacobsen and Knudsen, 1940; Sverdrup et al., 1942) and replaced by Chlorinity as the only concentration measure for dissolved material in seawater. Chlorinity was defined as a fixed multiple of the silver mass required for the titration in order to remove any future dependence on the continuously improving values of the atomic weights.

Later on, thermodynamic properties of SSW were measured in the lab with low uncertainty along with the temperature, pressure and Chlorinity of the samples. Additionally, in a series of chemical analyses, the mass fractions, expressed as multiples of the Chlorinity, of the main SSW constituents were determined. At this point it was possible to compute the Absolute Salinity of SSW from its Chlorinity (Millero
and Leung, 1976) but it was never suggested before 2008 to use this information to form a revised salinity scale. The uncertainty of this Absolute Salinity estimate (Millero et al., 2008) contains uncertainty contributions associated with the Chlorinity measurement plus the uncertainties of the other mass fractions measured relative to Chlorinity as well as the masses of possibly missing additional constituents. An additional uncertainty results from the estimation of the molar mass of the sodium fraction based on the condition of exact electric neutrality of the solute.

Concurrent with the improved determination of the thermodynamic properties of SSW, the use of conductivity ratio measurements to estimate the Chlorinity was developed and found to be more convenient and more precise than measurements made by silver titration. Moreover, conductivity measurements are well-suited for in-situ sensors (SeaBird, 1989). Unfortunately, the two methods did not always give consistent results, particularly in regions with known composition anomalies relative to SSW. This lack of consistency lead to the introduction of a new salinity scale, PSS-78, in order to define an unambiguous measure of salinity. Based on measurements of SSW, a regression polynomial was derived to compute an estimate for Chlorinity from a measured conductivity ratio. To avoid any confusion with previous titration Chlorinity, a fixed multiplier was applied to this conductivity-based Chlorinity estimate. The multiplier was taken from Knudsen’s formula at a selected point typical of open ocean conditions and the resulting formula was referred to as “Practical Salinity” ($S_P$). The dimensionless number $S_P = 35$ was chosen to correspond to the Chlorinity at which the Absolute Salinity was estimated to equal 35 g kg$^{-1}$ on the original dry-salt mass scale of 1900. Since then, certified samples of SSW used for the calibration of oceanographic instruments have been specified in terms of Practical Salinity rather than Chlorinity. The definition of Practical Salinity ensures that it provides a direct measure of Chlorinity for SSW provided the composition of SSW is unchanged. No similar statement can be made for the general case where composition anomalies may be present.

In 2006, at the first meeting of WG127, the Gibbs function of seawater (Feistel, 2003; Feistel and Hagen, 1995; Feistel et al., 2008) was chosen as the preferred future substitute for the International Equation of State of Seawater (EOS-80). At that time, it was recognized that a supporting standard composition model for sea salt was needed for a unique formulation of the theoretical limiting-law terms of very dilute seawater. This sea-salt model was to be derived from the most accurate chemical composition analysis results for SSW, to be consistent with the Chlorinity value linked to Practical Salinity, to be exactly electro-neutral, and to be based on the latest values for atomic weights. The result of two years of work on the details was the Reference Composition model of sea salt (Millero et al., 2008). This composition model provides a precisely defined best estimate of the ratio between the mass fraction of dissolved material, $S_A$, and the Chlorinity, $Cl$, or the Practical Salinity used to estimate $Cl$ from conductivity. This way, the Gibbs function established the currently best available quantitative relation between the mass of dissolved material, expressed as a multiple of Chlorinity, and the resulting thermodynamic properties of SSW, measured in turn for samples with known Chlorinity.

In 2008, at the third meeting of WG127, the lacking traceability of Practical Salinity measurements to the SI was an agenda item; practical possibilities were considered to improve their long-term stability and comparability. As the most attractive option for oceanographers, the empirical relation available from the Gibbs function between density and Reference Salinity was suggested as an SI-traceable alternative to the PSS-78 correlation between Reference Salinity and conductivity ratio measurements relative to an artefact like SSW.

Another useful aspect of the Reference Composition model is its role as a definite fixed point for the analysis of chemical composition anomalies. “Millero’s Rule” empirically states that the property changes of seawater, in particular density, resulting from small composition anomalies can be approximately determined based on the mass of the anomaly, independent of its chemical nature. Reference-Composition Salinity is the best estimate for the mass fraction of salt dissolved in SSW, and a correction of its value by the measured mass fraction anomaly can be used to estimate property anomalies from the Gibbs function available for SSW (McDougall et al., 2009; Millero, 2010; Pawlowicz, 2010).

As already discussed for SSW, the density-salinity relation available from the Gibbs function can also be inverted in the presence of composition anomalies to determine an estimate of Absolute Salinity from density measurements (Feistel et al., 2010b; Millero and Leung, 1976; Wright et al., 2011) the less predictable effects of the anomalous solute on the conductivity become irrelevant, including in particular the effects of non-conducting species such as silicate which is relatively abundant in the North Pacific. This approach, once generally recognised and practically established, may provide a reliable oceanographic measurement technology that is founded on stable and reliable SI-traceable measurement standards and naturally accounts for slight variations in the oceans composition, spatially, episodically, and systematically on climatic time scales.

Coming back to a metrological evaluation, this historical development has provided several measurement procedures to estimate Absolute Salinity, which include different measurement models. The measurement model is essential for traceability. Firstly, it forms the evaluation link between the measured input quantities to Absolute Salinity (the output quantity). Secondly, it is fundamental for an appropriate uncertainty calculation. In the following we will therefore outline the measurement models behind the different estimates of Absolute Salinity, which have been described above. The
Fig. 2. Illustration of metrological traceability of Chlorinity measurement results. Notes in the caption of Fig. 1 apply accordingly. Here the metrological reference is the declaration of the “General Conference of Weights and Measures (CGPM)” held in 1889 and 1901, which specified the platinum/iridium prototype stored in Paris as “1 kg”. Note that the illustration has been simplified for clarity. Depending on the titration method additional measurement results and the corresponding traceability chains must be considered, e.g. from density or volume measurements. In particular a purity measurement of the silver must be accounted for in the uncertainty calculation. Furthermore, there are typically several calibration levels between an end user’s mass calibrator and a primary mass calibrator.

The first four measurement models are related to measurements of seawater samples having Standard Seawater composition.

1. The first measurement model is based on the early Knudsen-Sørensen measurements (Forch et al., 1902; Jacobsen and Knudsen, 1940; Knudsen, 1903). In this case Absolute Salinity of a seawater sample is estimated as

\[ S_A = S_{AonCl} \times Cl. \]  

(8)

The multiplication factor \( S_{AonCl} = 1.80655 \) (an influence quantity, see Sect. 3) has been experimentally determined in 1900 for SSW with a salinity of \( S_A = 35 \text{ g kg}^{-1} \) as stated above. In Eq. (8) the measured input quantity is Chlorinity (Cl), measured by titration. Traceability of a Chlorinity titration result to the SI unit “kg” is qualitatively illustrated in Fig. 2. A titration, depending on the measurement procedure, includes several measurements like density or volumetric measurements, which measurement results needs to be traceable to the corresponding SI references. For simplicity Fig. 2 is restricted to the traceability chain of the corresponding mass measurements. In particular the link to the SI unit “kg” is given by the preparation and mass measurement of the silver in order to prepare a titration solution of known silver concentration. The uncertainty of Absolute Salinity \( u(S_A) \) of a sample under investigation using this measurement model can be calculated from Eq. (8)

\[ u^2(S_A) = (Cl \times u(S_{AonCl}))^2 + (S_{AonCl} \times u(Cl))^2. \]  

(9)
The uncertainty of a Chlorinity measurement result \( u(\text{Cl}) \) needs in particular to consider uncertainty contributions from the titration measurements and the purity of the silver in use. The uncertainty of SAonCl can also be calculated by solving Eq. (8) for SAonCl and building the derivatives according to GUM (2008)

\[
u^2(\text{SAonCl}) = \left( \frac{1}{\text{Cl}_{\text{Knud}}} u(S_{A_{\text{Knud}}}) \right)^2 + \left( \frac{S_{A_{\text{Knud}}}}{\text{Cl}^2} u(\text{Cl}_{\text{Knud}}) \right)^2
\]

(10)

with \( \text{Cl}_{\text{Knud}} \) and \( S_{A_{\text{Knud}}} \) being the measurement results of Sørensen and the corresponding uncertainties. \( u(S_{A_{\text{Knud}}}) \) is mainly related to missing volatile compounds and any residual water in the dried seawater, and introduces the largest uncertainty contribution to SAonCl and also \( S_A \). The overall relative uncertainty of \( S_A \) using this measurement model is about 0.5% (Millero et al., 2008).

2. The second measurement model is based on Chlorinity, estimated by conductivity ratio measurements. Firstly, measurements of conductivity ratio and Chlorinity are used to determine an empirically determined polynomial approximation for Chlorinity in terms of the conductivity ratio:

\[
\text{Cl} = \sum_{i=0}^{5} a_i^{\text{Cl}} R^{i/2}.
\]

(11a)

This estimate of Chlorinity is then converted to Practical Salinity using the Knudsen relation (Eq. 8):

\[
S_p = \text{SonCl} \sum_{i=0}^{5} a_i^{\text{Cl}} R^{i/2} = \sum_{i=0}^{5} a_i R^{i/2}.
\]

(11b)

where \( \text{SonCl} = \text{Sp}/\text{Cl} \) and \( a_i = a_i^{\text{Cl}} \times \text{SonCl} \). Note that \( S_p \) is dimensionless by definition and that the value of SonCl is equivalent to SAonCl/(g kg\(^{-1}\)) in Eq. (8). The second sum in Eq. (11b) represents the PSS-78 polynomial expression for Practical Salinity. Equation (11b) can be used directly to estimate Absolute Salinity, simply giving

\[
S_A \approx S_p \text{ g kg}^{-1}
\]

(11c)

as used in practice before 2010 (even though this was not the intended usage of \( S_p \)). The measured input quantity for the measurement model is the conductivity ratio \( R \). Measurement results for \( R \) are not traceable to the unit “kg”. In current practice, they are not even traceable to the SI (see Sect. 3). In measurement model 2 the link to the SI unit “kg” of an \( S_A \) estimate includes three elements. First the uncertainty associated with the (titration based) Chlorinity and of the conductivity ratio measurements, second the determination of the functional form (11a) and the estimation of the coefficients \( a_i^{\text{Cl}} \). The latter are due to the uncertainties associated with the underlying (titration and conductivity ratio) measurement results and fitting technique which served to determine the coefficients. The uncertainty of such a Chlorinity result is then given by

\[
u^2(\text{Cl}) = \sum_{i=1}^{5} \left( R^{i/2} u(a_i^{\text{Cl}}) \right)^2 + \left( \frac{\partial \text{Cl}}{\partial R} u(R) \right)^2.
\]

(12)

Note that no uncertainty has to be attributed to SonCl in Eq. (11b) since SonCl is specified as part of the definition of \( S_p \). In contrast to SAonCl in Eq. (8), which results from a measured relation between \( S_A \) and Cl and therefore has an uncertainty, SonCl just acts as a scaling factor. This is the reason to distinguish SAonCl from SonCl even though SonCl is derived directly from the estimate of SAonCl. The accuracy of the Cl-R relation depends on the uncertainty of the coefficients and the underlying measurement results only. However, the result of Eq. (12) must be substituted into Eq. (9) to calculate the uncertainty of an \( S_A \) estimate according to the measurement model (ii); the uncertainty associated with using SAonCl for this purpose enters at this point.

Estimates of Absolute Salinity calculated from measurement models 1 and 2 are actually of similar value. They just vary within the uncertainty associated with the coefficients of the polynomial relating Chlorinity to conductivity ratio. They have in common that \( S_p \) and Cl can each be measured with rather small uncertainty and therefore they can provide rather reproducible measurement results. However, used as estimates for Absolute Salinity they suffer from the large uncertainty that must be attributed to SAonCl. Therefore they are rather bad estimates for Absolute Salinity, i.e., the actual mass fraction of material dissolved in a sample of seawater under investigation. It must be emphasized that the estimate of \( S_A \) based on \( S_p \) can be used in compliance with the SI, in the sense discussed in Sect. 2.2, if and only if the uncertainty contributions of SAonCl to the Absolute Salinity result is considered.

3. The third measurement model is based on Reference Salinity \( S_R \). It takes advantage of the more precise
chemical analytical measurements of SSW done in the 1960s and 1970s (Millero and Leung, 1976) in order to formulate a stoichiometric chemical composition model for Standard Seawater. Water with this composition is said to have the Reference Composition (RC) and is referred to as Reference Composition Seawater (RCSW). The Absolute Salinity of RCSW is referred to as the Reference Salinity. It can be estimated from a Practical Salinity measurement result by the relation

\[ S_A = S_R = \frac{S_{35}^{A}}{S_{35}^{R}} \times S_P \]  \hspace{1cm} (13)

The quantity \( S_{35}^{A} \) is the estimated mass fraction of dissolved material in Reference Composition Seawater at a Practical Salinity of 35 (Millero et al., 2008). The traceability of this Absolute Salinity estimate to the SI unit “kg” is also given by the former Chlorinity titration measurements. However, in contrast to measurement model 2, where the SI link is established by the \( S_P - Cl \) relation, here the link is given by mass fraction measurements used to determine \( S_{35}^{A} \). Its value is calculated from the sum of the mass fractions \( r_i \) of the seawater components, which are measured with respect to Cl

\[ S_{35}^{A} = \sum_i r_i \times Cl \]  \hspace{1cm} (14)

The uncertainty of \( S_{35}^{A} \) for SSW then is given by

\[ u^2(S_{35}^{A}) = Cl^2 \times \sum_i u^2(r_i) + \left( \sum_i r_i \right)^2 \times u^2(Cl) \]  \hspace{1cm} (15)

\( u(r_i) \) are the standard uncertainties of \( r_i \) with respect to Cl and \( u(Cl) \) is the uncertainty of the titration measurement result for the halides. Note that Eqs. (14) and (15) can also include constituents, that have not been considered in the empirical measurement of \( S_{35}^{A} \) (e.g., Li\(^+\) (~0.18 mg kg\(^{-1}\)), Rb\(^+\) (~0.12 mg kg\(^{-1}\)) and dissolved gasses such as nitrogen and oxygen that are highly variable). Naturally, then the corresponding \( r_i \) is zero in Eq. (14), however, it is possible to include an estimated uncertainty \( u(r_i) \) in the uncertainty of \( S_{35}^{A} \) to account for missing values. Finally, from Eq. (13) the overall uncertainty of an \( S_A \) measurement, using measurement model 3, can be calculated from

\[ u^2(S_A) = \left( \frac{S_{35}^{A}}{35} \times u(S_P) \right)^2 + \left( \frac{S_{35}^{P}}{35} \times u(S_{35}^{A}) \right)^2 \]  \hspace{1cm} (16)

Note that in contrast to measurement model 2 here \( u(S_P) \) accounts for the repeatability of \( S_P \) results only (the uncertainty correlated to the (SI) reference is covered by \( u(S_{35}^{A}) \)).

4. The fourth measurement model is based on Reference Salinity and its link to density using the Gibbs function (Feistel, 2008)

\[ \rho = \frac{1}{g_P(S_R, T, P)} \]  \hspace{1cm} (17)

In this measurement model density \( \rho \) is the measurand embodied in a seawater sample under investigation. \( g_P \) is the Gibbs function. The subscript \( P \) indicates partial differentiation with respect to pressure \( P \) at constant Reference Salinity \( S_R \) and temperature \( T \). Using the Reference Salinity as an estimate of Absolute Salinity \( S_A = S_R \), Eq. (17) forms an implicit equation for Absolute Salinity that must be numerically solved. Density, temperature and pressure can easily be measured with respect to SI standards. On the other hand Eq. (17) is established from an empirical evaluation of density and Reference Salinity data measured from Standard Seawater. Since all measured quantity values in this measurement model are traceable to the SI, it can be used to calculate an SI consistent estimate of Absolute Salinity. In particular such an estimate is traceable to the SI unit “kg” via the Reference Salinity measurement results used to establish Eq. (17) and whose traceability is based on measurement model 3. Due to the implicit nature of Eq. (17) the uncertainty evaluation is not as straightforward as in the above models and numerical methods must be chosen in order to estimate the propagation of the uncertainties of the input quantities (e.g. see supplement 1 of GUM, 2008). Basically, besides the measurement uncertainties of the density, temperature and pressure measurement results of the actual sample under investigation, the uncertainty budget also needs to consider the accuracy of Eq. (17). In analogy to the foregoing measurement models this uncertainty contribution is determined from the uncertainties of the measurement results used to establish Eq. (17). Here in particular the uncertainties of Reference Salinity as an estimate for Absolute Salinity according to measurement model 3 enter into the calculation. Thus, measurement model 4 is an alternative to estimate Absolute Salinity, but it does not reduce its uncertainty, although density can be measured with a very low relative uncertainty of a few \( 10^{-6} \) (Wolf, 2008).

The measurement models 3 and 4 reduce the uncertainty of an Absolute Salinity estimate compared to the measurement models 1 and 2, since the \( S_A - Cl \) relation is more accurate in 3 and 4. However it is still about an order of magnitude larger than the precision of current Practical Salinity measurement results, which is necessary for oceanographic purposes. The definition of Reference Salinity therefore neglects this uncertainty contribution of necessity in order to take advantage of the low uncertainty of Practical Salinity results traceable to
$K_{15}$. As a consequence, although a Reference Salinity result is certainly a more adequate measure for the dissolved mass of material in an investigated sample of seawater having standard seawater composition than Practical Salinity or Chlorinity, it is nevertheless not consistent with the SI unit “kg”. Consequently, the usage of the unit “g kg$^{-1}$” for a Reference Salinity result of a measurement is formally inadmissible, unless the uncertainty contribution related to SI standards is considered.

Finally, we will qualitatively address two measurement models of Absolute Salinity estimates, when the composition of a seawater sample shows an anomaly with respect to Standard Seawater. Both measurement models make use of Eq. (17). In the presence of composition anomalies, no single salinity variable can fully characterize the salt content of the solution and Wright et al. (2011) discuss different possibilities. There the Absolute Salinity variable corresponding to the mass fraction of dissolved material in solution is referred to as Solution Absolute Salinity and represented by the symbol $S_{A}^{\text{soln}}$.

5. In measurement model 5 a Reference Salinity value is first calculated from a Practical Salinity measurement of a seawater sample under investigation using Eq. (13). Note that such a Reference Salinity value is not linked to the SI according to measurement model 3, since that link requires standard seawater composition. An estimate for the mass fraction of dissolved material in seawater is then calculated from

$$S_A = S_R + \lambda \delta S_A^{\text{dens}},$$

where the proportionality constant $\lambda = 1.75$ for open ocean sites and $\delta S_A^{\text{dens}}$ is taken from a lookup table that is correlated to the position where the sample was collected. The values of $\delta S_A^{\text{dens}}$ are empirically determined from salinity values that are calculated from direct density measurement results using Eq. (17). Reference Salinity calculated from Practical Salinity measurement results using Eq. (13) and composition anomalies estimates determined by various analytical measurement techniques (IOC, 2010; McDougall et al., 2009). The factor 1.75 was determined by Pawlowicz et al. (2010) using a model study that accounts for the influence of observed composition anomalies in the open ocean on both density and conductivity. Traceability to the SI unit “kg” can in principle be achieved by independent measurements of the composition anomalies in order to establish Eq. (18).

Qualitatively, in analogy to measurement models 1 to 4, the determination of the uncertainty of $S_A$ needs to consider the uncertainties of all measurement results with respect to the SI, which enter into the measurement model, in particular that of the $\delta S_A^{\text{dens}}$ values and the coefficient $\lambda$. In practice it is difficult to fully determine the uncertainty of such an Absolute Salinity estimate because the correlation between $S_A$, $S_R$ and $\delta S_A^{\text{dens}}$ is not unambiguous. For examples, the value of $\lambda$ may in reality vary with the nature of the composition anomalies and seawater samples of different composition can produce the same Practical Salinity and therefore the same Reference Salinity value. The uncertainty of the Absolute Salinity estimate provided by Eq. (18) must allow for the range of conditions to be considered and the ambiguity associated with $S_R$. Pawlowicz et al. (2010) estimate that the uncertainty for the range of deep ocean waters that have been sampled is approximately 0.003 g kg$^{-1}$.

6. The last measurement model is analogous to measurement model 5 but uses local density and conductivity measurements to estimate $\delta S_A^{\text{dens}}$ rather than a lookup table and the factor $\lambda$ is permitted to vary with location. For example, $\lambda = 1.75$ is appropriate for open ocean sites, but $\lambda = 1.0$ is apparently more appropriate for the Baltic Sea (Feistel et al., 2010a). In this case, the quantity $\delta S_A^{\text{dens}}$ is given by $S_A^{\text{dens}} - S_R$ where $S_A^{\text{dens}}$ is derived from a density measurement using Eq. (17). This measurement model has been applied in the past with $\lambda$ taken to be equal to 1 everywhere, an approximation based on indications that density is sensitive to changes in the mass fraction of dissolved material, but is less sensitive to composition anomalies (Chen and Millero, 1986; Millero, 1975). Whatever value is used for $\lambda$, the uncertainty budget of the Absolute Salinity estimate has to allow for its uncertainty, i.e. the validity of Eq. (18) with respect to anomalous seawater.

Note that taking $\lambda = 1$ in measurement model 6 gives simply $S_A = S_A^{\text{dens}}$, where $S_A^{\text{dens}}$ is determined from the solution of Eq. (17). Wright et al. (2011) give this model special status not because it provides a good measure of the mass fraction of dissolved material but because it provides a good measure of density and a measure of the mass fraction of dissolved material that is better than Reference Salinity. For most dynamic oceanography studies it is more critical to have good density results than good mass fraction results, so this is a desirable combination of properties. Here, however, we focus on the SI-traceability of the mass fraction of dissolved material in seawater.

Finally it must be stressed that the SI-traceability of results obtained by means of these measurement models is based on a fixed empirical relation, which has been established once, but has never been verified again. Strictly speaking this is not in compliance with the idea of metrological traceability of measurement results. Actually, the link between a results and the corresponding
SI measurement standard should be regularly established. In practice, this can not always be realized. Nevertheless, the validity of the coefficients corresponding to the measurement models should be verified occasionally in order to reveal changes that might affect the comparability of the measurement results. In particular, Chlorinity should be measured occasionally and verified against expectations since it is no longer regularly measured, but provides the fundamental bases for the SI-traceability of all Absolute (Solution) Salinity estimates.

6 Alternative SI traceability of Practical Salinity results

In practice Practical Salinity is and, in the foreseeable future, will remain the salinity measurand of choice. Looking at the foregoing sections, two major issues of Practical Salinity measurements have to be dealt with

1. Practical Salinity measurement results should be traceable to the quantity value of a stable SI measurement standard in order to guarantee comparability on climatic time scales.

2. The accuracy of the relation between Practical Salinity measurement results and Absolute Salinity needs to be improved in order to achieve sufficiently small uncertainties for estimates of Absolute Salinity that are based on Practical Salinity measurement results.

Improvements in the second issue depend on the uncertainty of mass fraction measurements. Modern methods of mass spectrometry could be applied to this end. However, a discussion of these measurement procedures is beyond the scope of this paper. Here we focus on the SI traceability for Practical Salinity measurement results. In principle, this can be accomplished without significant changes of the established production, calibration and measurement procedures, simply by measuring the absolute conductivities in order to calculate \( K_{15} \) of SSW (see Sect. 3). Unfortunately, as pointed out, the related uncertainty using present-day state-of-the-art primary conductivity measurement procedures (Brinkmann et al., 2003) is, with respect to short time scales, about a factor 5 larger than that of the results presently used for the ocean observation system (Seitz et al., 2010).

One way out of this practical dilemma is through the measurement of a different seawater quantity that is traceable to SI measurement standards and subject to smaller measurement uncertainties that are tolerable. The salinity would then be computed via an empirical relation to the measured quantity that is very precisely known. A potential candidate for this purpose is density, which has two important advantages, (i) SI-traceable density measurements of seawater can be carried out with a relative uncertainty of a few \( 10^{-6} \) (Wolf, 2008), which perfectly meets the needs of ocean observation, (ii) a relation between density and the Absolute Salinity of Standard Seawater is available in the form of the TEOS-10 Gibbs function (IOC, 2010).

It is important to note that the actual measuring procedure for a quantity value is irrelevant for its traceability. It is the quantity value that is traceable, not the measurement procedure to achieve this value. The method used is essential for the uncertainty of the result. So it is possible to measure the density of seawater (with fixed solute composition) with a conductivity sensor, since both quantities depend on the content of dissolved salt. Hence, following the metrological traceability concept, a conductivity (ratio) measurement device can serve to measure density if it is properly calibrated with respect to an SI-traceable density measurement standard. Such a density measurement device cannot reasonably be used for any kind of solution, since the dependence of conductivity and density on the composition of a solution is different. However, under the assumption of constant relative mass fractions of the dissolved components, i.e. if only the amount of water in the sample is variable, a conductivity sensor can serve well to measure density. Hence, the density of seawater having standard seawater composition can be measured in the proposed way, while composition anomalies can be covered as outlined in the measurement models 5 and 6 in the foregoing section.

Traceability of Practical Salinity results to density standards could be realized in the following way. An empirical relation between \( K_{15} \), using the current PSS-78 measurement procedure, and density of Standard Seawater needs to be established in order to remain consistent with current Practical Salinity measurement results. This relation then can be used to assign a \( K_{15} \) value to the Standard Seawater calibration solution from a density measurement. The production procedure of SSW would be unchanged, except for the additional density measurement. Using this approach, changes can be restricted to the manufacturers of Standard Seawater calibration solutions. The traceability chain for salinometer and CTD measurements will remain untouched. Thus, in Fig. 1 just the primary measurement procedure to assign the \( K_{15} \) value changes. The reference for its traceability would then be the density based definition of an SI coherent normalised \( K_{15} \) value of unit one according to a somewhat redefined PSS-78. Note that the “redefinition” does not affect the actual scale, but the procedure to assign \( K_{15} \) to the Standard Seawater calibration solution only.

The proposed change in traceability would have several advantages:

- Practitioners could maintain their usual calibration and measurement procedures without any changes.

- The indicated quantity of a salinometer or CTD measurement will continue to be Practical Salinity or a conductivity ratio consistent with PSS-78. Consequently, there will be no break in oceanographic data bases. However, a comparison of new results, traceable to the
density related $K_{15}$, to old results, traceable to the conductivity ratio related $K_{15}$, need to consider the uncertainty of the measurement results used to establish the $K_{15}$-density relation.

- Any change in the defined KCl solution that affects its conductivity will be revealed, since, the conductivity ratio that is calculated to adjust SSW will differ from the $K_{15}$ value calculated from density. However, even in that case comparability of Practical Salinity results will not be affected.

- A change in Standard Seawater composition that affects its conductivity or its density will also be revealed.

- Although the result of a measurement will be indicated as Practical Salinity or conductivity ratio, density will be the actually measured quantity, because the results will be measured traceable to density standards. Consequently, density can be directly calculated from Practical Salinity results. To this end an empirical conductivity ratio-density relation must be established over the complete validity range of Practical Salinity.

This conceptual proposal is still immature and needs to be worked out in more detail in the future. In particular, the effect of composition anomalies on density based salinity measurements needs to be investigated in more detail, which also includes density and temperature measurements under high pressure. However, the new concept is very promising regarding the long-term reliability of observations made by the coming generations for future climatic trend analyses. This approach will also be in compliance with the metrological traceability concept, which is increasingly recognized.

Appendix A

A common understanding of used concepts and associated terms is the key for a common understanding. So below we summarize some of the most important metrological concepts and terms from the “International Vocabulary of Metrology” (VIM, 2008) used throughout the text. In the list hereafter, the VIM entry number follows the concept definition listed

**calibration hierarchy (2.40):** sequence of calibrations from a reference to the final measuring system, where the outcome of each calibration depends on the outcome of the previous calibration

**coherent derived unit (1.12):** derived unit that, for a given system of quantities and for a chosen set of base units, is a product of powers of base units with no other proportionality factor than one

**input quantity in a measurement model (2.50):** quantity that must be measured, or a quantity, the value of which can be otherwise obtained, in order to calculate a measured quantity value of a measurand

**measurand (2.3):** quantity intended to be measured

**measurement function (2.49):** function of quantities, the value of which, when calculated using known quantity values for the input quantities in a measurement model, is a measured quantity value of the output quantity in the measurement model. If a measurement model $h(Y, X_1, \ldots, X_n) = 0$ can explicitly be written as $Y = f(X_1, \ldots, X_n)$, where $Y$ is the output quantity in the measurement model, the function $f$ is the measurement function.

**measurement model (2.48):** mathematical relation among all quantities known to be involved in a measurement. A general form of a measurement model is the equation $h(Y, X_1, \ldots, X_n) = 0$.

**measurement repeatability (2.21):** measurement precision under a set of repeatability conditions of measurement

**measurement reproducibility (2.25):** measurement precision under reproducibility conditions of measurement

**measurement result (2.9):** set of quantity values being attributed to a measurand together with any other available relevant information

A measurement result is generally expressed as a single measured quantity value and a measurement uncertainty.

**measurement standard (5.1):** realization of the definition of a given quantity, with stated quantity value and associated measurement uncertainty, used as a reference

**measurement uncertainty (2.26):** non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used

NOTE 1: Measurement uncertainty includes components arising from systematic effects, such as components associated with corrections and the assigned quantity values of measurement standards, as well as the definitional uncertainty. Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated.

NOTE 2: The parameter may be, for example, a standard deviation called standard measurement uncertainty (or a specified multiple of it), or the half-width of an interval, having a stated coverage probability.

NOTE 3: Measurement uncertainty comprises, in general, many components. Some of these may be evaluated by Type A evaluation of measurement uncertainty from the statistical distribution of the quantity values from series of measurements and can be characterized by standard deviations. The other components, which may be evaluated by Type B evaluation of measurement uncertainty, can also be characterized by standard deviations, evaluated from probability density functions based on experience or other information.

NOTE 4: In general, for a given set of information, it is understood that the measurement uncertainty is associated with a stated quantity value attributed to the measurand. A modification of this value results in a modification of the associated uncertainty.
metrological comparability of measurement results (2.46): comparability of measurement results, for quantities of a given kind, that are metrologically traceable to the same reference

EXAMPLE: Measurement results, for the distances between the Earth and the Moon, and between Paris and London, are metrologically comparable when they are both metrologically traceable to the same measurement unit, for instance the metre.

Metrological comparability of measurement results does not necessitate that the measured quantity values and associated measurement uncertainties compared be of the same order of magnitude.

metrological compatibility of measurement results (2.47): property of a set of measurement results for a specified measurand, such that the absolute value of the difference of any pair of measured quantity values from two different measurement results is smaller than some chosen multiple of the standard measurement uncertainty of that difference

metrological traceability (2.41): property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty

metrological traceability chain (2.42): a sequence of measurement standards and calibrations that is used to relate a measurement result to a reference

primary measurement standard (5.4): measurement standard established using a primary reference measurement procedure, or created as an artifact, chosen by convention

primary reference measurement procedure (2.8): reference measurement procedure used to obtain a measurement result without relation to a measurement standard for a quantity of the same kind

output quantity (2.51): quantity, the measured value of which is calculated using the values of input quantities in a measurement model

quantity (1.1): property of a phenomenon, body, or substance, where the property has a magnitude that can be expressed as a number (the quantity value) and a reference

repeatability condition of measurement (2.20): condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time

reproducibility condition of measurement (2.24): condition of measurement, out of a set of conditions that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects

stability of a measuring instrument (4.19): property of a measuring instrument, whereby its metrological properties remain constant in time

sensitivity of a measuring system (4.12): quotient of the change in an indication of a measuring system and the corresponding change in a value of a quantity being measured

Appendix B

Abbreviations and notations

\[ \begin{align*}
\kappa & \quad \text{conductivity} \\
G & \quad \text{conductance} \\
R & \quad \text{conductivity ratio of a seawater sample and the defined KCl-solution} \\
K_{15} & \quad \text{conductivity ratio of IAPSO-Standard Seawater} \\
S_P & \quad \text{Practical Salinity} \\
S_A & \quad \text{Absolute Salinity} \\
S_R & \quad \text{Reference Composition Salinity} \\
\text{Cl} & \quad \text{Chlorinity} \\
\text{SSW} & \quad \text{(IAPSO) Standard Seawater} \\
\text{SAnCl} & \quad \text{factor that correlates Chlorinity and an Absolute Salinity estimate, based on the Knudsen formula} \\
\text{SonCl} & \quad \text{factor that correlates Chlorinity and Practical Salinity} \\
S^{35}_{A} & \quad \text{estimated mass fraction of dissolved material in Reference Composition Seawater}
\end{align*} \]

Edited by: R. Tailleux

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