**Ocean Science
Discussions**

Metrological traceability of oceanographic salinity measurement results

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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. In 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 "g/kg". 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 $t = 25\,°C$ and $P = 101\,325\,Pa$ (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 "g/kg"), 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 IAPSO[1] Standard Seawater (SSW)
5 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 "g/kg". 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
10 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 there-
15 fore 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
20 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).
25 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;

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[1]IAPSO: International Association for the Physical Sciences of the Ocean, http://iapso.sweweb.net

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De Bièvre et al., 2009). 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 can not 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)[2]. 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) often ends 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

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[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.

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 an associated inevitable "measurement uncertainty" (uncertainty) (VIM, 2008). This is due to uncertainties of the procedures used to assign the value as well as to potential instabilities of the measurement standard itself. The uncertainty of any measured quantity value must include the uncertainty associated with the measurement standard and those associated with the measurement procedure itself. Therefore, the measurement uncertainty is a quantitative measure of the reliability of the measured quantity value *with respect to the reference it is related to*. A useful measurement result therefore always has to indicate the measured quantity value in conjunction with its unit and its uncertainty. Obviously, the measurement uncertainty increases with the number of calibration levels between the measurement result and the primary standard. In a comparison, measurement results are equivalent within the measurement uncertainty if – and only if – their difference is smaller than the uncertainty of their difference ("compatibility"; VIM, 2008). On the other hand they are reliably different if – and only if – the difference is larger than the uncertainty of the difference.

To ensure the most wide-spread comparability of measurement results in practice, the SI was adopted by the International Conference of Weights and Measures. It is based on a "set of base quantities together with a set of non-contradictory equations relating those quantities" (VIM, 2008). National Metrological Institutes (NMIs) have developed procedures to realize primary measurement standards for six out of seven base quantities[3] of the SI and for (many) derived quantities. Extensive (ongoing) efforts are made to realise the SI base units by coupling them to stable physical phenomena

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[3]There 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.

in order to guarantee the most stable, replicable primary measurement standards possible for the SI units. Additionally, the NMIs periodically conduct international comparison measurements under the umbrella of the International Bureau of Weights and Measures, in order to verify the equivalence of the quantity values of national measurement standards (MRA, 1999).

In the next section the current metrological traceability of Practical Salinity measurement results is discussed.

3 Traceability of practical salinity measurement results

The Practical Salinity Scale 1978 (PSS-78) is defined by a polynomial in the conductivity ratio (Perkin and Lewis, 1980)

$$R = \frac{\kappa_s}{\kappa_{KCl}} . \tag{1}$$

κ_{KCl} is the electrolytic conductivity of a potassium chloride solution, having a KCl mass fraction of 32.4356 g/kg. κ_s 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 κ_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 is defined such that the Practical Salinity value is 35 if $\kappa_s = \kappa_{KCl}$,

5 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

10 opportunity and sold in the form of ampoules. The conductivity of such a sample is adjusted by the manufacturer, typically by dilution, to the conductivity of the KCl solution defined in PSS-78 (Bacon et al., 2007). To this end its conductance G_{SSW}^m is accurately measured and adjusted until it is near that of the KCl solution G_{KCl}^m. Since it is impossible to prepare the defined KCl solution with the desired accuracy, solutions with slightly

15 higher and lower concentrations are prepared and G_{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_{SSW}^m and G_{KCl}^m the so-called K_{15} ratio is calculated and inscribed on the labels of

20 the SSW ampoules

$$K_{15} = \frac{G_{SSW}^m}{G_{KCl}^m}. \qquad (2)$$

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

$$R = \frac{G_s^u}{G_{SSW}^u} K_{15}, \qquad (3)$$

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G_s^u 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 κ of the solution by the cell constant K of the specific measuring cell in use (not to be confused with K_{15}):

$$G = \frac{\kappa}{K} . \tag{4}$$

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 Eqs. (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., 2009). 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,

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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 uncertainty of R is calculated from the input quantities of Eq. (3) as

$$u(R)^2 = \left(\frac{K_{15}}{G_{SSW}^u} u\left(G_s^u\right) \right)^2 + \left(\frac{G_s^u}{\left(G_{SSW}^u\right)^2} u\left(G_{SSW}^u\right) \right)^2 + \left(\frac{G_s^u}{G_{SSW}^u} u(K_{15}) \right)^2. \tag{5a}$$

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

$$u(K_{15})^2 = \left(\frac{1}{G_{KCl}^m} u\left(G_{SSW}^m\right) \right)^2 + \left(\frac{G_{SSW}^m}{\left(G_{KCL}^m\right)^2} u\left(G_{KCl}^m\right) \right)^2. \tag{5b}$$

Note that uncertainties are typically stated as "standard uncertainties" (GUM, 2008), i.e. related to a normally distributed probability function at a level of confidence of 68%, so that they can be used in propagation of measurement uncertainties, e.g., when used in quantity equations. Multiples of the standard uncertainty can be used in the end measurement result if an increased level of assurance is desired. Equation (5b) 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 $u(K_{15})$ to be 5×10^{-6} 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).

It must be emphasized that the *absolute*[4] conductivity values corresponding to Eqs. (1) to (3) are not measured, i.e. they are not measured traceable to the SI (in units of $\Omega^{-1}\,m^{-1}$), 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 κ_{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. Hence, conductivity ratio measurement results from Eq. (3) are not traceable to the SI either. The crucial difference in metrological reference of K_{15} becomes obvious in the uncertainty contributions of K_{15}. In case

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[4]In fact from a metrological point of view there are no "absolute" measurement results at all. The numerical values (quantity value and uncertainty) of every measurement result are given relative to the quantity value assigned to a reference of some sort. However, it is common habit to use the expression "absolute conductivity" as a synonym for a conductivity measurement in SI units, so we will maintain this habit.

K_{15} is referred to the SI, its uncertainty needs to consider the uncertainties of G_{SSW}^m and G_{KCl}^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_{SSW}^m and G_{KCl}^m are then given by

$$u\left(G_{KCl}^m\right)^2 = \left(\frac{1}{K^m}u(\kappa_{KCl})\right)^2 + \left(\frac{\kappa_{KCl}}{(K^m)^2}u(K^m)\right)^2, \tag{6a}$$

$$u\left(G_{SSW}^m\right)^2 = \left(\frac{1}{K^m}u(\kappa_{SSW})\right)^2 + \left(\frac{\kappa_{SSW}}{(K^m)^2}u(K^m)\right)^2. \tag{6b}$$

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

$$u^2(K^m) = \left(\frac{1}{G_{ref}}u(\kappa_{ref})\right)^2 + \left(\frac{\kappa_{ref}}{G_{ref}^2}u(G_{ref})\right)^2. \tag{6c}$$

G_{ref} is the measured conductance of a solution of known absolute conductivity κ_{ref} and known uncertainty $u(\kappa_{ref})$. $u(G_{ref})$, $u(\kappa_{KCl})/K^m$ and $u(\kappa_{SSW})/K^m$ account for sensitivity and stability of the measuring device during the conductance measurements of the reference solution, SSW and the KCl-solutions, respectively. They can be statistically determined by measurements under repeatability conditions. 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-raceable 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 t and salinities, with the salinities represented by Practical Salinity measurements $S_{\text{P-cal}}$ 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 G_{CTD} to the temperature and Practical Salinity data. Consequently a CTD measurement of Practical Salinity $S_{\text{P-CTD}}$ includes an additional level within the calibration hierarchy (see Fig. 1), which necessarily results in an additional contribution to the total uncertainty $u(S_{\text{P-CTD}})$

$$u^2(S_{\text{P-CTD}}) = \left(\frac{\partial S_{\text{P-CTD}}}{\partial G_{\text{CTD}}} u(G_{\text{CTD}})\right)^2 + \left(\frac{\partial S_{\text{P-CTD}}}{\partial t} u(t)\right)^2 + \left(\frac{\partial S_{\text{P-CTD}}}{\partial p} u(p)\right)^2 + u^2(S_{\text{P-cal}}). \quad (7)$$

$u(G_{\text{CTD}})$ includes contributions related to the sensitivity and stability of the CTD during the calibration, the sensitivity and stability during the seawater sample measurement and reproducibility during the cruise. The first two contributions are statistically determined from several measurements. The last is estimated by a verification calibration after the cruise or by comparison measurements during the cruise. Here water samples from a well mixed layer are collected and measured in the lab with a salinometer and compared with the result of the conductance sensor of the CTD-probe. Additionally the temperature measurement of the CTD-probe is compared in situ with a standard thermometer. $u(t)$ considers the uncertainties associated with the temperature measurement results during the calibration and the seawater measurements. The influence of water pressure on the conductance sensor in deep sea measurements is corrected with coefficients provided by the manufacturer. $u(p)$ should account for uncertainties in the correction, but is not yet considered. $u(S_{\text{P-cal}})$ is the uncertainty of the Practical Salinity calibration results, which accounts for the stability of salinity in the calibration

bath $u(S_{bath})$, the accuracy of the fitting procedure $u(S_{fit})$ and the uncertainty of the salinometer results $u(S_P)$:

$$u^2(S_{P\text{-cal}}) = u^2(S_{bath}) + u^2(S_{fit}) + u(S_P)^2 .\tag{8}$$

It must be emphasised that due to this calibration hierarchy and the corresponding uncertainties, the uncertainties associated with Practical Salinity results obtained from CTD measurements are inevitably larger than those obtained from salinometer measurements. The resulting measurement uncertainty for Practical Salinity is given by a CTD-manufacturer as 0.007 to 0.009 (Larson, 1993). Dynamic effects and fouling of the conductivity- sensor of the CTD may cause additionally much bigger uncertainties but are not discussed here.

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 K_{15} and calcu-

5 lated an overall standard uncertainty of 5×10^{-6}, which in fact would be negligible. That investigation quantified variability in the production of SSW and ensuing measurement uncertainties in the calculation of K_{15}. As such it characterizes the *current* capability of a *single* manufacturer to replicate SSW. In oceanography salinity measurement results are compared over several decades and eventually they will be compared over sev-

10 eral centuries. Consequently, an uncertainty contribution quantifying the replicability of SSW has to cover this period. Unfortunately it is impossible to foresee and quantify all possible influences that might one day affect the SSW, which makes the determination of an adequate uncertainty practically impossible or too large to be of any use.

Another possibility to deal with the problem is to verify the stability and replicability

15 of produced SSW samples over a long time. To this end comparison measurements are regularly performed, in which Practical Salinities (or the conductivity ratios) 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

20 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

25 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 as follows. The uncertainty

of a Practical Salinity measurement using a Guildline salinometer is stated to be 0.002 by the manufacturer. 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 of results in the older investigation, then the combined uncertainty of the corrected values is $u^2_{corr}=3\times0.002^2$. This procedure can be continued. Going N steps back in time therefore results in a combined uncertainty of $u^2_N=(2\cdot N+1)\times0.002^2$, or $u_N=\sqrt{2\cdot N+1}\times0.002$, 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 0.009.

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 6×10^{-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 Δs that light travels in a time Δt. Δs and Δt are related by the speed of light

$$c_0 = \frac{\Delta s}{\Delta t}.$$ (9)

c_0 is defined as a fixed value, while the quantity value of Δt is linked to the microwave transition of caesium (Quinn, 1995). Thus an independent reference for the measurement of Δs would violate Eq. (9), 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 depends on c_0 and the definition of the unit "second". This concept can be extended to the entire SI. It is not possible to introduce a further independent measurement standard into the SI without running into contradictions, if the corresponding quantity is correlated to other SI quantities. Clearly the choice of reference values is critical to the reliability of the SI. Any measurement results, such as current Practical Salinity data, which are traceable to other than the SI measurement standards, are therefore inconsistent with the SI, as long as those proprietary measurement standards are not themselves traceable and consistently linked to the SI. Using them in calculations together with other measurement results which are traceable to the SI inevitably results in inconsistencies, the consequences of which may be very difficult to anticipate.

5   Estimates of absolute salinity

Absolute Salinity is defined as the mass fraction of dissolved material in a given mass of seawater, i.e., (mass of dissolved material)/(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 $35\,\mathrm{g\,kg^{-1}}$ 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, 2009).

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., 2010; Millero and Leung, 1976; Wright et al., 2010) 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

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different estimates of Absolute Salinity, which have been described above. The first four measurement models are related to measurements of seawater samples having Standard Seawater composition.

(i) 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

$$S_A = \text{SAonCl} \cdot Cl. \tag{10}$$

The multiplication factor SAonCl=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. (10) 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. (10)

$$u^2(S_A) = (Cl \cdot u(\text{SAonCl}))^2 + (\text{SAonCl} \cdot u(Cl))^2. \tag{11}$$

The uncertainty of a Chlorinity measurement result $u(Cl)$ 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. (10) for SAonCl

and building the derivatives according to GUM (GUM, 2008)

$$u^2(\text{SAonCl}) = \left(\frac{1}{Cl_{\text{Knud}}}u(S_{\text{A\_Knud}})\right)^2 + \left(\frac{S_{\text{A\_Knud}}}{Cl_{\text{Knud}}^2}u(Cl_{\text{Knud}})\right)^2 \tag{12}$$

with Cl_{Knud} and $S_{\text{A\_Knud}}$ being the measurement results of Sørensen and the corresponding uncertainties. $u(S_{\text{A\_Knud}})$ 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).

(ii) 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:

$$Cl = \sum_{i=0}^{5} a_i^{Cl} R^{i/2}. \tag{13a}$$

This estimate of Chlorinity is then converted to Practical Salinity using the Knudsen relation (Eq. 10):

$$S_{\text{P}} = \text{SonCl} \sum_{i=0}^{5} a_i^{Cl} R^{i/2} = \sum_{i=0}^{5} a_i R^{i/2}. \tag{13b}$$

where $\text{SonCl}=S_{\text{P}}/Cl$ and $a_i = a_i^{Cl} \cdot \text{SonCl}$. Note that S_{P} is dimensionless by definition and that the value of SonCl is equivalent to $\text{SAonCl}/(\text{g kg}^{-1})$ in Eq. (10). The second sum in (Eq. 13b) represents the PSS-78 polynomial expression for Practical Salinity. Equation. (13b) can be used directly to estimate Absolute Salinity, simply giving

$$S_{\text{A}} \approx S_{\text{P}} \, \text{g kg}^{-1} \tag{13c}$$

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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 (ii) the link to the

5　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 (Eq. 13a) and the estimation of the coefficients a_i^{Cl}, and finally, there is the usage of S_P as an estimate of the mass fraction of dissolved material, expressed by (Eq. 13c).

10　　A Chlorinity result calculated from Eq. (13a) has to account for both the uncertainty of the R measurement result of the actual sample under investigation and the uncertainty of the coefficients $u(a_i^{Cl})$. 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

15　is then given by

$$u^2(Cl) = \sum_{i=0}^{5} \left(R^{i/2} u\left(a_i^{Cl}\right) \right)^2 + \left(\frac{\partial Cl}{\partial R} u(R) \right)^2 . \tag{14}$$

Note that no uncertainty has to be attributed to SonCl in Eq. (13b) since SonCl is specified as part of the definition of S_P. In contrast to SAonCl in Eq. (10), which results from a measured relation between S_A and Cl and therefore has an uncertainty, SonCl

20　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. (14) must be substituted into Eq. (11) to calculate the uncertainty of an S_A estimate according to the measurement

25　model (ii); the uncertainty associated with using SAonCl for this purpose enters at this point.

Estimates of Absolute Salinity calculated from measurement models (i) and (ii) 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. 4.2, if and only if the uncertainty contributions of SAonCl to the Absolute Salinity result is considered.

(iii) 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

$$S_A = S_R = \frac{S_A^{35}}{35} \cdot S_P \tag{15}$$

The quantity S_A^{35} 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 (ii), 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_A^{35}. Its value is calculated from the sum of the mass fractions r_i of the seawater components, which are measured with respect to Cl

$$S_A^{35} = \sum_i r_i \cdot Cl \tag{16}$$

The uncertainty of S_A^{35} for SSW then is given by

$$u^2\left(S_A^{35}\right) = Cl^2 \cdot \sum_i u^2(r_i) + \left(\sum_i r_i\right)^2 \cdot u^2(Cl) \qquad (17)$$

$u(r_i)$ 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. (16) and (17) can also include constituents, that have not been considered in the empirical measurement of S_A^{35} (e.g., Li$^+$ ($\sim$0.18 mg kg^{-1}), Rb$^+$ ($\sim$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. (16), however, it is possible to include an estimated uncertainty $u(r_i)$ in the uncertainty of S_A^{35} to account for missing values. Finally, from Eq. (15) the overall uncertainty of an S_A measurement, using measurement model (iii), can be calculated from

$$u^2(S_A) = \left(\frac{S_A^{35}}{35}u(S_P)\right)^2 + \left(\frac{S_P}{35}u\left(S_A^{35}\right)\right)^2 \qquad (18)$$

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

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

$$\rho = \frac{1}{g_P(S_R, T, P)}. \qquad (19)$$

In this measurement model density ρ 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. (19) forms

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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. (19) 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. (19) and whose traceability is based on measurement model (iii). Due to the implicit nature of Eq. (19) the uncertainty evaluation is not as straight forward 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. (19). In analogy to the foregoing measurement models this uncertainty contribution is determined from the uncertainties of the measurement results used to establish Eq. (19). Here in particular the uncertainties of Reference Salinity as an estimate for Absolute Salinity according to measurement model (iii) enter into the calculation. Thus, measurement model (iv) 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 (iii) and (iv) reduce the uncertainty of an Absolute Salinity estimate compared to the measurement models (i) and (ii), since the S_A-Cl relation is more accurate in (iii) and (iv). 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. (19). In the presence of composition anomalies, no single salinity variable can fully characterize the salt content of the solution and Wright et al. (2010) discuss different possibilities. 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^{soln}. We adopt this notation below.

(v) In measurement model (v) a Reference Salinity value is first calculated from a Practical Salinity measurement of a seawater sample under investigation using Eq. (15). Note that such a Reference Salinity value is not linked to the SI according to measurement model (iii), since that link requires standard seawater composition. An estimate for the mass fraction of dissolved material in seawater is then calculated from

$$S_A = S_R + \lambda \delta S_A^{dens}, \tag{20}$$

where the proportionality constant $\lambda{=}1.75$ for open ocean sites and δS_A^{dens} is taken from a lookup table that is correlated to the position where the sample was collected. The values of δS_A^{dens} are empirically determined from salinity values that are calculated from direct density measurement results using Eq. (19), Reference Salinity calculated from Practical Salinity measurement results using Eq. (15) and composition anomalies estimates determined by various analytical measurement techniques (IOC, 2010; Mc-Dougall 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. (20).

Qualitatively, in analogy to measurement models (i) to (iv), 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 δS_A^{dens} values and the coefficient λ. 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 δS_A^{dens} is not unambiguous. For examples, the value of λ 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. (20) 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 $0.003\,\mathrm{g\,kg^{-1}}$.

(vi) The last measurement model is analogous to measurement model (v) but uses local density and conductivity measurements to estimate δS_A^{dens} rather than a lookup table and the factor λ 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., 2010). In this case, the quantity δS_A^{dens} is given by $S_A^{dens} - S_R$ where S_A^{dens} is derived from a density measurement using Eq. (19). This measurement model has been applied in the past with λ 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 λ, the uncertainty budget of the Absolute Salinity estimate has to allow for its uncertainty, i.e. the validity of Eq. (20) with respect to anomalous seawater.

Note that taking $\lambda = 1$ in measurement model (vi) gives simply $S_A = S_A^{dens}$, where S_A^{dens} is determined from the solution of Eq. (19). Wright et al. (2010) 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-tracability 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.

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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.

5 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

10 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

15 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

20 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. To measure the weight of a person, a mass balance can be used, a spring or a magnetic coil. It is the quantity value that is traceable, not the measurement procedure to achieve this value. The method used is essential for the uncertainty of the result.

25 Hence, we could measure the density of seawater with a conductivity sensor, if the sensor were properly calibrated with respect to an SI-traceable density measurement standard.

Such a traceability of Practical Salinity results 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 figure 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. 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.

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– 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.

Abbreviations and notations

κ	conductivity
G	conductance
R	conductivity ratio of a seawater sample and the defined KCl-solution
K_{15}	conductivity ratio of IAPSO-Standard Seawater
S_P	Practical Salinity
S_A	Absolute Salinity
S_R	Reference Composition Salinity
Cl	Chlorinity
SSW	(IAPSO) Standard Seawater
SAonCl	factor that correlates Chlorinity and an Absolute Salinity estimate, based on the Knudsen formula
SonCl	factor that correlates Practical Salinity and Chlorinity
S_A^{35}	estimated mass fraction of dissolved material in Reference Composition Seawater

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(i) **metrological reference**: definition of conductivity ratio of unit one according to PSS-78 (documentation)

(ii) primary measurement procedure: preparation of KCl-solutions and IAPSO-SSW; G_{KCl} and G_{SSW} measurements

conductance-meter, (typically a salinometer)

assign

not assigned

(iii) $K_{15} = 0.99986$

IAPSO-SSW

calibrate

(iv) measurement procedure for R; (vi) for CTD calibration: preparation of seawater bath, measurement procedure for R

salinometer, conductivity meter

$u(S_P) = 0.0024$

(v) $R = 0.999110$ ↓ $S_P(R) = 34.9650$

seawater sample

(vii) CTD: sea-water bath

assign

calibrate

(viii) measurement procedure for $S_{P\text{-}CTD}$

$u(S_{P\text{-}CTD}) = 0.0032$

(ix) $S_{P\text{-}CTD}(t, p, G_{CTD}) = 34.8856$

seawater sample

assign

conductivity, temperature-depth probe (CTD)

calibration hierarchy
metrological traceability chain

uncertainty | quantity value | calibrator (sample) | action | measuring system | measurement procedure

measurement result

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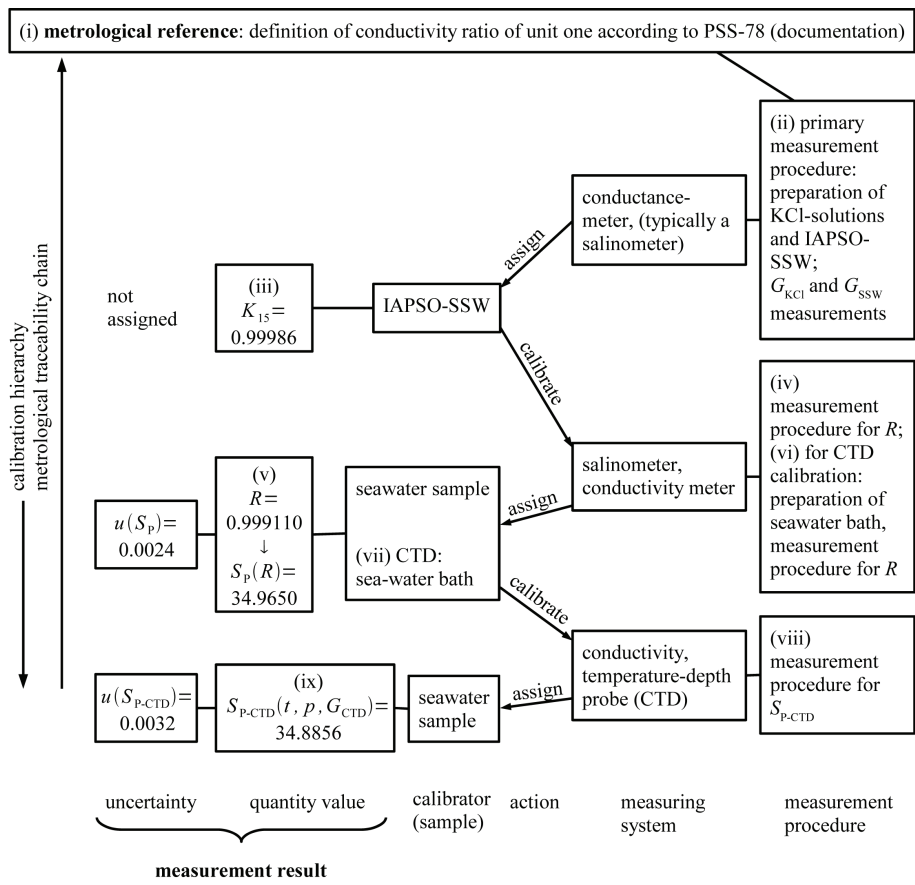
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Fig. 1. Illustration of the current traceability of a measured conductivity ratio R and the derived Practical Salinity result S_P, respectively to the K_{15} ratio of Standard Seawater (SSW). Starting from the top of the figure and working towards the bottom, it indicates (i) the metrological reference for conductivity ratio measurement results, which is the (standardizing) documentation of PSS-78 (UNESCO, 1998[1]), in particular the definition of the conductivity ratio. This also describes (ii) the procedure how to realize (embody) the (iii) K_{15} ratio in IAPSPO-SSW. In turn, SSW is used for the calibration of a salinometer. According to (iv) 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 measurement 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 result 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 onto other 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 measuring system.
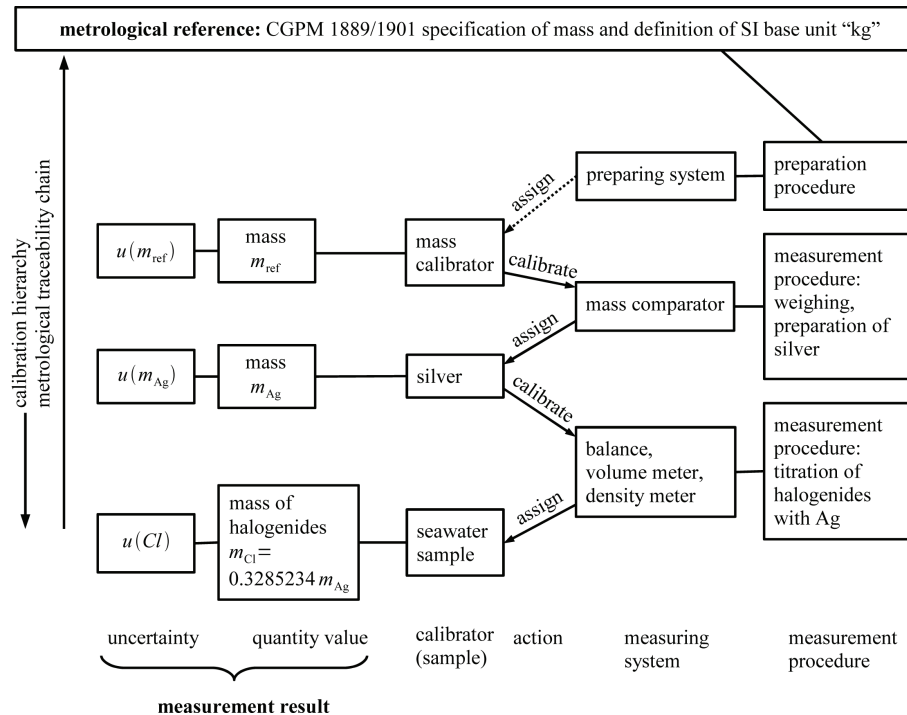
Fig. 2. Illustration of metrological traceability of Chlorinity measurement results. Notes in the caption of Fig. 1 apply accordingly. Here the metrological reference is the declaration of the "General Conference of Weights and Measures (CGPM)" held in 1889 and 1901, which specified the platinum/iridium prototype stored in Paris. 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 measurement results. In particular a purity measurement of the silver must be accounted for in the uncertainty calculation. Furthermore, there are in fact several calibration levels between an end user's mass calibrator and a primary mass calibrator.