

IAPSO Standard Seawater: Definition of the Uncertainty in the Calibration Procedure, and Stability of Recent Batches

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ABSTRACT

Standard seawater (SSW) has been employed by oceanographers as a reference material in the determination of salinity for over a century. In all that time, this is the first study to determine the uncertainty of the SSW manufacturing process. SSW is calibrated in reference to carefully prepared solutions of potassium chloride (KCl). All uncertainties in the preparation and measurement of KCl solutions and of new SSW are calculated. The expanded uncertainty of the SSW conductivity ratio is found to be 1×10^{-5} , based on a coverage factor of 2, at the time of manufacture. There is no discernible “within batch” variability. No significant variability of quality within or between batches of KCl is found. Measurement of SSW “offsets” from the label conductivity ratio as long as 5 yr after the SSW batch manufacture are reported, and no significant change in label conductivity ratio for SSW batches P130 through P144 outside the expanded uncertainty of 1×10^{-5} is found. This last result is in contrast to some other studies, and herein are suggestions as to why this may be the case.

1. Introduction

Standard seawater (SSW) has now been used for salinity determinations for over a century. It was first introduced to the oceanographic community by Martin Knudsen in 1900, when it was used as a chemical standard in the determination of the chlorinity (and hence salinity) of seawater. SSW, as approved by the International Association for the Physical Sciences of the Ocean (IAPSO), is still required today, although it is now used as a reference standard in the measurement of the electrical conductivity (and hence salinity) of seawater. Culkin and Smed (1979) provide a history of SSW.

Even though SSW has been calibrated in electrical conductivity for many decades, an analysis of the un-

certainty of the IAPSO SSW manufacturing procedure has never been published. It is important that this omission be rectified for a number of reasons. Ever-greater accuracy and stability is being achieved by the manufacturers of ocean-going conductivity-measuring instruments [conductivity–temperature–depth (CTD)], whether deployed from research vessels or attached to autonomous drifting floats, marine gliders, or powered submersibles. The quest for early signals of climate change, particularly in the deep waters of the world’s oceans, requires the highest-accuracy measurements of salinity. Consequently, attention has been focused, albeit intermittently through the years, on the accuracy of the “label value” of the salinity of SSW.

This paper is structured as follows. In section 2, we summarize the SSW preparation and manufacturing process, and describe the calibration procedure. Sections 3, 4, and 5 work through all elements of the calibration procedure and conclude with its combined standard uncertainty. In section 6, we describe how our uncertainty determination relates to previous publications on the question of the accuracy of the SSW label value. We present our conclusions in section 7.

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2. SSW preparation, manufacture, and calibration

a. Scales, units, and conventions

All original temperature definitions in the calibration procedure are in terms of the International Practical Temperature Scale of 1968 (IPTS-68). It may be that salinity will be redefined in the future to accommodate the International Temperature Scale of 1990 (ITS-90). Until then, the SSW calibration procedure requires conversions between temperature measurements made with instruments calibrated with ITS-90, and their use in quantities defined in IPTS-68. In what follows, all temperature measurements are made on the ITS-90 scale and are converted for use in all SSW equations to IPTS-68 (Preston-Thomas 1990; Weir and Goldberg 1996).

The original definitions refer to atmospheric pressure in terms of “one standard atmosphere” (1 atm = $1.013\,25 \times 10^5$ Pa). Reference is also made to vapor pressures in terms of millimeters of mercury (mm Hg; where 1 Pa = 0.0075 mm Hg).

Measurements of conductivity and conductivity ratio are central to the calibration procedure, but often the term “ratio” is dropped, even though conductivity [in siemens per meter ($S\,m^{-1}$), or equivalent] is not directly involved. It has been suggested (A. Dickson 2006, personal communication) that, on the one hand, a conductivity ratio is properly the ratio of two measured conductivities, so that K_{15} and related quantities are indeed conductivity ratios. On the other hand, the measurements made by Guildline Autosal salinometers are, in principle, conductivities, which in practice are “scaled” by an internal resistance of the salinometer and appear as conductivity ratios, but perhaps should be called “scaled conductivities.” We choose to adopt the simple convention of calling quantities with units of Siemens per meter (or related) conductivities; conductivity ratios are dimensionless measures of conductivity, whether they are true ratios or scaled conductivities.

In accordance with the recommendations of the ISO (1993), we determine standard uncertainties of each element of the calibration procedure, where “standard uncertainty” means one standard deviation. The final net uncertainty for the whole procedure is the combined standard uncertainty obtained by taking the root of the sum of the squares of all standard uncertainties. The reported uncertainty is the expanded uncertainty, which is the combined standard uncertainty multiplied by a coverage factor.

b. Background

Until 1978 the standard for salinity determinations was a primary standard seawater (stored in glass am-

poules), which itself had been calibrated against the ultimate standard—pure silver. The introduction of electrical conductivity for estimating salinity led to suggestions that there was a need for a reproducible standard that was independent of any stored solution which could change composition as a result of long-term contact with a glass container [see Poisson (1976, 1978) and Poisson et al. (1978); for full references, see references 3, 4, and 7 in the reference list of Poisson (1980)]. Consequently, the Joint Panel on Oceanographic Tables and Standards (JPOTS) recommended (UNESCO 1979) that KCl be investigated for use as such a standard. Measurements made in three laboratories (in Canada, the United Kingdom, and France) obtained excellent agreement regarding the conductivity of KCl prepared in deionized or double-distilled water. From this work JPOTS formulated the Practical Salinity Scale 1978 (Perkin and Lewis 1980; UNESCO 1981), in which the conductivity at 15°C (on IPTS-68) and 1 standard atmosphere pressure of a KCl solution containing $32.4356\,g\,kg^{-1}$ was adopted as the reference standard for salinity determination. This was chosen as giving the same conductivity as seawater of salinity of exactly 35 on the previous salinity scale.

Among the reasons for choosing KCl were the following: (i) KCl was the accepted standard in electrical conductivity measurements, and (ii) Merck “Suprapur” (brand-named “Aristar” in the United Kingdom) KCl was of sufficient purity for use as a standard (Poisson 1980) and (iii) it was consistent within and between batches (Dauphinee et al. 1980). It was also claimed that the major impurity was sodium chloride (NaCl), but that at the level of interest the molal conductivities of the two salts were sufficiently similar as to minimize the effect of the impurity (Lewis 1980). We note that according to the most recent information from the manufacturer, the major impurity in Aristar KCl is nitrogen (species unspecified), some of which is in the form of nitrate, which is decomposed on fusion (see section 3f).

Thus, SSW is calibrated in electrical conductivity ratio (K_{15}) relative to a KCl solution containing $32.4356\,g\,kg^{-1}$ solution,

$$K_{15} = \frac{R_{15}}{Z_{N,15}}, \quad (1)$$

where R_{15} is the conductivity ratio of SSW at a temperature of 15°C (IPTS-68) and a pressure of 1 standard atmosphere, and $Z_{N,15}$ is the conductivity ratio of the KCl solution ($32.4356\,g\,kg^{-1}$) at 15°C (IPTS-1968) and 1 standard atmosphere.

c. Single-point calibration

Great pains are taken to measure, to very high accuracy, the conductivity ratio of a KCl solution when we know its conductivity ratio (by design) is exactly 1 (to within measurement accuracy) at 15°C. We are not disconcerted when the result is (however slightly) significantly different from 1, because the single-point calibration procedure eliminates (to first order) any bias that is common to both numerator and denominator in Eq. (1). Such (small) biases arise in the use of salinometers. Hibbert (2003) gives a complete derivation of the measurement uncertainty of ratios sharing uncertainty components in numerator and denominator. We provide below a simple demonstration of bias elimination.

Suppose the real (and unknown) conductivity ratio of the KCl is $Z_{N,15}$ (which we shall temporarily abbreviate to Z for convenience), and the measured KCl conductivity ratio to be Z_m ; similarly, the real (and unknown) conductivity ratio of the new SSW is R , and its measured value is R_m . Then,

$$Z_m = Z + \beta_Z \pm \varepsilon_Z, \quad (2a)$$

$$R_m = R + \beta_R \pm \varepsilon_R, \quad (2b)$$

where β is specific measurement bias (attributed to the salinometer), ε is all other measurement uncertainty, and subscripts Z and R indicate attribution to KCl and SSW measurement, respectively. Then, the measured conductivity ratio K_{15} of the new SSW to the KCl standard is

$$\begin{aligned} K_{15} &= \frac{R + \beta_R \pm \varepsilon_R}{Z + \beta_Z \pm \varepsilon_Z} \\ &= \frac{R(1 + \beta'_R \pm \varepsilon'_R)}{Z(1 + \beta''_Z \pm \varepsilon''_Z)}, \end{aligned} \quad (3)$$

where primes indicate division by R and double primes note division by Z (i.e., $\beta'_R = \beta_R/R$, etc.). Now the uncertainties and biases are very small and are the same order of magnitude by which Z and R are different from 1: $|\beta| \sim |\varepsilon| \sim |R - 1| \sim |Z - 1| \sim O(10^{-5})$; therefore, to first order, we can drop the primes, $\beta'_R \approx \beta_R$, etc.; resulting second-order errors are $O(10^{-10})$. We can now proceed to expand the term in parentheses in the denominator of the second line of (3):

$$\begin{aligned} K_{15} &= \frac{R}{Z} (1 + \beta_R \pm \varepsilon_R)(1 - \beta_Z \pm \varepsilon_Z) \\ &= \frac{R}{Z} (1 + \beta_R - \beta_Z \pm \varepsilon_R \pm \varepsilon_Z), \end{aligned} \quad (4)$$

where second-order (and higher) terms have been ignored in the expansions. Therefore, if the measurement biases are the same, they are eliminated from the cal-

ulation; R_m/Z_m is an unbiased estimator of $K_{15} = R/Z$; and the combined uncertainty of the measured estimate of K_{15} is given by the root of the sum of the squares of the individual uncertainties. For the salinometer biases in the measurement of both R and Z to be the same, the same salinometer must have been used and it must have remained stable throughout the procedure, as confirmed by the monitoring described below.

d. SSW preparation, manufacture, and calibration

We describe in this section the standard method for the manufacture and calibration of SSW as set out in Culkin (1986).

Seawater used for the preparation of SSW is northeast Atlantic surface water, collected well away from land and transported, unfiltered, in 1000-L containers to the Ocean Scientific International Limited (OSIL) laboratory, formerly in Petersfield, now (as of December 2006) in Havant, United Kingdom. It is passed through 2.0- and 0.2- μm cartridge filters and an in-line ultraviolet sterilizing module into a 5000-L polyvinyl carbonate (PVC)-lined tank with paddle stirrer. The water is then mixed by circulating through 0.2- μm cartridge filters for at least 30 days with periodic use of ultraviolet sterilization, during which time sufficient deionized water is added to adjust the salinity to somewhere in the range of 34.99–35.0.

Finally, the seawater is sealed in borosilicate bottles (capacity 230 mL), which have previously been rinsed with deionized water and dried at 180°C for 8 h. This final filling process includes further filtering of the seawater through cartridge filters, and ultraviolet sterilization. One bottle out of every 130 is reserved for calibration.

The two elements on the rhs of Eq. (1) must be determined: (i) R_{15} and (ii) $Z_{N,15}$. The determination of R_{15} is relatively straightforward; the conductivity of the new SSW batch is measured (on a Guildline 8400B Autosal salinometer) at a suitable set temperature (usually 21°C), and the resulting conductivity is converted to 15°C.

The determination of $Z_{N,15}$ is rather more complicated. The definition requires a KCl solution of concentration 32.4356 g kg⁻¹, which is impossible to prepare in practice. Therefore, the required value is obtained by interpolation. Four or five KCl solutions in the concentration range of 32.2–32.6 g kg⁻¹ are prepared. A straight line is fitted between concentration and conductivity, and the value of conductivity, at the required concentration, is found. The procedure for preparing the KCl solutions is described next.

KCl of high purity (melting point 790°C) is fused in a platinum crucible at 850°C for 20 min. The molten KCl

is then poured onto a stainless steel plate. The plate has been previously degreased, washed (with deionized water), and then dried at 120°C. The resulting lumps of KCl are broken into smaller pieces with an agate pestle, transferred to a clean, dry platinum basin, and stored under vacuum with a desiccant until required.

A suitable quantity (ca. 9 g) of fused KCl is transferred, using a stainless steel scoop, to a conical flask. The mass of KCl is determined by first weighing the scoop plus KCl, and then after transference, weighing the scoop plus any residual KCl, with the difference being the mass of KCl transferred into the flask. Then, the mass of KCl is corrected for buoyancy in air.

A 300-mL flask, containing the dry weight of KCl determined above and a magnetic stirring bar, is stoppered and weighed. A quantity of deionized water, having been predetermined to attain the desired concentration of KCl, is then added, the KCl is dissolved, and the solution, flask, stopper, and bar are reweighed. The solution mass then is corrected for buoyancy in air. A correction can be made for the mass of water lost as vapor into the airspace at the top of the flask. The solution concentration can then be calculated.

Finally, KCl solution conductivity is measured on a salinometer at a set temperature (usually 21°C), and a conversion applied to reduce the conductivity to 15°C.

3. KCl solution concentration and conductivity uncertainties

We proceed to examine the SSW calibration procedure to determine the standard uncertainty of each element of the procedure. As will become apparent, we seek to define relative uncertainties (standard uncertainty divided by mean of quantity) to the order of 10×10^{-6} or better. We will retain, for calculation of the combined standard uncertainty, relative uncertainties of 0.1×10^{-6} or greater. Anything smaller we will treat as negligible and assign to it a value of zero.

KCl solution concentration is a linear function of KCl mass in solution, and (over the very small ranges of values under consideration) KCl solution conductivity is a linear function of KCl solution concentration. In this section, all uncertainties will be calculated as relative uncertainties (either in the determination of KCl mass or KCl solution conductivity) and employed directly in the calculation of the combined standard uncertainty.

a. Preparation of dry KCl

The experiments of Dauphinee et al. (1980) and Gates and Wood (1985) have confirmed that the prepa-

ration of dry KCl by fusion, as described in section 2d, leaves no reasonably quantifiable amount of residual water in the KCl to contribute to the combined standard uncertainty.

b. Weighing of dry KCl

The fused KCl (ca. 9 g) is transferred, using a stainless steel scoop, to a conical flask. The mass of KCl is determined by first weighing the scoop plus KCl, and then after transference, weighing the scoop plus any residual KCl (the tare), with the difference being the weight of KCl transferred into the flask. The balance used to perform the weighings has a resolution of 10 μg . On each use, the balance is calibrated against its own internal balance weights, and checked with an external 50-g E2-class calibration weight, which is annually certified by the U.K. National Weights and Measures Laboratory, in Teddington; the balance itself is calibrated annually by the manufacturer. We take the standard uncertainty resulting from each of the two weighings as the certified standard uncertainty in the determination of the external calibration weight, 15 μg (the calibration certificate actually reports an expanded uncertainty of 30 μg based on a coverage factor of 2). For a scoop mass of 31 g, with a loading of 9-g KCl, the resulting relative standard uncertainties are therefore 15 $\mu\text{g}/31$ g for the tare (the scoop with any residual KCl), or 0.5×10^{-6} , and 15 $\mu\text{g}/40$ g, for the scoop plus KCl, or 0.4×10^{-6} .

Having weighed the KCl, the weight is corrected for buoyancy in air. This is the correct form of the buoyancy correction:

$$w_v = w_A [1 - (\rho_A/\rho_{\text{BW}})] / [1 - (\rho_A/\rho_{\text{KCl}})]. \quad (5a)$$

However, the approximate form below is normally employed:

$$w_v = w_A \left[1 + \rho_A \left(\frac{1}{\rho_{\text{KCl}}} - \frac{1}{\rho_{\text{BW}}} \right) \right], \quad (5b)$$

where w_v is the mass of KCl; w_A is the (measured) weight of KCl in air; and ρ_A , ρ_{KCl} , and ρ_{BW} are the densities of air, the dry KCl, and the balance weights, respectively. The approximate form (5b) is obtained by expanding the denominator of (5a) and ignoring terms higher than first order.

Now $\rho_A \sim 1.2 \text{ kg m}^{-3}$, $\rho_{\text{BW}} = 8.0 \times 10^3 \text{ kg m}^{-3}$, and $\rho_{\text{KCl}} = 1.988 \times 10^3 \text{ kg m}^{-3}$, and therefore the whole density term within the parentheses on the rhs of (5b) is $\sim 5 \times 10^{-4}$. The uncertainty in the buoyancy correction mainly results from the uncertainties in determining ρ_A from measurements of atmospheric pressure, tempera-

ture, and relative humidity, and the dominant fractional uncertainty is the ratio of the uncertainty in ρ_A to ρ_{KCl} .

During SSW calibration, atmospheric properties are measured with the following standard uncertainties: 0.2°C (temperature), 20 Pa (pressure), and 2% (relative humidity). Using a suitable equation for the density of moist air (e.g., Davis 1992), these are equivalent to standard uncertainties in ρ_A of 8×10^{-4} , 2×10^{-4} , and $2 \times 10^{-4} \text{ kg m}^{-3}$, respectively; and relative standard uncertainties of 0.4×10^{-6} , 0.1×10^{-6} , and 0.1×10^{-6} , respectively.

How accurately is the density of solid KCl known? Hutchison (1944) found $\rho_{\text{KCl}} = 1987.15 \text{ kg m}^{-3}$ (with a quoted uncertainty of 0.02 kg m^{-3}) at 25°C. The KCl thermal expansion coefficient is $133 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, so at 20°C, the density is $1988.47 \text{ kg m}^{-3}$, and an uncertainty in temperature of 0.2°C results in an uncertainty in density of 0.05 kg m^{-3} . This is negligible for the contribution to the uncertainty of determination of KCl mass via the buoyancy correction.

c. Determination of required quantity of water

We include this section for completeness. The weight of water (in air) required to produce a concentration X (g kg^{-1}) is calculated as follows. First, the required mass (g) of water is $w_r = [(1000/X) - 1] w_v$. The buoyancy correction (k) has the same form as in (5b): $k = \rho_A[(1/\rho_{\text{sol}}) - (1/\rho_{\text{BW}})]$, where ρ_{sol} is KCl solution density. Then, the required weight of water (in air) is $w_r/(1 + k)$. This calculation does not contribute to the combined standard uncertainty because the actual amount of water added is determined below (section 3d).

d. Preparation and weighing of KCl solution

A 300-mL flask, containing the dry mass of KCl determined in section 3c and a magnetic stirring bar, is stoppered and weighed using a balance with 0.1-mg resolution and 0.2-mg standard uncertainty. The quantity of deionized water, as determined in section 3d, is then added, the KCl is dissolved, and the solution, flask, stopper, and bar are reweighed. The mass of the flask, etc., is $\sim 180 \text{ g}$; the mass of the water is 270–280 g. The relative standard uncertainties are therefore 0.2 mg/180 g, or 1.1×10^{-6} , for the flask with the dry KCl, bar, and stopper, and 0.2 mg/450 g, or 0.4×10^{-6} , for the flask, etc., plus solution.

Next, as in section 2c, the weight of water is corrected for buoyancy in air, and a similar approximate form is used for the correction:

$$W_v = W_A \left[1 + \rho_A \left(\frac{1}{\rho_{\text{sol}}} - \frac{1}{\rho_{\text{BW}}} \right) \right], \quad (6)$$

where W_v and W_A are the mass of KCl solution, and the (measured) weight of KCl solution in air, respectively, and ρ_{sol} is the density of the KCl solution; other terms are as defined previously. The main difference over the previous calculation of relative uncertainty results from ρ_{sol} being approximately half ρ_{KCl} , and so the relative standard uncertainties resulting from atmospheric temperature, pressure, and humidity are doubled: 0.8×10^{-6} , 0.2×10^{-6} , and 0.2×10^{-6} , respectively.

The density of KCl in aqueous solution is given by Söhnel and Novotny (1985) as a function of KCl concentration and temperature (see also Chen et al. 1977). Uncertainty in temperature of 0.2°C results in an uncertainty in ρ_{sol} of 0.05 kg m^{-3} , similar to the accuracy of determination of the density of KCl solutions in Gates and Wood (1985), so we ignore this as a significant uncertainty.

Finally, a correction can be made for the mass of water (m_{vap} , in g) lost as vapor into the airspace at the top of the flask (Poisson 1981). This is the original form of the equation:

$$m_{\text{vap}} = \frac{18.001 V_A \pi^t}{22415[1 + (t/273)]760}, \quad (7a)$$

where V_A is the volume of air (cm^3) in the flask with the stopper inserted, and π^t is the partial pressure (mm Hg) of saturated water vapor at the solution temperature t ($^\circ\text{C}$). Reducing the three numerical factors to a single value, and incorporating a conversion factor of π^t (mm Hg) = $133.32 p^t$ (Pa), we obtain

$$m_{\text{vap}} = \frac{V_A p^t}{1 + (t/273)} \times 1.4088 \times 10^{-4} \quad (7b)$$

for $t = 20^\circ\text{C}$, $p^t = 2.34 \text{ kPa}$ (e.g., Wagner and Pruss 1993), with $V_A = 25 \text{ cm}^3$, $m_{\text{vap}} = 0.5 \text{ mg}$. Given 270–280 g water, this represents a (relative) correction of 1.8×10^{-6} . A temperature uncertainty of 0.2°C corresponds to an uncertainty in p^t of 30 Pa, and in m_{vap} of $6 \text{ } \mu\text{g}$, which is negligible.

e. Solvent conductivity

The deionizing columns (“Elgastat,” manufactured by Elga, Ltd., High Wycombe, United Kingdom) produce water of 18 M Ω cm minimum resistivity, which is equivalent to a maximum conductivity of $0.05 \text{ } \mu\text{S cm}^{-1}$. We can compare this with the conductivity of pure water (Light 1984; Marshall 1987), which at 20°C is $0.0420 \text{ } \mu\text{S cm}^{-1}$.

Poisson (1980) considered the conductivity of water, in one of the papers leading to the definition of practical salinity, in the context of its contribution to the

TABLE 1. Conductivity of major impurities in Aristar KCl compared with equivalent quantity of KCl. Total (1) shows the sums of the maximum assay concentrations and resulting calculated conductivities in the preceding 6 rows. Note that the assay quotes a maximum concentration of 10 ppm for nitrogen (N); making the worst-case assumption that the nitrogen is present as nitrate, then the nitrate concentration is 44 ppm ($= 10 \times 62/14$, where 62 and 14 are the molecular and atomic weights of nitrate and nitrogen, respectively). Total (2) repeats the calculation of Total (1) but substitutes the measured values of nitrate and phosphate for the assay values. Totals (3) and (4) use the maximum total concentrations of Totals (1) and (2), respectively, equally divided between potassium and chloride, to obtain conductivity estimates for KCl in equivalent total concentrations to the impurities. "Diff" gives the stated total conductivity differences. See section 2d for discussion.

Substance	Conductance $S\ m^{-1}\ (mmol\ cm^{-3})^{-1}$	Max. conc. ppm	Molecular wt. $g\ mol^{-1}$	Ion conc., N $mmol\ cm^{-3}$	Conductivity $mS\ cm^{-1}$
Nitrogen (as nitrate)	71.4	44	62	7.097×10^{-7}	5.067×10^{-4}
Phosphate	92.8	5	95	5.263×10^{-8}	4.884×10^{-5}
Sulfate	79.8	10	96	1.042×10^{-7}	8.313×10^{-5}
Barium	130.0	1	137.3	7.283×10^{-9}	9.468×10^{-6}
Lithium	38.7	0.4	6.94	5.764×10^{-8}	2.231×10^{-5}
Sodium	50.1	5	23	2.174×10^{-7}	1.089×10^{-4}
Total (1)		65.4			7.794×10^{-4}
Nitrate (measured)	71.4	1	62	1.6129×10^{-8}	1.152×10^{-5}
Phosphate (measured)	92.8	0.02	95	2.1052×10^{-10}	1.954×10^{-7}
Total (2)		17.4			2.355×10^{-4}
Potassium	73.5	33	39.1	8.440×10^{-7}	6.203×10^{-4}
Chloride	76.3	33	35.5	9.296×10^{-7}	7.093×10^{-4}
Total (3)		66			1.330×10^{-3}
Potassium	73.5	8.7	39.1	2.2276×10^{-7}	1.637×10^{-4}
Chloride	76.3	8.7	35.5	2.4535×10^{-7}	1.872×10^{-4}
Total (4)		17.4			3.509×10^{-4}
Diff (3) – (1)					5.506×10^{-4}
Diff (4) – (2)					1.154×10^{-4}

conductivity of KCl solutions. The conductivity of distilled water in equilibrium with air was measured to be $1.0\ \mu S\ cm^{-1}$. More recently, Pratt et al. (2001) measured the conductivity of CO_2 -saturated water to be $0.99\ \mu S\ cm^{-1}$ at $20^\circ C$, which is in good agreement with Poisson (1980). Poisson (1980) considered the conductivity of the solvent to be a component of the conductivity of the defined KCl solution ($32.4356\ g\ kg^{-1}$ concentration). Pratt et al. (2001) find that the conductivity of CO_2 -saturated water increases by $0.02\ \mu S\ cm^{-1}\ ^\circ C^{-1}$, which would correspond to a relative standard uncertainty in conductivity (for a temperature uncertainty of $0.2^\circ C$) of 0.1×10^{-6} . However, Poisson (1980) also states that the solvent conductivity can range more widely, depending on the level of the CO_2 saturation of the solvent. We choose, therefore, to associate a standard uncertainty of $0.1\ \mu S\ cm^{-1}$ with the amount of CO_2 dissolved in the solvent, or 2.3×10^{-6} relative standard uncertainty. This is equivalent to a 10% uncertainty (at laboratory temperature) in the level of CO_2 saturation of the deionized water. However, we note that this is the most uncertain of the uncertainties described here in section 3. An alternate (higher) uncertainty is also employed in calculating the combined standard uncertainty in section 3h, and both are compared with measurements in section 4b.

f. Impurities in the KCl

Although KCl is produced to a high degree of purity, nevertheless it does contain impurities, and we now consider the net difference between the conductivity of the impurities at the levels stated in the manufacturer's assay and KCl conductivity. Table 1 presents data relating to the assayed impurities and KCl. The six major impurities are listed, together with the maximum concentration (ppm) obtained from the assay, except for nitrogen (N), for which the species is unspecified; thus, we made the worst-case assumption that the nitrogen was present as nitrate, and converted the concentration accordingly (see Table 1 caption). All six of these impurities are recorded as being at or below the detection limit, so any calculated estimate of conductivity will be the maximum possible, rather than the probable. Conductance and molecular weight are obtained from Lide (2005). The ion concentration is the maximum concentration divided by the molecular weight, and the conductivity is then the ion concentration multiplied by the conductance. The results of the same calculations are listed in the table for potassium and chloride ions, with the same total maximum concentration as for the impurities. It can be seen from Table 1 that the net impurity conductivity minus the net equivalent KCl con-

TABLE 2a. Summary of nonnegligible uncertainties in the determination of KCl solution conductivity, as described in section 3. RSU is relative standard uncertainty. The final item (combined standard uncertainty) is the root of the sum of the squares of all preceding items.

Uncertainty source	RSU ($\times 10^{-6}$)
KCl weight	0.4
Tare (of above)	0.5
KCl buoyancy (temperature)	0.4
KCl buoyancy (pressure)	0.1
KCl buoyancy (humidity)	0.1
Solution weight	0.4
Tare (of above)	1.1
Solution buoyancy (temperature)	0.8
Solution buoyancy (pressure)	0.2
Solution buoyancy (humidity)	0.2
Solvent conductivity	2.3
KCl impurity conductivity	1.5
KCl solution conductivity	2.9
Combined standard uncertainty (relative)	4.3

ductivity is -5.5×10^{-4} mS cm $^{-1}$. With seawater conductivity ~ 43 mS cm $^{-1}$, this represents a relative bias of 13.0×10^{-6} , which is not negligible.

We decided to investigate this issue further. The major contributor to calculated impurity conductivity is nitrogen, where we had assumed it to be present as nitrate in the supplied KCl. We tested this assumption by measuring the nitrate (and phosphate) content of a KCl solution prepared as described above. The results are included in Table 1. The measured nitrate content was 0.03 mg kg $^{-1}$ in a 32 g kg $^{-1}$ KCl solution, or 0.9 ppm; phosphate was at or below the detection limit of 0.02 ppm. Using these values, we now calculate the maximum relative bias to be -2.7×10^{-6} . We treat this (conservatively) as a relative standard uncertainty of 1.5×10^{-6} .

g. KCl solution conductivity measurement

The standard uncertainty of the measurement of KCl solution conductivity ratios using a Guildline Autosol 8400B salinometer is 2.9×10^{-6} , based on a minimum of three measurements of the conductivity ratio of each KCl solution. This is discussed in detail in section 5.

h. Combined standard uncertainty

The uncertainties attributed to the measured conductivity of a prepared KCl solution, as described in the preceding sections, are summarized in Table 2. The combined (relative) standard uncertainty is 4.3×10^{-6} . The dominant uncertainties are those resulting from the (i) salinometer conductivity measurement and (ii) solvent conductivity. We note that doubling the solvent uncertainty, which is equivalent to 20% uncertainty in

TABLE 2b. Summary of uncertainties in SSW K_{15} , as described in sections 4 and 5. The final item (combined standard uncertainty) is the root of the sum of the squares of all preceding items.

Uncertainty source	RSU ($\times 10^{-6}$)
KCl conductivity at defined concentration	4.0
KCl conductivity temperature conversion	1.4
New SSW conductivity	2.0
Combined standard uncertainty (relative)	4.7

the CO $_2$ saturation level, produces a combined (relative) standard uncertainty of 5.9×10^{-6} .

4. Regression statistics, temperature correction, and K_{15} uncertainty

Having considered the uncertainty of the preparation of a single KCl solution in section 3, in this section we consider the uncertainties in the regressions involving multiple KCl solutions and subsequent uncertainties.

a. Regression statistics

Given measured conductivity ratios for four or five KCl solutions of known concentrations (in the range of 32.2–32.6 g kg $^{-1}$), we need to determine the conductivity at a specific concentration (32.4356 g kg $^{-1}$). Concentration is the independent variable (x) and conductivity ratio the dependent variable (y). However, because most of the uncertainties are in concentration, instead of regressing x on y we regress y on x . This is called “controlled calibration” by Brown (1993), who calls it “the favored route, at least since Eisenhart (1939).” Instead of fitting $y = a + bx$, we fit $x = \alpha + \beta y$, where $b = 1/\beta$ and $a = -\alpha/\beta$. Typical results are shown in Fig. 1. Also, we subtract from x and y their means, so we regress $y' = y - \bar{y}$ on $x' = x - \bar{x}$. In this form, $a = \alpha = 0$, and $\beta = \Sigma x'y' / \Sigma y'^2$. This effectively decouples the standard errors of the regression coefficients, so that

$$se(\beta) = \left[\frac{\sum (x' - \beta y')^2}{\nu \sum y'^2} \right]^{1/2}, \quad (8a)$$

$$se(\alpha) = \left[\frac{\sum (x' - \beta y')^2}{\nu n} \right]^{1/2}, \quad (8b)$$

where se is the standard error of the relevant regression coefficient, n is the number of data points, and ν ($\nu = n - 2$) is the degrees of freedom of deviations about the regression (e.g., Draper and Smith 1998). With the small standard error of β compared with β , we find that $se(b) = se(\beta)/\beta^2$, and $se(a) = se(\alpha)/\beta$. While $a = \alpha = 0$, $se(a)$ and $se(\alpha)$ are nonzero because of measurement uncertainty.

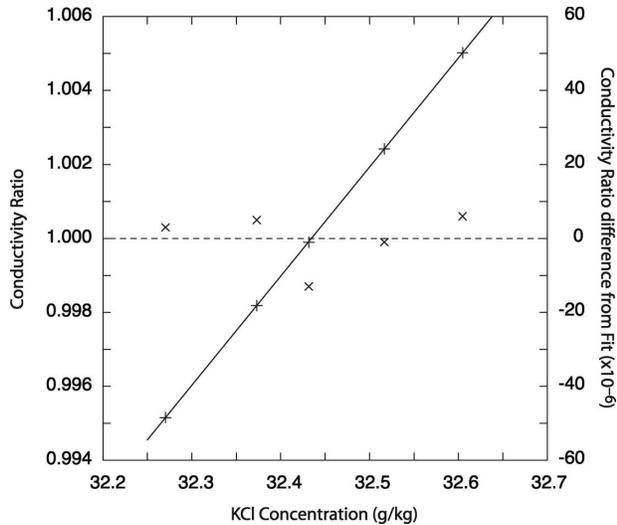


FIG. 1. KCl solution concentration vs conductivity ratio (data points are plus signs; the fitted line is solid), and KCl concentration vs fit residual (data points are crosses; the zero conductivity ratio difference line is dashed) for analysis of batch P145 by operator B. The rms residual for this example is 7.0×10^{-6} .

Given the standard errors of slope and intercept, we can calculate the conductivity ratio standard error resulting from the regression (δr) at the point of interest:

$$\delta r = \{[se(b)\delta x]^2 + se(a)^2\}^{1/2}, \quad (9)$$

where $\delta x = 32.4356 - \bar{x}$.

b. Results of regression

We would expect similarity between (a) KCl solution conductivity ratio combined (relative) standard uncertainty of 4.3×10^{-6} calculated in section 3h, (b) conductivity ratio standard error resulting from the regressions (δr) defined in (9) above, and (c) the root-mean-square (rms) of conductivity deviations about the regression, with ν degrees of freedom as above. We are interested in item (c) because it is effectively an independent measurement of item (a) for each KCl solution. Values of (b) and (c) are shown in Fig. 2 for 22 regressions, covering SSW batches P136–P146. We now treat relative standard uncertainties as conductivity ratio standard uncertainties with no significant loss of accuracy.

Initially, we note that in Fig. 2 there is an outlier—regression number 8, associated with batch P139. First, while this has an unusually large standard error and rms residual deviance, it corresponds to one of three such determinations for P139, the other two being of “normal” quality; second, although the uncertainties are large, in this case the mean was not significantly differ-

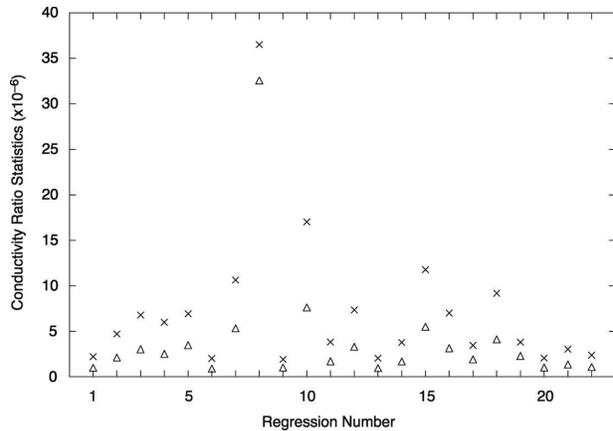


FIG. 2. The conductivity standard error due to the regression (triangles), and the rms of conductivity deviations about the regression (crosses), for SSW batches P136 to P146, with (typically) two sets of determinations per batch, for the regressions described in section 4.

ent from the other two means, so the quality of the determination of the “label value” for P139 was not compromised.

Excluding the outlier, the overall residual standard deviation for the remaining 21 regressions is 6.8×10^{-6} , with 58 degrees of freedom (100 data points from 21 regressions and two parameters per regression). This is similar to the combined standard uncertainty of the conductivity ratio of a single KCl solution (4.3×10^{-6}), but the value with the increased solvent conductivity uncertainty (5.9×10^{-6}) is closer. The conductivity ratio standard errors resulting from the regression (δr) are generally about half of these values, because by regressing about the center of gravity of the data (\bar{x}, \bar{y}), the contribution to δr from $se(b)$ is very small as a result of δx being very small. The smaller value (δr) is the appropriate value to take forward as the standard uncertainty of the conductivity of a KCl solution of $32.4356 \text{ g kg}^{-1}$ concentration, being the uncertainty calculated at that concentration. We choose to take forward an uncertainty of 4.0×10^{-6} to the final combined standard uncertainty.

c. Temperature correction

The measurements of KCl conductivity ratio are made at a set temperature, usually 21°C , and must be reduced to the standard temperature of 15°C . This is done using Eq. (4) of Dauphinee et al. (1980), which (as written) is

$$Z_{N,t} = 1 - 1.4655 \times 10^{-3}(\Delta t) + 9.103 \times 10^{-6}(\Delta t)^2, \quad (10a)$$

where $\Delta t = t - 15^\circ\text{C}$. However, this equation cannot be used for the purpose as written because it lacks $Z_{N,15}$ as a variable. We know, in principle, that $Z_{N,15} = 1$ by definition, but the purpose of the exercise is to calibrate SSW with a measurement of $Z_{N,t}$ converted to $Z_{N,15}$, and it will usually be slightly different from 1. There are two logical possibilities: either the whole of the rhs is multiplied by $Z_{N,15}$, or the first “1” on the rhs should actually be $Z_{N,15}$. It makes no practical difference which form we choose because, to first order, the multiplication of two numbers that are slightly (by the order of 10^{-5}) different from 1 is the same as the addition of the two small differences to 1. Resulting higher-order uncertainties are negligible. We choose the first form, which we write as

$$\frac{Z_{N,t}}{Z_{N,15}} = 1 - 1.4655 \times 10^{-3}(\Delta t) + 9.103 \times 10^{-6}(\Delta t)^2. \quad (10b)$$

The temperature of the salinometer’s water bath is monitored with a platinum resistance thermometer (PRT), which is annually calibrated (ITS-90) using the melting point of gallium, the triple point of water, and the triple point of mercury. The PRT’s resolution is 0.3 m°C and its standard uncertainty is 1.0 m°C. The resulting standard uncertainty in the temperature conversion from $Z_{N,t}$ to $Z_{N,15}$ is 1.4×10^{-6} .

5. SSW R_{15} and K_{15} uncertainties

Having calculated uncertainties pertaining to the KCl solutions in the preceding two sections, in this section we calculate SSW measurement uncertainties, and derive the final combined standard uncertainty for the whole calibration procedure.

Guildline Autosal 8400B salinometers are used for all conductivity ratio measurements. They can undergo drifts (trends) in calibration. The SSW manufacturing process eliminates such trends by careful monitoring, in particular by regular checks of the standardization against other batches of SSW, monitoring the salinometer bath temperature with a high-precision PRT, and monitoring the “standby” (“SBY”) and “zero” salinometer diagnostics. If any of these quantities is seen to vary significantly during measurement, then the calibration is abandoned until any problems are identified and rectified.

The resolution of Autosals is 5.0×10^{-6} in the conductivity ratio, because they read in double-conductivity ratio with a resolution of 10.0×10^{-6} . Laboratory best practice combined with multiple measurements (to reduce the standard error of the mean of

the measurements) enables a standard uncertainty of 5.0×10^{-6} in conductivity ratio to be achieved. All sample conductivity ratio values are obtained from a minimum of three measurements; therefore, the standard error of the mean of each value is $5.0 \times 10^{-6}/\sqrt{3} = 2.9 \times 10^{-6}$, which we take as the standard uncertainty associated with the measured conductivity ratio of a sample of SSW (and of a KCl solution; see section 3g).

The final value of R_{15} for each new batch of SSW is obtained not from measurement of a single sample of SSW, but from multiple samples. For each new batch, 11 or 12 bottles (previously ampoules) were each analyzed by two (occasionally three) operators, which is a total of 22–24 samples (for two operators, and more for three). The maximum observed standard deviation in the batches examined for this study (P136–P146) was 10.0×10^{-6} ; for 22 samples, the standard error of the mean is thus 2.1×10^{-6} (P144). The typical standard deviation for all other batches is 5.0×10^{-6} , so the standard error of the mean is correspondingly lower, 1.0×10^{-6} . It is important to note, in the context of possible within-batch variability of SSW conductivity, that *no such variability is observed, at the time of SSW production*, above the expected uncertainty of salinometer conductivity ratio measurements, as demonstrated by these observations.

We now consider the conversion from R_t to R_{15} , where R_t is the new SSW conductivity ratio at temperature t (°C), and t is usually 21°C. The (empirical) relationship for obtaining practical salinity from R_t and t , $S(R_t, t)$, is a fifth-order polynomial in the square root of R_t , and a second such polynomial with a temperature-dependent multiplying factor (Fofonoff and Millard 1983),

$$S(R_t, t) = \sum_{i=0}^5 a_i R_t^{i/2} + \frac{t - 15}{1 + k(t - 15)} \sum_{i=0}^5 b_i R_t^{i/2}. \quad (11a)$$

The coefficients are listed in Table 3. By construction,

$$\sum_{i=0}^5 a_i = 35.0000 \quad \text{and} \quad \sum_{i=0}^5 b_i = 0.0000, \quad (11b)$$

therefore, when $R_t = 1$ (exactly) for any t , salinity = 35, and the temperature dependence of salinity in the vicinity of $R_t = 1$ is extremely weak. For example, for a conductivity ratio of 0.999 95, the resulting calculated salinity is 34.9980 at 15°C, with zero temperature-dependent contributions [Eq. (2), the second term on the rhs, equals zero for $t = 15^\circ\text{C}$, by construction]. The temperature-dependent contribution for 21°C for the same conductivity is -7×10^{-6} in salinity. Therefore,

TABLE 3. Coefficients in the equation for conversion of temperature ($^{\circ}\text{C}$) and conductivity ratio to salinity, $S(R, t)$; see section 5.

Index (i)	a_i	b_i	k
0	0.0080	0.0005	0.0162
1	-0.1692	-0.0056	
2	25.3851	-0.0066	
3	14.0941	-0.0375	
4	-7.0261	0.0636	
5	2.7081	-0.0144	
Σ	35.0000	0.0000	

in practice, R_{21} is taken to be equal to R_{15} with zero error, and no correction is applied.

Thus, we associate a (conservative) standard uncertainty of 2.0×10^{-6} with the determination of the value of R_{15} ; the standard uncertainties associated with the measurement of $Z_{N,t}$ and temperature correction to $Z_{N,15}$ are 4.0×10^{-6} and 1.4×10^{-6} , respectively (summarized in Table 2); therefore, the combined standard uncertainty of SSW K_{15} is 4.7×10^{-6} . The expanded uncertainty, based on a coverage factor of 2, is (rounded) 10×10^{-6} , or 1×10^{-5} .

6. Discussion

In this section, we consider whether other observable factors might contribute to increasing the uncertainty of

SSW conductivity ratio above that derived from the calibration procedure in the preceding three sections. We consider KCl quality specifically, in addition to possible changes in SSW conductivity ratio over time.

a. KCl quality

As stated in section 2a above, Dauphinee et al. (1980) and Poisson (1980) found no difference between KCl lots. Therefore, it is only relatively recently (since 2000) that the manufacturers of SSW have been recording the KCl (Aristar) lot number as part of the SSW production documentation. It is right that the KCl lot number should be recorded and the SSW calibration results examined for changes in KCl quality, and this practice will continue. Each batch of SSW is calibrated either 2 or 3 times by the procedures described above. Each calibration uses a fresh preparation of KCl standards, and two or three different operators (from a total of four) perform the work. The results are presented in Table 4 for three batches of KCl, used to calibrate SSW batches P139 (2000)–P146 (2005). Measurements are the same as previously described: each operator makes a minimum of three measurements of the conductivity ratio of each of 10–12 bottles of SSW, each KCl R_{15} is obtained by fitting a line to conductivity ratio measurements of either four or five KCl solutions, and the conductivity ratio of each solution is measured a minimum of 3 times. The maximum rejection rate for KCl solutions is 10%, that is, one solution out of five may be

TABLE 4. Measurements of K_{15} using three lots of Aristar KCl. The KCl lot numbers in column 1 correspond to 1 (734 739 622); 2 (544 439 020); 3 (B886 139 204); U (unrecorded). Analysts are identified in column 2; column 3 gives values of R_{15} for a KCl concentration of $32.4356 \text{ g kg}^{-1}$; column 4 gives the R_{21} mean for the new batch of SSW; column 5 gives K_{15} for the new batch of SSW; columns 6 and 7 give SSW batch number and calibration date, respectively. The date is shown as day/month/year.

KCl lot	Operator	R_{15}	R_{21}	K_{15}	SSW batch	Date
3	A	1.000 011	0.999 803	0.999 79	P146	06/05/2005
3	B	0.999 999	0.999 778	0.999 78	P146	12/05/2005
1	A	1.000 005	0.999 815	0.999 81	P145	09/07/2004
2	B	1.000 028	0.999 827	0.999 80	P145	15/07/2004
1	A	1.000 006	0.999 878	0.999 87	P144	23/09/2003
2	B	1.000 015	0.999 879	0.999 86	P144	10/09/2003
2	C	1.000 029	0.999 884	0.999 86	P144	18/09/2003
2	A	1.000 012	0.999 897	0.999 89	P143	24/02/2003
2	C	1.000 003	0.999 897	0.999 89	P143	18/02/2003
1	A	0.999 998	0.999 910	0.999 91	P142	30/10/2001
U	B	0.999 979	0.999 896	0.999 91	P142	14/11/2001
2	A	0.999 994	0.999 924	0.999 93	P141	09/05/2002
U	B	0.999 985	0.999 926	0.999 94	P141	15/05/2002
U	B	1.000 001	0.999 922	0.999 92	P141	12/06/2002
1	A	1.000 012	0.999 920	0.999 91	P140	10/10/2000
2	A	1.000 007	0.999 920	0.999 91	P140	10/10/2000
1	D	0.999 990	0.999 915	0.999 92	P140	10/11/2000
1	A	1.000 012	0.999 940	0.999 93	P139	10/10/2000
2	A	1.000 007	0.999 940	0.999 93	P139	10/10/2000
1	D	0.999 990	0.999 937	0.999 94	P139	10/11/2000

rejected by one out of two operators during the calibration procedure, either by identifying a flaw in the KCl preparation process, such as inadvertent splashing of water, or by discerning an anomalous value of conductivity ratio postmeasurement.

No group of either two or three calibrations in Table 4 contains results of a greater difference from the mean than $\pm 1 \times 10^{-5}$ in K_{15} , and we attribute this to the salinometer uncertainty described in section 5. We conclude that (i) there is no significant variability within lots of KCl discernible above salinometer uncertainty, (ii) there is no significant bias between lots of KCl discernible above salinometer uncertainty, and (iii) there is no significant operator bias.

We examined the possible effect of impurities on the KCl conductivity in section 3f. Our “worst case” assumptions led us to suspect a possible bias, mainly resulting from nitrate content, of -5.5×10^{-4} mS cm⁻¹. Actual measurements of nitrate content reduced this to -1.2×10^{-4} mS cm⁻¹. The consistency demonstrated in the results in Table 4 leads us to conclude that our examination of the nitrate content for one batch of KCl is therefore representative of the quality of all batches used in the analysis.

Kawano et al. (2005) have suggested that variations in the lot (batch) quality of the KCl used in SSW calibration could affect the traceability of salinity data. Our results are different from theirs, but then our methods are also different from theirs. For example, in their preparation of KCl solutions, they heat but do not fuse the KCl. Also, they “reverse” the calibration process, that is, they use salinometers standardized with SSW to measure KCl conductivity. They use one batch of SSW—P132, manufactured in 1997 and employed in their analyses in 1999 and 2000. We suggest that the simplest means whereby our results may be reconciled is that their supply of P132 had drifted from its label value of conductivity ratio in the 2–3 yr since manufacture. This leads us to consider further the issue of SSW “offsets.”

b. SSW offsets

In recent years a number of independent investigations of the reliability and accuracy of SSW have been carried out (Mantyla 1980, 1987, 1994; Saunders 1986; Takatsuki et al. 1991; Culkin and Ridout 1998; Bacon et al. 2000; Aoyama et al. 2002; Kawano et al. 2005). Some of these investigations have suggested that changes in the conductivity of SSW can take place during storage, which is perhaps not surprising for seawater stored in a glass container, and some of these authors have suggested that the offsets can be used to correct field salinity data. The question of whether these offsets

should be used for this purpose is one that should be carefully considered by individual scientists and program organizers. Offset values have been shown to be time dependent (Culkin and Ridout 1998; Bacon et al. 2000); SSW salinity can evolve in vitro over a period of several years. Therefore, the age of the standard at the time of use is important, and any correction applied for subsequent offset could lead to greater inaccuracy in the field data.

Gouretski and Jancke (2000) performed the most comprehensive data quality analysis of marine salinity measurements to date. They compared direct inter-cruise salinity offsets (“crossover analysis”) computed with and without differences of SSW salinity from label salinity as suggested by Aoyama et al. (1998). There were 299 cruise pairs selected, including 131 pairs of cruises from the World Ocean Circulation Experiment (WOCE; Siedler et al. 2001). Accounting for the differences resulted in a rather small reduction of the mean absolute offset value, only for WOCE cruise pairs from 0.001 93 to 0.001 51 in salinity. In contrast, there was a slight increase in the mean absolute offset for the non-WOCE and WOCE/non-WOCE crossovers. They concluded that their “analysis demonstrates that applying the fixed ‘corrections’ as reported by Aoyama et al. (1998) has no appreciable effect.”

Now when each batch of SSW is calibrated, at the same time archived standards from previous batches are checked for change relative to their original label value (offsets). We emphasize that the recorded change is referenced to the defined KCl solution and is therefore independent of any previous batch (which may itself have changed with time). These offsets have already been reported for batches P120–P129 (Culkin and Ridout 1998). The offsets for batches P130–P144, using the same methodology, are shown in Table 5 and Fig. 3. The number of ampoules or bottles measured on each occasion is listed in the final column.

The changes in conductivity ratio (R_t) with time after calibration for SSW batches P130–P144 are within the range (from -2 to $+3$) $\times 10^{-5}$ (<0.001 in salinity) for storage periods up to 282 weeks. Figure 3 includes 6-month binned mean offsets, with errors bars ± 1 standard error. Out to 2 yr in age, the offsets are not significantly different from zero. Between 2 and 4 yr, the 6-month means are between 0 and 1×10^{-5} . Fitting a straight line to all data yields a slope of 0.3×10^{-5} yr⁻¹, which is significantly different from zero at the 5% level but not at the 1% level, and it only explains 12% of the variance. The values are consistent, for the bulk of the data, with (a) the expanded uncertainty of SSW conductivity ratio of 1×10^{-5} (described in section 5), and (b) no change of SSW conductivity ratio in vitro.

TABLE 5. Changes in K_{15} values of IAPSO standard seawaters after storage. In column 1, the batch number is identified in the first row for each batch, with container type (bottle or ampoule) in the second row. Date is given as day/month/year. Diff is (New K_{15} – Label K_{15}).

Batch/container	Date	Age (weeks)	Label K_{15}	New K_{15}	Diff ($\times 10^{-5}$)	No. of checks
P130	21/03/1996		0.999 97			
Ampoules	17/10/1996	30		0.999 97	0	2
	09/04/1997	55		0.999 97	0	5
	11/11/1997	86		0.999 95	-2	2
P131	10/10/1996		0.999 86			
Ampoules	15/01/1997	14		0.999 86	0	4
	09/04/1997	26		0.999 87	1	6
	11/11/1997	57		0.999 86	0	5
	04/06/1998	86		0.999 86	0	4
P132	09/04/1997		0.999 93			
Ampoules	11/11/1997	31		0.999 93	0	6
	04/06/1998	60		0.999 92	-1	5
	09/02/1999	96		0.999 93	0	4
	16/04/1999	105		0.999 92	-1	3
	02/06/2000	112		0.999 92	-1	2
P133	11/11/1997		0.999 86			
Ampoules	04/06/1998	27		0.999 85	-1	13
	09/02/1999	60		0.999 87	1	9
	16/04/1999	69		0.999 84	-2	5
P134	04/06/1998		0.999 89			
Ampoules	09/02/1999	36		0.999 91	2	7
	16/04/1999	45		0.999 90	1	6
	09/06/1999	53		0.999 89	0	4
	09/12/1999	79		0.999 91	2	3
	09/05/2002	205		0.999 90	1	1
	25/03/2003	255		0.999 92	3	1
P135	09/02/1999		0.999 92			
Ampoules	16/04/1999	9		0.999 92	0	6
	08/06/1999	16		0.999 91	-1	4
	09/12/1999	42		0.999 93	1	8
	11/10/2000	91		0.999 92	0	7
	09/05/2002	169		0.999 93	1	1
	09/07/2004	282		0.999 93	1	2
P136	16/04/1999		0.999 96			
Ampoules	09/06/1999	8		0.999 96	0	6
	09/12/1999	34		0.999 97	1	6
	10/11/2000	82		0.999 96	0	6
	30/10/2001	133		0.999 97	1	1
	09/05/2002	160		0.999 97	1	1
P137	09/12/1999		0.999 95			
Ampoules	02/06/1999	27		0.999 93	-2	2
	10/11/2000	48		0.999 94	-1	6
	14/11/2001	101		0.999 94	-1	4
	09/05/2002	126		0.999 94	-1	1
P138	09/06/1999		0.999 94			
Ampoules	14/11/2001	127		0.999 94	0	4
	09/05/2002	152		0.999 94	0	3
P139	10/11/1999		0.999 93			
Ampoules	14/11/2001	105		0.999 94	1	5
	15/05/2002	131		0.999 94	1	4
	25/02/2003	176		0.999 94	1	1
P140	10/11/2000		0.999 91			
Bottles	14/11/2001	53		0.999 91	0	5
	15/05/2002	79		0.999 91	0	5
	09/07/2004	191		0.999 91	0	2
P141	12/06/2002		0.999 93			
Bottles	15/07/2004	109		0.999 94	1	4

TABLE 5. (Continued)

Batch/container	Date	Age (weeks)	Label K_{15}	New K_{15}	Diff ($\times 10^{-5}$)	No. of checks
P142	14/11/2001		0.999 91			
Ampoules	15/05/2002	26		0.999 92	1	2
	23/10/2003	101		0.999 90	-1	2
	09/07/2004	138		0.999 92	1	1
P143	25/02/2003		0.999 89			
Bottles	23/10/2003	34		0.999 88	-1	4
	15/07/2004	72		0.999 88	-1	8
P144	23/09/2003		0.999 87			
Bottles	09/07/2004	41		0.999 86	-1	2
	15/07/2004	42		0.999 88	1	3

These measurements now also include batch P132, which we suggested above may have drifted in conductivity ratio by the time it was used by Kawano et al. (2005), but remained unchanged according to the results presented in Table 5. Furthermore, Bacon et al. (2000) clearly demonstrated the evolution of the conductivity ratio in vitro over time scales of a few years. How are we to reconcile these apparently contradictory observations? We hypothesize that motion and temperature may have been important agents in causing offsets. The SSW produced and measured in the same place has not had to travel far (a few tens of meters, at most), and has experienced no extremes of temperature. SSW used at sea or in another country will have experienced forklift trucks, ships, planes, road transport, and cranes; so it will have been shaken for long periods, and over long distances, and may well have experienced quite high or low temperatures while in transit. One can imagine that this might promote any slow processes leading to change in conductivity ratio, but we have no evidence with which to confirm or deny the hypothesis. We expect, however, that the replace-

ment of ampoules by bottles may improve the situation. The bottles are made from borosilicate glass, which is of a higher quality than the glass of the ampoules. Also, the bottles are packaged upright, unlike the ampoules, which were laid down flat. Because the ampoules had a larger airspace than the bottles, this will have led to greater “sloshing” inside ampoules in response to any motion. We expect to see, in coming years, an improved performance from the bottles in respect to “holding” the labeled value of conductivity ratio over long periods, including transportation.

7. Conclusions

First, we find the expanded uncertainty of new SSW conductivity ratio to be 1×10^{-5} , based on a coverage factor of 2, at the time of manufacture. The largest standard uncertainties contributing to the combined standard uncertainty on which this is based are the (i) measurement of the KCl solution conductivity ratio, (ii) solvent conductivity in the KCl solutions, and (iii) measurement of the new SSW conductivity ratio. Two of these (i and iii) are salinometer measurement uncertainties, and one (ii) is effectively CO_2 saturation uncertainty, which we believe to be the most “uncertain uncertainty,” deserving further investigation. Second, we report that SSW batches P130–P144 have effectively zero offset, within the same range of uncertainty, over periods of a few years. Third, we find no reason to support any “lot dependency” of uncertainties in the KCl used for SSW calibration, although we note that it would be useful to examine further the KCl impurity content. Fourth, we find no SSW “within-batch variability” at the time of production. The consequence of these four conclusions is that the reported uncertainty is not just the calibration uncertainty, it incorporates all of the other sources of uncertainty for which we have data. Finally, further work is required to explain both the apparent discrepancy between reports of SSW changing conductivity ratio in vitro, and the evidence

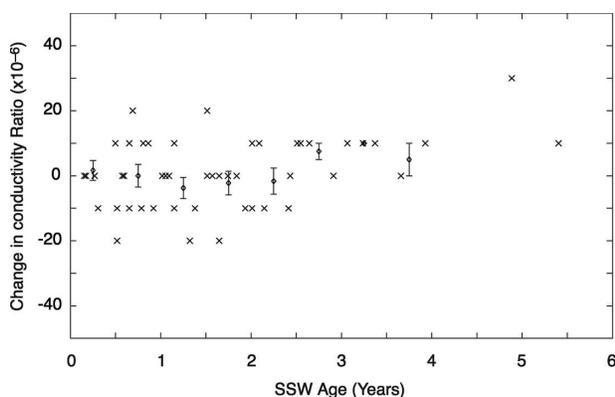


FIG. 3. Change in K_{15} with storage time (yr) for various batches of IAPSO SSW, as detailed in Table 3. Individual data are crosses; 6-month binned mean values are plotted as diamonds, with error bars as ± 1 standard error for each bin.

for no such change presented in this paper. A direct implication of this evidence is that any “correction tables,” which are intended to allow for offsets in modern SSW, should be treated with great caution.

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