

IAPSO STANDARD SEAWATER: DEFINITION OF THE UNCERTAINTY IN THE CALIBRATION  
PROCEDURE, AND STABILITY OF RECENT BATCHES

by

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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 by reference to carefully prepared solutions of potassium chloride (KCl). We calculate all uncertainties in the preparation and measurement of KCl solutions and of new SSW. We find the expanded uncertainty of SSW conductivity ratio to be  $1 \times 10^{-5}$ , based on a coverage factor of 2, at the time of manufacture. There is no discernible “within-batch” variability. We find no significant variability of KCl quality within or between batches of KCl. We report on measurement of SSW “offsets” from label conductivity ratio as long as 5 years after SSW batch manufacture, and we find no significant change in label conductivity ratio for SSW batches P130 through P144 outside the expanded uncertainty of  $1 \times 10^{-5}$ . This last result is in contrast to some other studies, and we suggest why this may be the case.

## **1 Introduction**

Standard Seawater (SSW) has now been in use 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 uncertainty 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 (CTDs – Conductivity, Temperature, Depth), 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 summarise 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.

## 2 SSW Preparation, Manufacture and Calibration

### 2.1 Scales, Units and Conventions

All original temperature definitions in the calibration procedure are in terms of IPTS-68. It may be that salinity will be redefined in the future to accommodate the ITS-90 temperature scale. 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 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), where  $1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$ . Reference is also made to vapour pressures in terms of mm Hg, where  $1 \text{ Pa} = 0.0075 \text{ mm Hg}$ .

Measurements of conductivity and conductivity ratio are central to the calibration procedure, but often the term “ratio” is dropped, even though a conductivity (in  $\text{S m}^{-1}$  or equivalent) is not directly involved. It has been suggested (Andrew Dickson, *pers. comm.*, 2006) 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 should perhaps be called “scaled conductivities”. We choose to adopt the simple convention of calling quantities with units of  $\text{S m}^{-1}$  (or related) “conductivities”, and “conductivity ratios” are dimensionless measures of conductivity, whether true ratios or “scaled conductivities”.

In accordance with the recommendations of the International Standardisation Organisation (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.

## 2.2 Background

Until 1978 the standard for salinity determinations was a Primary Standard Seawater (stored in glass ampoules) 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, UK and France) obtained excellent agreement of the conductivity of KCl prepared in de-ionised or double distilled water. From this work JPOTS formulated the Practical Salinity Scale 1978 (UNESCO, 1981), in which the conductivity, at 15 °C (on the 1968 temperature scale, IPTS-68) and 1 standard atmosphere pressure, of a KCl solution containing  $32.4356 \text{ g kg}^{-1}$  was adopted as the reference standard for salinity determination. This was chosen as giving the same conductivity as a seawater of salinity exactly 35 on the previous salinity scale.

Among the reasons for choosing KCl were: (i) KCl was the accepted standard in electrical conductivity measurements; (ii) Merck “Suprapur” (brand-named “Aristar” in the UK) KCl

was of sufficient purity for use as a standard (Poisson, 1980); (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 near 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 3.6).

So SSW is calibrated in electrical conductivity ratio ( $K_{15}$ ) relative to a KCl solution containing 32.4356 g KCl per kg 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<sup>-1</sup>) at 15 °C (IPTS-1968) and 1 standard atmosphere.

### 2.3 *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) to be 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 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 to be  $Z_{N,15}$  (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  $R_m$ . Then:

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

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

where  $\beta$  is specific measurement bias (attributed to the salinometer),  $\epsilon$  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:

$$\begin{aligned} K_{15} &= \frac{R + \beta_R \pm \epsilon_R}{Z + \beta_Z \pm \epsilon_Z} \\ &= \frac{R (1 + \beta'_R \pm \epsilon'_R)}{Z (1 + \beta''_Z \pm \epsilon''_Z)} \end{aligned} \quad (3)$$

where primes indicate division by  $R$  and double primes division by  $Z$  (ie  $\beta'_R = \beta_R/R$ , etc).

Now the uncertainties and biases are very small, and of the same order of magnitude by which  $Z$  and  $R$  are different from 1:  $|\beta| \sim |\epsilon| \sim |R-1| \sim |Z-1| \sim O(10^{-5})$ ; 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):

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

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 calculation;  $R_m/Z_m$  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.

#### *2.4 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 North East Atlantic surface water, collected well away from land and transported, unfiltered, in 1000 litre containers to the OSIL laboratory in Petersfield, UK. It is passed through 2.0 and 0.2  $\mu\text{m}$  cartridge filters and an in-line ultraviolet sterilising module into a 5000 litre PVC-lined tank with paddle stirrer. The water is then mixed by circulating through 0.2  $\mu\text{m}$  cartridge filters for at least 30 days with periodic use of ultraviolet sterilisation, during which time sufficient de-ionised water is added to adjust the salinity to somewhere in the range 34.99 – 35.0.

Finally, the seawater is sealed in borosilicate bottles (capacity 230 ml), which have previously been rinsed with de-ionised water and dried at 180 °C for 8 hours. This final filling process includes further filtering of the seawater through cartridge filters, and ultraviolet sterilisation. 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 Autosol 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<sup>-1</sup>, which is impossible to prepare in practice. Therefore the required value is obtained by interpolation. Four or five KCl solutions in the concentration range 32.2–32.6 g kg<sup>-1</sup> 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 deionised water, 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, then after transference, weighing the scoop plus any residual KCl, 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 deionised 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 re-weighed. Then the solution mass is corrected for buoyancy in air. A correction can be made for the mass of water lost as vapour into the air space 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  $10 \times 10^{-6}$  or better. We will retain, for calculation of the combined standard uncertainty, relative uncertainties of  $0.1 \times 10^{-6}$  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.

#### *3.1 Preparation of dry KCl*

The experiments of Dauphinee *et al.* (1980) and Gates and Wood (1985) have confirmed that the preparation of dry KCl by fusion, as described in section 2.4, leaves no reasonably quantifiable amount of residual water in the KCl to contribute to the combined standard uncertainty.

#### *3.2 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, then after transference,

weighing the scoop plus any residual KCl (the tare), the difference being the weight of KCl transferred into the flask. The balance used to perform the weighings has a resolution of 10  $\mu\text{g}$ . 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 UK National Weights and Measures Laboratory, Teddington; the balance itself is calibrated annually by the manufacturer. We take the standard uncertainty due to each of the two weighings as the certified standard uncertainty in the determination of the external calibration weight, 15  $\mu\text{g}$  (the calibration certificate actually reports an expanded uncertainty of 30  $\mu\text{g}$  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  $0.5 \times 10^{-6}$ ; and 15  $\mu\text{g}$  / 40 g, for the scoop plus KCl, or  $0.4 \times 10^{-6}$ .

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

$$w_v = w_A \left(1 - (\rho_A / \rho_{BW})\right) / \left(1 - (\rho_A / \rho_{KCl})\right) \quad (5a)$$

However, the approximate form below is normally employed:

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

where  $w_v$  is the mass of KCl;  $w_A$  is the (measured) weight of KCl in air; and  $\rho_A$ ,  $\rho_{KCl}$  and  $\rho_{BW}$  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  $\rho_A \sim 1.2 \text{ kg m}^{-3}$ ,  $\rho_{BW} = 8.0 \times 10^3 \text{ kg m}^{-3}$  and  $\rho_{KCl} = 1.988 \times 10^3 \text{ kg m}^{-3}$ , 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  $\rho_A$  from measurements of atmospheric pressure, temperature and relative humidity, and the dominant fractional uncertainty is the ratio of the uncertainty in  $\rho_A$  to  $\rho_{KCl}$ .

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

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

### 3.3 Determination of Required Quantity of Water

We include this section for completeness. The weight of water (in air) required to produce a concentration  $X \text{ (g kg}^{-1}\text{)}$  is calculated as follows. Firstly, 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):  $k = \rho_A[(1/\rho_{sol}) - (1/\rho_{BW})]$ , where  $\rho_{sol}$  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 3.4).

### 3.4 Preparation and Weighing of KCl Solution

A 300 ml flask, containing the dry mass of KCl determined in section 3.3, and a magnetic stirring bar, is stoppered and weighed using a balance with resolution 0.1 mg and standard uncertainty 0.2 mg. The quantity of deionised water, as determined in section 3.4, is then added, the KCl is dissolved, and the solution, flask, stopper and bar re-weighed. The mass of flask etc. is ~180 g; the mass of water is 270-280 g. The relative standard uncertainties are therefore 0.2 mg / 180 g, or  $1.1 \times 10^{-6}$  for the flask with dry KCl, bar and stopper; and 0.2 mg / 450 g, or  $0.4 \times 10^{-6}$  for the flask etc. plus solution.

Next, as in section 2.3, the weight of water is corrected for buoyancy in air, and a similar approximate form used for the correction:

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

where  $W_v$  and  $W_A$  are the mass of KCl solution, and the (measured) weight of KCl solution in air, respectively, and  $\rho_{sol}$  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  $\rho_{sol}$  being approximately half  $\rho_{KCl}$ , and so the relative standard uncertainties due atmospheric temperature, pressure and humidity are doubled:  $0.8 \times 10^{-6}$ ,  $0.2 \times 10^{-6}$  and  $0.2 \times 10^{-6}$ , 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 uncertainty in  $\rho_{sol}$  of  $0.05 \text{ kg m}^{-3}$  – 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 ( $m_{\text{vap}}$ , g) lost as vapour into the air space 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 ( $\text{cm}^3$ ) in the flask with the stopper inserted, and  $\pi^t$  is the partial pressure (mm Hg) of saturated water vapour at the solution temperature  $t$  ( $^{\circ}\text{C}$ ). Reducing the three numerical factors to a single value, and incorporating a conversion factor of  $\pi^t$  (mm Hg) = 133.32  $\text{p}^t$  (Pa), we obtain:

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

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

### 3.5 Solvent Conductivity

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

Now 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 conductivity of KCl solutions. The conductivity of distilled water in equilibrium with air was measured to be 1.0  $\mu\text{S cm}^{-1}$ . More recently, Pratt *et al.* (2001) measured the conductivity of  $\text{CO}_2$ -saturated water

to be  $0.99 \mu\text{S cm}^{-1}$  at  $20 \text{ }^\circ\text{C}$ , 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 (concentration  $32.4356 \text{ g kg}^{-1}$ ). Pratt *et al.* (2001) find that the conductivity of  $\text{CO}_2$ -saturated water increases by  $0.02 \mu\text{S cm}^{-1} \text{ }^\circ\text{C}^{-1}$ , which would correspond to a relative standard uncertainty in conductivity (for a temperature uncertainty of  $0.2 \text{ }^\circ\text{C}$ ) of  $0.1 \times 10^{-6}$ . However, Poisson (1980) also states that the solvent conductivity can range more widely, depending on the level of  $\text{CO}_2$  saturation of the solvent. We choose, therefore, to associate a standard uncertainty of  $0.1 \mu\text{S cm}^{-1}$  with the amount of  $\text{CO}_2$  dissolved in the solvent, or  $2.3 \times 10^{-6}$  relative standard uncertainty. This is equivalent to a 10% uncertainty (at laboratory temperature) in the level of  $\text{CO}_2$  saturation of the deionised 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 3.8, and both are compared with measurements in section 4.2.

### 3.6 *Impurities in the KCl*

Although KCl is produced to a high degree of purity, it does nevertheless 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 to 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, so 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 conductivity is  $-5.5 \times 10^{-4} \text{ mS cm}^{-1}$ . With seawater conductivity  $\sim 43 \text{ mS cm}^{-1}$ , this represents a relative bias of  $13.0 \times 10^{-6}$ , 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  $0.03 \text{ mg kg}^{-1}$  in a  $32 \text{ g kg}^{-1}$  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  $-2.7 \times 10^{-6}$ . We treat this (conservatively) as a relative standard uncertainty of  $1.5 \times 10^{-6}$ .

### *3.7 KCl Solution Conductivity Measurement*

The standard uncertainty of the measurement of KCl solution conductivity ratios using a Guildline Autosol 8400B salinometer is  $2.9 \times 10^{-6}$ , based on a minimum of 3 measurements of the conductivity ratio of each KCl solution. This is discussed in detail in section 5.

### *3.8 Combined Standard Uncertainty*

The uncertainties attributed to the measured conductivity of a prepared KCl solution, as described in the preceding sections, are summarised in Table 2. The combined (relative) standard uncertainty is  $4.3 \times 10^{-6}$ . The dominant uncertainties are those due (i) to the salinometer conductivity measurement, and (ii) to the solvent conductivity. We note that



doubling the solvent uncertainty – equivalent to 20% uncertainty in the CO<sub>2</sub> saturation level – produces a combined (relative) standard uncertainty of  $5.9 \times 10^{-6}$ .

#### 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.

##### 4.1 Regression Statistics

Given measured conductivity ratios for four or five KCl solutions of known concentrations (in the range 32.2–32.6 g kg<sup>-1</sup>), we need to determine the conductivity at a specific concentration (32.4356 g kg<sup>-1</sup>). Concentration is the independent variable ( $x$ ) and conductivity ratio the dependent variable ( $y$ ). However, since 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 favoured 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 figure 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

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

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

where  $se$  is the standard error of the relevant regression coefficient,  $n$  is the number of data points, and  $\nu$  ( $\nu = n-2$ ) is the degrees of freedom of deviations about the regression (eg Draper and Smith, 1985). With the standard error of  $\beta$  small compared with  $\beta$ , 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 non-zero due to measurement uncertainty.

Given the standard errors of slope and intercept, we can calculate the conductivity ratio standard error due to the regression ( $\delta r$ ) at the point of interest:

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

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

#### 4.2 Results of regression

We would expect similarity between (a) KCl solution conductivity ratio combined (relative) standard uncertainty of  $4.3 \times 10^{-6}$  calculated in section 3.9, (b) the conductivity ratio standard error due to the regressions ( $\delta r$ ) defined in (9) above, and (c) the root-mean-square (rms) of conductivity deviations about the regression, with  $\nu$  degrees of freedom as above. We are interested in (c) because it is effectively an independent measurement of (a) for each KCl solution. Values of (b) and (c) are shown in figure 2 for 22 regressions, covering SSW batches P136 to P146. We now treat relative standard uncertainties as conductivity ratio standard uncertainties with no significant loss of accuracy.

Firstly we note that in figure 2 there is an outlier: regression number 8, associated with batch P139. Firstly, while these are an unusually large standard error and rms residual deviance, they correspond to one of three such determinations for P139, the other two being of “normal” quality; secondly, although the uncertainties are large, in this case the mean was not

significantly different 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  $6.8 \times 10^{-6}$ , with 58 degrees of freedom (100 data points from 21 regressions, 2 parameters per regression). This is similar to the combined standard uncertainty of the conductivity ratio of a single KCl solution ( $4.3 \times 10^{-6}$ ), but the value with increased solvent conductivity uncertainty ( $5.9 \times 10^{-6}$ ) is closer. The conductivity ratio standard errors due to the regression ( $\delta r$ ) are generally about half of these values, because by regressing about the centre of gravity of the data  $(\bar{x}, \bar{y})$ , the contribution to  $\delta r$  from  $\text{se}(b)$  is very small because  $\delta x$  is very small. The smaller value ( $\delta r$ ) is the appropriate value to take forwards as the standard uncertainty of the conductivity of a KCl solution of concentration  $32.4356 \text{ g kg}^{-1}$ , being the uncertainty calculated at that concentration. We choose to take forwards an uncertainty of  $4.0 \times 10^{-6}$  to the final combined standard uncertainty.

### 4.3 Temperature Correction

The measurements of KCl conductivity ratio are made at a set temperature, usually  $21 \text{ }^\circ\text{C}$ , and must be reduced to the standard temperature of  $15 \text{ }^\circ\text{C}$ . 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  $\Delta t = t - 15 \text{ }^\circ\text{C}$ . 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 since to first order, multiplication of two numbers slightly (by the order of  $10^{-5}$ ) different from 1 is the same as adding 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 1.0 m°C. The resulting standard uncertainty in the temperature conversion from  $Z_{N,t}$  to  $Z_{N,15}$  is  $1.4 \times 10^{-6}$ .

## 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 standardisation against other batches of SSW; by monitoring the salinometer bath temperature with a high-precision PRT; and by monitoring the salinometer diagnostics “standby” (SBY) and “zero”. 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  $5.0 \times 10^{-6}$  in conductivity ratio, since they read in double conductivity ratio with a resolution of  $10.0 \times 10^{-6}$ . Laboratory best practice combined with multiple measurements (to reduce the standard error of the mean of the measurements) enables a standard uncertainty of  $5.0 \times 10^{-6}$  in conductivity ratio to be achieved. All sample conductivity ratio values are obtained from a minimum of 3 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: section 3.7).

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 analysed by 2 (occasionally 3) operators: a total of 22-24 samples (for 2 operators; more for 3). The maximum observed standard deviation in the batches examined for this study (P136 to P146) was  $10.0 \times 10^{-6}$ ; for 22 samples, the standard error of the mean is thus  $2.1 \times 10^{-6}$  (P144). The typical standard deviation for all other batches is  $5.0 \times 10^{-6}$ , the standard error of the mean being correspondingly lower,  $1.0 \times 10^{-6}$ . 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 of  $R_t$  to  $R_{15}$ , where  $R_t$  is the new SSW conductivity ratio at temperature  $t$  ( $^{\circ}\text{C}$ ), and  $t$  is usually  $21$   $^{\circ}\text{C}$ . 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,

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

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 0.99995, the resulting calculated salinity is 34.9980 at 15°C, with zero temperature-dependent contribution (equation 2, second term on RHS, equals zero for  $t=15^\circ\text{C}$ , by construction). The temperature-dependent contribution for 21°C for the same conductivity is  $-7 \times 10^{-6}$  in salinity. Therefore, in practice,  $R_{21}$  is taken to be equal to  $R_{15}$  with zero error and no correction is applied.

So we associate a (conservative) standard uncertainty of  $2.0 \times 10^{-6}$  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  $4.0 \times 10^{-6}$  and  $1.4 \times 10^{-6}$  respectively (summarised in Table 2); therefore the combined standard uncertainty of SSW  $K_{15}$  is  $4.7 \times 10^{-6}$ . The expanded uncertainty, based on a coverage factor of 2, is (rounded)  $10 \times 10^{-6}$ , or  $1 \times 10^{-5}$ .

## 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 specifically KCl quality, and possible changes in SSW conductivity ratio over time.

### 6.1 KCl quality

As stated in section 2.1 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 KCl (“Aristar”) lot number as part of the SSW production documentation. It is right that KCl lot number should be recorded, and SSW calibration results examined for changes in KCl quality, and this practice will continue. Each batch of SSW is calibrated two or three 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) to P146 (2005). Measurements are as previously described: each operator makes a minimum of 3 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 4 or 5 KCl solutions; the conductivity ratio of each solution is measured a minimum of 3 times. The maximum rejection rate for KCl solutions is 10%: ie, one solution out of 5 may be 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 post-measurement an anomalous value of conductivity ratio.

No group of two or three calibrations in Table 4 contains results of 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; (iii) there is no significant operator bias.

We examined the possible effect of impurities on the KCl conductivity in section 3.6. Our “worst-case” assumptions led us to suspect a possible bias, mainly due to nitrate content, of

$-5.5 \times 10^{-4} \text{ mS cm}^{-1}$ . Actual measurements of nitrate content reduced this to  $-1.2 \times 10^{-4} \text{ mS cm}^{-1}$ . 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 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: they use salinometers standardised 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 years since manufacture. This leads us to consider further the issue of SSW “offsets”.

## 6.2 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 have suggested that changes in the conductivity of SSW can take place during storage, which is perhaps not surprising for a 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 programme 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 periods 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 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). 299 cruise pairs were 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 0.00193 to 0.00151 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 emphasise that the change recorded 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 through P129 (Culkin and Ridout, 1998). The offsets for batches P130 through P144, using the same methodology, are shown in Table 5 and figure 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 to P144 are within the range  $(-2 \text{ to } +3) \times 10^{-5}$  ( $<0.001$  in salinity) for storage periods up to 282 weeks. Figure 3 includes 6-month binned mean offsets, with errors bars  $\pm 1$  standard error. Out to 2 years age, the offsets are not significantly different from zero. Between 2 and 4

years, the 6-month means are between 0 and  $1 \times 10^{-5}$ . Fitting a straight line to all data yields a slope of  $0.3 \times 10^{-5} \text{ year}^{-1}$ , 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  $1 \times 10^{-5}$  (described in section 5), and (b) no change of SSW conductivity ratio *in vitro*.

Now these measurements 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 evolution of conductivity ratio *in vitro* over timescales of a few years. How are we to reconcile these apparently contradictory observations? We hypothesise that motion and temperature may have been important agents in causing “offsets”. SSW produced and measured in the same place has not had to travel far: a few tens of metres, at most, experiencing no extremes of temperature. SSW used at sea or in another country will have experienced forklift trucks, ships, planes, road transport, 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 replacement of ampoules by bottles may improve the situation. The bottles are made from borosilicate glass, of higher quality than the glass of the ampoules. Also, the bottles are packaged upright, unlike the ampoules, which were laid down flat. Since ampoules had a larger air space than the bottles, this will have led to greater “sloshing” inside ampoules in response to any motion. We expect to see, in coming years, improved performance from the bottles in respect of “holding” label value of conductivity ratio over long periods, including transportation.

## 7. Conclusions

Firstly, we find the expanded uncertainty of new SSW conductivity ratio to be  $1 \times 10^{-5}$ , 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 (i) the measurement of KCl solution conductivity ratio, (ii) solvent conductivity in the KCl solutions, and (iii) the measurement of new SSW conductivity ratio. Two of these (i and iii) are salinometer measurement uncertainties; one (ii) is effectively CO<sub>2</sub> saturation uncertainty, and we believe this to be the most “uncertain uncertainty”, deserving of further investigation. Secondly, we report that SSW batches P130–P144 have effectively zero “offset”, within the same range of uncertainty, over periods of a few years. Thirdly, 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. Fourthly, 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 other sources of uncertainty for which we have data. Finally, further work is required to explain the apparent discrepancy between reports of SSW changing conductivity ratio *in vitro*, and the evidence for no such change presented in this paper. A direct implication of this evidence is that any “correction tables”, intended to allow for “offsets” in modern SSW, should be treated with great caution.

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## References

- Aoyama, M., T. M. Joyce, T. Kawano and Y. Takatsuki, 1998: Offsets of the IAPSO Standard Seawater through batch P129 and its application to Pacific WHP crossovers. *International WOCE Newsletter*, No. 32, 5-7.
- Aoyama, M., T. M. Joyce, T. Kawano and Y. Takatsuki, 2002: Standard seawater comparison up to P129. *Deep-Sea Res. I* **49** 1103-1114.
- Bacon, S., H. M. Snaith and M. J. Yelland, 2000: An evaluation of some recent batches of IAPSO standard seawater. *J. Atmos. Oceanic Tech.* **17** 854-861.
- Brown, P. J., 1993: Measurement, regression and calibration. Clarendon Press, Oxford, 201 pp.
- Chen, C.-T., R. T. Emmet and F. J. Millero, 1977: The apparent molal volumes of aqueous solutions of NaCl, KCl, MgCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, and MgSO<sub>4</sub> from 0 to 1000 bars at 0, 25, and 50 °C. *J. Chem. Eng. Data* **22** 201-207.
- Culkin, F., 1986: Calibration of standard seawater in electrical conductivity. *The Science of the Total Environment* **49** 1-7.
- Culkin, F. and P. Ridout, 1998: Stability of IAPSO standard seawater. *J. Atmos. Oceanic Tech.* **15** 1072-1075.
- Culkin, F. and J. Smed, 1979: The history of standard seawater. *Oceanologica Acta* **2** 355-364.

- Dauphinee, T. M., J. Ancsin, H. P. Klein and M. J. Phillips, 1980: The effect of concentration and temperature on the conductivity ratio of potassium chloride solutions to Standard Seawater of salinity 35‰ (chlorinity 19.374‰). *IEEE J. Oceanic Eng.* **OE-5** 17-21.
- Davis, R. S., 1992: Equation for the determination of the density of moist air (1981/91). *Metrologia* **29** 67-70.
- Draper, N. R. and H. Smith, 1998: Applied Regression Analysis (3<sup>rd</sup> ed.). Wiley, New York, 726 pp.
- Eisenhart, C., 1939: The interpretation of certain regression methods and their use in biological and industrial research. *Annals of Mathematical Statistics* **10** 162-186.
- Fofonoff, N. P. and R. C. Millard, Jr., 1983: Algorithms for computation of fundamental properties of seawater. *UNESCO Tech. Pap. Mar. Sci.* **44** 1-53.
- Gates, J. A. and R. H. Wood, 1985: Densities of aqueous solutions of NaCl, MgCl<sub>2</sub>, KCl, NaBr, LiCl and CaCl<sub>2</sub> from 0.05 to 5.0 mol kg<sup>-1</sup> and 0.01013 to 40 MPa at 298.15 K. *J. Chem. Eng. Data* **30** 44-49.
- Gouretski, V. V. and K. Jancke, 2001: Systematic errors as the cause for an apparent deep water property variability: global analysis of the WOCE and historical hydrographic data. *Prog. Oceanog.* **48** 337-402.
- Hibbert, D. B., 2003: The measurement uncertainty of ratios which share uncertainty components in numerator and denominator. *Accred. Qual. Assur.* **8** 195-199.
- Hutchison, D. A., 1944: Density of Potassium Chloride. *Physical Review* **66** 144-148.

- International Standardisation Organisation (ISO), 1993: Guide to the Expression of Uncertainty of Measurement. ISO, Geneva, 101 pp.
- Kawano, T., M. Aoyama and Y. Takatsuki, 2005: Inconsistency in the conductivity of standard potassium chloride solutions made from different high-quality reagents. *Deep-Sea Res. I* **52** 389-396.
- Lewis, E. L., 1980: The Practical Salinity Scale 1978 and its antecedents. *IEEE J. Oceanic Eng.* **OE-5** 3-8.
- Lide, D. R. (editor), 2005: CRC Handbook of Chemistry and Physics, 86<sup>th</sup> Edition. CRC Press, Boca Raton, Florida, USA, 2626 pp.
- Light, T. S., 1984: Temperature dependence and measurement of resistivity of pure water. *Anal. Chem.* **56** 1138-1142.
- Mantyla, A. W., 1980: Electric conductivity comparisons of Standard Seawater batches P29 to P84. *Deep-Sea Res.* **27A** 837-846.
- Mantyla, A. W., 1987: Standard Seawater comparison updated. *J. Phys. Oceanogr.* **17** 543-548.
- Mantyla, A. W., 1994: The treatment of inconsistencies in Atlantic deep water salinity data. *Deep-Sea Res.*, **41** (9) 1387-1405.
- Marshall, W. L., 1987: Electrical conductance of liquid and supercritical water evaluated from 0 °C and 0.1 MPa to high temperature and pressures. Reduced-state relationships. *J. Chem. Eng. Data* **32** 221-226.

- Perkin, R. G. and E. L. Lewis, 1980: The Practical Salinity Scale 1978: fitting the data. *IEEE J. Oceanic Eng.* **OE-5** 9-16.
- Poisson, A., 1980: The concentration of the KCl solution whose conductivity is that of Standard Seawater (35‰) at 15°C. *IEEE J. Oceanic Eng.* **OE-5** 24-28.
- Poisson, A., 1981: Conductivity ratio measurement of diluted or concentrated Standard Seawater and KCl solution used to establish the new Practical Salinity Scale 1978. *UNESCO Tech. Pap. Mar. Sci.* **37** 73-104.
- Pratt, K. W., W. F. Koch, Y. C. Wu and P. A. Berezansky, 2001: Molality-based primary standards of electrolytic conductivity. *Pure Appl. Chem.* **73** 1783-1793.
- Preston-Thomas, H., 1990: The International Temperature Scale of 1990 (ITS-90). *Metrologia* **27** 3-10.
- Saunders, P. M., 1986: The accuracy of measurement of salinity, oxygen and temperature in the deep ocean. *J. Phys. Oceanogr.*, **16** (1) 189-195.
- Siedler, G., J. Church and W. J. Gould, 2001 (eds.): Ocean Circulation and Climate: Observing and Modelling the Global Ocean. Academic Press, San Diego, USA, 715 pp.
- Söhnel, O. and P. Novotny, 1985: Densities of aqueous solutions of inorganic substances. Elsevier, Amsterdam, 335 pp.
- Takatsuki, Y., M. Aoyama, T. Nakano, H. Miyagi, T. Ishihara and T. Tsutsumida, 1991: Standard seawater comparisons of some recent batches. *J. Atmos. Oceanic. Tech.* **8** 985-987.

UNESCO, 1979: Ninth report of the Joint Panel on Oceanographic Tables and Standards.

*UNESCO Tech. Pap. Mar. Sci.* No. 30, 32 pp.

UNESCO, 1981: Tenth report of the Joint Panel on Oceanographic Tables and Standards.

*UNESCO Tech. Pap. Mar. Sci.* No. 36, 25 pp.

Wagner, W. and A. Pruss, 1993: International equations for the saturation properties of ordinary water substance. Revised according to the international temperature scale of 1990. Addendum to *Journal of Physical and Chemical Reference Data* **16**, 893 (1987).

*J. Phys. Chem. Reference Data* **22** 783-787.

Weir, R. D. and R. N. Goldberg, 1996: On the conversion of thermodynamic properties to the basis of the International Temperature Scale of 1990. *J. Chem. Thermodynamics* **28**

261-276.

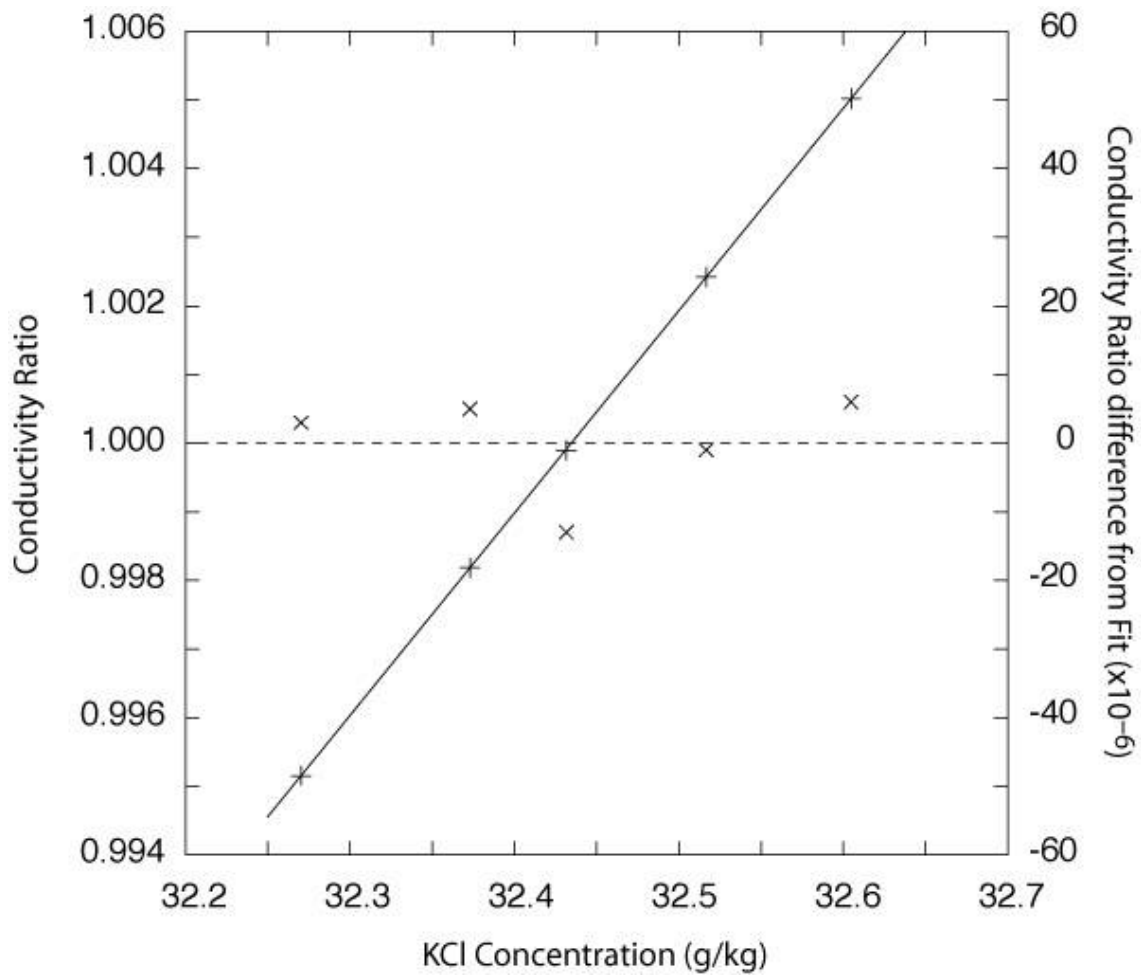


## Figure Captions

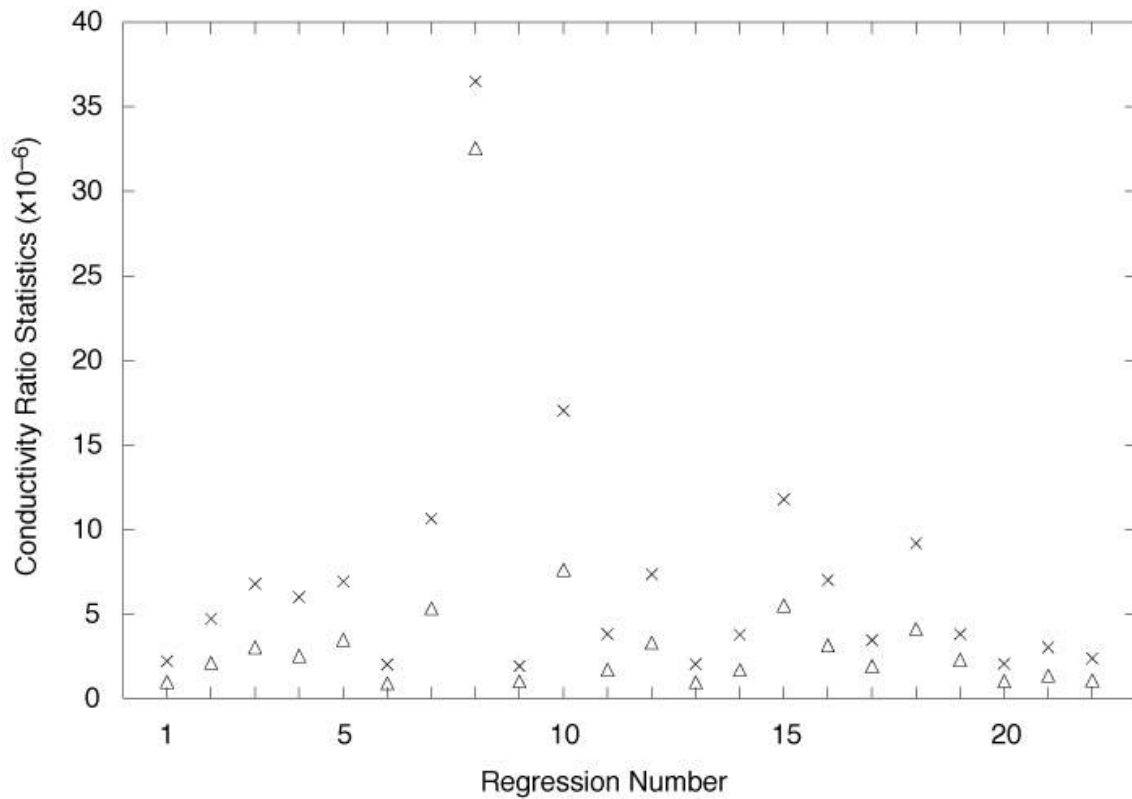
**Figure 1:** KCl solution concentration vs. conductivity ratio (data points are plus signs; the fitted line is solid), and KCl concentration vs. fit residual (data points are crosses; the zero conductivity ratio difference line is dashed) for analysis of batch P145 by operator B. The rms residual for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

**Figure 2:** For the regressions described in section 4, 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.

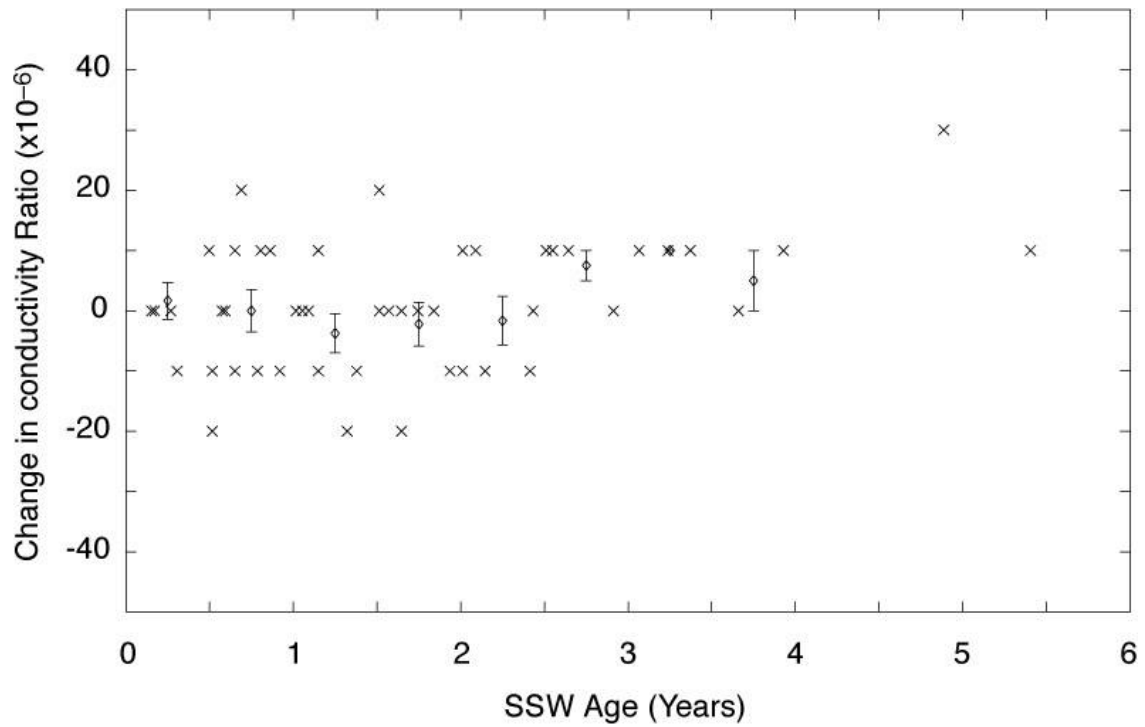
**Figure 3:** Change in  $K_{15}$  with storage time (in years) for various batches of IAPSO SSW, as detailed in Table 3. Individual data are crosses; six-month binned mean values are plotted as diamonds, with error bars as  $\pm 1$  standard error for each bin.



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**Figure 3:** Change in  $K_{15}$  with storage time (in years) for various batches of IAPSO SSW, as detailed in Table 3. Individual data are crosses; six-month binned mean values are plotted as diamonds, with error bars as  $\pm 1$  standard error for each bin.

**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 (=10x62/14, where 62 and 14 are the molecular / atomic weights of nitrate and nitrogen respectively). Total (2) repeats the calculation of Total (1) but substituting 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 2.4 for discussion.

Substance	Conductance $S\ m^{-1}\ per\ mmol\ cm^{-3}$	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	7.097E-07	5.067E-04
Phosphate	92.8	5	95	5.263E-08	4.884E-05
Sulphate	79.8	10	96	1.042E-07	8.313E-05
Barium	130.0	1	137.3	7.283E-09	9.468E-06
Lithium	38.7	0.4	6.94	5.764E-08	2.231E-05
Sodium	50.1	5	23	2.174E-07	1.089E-04
Total (1)		65.4			7.794E-04
Nitrate (measured)	71.4	1	62	1.6129E-08	1.152E-05
Phosphate (measured)	92.8	0.02	95	2.1052E-10	1.954E-07
Total (2)		17.4			2.355E-04
Potassium	73.5	33	39.1	8.440E-07	6.203E-04
Chloride	76.3	33	35.5	9.296E-07	7.093E-04
Total (3)		66			1.330E-03
Potassium	73.5	8.7	39.1	2.2276E-07	1.637E-04
Chloride	76.3	8.7	35.5	2.4535E-07	1.872E-04
Total (4)		17.4			3.509E-04
Diff (3)–(1)					5.506E-04
Diff (4)–(2)					1.154E-04

**Table 2a:** Summary of non-negligible uncertainties in the determination of KCl solution conductivity, as described in Section 3. RSU is relative standard uncertainty.

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

**Table 2b:** Summary of uncertainties in SSW  $K_{15}$ , as described in sections 4 and 5.

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

**Table 3:** Coefficients in the equation for conversion of temperature ( $^{\circ}\text{C}$ ) and conductivity ratio to salinity,  $S(R_t, t)$ : 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	
$\Sigma$	35.0000	0.0000	

**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 g/kg; 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.

KCl Lot	Operator	$R_{15}$	$R_{21}$	$K_{15}$	SSW Batch	Date dd/mm/yyyy
3	A	1.00001 1	0.99980 3	0.99979	P146	06/05/2005
3	B	0.99999 9	0.99977 8	0.99978	P146	12/05/2005
1	A	1.00000 5	0.99981 5	0.99981	P145	09/07/2004
2	B	1.00002 8	0.99982 7	0.99980	P145	15/07/2004
1	A	1.00000 6	0.99987 8	0.99987	P144	23/09/2003
2	B	1.00001 5	0.99987 9	0.99986	P144	10/09/2003
2	C	1.00002 9	0.99988 4	0.99986	P144	18/09/2003
2	A	1.00001 2	0.99989 7	0.99989	P143	24/02/2003
2	C	1.00000 3	0.99989 7	0.99989	P143	18/02/2003
1	A	0.99999 8	0.99991 0	0.99991	P142	30/10/2001
U	B	0.99997 9	0.99989 6	0.99991	P142	14/11/2001
2	A	0.99999 4	0.99992 4	0.99993	P141	09/05/2002
U	B	0.99998 5	0.99992 6	0.99994	P141	15/05/2002
U	B	1.00000 1	0.99992 2	0.99992	P141	12/06/2002
1	A	1.00001 2	0.99992 0	0.99991	P140	10/10/2000
2	A	1.00000 7	0.99992 0	0.99991	P140	10/10/2000
1	D	0.99999 0	0.99991 5	0.99992	P140	10/11/2000
1	A	1.00001 2	0.99994 0	0.99993	P139	10/10/2000
2	A	1.00000 7	0.99994 0	0.99993	P139	10/10/2000
1	D	0.99999 0	0.99993 7	0.99994	P139	10/11/2000



**Table 5:** Changes in K15 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. Diff is (New K15 – Label K15).

Batch / Container	Date	Age (weeks)	Label K15	New K15	Diff ( $\times 10^{-5}$ )	No. of Checks
P130	21/03/1996		0.99997			
Ampoules	17/10/1996	30		0.99997	0	2
	09/04/1997	55		0.99997	0	5
	11/11/1997	86		0.99995	-2	2
P131	10/10/1996		0.99986			
Ampoules	15/01/1997	14		0.99986	0	4
	09/04/1997	26		0.99987	1	6
	11/11/1997	57		0.99986	0	5
	04/06/1998	86		0.99986	0	4
P132	09/04/1997		0.99993			
Ampoules	11/11/1997	31		0.99993	0	6
	04/06/1998	60		0.99992	-1	5
	09/02/1999	96		0.99993	0	4
	16/04/1999	105		0.99992	-1	3
	02/06/2000	112		0.99992	-1	2
P133	11/11/1997		0.99986			
Ampoules	04/06/1998	27		0.99985	-1	13
	09/02/1999	60		0.99987	1	9
	16/04/1999	69		0.99984	-2	5
P134	04/06/1998		0.99989			
Ampoules	09/02/1999	36		0.99991	2	7
	16/04/1999	45		0.99990	1	6
	09/06/1999	53		0.99989	0	4
	09/12/1999	79		0.99991	2	3
	09/05/2002	205		0.99990	1	1
	25/03/2003	255		0.99992	3	1
P135	09/02/1999		0.99992			
Ampoules	16/04/1999	9		0.99992	0	6
	08/06/1999	16		0.99991	-1	4
	09/12/1999	42		0.99993	1	8
	11/10/2000	91		0.99992	0	7

	09/05/2002	169	0.99993	1	1
	09/07/2004	282	0.99993	1	2
P136	16/04/1999		0.99996		
Ampoules	09/06/1999	8	0.99996	0	6
	09/12/1999	34	0.99997	1	6
	10/11/2000	82	0.99996	0	6
	30/10/2001	133	0.99997	1	1
	09/05/2002	160	0.99997	1	1
P137	09/12/1999		0.99995		
Ampoules	02/06/1999	27	0.99993	-2	2
	10/11/2000	48	0.99994	-1	6
	14/11/2001	101	0.99994	-1	4
	09/05/2002	126	0.99994	-1	1
P138	09/06/1999		0.99994		
Ampoules	14/11/2001	127	0.99994	0	4
	09/05/2002	152	0.99994	0	3
P139	10/11/1999		0.99993		
Ampoules	14/11/2001	105	0.99994	1	5
	15/05/2002	131	0.99994	1	4
	25/02/2003	176	0.99994	1	1
P140	10/11/2000		0.99991		
Bottles	14/11/2001	53	0.99991	0	5
	15/05/2002	79	0.99991	0	5
	09/07/2004	191	0.99991	0	2
P141	12/06/2002		0.99993		
Bottles	15/07/2004	109	0.99994	1	4
P142	14/11/2001		0.99991		
Ampoules	15/05/2002	26	0.99992	1	2
	23/10/2003	101	0.99990	-1	2
	09/07/2004	138	0.99992	1	1
P143	25/02/2003		0.99989		
Bottles	23/10/2003	34	0.99988	-1	4
	15/07/2004	72	0.99988	-1	8
P144	23/09/2003		0.99987		
Bottles	09/07/2004	41	0.99986	-1	2
	15/07/2004	42	0.99988	1	3