**Ocean Science
Discussions**

About uncertainties in practical salinity calculations

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6, 2461–2485, 2009

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Abstract

Salinity is a quantity computed, in the actual state of the art, from conductivity ratio measurements, knowing temperature and pressure at the time of the measurement and using the Practical Salinity Scale algorithm of 1978 (PSS-78) which gives prac-
5 tical salinity values S. The uncertainty expected on PSS-78 values is ±0.002, but nothing has ever been detailed about the method to work out this uncertainty, and the sources of errors to include in this calculation. Following a guide edited by the Bureau International des Poids et Mesures (BIPM), this paper assess, by two independent methods, the uncertainties of salinity values obtained from a laboratory salinometer
10 and Conductivity-Temperature-Depth (CTD) measurements after laboratory calibration of a conductivity cell. The results show that the part due to the PSS-78 relations fits is sometimes as much significant as the instruments one's. This is particularly the case with CTD measurements where correlations between the variables contribute to decrease largely the uncertainty on S, even when the expanded uncertainties on con-
15 ductivity cells calibrations are largely up of 0.002 mS/cm. The relations given in this publication, and obtained with the normalized GUM method, allow a real analysis of the uncertainties sources and they can be used in a more general way, with instruments having different specifications.

1 Introduction

20 Salinity is one of the fundamental quantities which measurement or computation is essential to determine the fundamental properties of seawater. In the actual state of the art, salinity is computed from conductivity ratio measurements, knowing temperature and pressure at the time of the measurement and using the Practical Salinity Scale algorithm defined by Perkin and Lewis (1980). This algorithm gives practical salinities
25 related to the electrical conductivity of seawater at 15°C to that of a standard potassium chloride solution (KCl).

In practice, in laboratories the salinity is computed from conductivity ratio measured up with salinometers calibrated with IAPSO standard seawater bottles which salinity and conductivity ratio at 15°C or K_{15} are known. At sea, instruments are equipped with conductivity cells calibrated and linearised in seawater baths which temperature is controlled and measured with a great accuracy and which salinity is determined by salinometers.

The World Ocean Circulation Experiments (WOCE) program suggested that temperature and conductivities could be measured to, respectively 0.002°C and 0.002 mS/cm, leading to an accuracy on salinity measurement of ±0.002 (Saunders et al., 1991), but nothing was detailed about the method to work out measurements uncertainties and which sources of errors have to be included in this calculation. Several Conductivity-Temperature-Depth (CTD) instruments manufacturers propose equipments which specifications fill these criteria but, with which uncertainties can they be controlled? A simple summing of uncertainties, as often seen in manuscripts, (see Uschida et al., 2008, for example) is not correct because sensitivities and correlations of input quantities must, also, be taken into account in the calculations.

Since 1995, the Bureau International des Poids et Mesures (BIPM) has edited a guide for the evaluation of measurement data and the expression of uncertainty in measurement (GUM) (BIPM, 2008) based on combined variance of input quantities and since 2008, it proposes a supplement to the GUM based on the propagation of distributions using a Monte Carlo method (BIPM, 2006). A probability density function is affected to each input variable of a mathematical relation and a software works out the output variable of the relation by generating random numbers for each input variable. This software can gives, as result, the histogram of the output variable distribution and its statistics of variation (mean, standard deviation. . .). The GUM and the Monte Carlo methods are two independent ways to calculate a measurement uncertainty.

The goal of this paper is to assess uncertainties of practical salinity calculations using these two methods, when salinity is obtained from laboratory salinometer measurements or from CTD measurements after laboratory calibration of conductivity cells.

2 Uncertainties on salinities calculated from salinometers measurements

Laboratories salinometers are calibrated with IAPSO standard seawater bottles distributed by OSIL Company (www.osil.co.uk) which has the world exclusive rights for that. The ratio K_{15} of the seawater bottle is determined by OSIL and written on each bottle. Then the conductivity cell of a salinometer at the temperature t measures up the conductivity $G_{st}(t)$, so that :

$$G_{st}(t) = K_{15}C(35, 15, 0)k_{\text{cellst}} \tag{1}$$

$C(35, 15, 0)$ is the conductivity of a standard seawater which salinity is 35 to the temperature 15°C and the pressure 0 dbar. k_{cellst} is a value adjusted by the salinometer and which is proportional to the cell constant at the time and at the temperature of the measurement. For a seawater sample, the cell will measure up $G(t)$, so that:

$$G(t) = R_t r_t C(35, 15, 0)k_{\text{cell}} \tag{2}$$

k_{cell} being the constant of the cell at the time and at the temperature of the measurement. R_t is the ratio displayed by the salinometer. R_t is equivalent to the K_{15} for the seawater sample. r_t is the temperature correction polynomial of the PSS-78, used to compensate for the temperature effect of the sample:

$$r_t = c_0 + c_1 t + c_2 t^2 + c_3 t^3 + c_4 t^4 \tag{3}$$

where c_0, c_1, c_2, c_3 and c_4 are constants given for the calculation of salinity (Perkin et al., 1980). See Appendix A to have the numerical values of the PSS-78 constants. If we call δk_{cell} the ratio $k_{\text{cellst}}/k_{\text{cell}}$, R_t is given by:

$$R_t = \frac{G(t)}{G_{st}(t)} \frac{K_{15}}{r_t} \delta k_{\text{cell}} \tag{4}$$

In the relation (4), $G(t)$ and $G_{st}(t)$ are two quantities correlated by the temperature. Conductivity is dependent to more than 80% of temperature so, $G(t)$ and $G_{st}(t)$ are

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strongly dependent on the stability of the cell temperature. The other quantities can be considered as being independent. Then, the GUM method applied to this relation gives the combined standard uncertainty $u_c(R_t)$ of R_t measurement:

$$
u_c(R_t)^2 = \left(\frac{\partial R_t}{\partial G}\right)^2 u_G^2 + \left(\frac{\partial R_t}{\partial G_{st}}\right)^2 u_{G_{st}}^2 + \left(\frac{\partial R_t}{\partial K_{15}}\right)^2 u_{K_{15}}^2 + \left(\frac{\partial R_t}{\partial r_t}\right)^2 u_{r_t}^2
$$

$$
+ \left(\frac{\partial R_t}{\partial \delta k_{\text{cell}}}\right)^2 u_{\delta k_{\text{cell}}}^2 + 2\frac{\partial R_t}{\partial G}\frac{\partial R_t}{\partial G_{st}}u_G u_{G_{st}} r_{G,G_{st}} \tag{5}
$$

u_G and $u_{G_{st}}$ are the standard measurement uncertainties of G and G_{st} and $r_{G,G_{st}}$ is their estimated correlation coefficient. We can suppose that $u_G=u_{G_{st}}$ because measurements are made with the same instrument. To simplify the calculation without to loose a lot of its accuracy, we can take $r_{G,G_{st}}=1$. $u_{K_{15}}$, u_{r_t}, and $u_{\delta k_{\text{cell}}}$ are, respectively the standard measurement uncertainties of K_{15}, r_t and δk_{cell}. With those elements, the calculation of $u_c(R_t)$ gives:

$$
u_c(R_t)^2 = R_t^2 \left[\left(1 - \frac{G}{G_{st}}\right)^2 \left(\frac{u_G}{G}\right)^2 + \left(\frac{u_{K_{15}}}{K_{15}}\right)^2 + \left(\frac{u_{r_t}}{r_t}\right)^2 + \left(\frac{u_{\delta k_{\text{cell}}}}{\delta k_{\text{cell}}}\right)^2\right] \tag{6}
$$

The advantage of measuring conductivity ratio appears clearly with the minus sign in the first member of this relation, so that the fact that, measurements are more precise when $G \approx G_{st}$, that is to say when the salinity of the sample is near of the salinity of the seawater standard used to calibrate the salinometer.

The numerical estimation of $u_c(R_t)$ has been made with the specification values of a Guildline Instruments Limited (Ontario, Canada) Portasal salinometer. Portasal is one of the most well known salinometer because, according to Guildline, it can "deliver salinity calculations on-board ships with laboratory level accuracy". Then, it is interesting to calculate its measurement uncertainties.

u_G can be assessed by the specified conductivity resolution of this instrument which is of 3×10^{-4} mS/cm at $S=35$ and $t=15°C$ or $G=42.9175$ mS/cm. The measurement range of the Portasal being of 0.004 to 76 mS/cm, its resolution can vary from

r_{min}=2×10^{-4} mS/cm to r_{max}=5.3×10^{-4} mS/cm. According to the GUM supplement 1 (BIPM, 2006), with these available information, a right-angled triangular probability density function (pdf) can be assigned to u_G, with a likeliest probability to the maximum value 5.3×10^{-4} mS/cm. The standard deviation of such a function leads to express u_G as:

$$u_G = \frac{(r_{max} - r_{min})}{\sqrt{18}}$$ (7)

which gives: u_G=1.7×10^{-4} mS/cm.

$u_{K_{15}}$ has been estimated by Bacon et al. (2007). According to this paper, the expanded uncertainty of the standard seawater conductivity ratio has been found to be 1×10^{-5} with a coverage factor of 2 at the time of manufacture. The way in which this uncertainty has been calculated, leads to chose a Normal pdf to assess $u_{K_{15}}$ and then: $u_{K_{15}}$=5×10^{-6}. This value includes the uncertainty due to the KCl quality used to prepare the reference conductivity according to Bacon et al. A default of quality could include an uncertainty of 0.001 on the value of the standard salinity S according to Kawano et al. (2005). The value 1×10^{-5} has been recently analysed by members of the Euromet project 918 (Seitz et al., 2008), and it appears that this uncertainty value quantify the current capability of the standard seawater manufacturer to replicate the conductivity of the KCl solutions on the short term, but no value has been given to quantify the long term variations (on several years or decades) in the production of KCl solutions. Then, the numerical results for $u_c(R_t)$ and U_S given in Table 1 and 2 are valid only for a short term.

u_{r_t} can be easily estimated by applying the GUM method to the relation (3) which depends only on t. That gives:

$$u_{r_t} = \left(c_1 + 2c_2t + 3c_3t^2 + 4c_4t^3\right) u_t$$ (8)

t is the temperature of the bath chosen to make the measurements and u_t is given by the stability of this temperature. t is often chose to be up of the ambient temperature

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or 24°C. The stability of this temperature is given to be ±0.001°C which is already a value difficult to hold during long periods of time. This value has been checked by measurements on the three Portasal of the SHOM laboratory. The standard deviation of those measurements has never been less than 0.001°C during periods of 1 to 24 h. Then: $u_t = 0.001$°C.

$u_{\delta k_{cell}}$ represents the variability of the constant of the cell under function of time and temperature. This variability depend a lot of the stability of the temperature and of the humidity of the laboratory. It can be reckoned only by recording the fluctuations of the value of R_t displayed by the salinometer. These fluctuations are random and δk_{cell} follow a Normal pdf with a standard deviation $u_{\delta k_{cell}} = 2 \times 10^{-5}$.

With those elements, $u_c(R_t)$ has been computed for different salinities with the GUM and the Monte Carlo methods. In order to realise reckonings according to the Monte Carlo method, the software Oracle Cristall Ball realise 11.1.1.1.000, has been used under a Microsoft Excel 2002. The Table 1 summarizes the parameters of the input quantities and the results. It appears that the biggest contribution to the uncertainty on R_t comes from the temperature stability via r_t variations. The second contribution comes from the uncertainty on the K_{15} ratio.

Then, the uncertainty on S has been calculated using the relation of the PSS-78:

$$S = \sum_{j=0}^{5} a_j R_t^{j/2} + \frac{(t-15)}{1+k(t-15)} \sum_{j=0}^{5} b_j R_t^{j/2} \tag{9}$$

where k, a_j and b_j are constants given for the calculation of salinity (Perkin et al., 1980). This relation has two input variables: R_t and t. R_t depends of t by the ratio r_t. The correlation coefficient $r_{R_t,t}$ can be calculated. At atmospheric pressure, for $S=35$, $r_{R_t,t}=0.55$, for $S=40$, $r_{R_t,t}=0.54$, so that for $S=10$, $r_{R_t,t}=0.97$. The combined standard uncertainty $u_c(S)$ of S is then given by the relation:

$$u_c^2(S) = \left(\frac{\partial S}{\partial R_t}\right)^2 u_c^2(R_t) + \left(\frac{\partial S}{\partial t}\right)^2 u_t^2 + 2r_{R_t,t}\frac{\partial S}{\partial R_t}\frac{\partial S}{\partial t}u_c(R_t)u_t \tag{10}$$

where:

$$\frac{\partial S}{\partial R_t} = \left(\frac{a_1}{2} R_t^{-1/2} + a_2 + \frac{3a_3}{2} R_t^{1/2} + 2a_4 R_t + \frac{5a_5}{2} R_t^{3/2} \right) + \frac{(t-15)}{1 + k(t-15)}$$
$$\times \left(\frac{b_1}{2} R_t^{-1/2} + b_2 + \frac{3b_3}{2} R_t^{1/2} + 2b_4 R_t + \frac{5b_5}{2} R_t^{3/2} \right) \qquad (11)$$

and,

$$\frac{\partial S}{\partial t} = \frac{1}{[1 + k(t-15)]^2} \left(\sum_{j=0}^{5} b_j R_t^{j/2} \right) \qquad (12)$$

The Table 1 gives the values of $u_c(S)$ obtained with GUM computation (0.00081) and with Monte Carlo simulation (0.00085) for the salinity $S=35$. For $S=10$, the same computations give 0.00023 and 0.00025 and for $S=40$: 0.00099 and 0.0011. These calculations show that relation (10) can be simplified because the contribution of the first term is largely superior the contribution of the others, and it can be written:

$$u_c(S) \approx \left(\frac{\partial S}{\partial R_t} \right) u_c(R_t) \qquad (13)$$

But, other uncertainties must be taken into account in the calculation of the uncertainty on salinity. At first, salinometers must be controlled at other standard salinities than 35, to correct for their linearity errors. These errors can be of 0.003 or more at $S=2$, as seen in calibration reports made by OSIL on Portasal salinometers (see Fig. 1). Hardware corrections are difficult to realise because linearity can be un-constant in the range of measurement. Then, salinity values must be corrected by linear relations on different sub-ranges. These corrections have a standard uncertainty u_l which is at least equal to the linear regression remainder or 0.0001.

At second, standard salinity bottles used for the calibration and the linearization can show salinity variations of 0.001 to the maximum, for 96 days of storage, according to Culkin et al. (1997). This available information leads to assign a rectangular pdf to

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this uncertainty (u_{sb}) according to the GUM. The standard deviation of such a function leads to express u_{sb} as: $u_{sb}=0.001/\sqrt{3}$.

At third, PSS-78 relations fits have a standard deviation which is of 0.0007 at atmospheric pressure according to Perkin and Lewis (1980) and of 0.0015 if the pressure term R_p is different of 1. The pdf of this uncertainty (u_{PSS}) can be considered as being Normal. In the case of salinometers, $u_{PSS}=0.0007$.

u_l , u_{sb} , u_{PSS} and $u_c(S)$ being independent variables, the expanded uncertainty U_S on the salinity can be express as:

$$U_S = 2\sqrt{u_c(S)^2 + u_l^2 + u_{sb}^2 + u_{PSS}^2} \tag{14}$$

Table 1 gives the values of U_S computed with the GUM and the Monte Carlo methods and it is the same whatever the method: $U_S=0.0022$ for $S=35$ for a Portasal salinometer. Table 2 gives the values obtained for $S=10$ and 40. It appears that the two methods give close results and that for 35 and 40 the expected accuracy of 0.002 cannot be respected. The main sources of errors are the stability of the bath temperature, the linearity of the salinometer, the salinity of the bottles of standard seawater and the PSS-78 itself.

3   Uncertainties on reference conductivities calculations

Calibration of conductivity sensors needs the calculation of reference conductivities C_{ref}. When calibrations are made at atmospheric pressure, C_{ref} is calculated with the relation:

$$C_{ref} = R_t r_t C(35, 15, 0) \tag{15}$$

where r_t is given by the relation (3) and R_t is obtained according to Fofonoff et al. (1983), with a Newton–Raphson iteration and the formula:

$$R_{tn+1} = R_{tn} + (S - S_n)\left(\frac{\partial S}{\partial R_t}\right)^{-1} \tag{16}$$

on condition to calculate $(\partial S/\partial R_t)$ with the first part of the relation (11).

$C(35, 15, 0)$ is a constant which value is much debated. According to Culkin and Smith (1980), $C(35, 15, 0)=42.914\,\text{mS/cm}$ and according to Poisson (1980), $C(35, 15, 0)=42.933\,\text{mS/cm}$. A recent study to be published by a BIPM working group (CCQM pilot study P111) has attributed the value $42.9104\,\text{mS/cm}$ to $C(35, 15, 0)$, after inter-comparisons made by different metrology laboratories (Seitz et al., 2009). In fact, in the case of CTD conductivity sensors calibrations, it does no matter which value is used, provided that the same value be used during data reduction and reference conductivities computations. Most of recent instruments are referenced to 42.914, then, let us take this value in uncertainties calculations, $C(35, 15, 0)$ being considered as a constant.

The value of R_t obtained with the relation (16), depends essentially of S which is measured by a laboratory salinometer and r_t depends of t. Then, we can write that $u_{R_t}=(\partial R_t/\partial S)u(S)$ and $u_{r_t}=(\partial r_t/\partial t)u_t$. But, the computation of numerical values of R_t and r_t for different temperatures between 0 and 40°C, shows that the correlation coefficient r_{R_t,r_t} is not equal to zero. For $p=0$ and $S=35$, $r_{R_t,r_t}=0.53$, for $S=40$, $r_{R_t,r_t}=0.56$ and for $S=10$, $r_{R_t,r_t}=0.964$. Then, they can't be considered as two independent variables, and the combined uncertainty on C_{ref} is given by:

$$u_{C_{\text{ref}}} = C(35, 15, 0)$$

$$\times \left[r_t^2 \left(\frac{\partial R_t}{\partial S} \right)^2 u^2(S) + R_t^2 \left(\frac{\partial r_t}{\partial t} \right)^2 u_t^2 + R \left(\frac{\partial R_t}{\partial S} \right) \left(\frac{\partial r_t}{\partial t} \right) u(S) u_t r_{R_t,r_t} \right]^{1/2} \quad (17)$$

$(\partial S/\partial R_t)$ can be calculated with the main part of the relation (11) and $u(S)=U_S/2$, U_S being calculated with the relation (14).

$(\partial r_t/\partial t)$ is the polynomial of the relation (8), but in the relation (17) u_t is the uncertainty on the reference temperatures measured during the calibration of the conductivity sensor. u_t depends on the uncertainties of the calibration of the reference thermometer to the fixed points of the ITS-90, but also, on the drift of this thermometer between

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two calibrations, of its self-heating during the measurements and on the stability and uniformity of the calibration bath temperature.

In 2002, the BIPM has edited a guide (Fellmuth et al., 2002) about calibration uncertainties budgets of standard platinum reference thermometers (SPRT) to the fixed points of the ITS-90. It takes into account the calibration uncertainties of the fixed points cells themselves, the realisation of the points, the self-heating errors and the repetability of the sensors but also, the non-unicities of the scale. This uncertainties budget can be applied to other kind of reference thermometers like Sea Bird Electronics SBE 35 which are used to calibrate CTD profilers at sea. In the best case, it leads to a combined standard uncertainty of 0.39 mK. This value is largely dependent of the uncertainty of the temperature assigned to the reference cells, which is given by the primary calibration laboratories. For example, a gallium melting point cell calibrated in UK with a UKAS certificate will have an expanded uncertainty of ±0.25 mK. The same calibration made in France by the National Calibration Laboratory (LNE) under the same procedure, with a COFRAC certificate, will be given with an expanded uncertainty of 1.2 mK, which will give a combined uncertainty of 0.7 mK.

The drift of a reference thermometer between two annual calibrations can be equivalent to a standard uncertainty of 0.1 mK and the self-heating correction can lead to a standard uncertainty of 0.2 mK. The stability and the uniformity of the temperature of the calibration bath can be evaluated by the shifts and the standard deviations of series of data measured at different places in the bath. It will express the reproducibility of measurements at all places in the bath. This reproducibility can be estimated, in the best case for seawater bath, to 0.3 mK in the range 0–40°C.

Then, the reference temperature combined uncertainty can be, in the best case, of: u_t=0.54 mK. With a COFRAC certificate on the fixed points cell: u_t=0.80 mK.

Table 3 shows values of $u_{C_{ref}}$ calculated for different temperatures, conductivities and S=35, with u_t=0.54 mK and $u(S)$=0.0011. Monte Carlo assessments and GUM calculations give very close values, and it appears that even with a very good measure of temperature, standard combined uncertainties on reference conductivities are close

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or superior to 0.002 mS/cm for high conductivity values. It appears also that the cross-term of the expression (17) can't be neglected.

Conductivity sensors of CTD floats or profilers are linearized with polynomials before to be used at sea. Then, in order to know the uncertainty on the measured conductivity, one must add to $u_{C_{ref}}$, the square sum of the polynomial residuals u_{C_l} and the uncertainty on the CTD sensor readings which can be assessed by the repetability of the sensor measurements u_{C_r}. $u_{C_{ref}}$, u_{C_l} and u_{C_r} being independent variables, the expanded uncertainty U_C on the conductivity values measured at sea, can be express as:

$$U_C = 2\sqrt{u_{C_{ref}}^2 + u_{C_l}^2 + u_{C_r}^2} \tag{18}$$

An estimate of the annual drifting of the sensor could be adds to this sum to have a real idea of the uncertainty on conductivity measurement. This source of errors has very variable amplitudes because it depends on the environment and the duration of measurements but also on the using of anti-fouling devices or on the regularity of the sensor cleaning. It varies from 0.001 mS/cm/year to several 0.01 mS/cm/year. In order to illustrate this variation, Fig. 2 shows the statistics of 32 thermosalinographs SBE 21 calibrated yearly to the SHOM calibration laboratory since 2003, in the shame of the French operational oceanography project Coriolis which contributes to ARGO and GODAE experiences. This figure shows the drifts of conductivity cells submitted to strong environmental conditions.

So, in order to assess the value of U_C, we will just consider the initial uncertainty of the measurements. A usual value for u_{C_l} is 0.0002 mS/cm and we can take as an example the repetability of a Sea Bird Electronics SBE 4 conductivity cell, which can be considered as equivalent to their resolution or u_{C_r} =0.0004 mS/cm and it follows a Normal law. U_C has been calculated with these values and the results are also given in Table 3. It appears that expanded uncertainties on conductivity measured values, obtained with the two methods, are largely superior to 0.002 mS/cm, particularly for high conductivity values.

4   Uncertainties on salinities calculated from CTD sensors data

Salinity is calculated with relation (9) when data are measured up with CTD sensors, but pressure effect must be taken into account and in this case, R_t is obtain with:

$$R_t = \frac{R}{r_t R_p} \qquad (19)$$

In this relation, r_t is given by the relation (3) and its uncertainty by the relation (8), in which u_t is the standard uncertainty on the temperatures measured by the CTD sensor. Taking into account the elements given in the previous paragraph about temperature calibration and the quality of the CTD's temperature sensors, u_t can be estimated to be equal to 0.001°C.

R is the ratio:

$$R = \frac{C(S, t, p)}{C(35, 15, 0)} \qquad (20)$$

$C(S, t, p)$ is the conductivity measured by the conductivity sensor and which expanded uncertainty is given by the relation (18). $C(35, 15, 0)$ is the constant which value has been discussed in the previous paragraph. $C(35, 15, 0)=42.914\,\text{mS/cm}$ and $u_R=u_C=U_C/2$, values of U_C being given in Table 3.

R_p is the coefficient for pressure effects correction. R_p is given by:

$$R_p = 1 + \frac{p\left(e_1 + e_2 p + e_3 p^2\right)}{\left(1 + d_1 t + d_2 t^2 + (d_3 + d_4 t) R\right)} \qquad (21)$$

e_1, e_2, e_3 et d_1, d_2, d_3, d_4 are constants which values are given in Perkin and Lewis (1980). p and t are two independent quantities, but R, which is proportional to $C(S, t, p)$, is strongly correlated to t. The calculation of the correlation coefficient $r_{R,t}$,

with the temperature – conductivity data of Table 3 gives $r_{R,t}=0{,}9995$. Let us take $r_{R,t}\approx 1$. In this case, the combined standard uncertainty on R_p (u_{R_p}) can be written:

$$u_{R_p}^2 = \left(\frac{\partial R_p}{\partial p}\right)^2 u_p^2 + \left(\frac{\partial R_p}{\partial t}u_t + \frac{\partial R_p}{\partial R}u_R\right)^2 \qquad (22)$$

The calculation of the sensitivity coefficients leads to write the final relation:

$u_{R_p} =$

$$\frac{\left[\left(e_1 + 2e_2 p + 3e_3 p^2\right)^2 u_p^2 + \left(R_p - 1\right)^2 \left[(d_1 + 2d_2 t + d_4 R)\, u_t + (d_3 + d_4 t)u_R\right]^2\right]^{1/2}}{\left(1 + d_1 t + d_2 t^2 + (d_3 + d_4 t)R\right)} \qquad (23)$$

It stays to find the value of u_p, the standard uncertainty on pressure measurements. Accuracy and precision of pressure sensors depend of their range of measurement. Pressure balances used to calibrate them, must be corrected to the normal gravity, of the height difference with the sensor, of the thermal and pressure expansion of the piston and of the air – mass hydrostatic pressure difference. After that, the expanded uncertainty of a reference pressure given by a 8000 dbar balance is calculated by a relation of this kind:

$$U_{\text{Pref}} = 0.12 + 0.00013p \quad \text{(dbar)} \qquad (24)$$

If the repeatability of a 6000 dbar sensor, and its electronics, is 0.2 dbar so that its residual temperature drift, then $u_p=0.53$ dbar at 6000 or 0.34 dbar at 2000 dbar.

With those elements, it stays to write the expression of the standard combined uncertainty on R_t, obtained with relation (19). Then, the GUM method applied to relation (19) leads to write:

$$u_c(R_t)^2 = \left(\frac{\partial R_t}{\partial R}\right)^2 u_R^2 + \left(\frac{\partial R_t}{\partial R_p}\right)^2 u_{R_p}^2 + \left(\frac{\partial R_t}{\partial r_t}\right)^2 u_{r_t}^2 + 2\frac{\partial R_t}{\partial R}\frac{\partial R_t}{\partial R_p}u_R u_{R_p} r_{R,R_p}$$

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$$+2\frac{\partial R_t}{\partial r_t}\frac{\partial R_t}{\partial R_p}u_{r_t}u_{R_p}r_{r_t,R_p} + 2\frac{\partial R_t}{\partial R}\frac{\partial R_t}{\partial r_t}u_R u_{r_t}r_{R,r_t} \tag{25}$$

The development of the relation (25) gives:

$$u_c(R_t) = R_t\left[\left(\frac{u_R}{R}\right)^2 + \left(\frac{u_{R_p}}{R_p}\right)^2 + \left(\frac{u_{r_t}}{r_t}\right)^2 - 2\frac{u_R}{R}\frac{u_{R_p}}{R_p}r_{R,R_p} + 2\frac{u_{R_p}}{R_p}\frac{u_{r_t}}{r_t}r_{r_t,R_p}\right.$$
$$\left. -2\frac{u_R}{R}\frac{u_{r_t}}{r_t}r_{R,r_t}\right]^{1/2} \tag{26}$$

The correlation coefficients of the variables R, R_t and r_t have been computed for the salinities S=10, 35, 38 and 40, with the numerical values of t, C and p displayed in Table 4. That gives: $r_{R,R_p}=-0.44$, $r_{R,r_t}=0.998\approx1$ and $r_{R_p,r_t}=-0.50$, and show that cross-terms can't be neglected. More, neglecting these terms would leads to increase the uncertainty. For example, for t=2°C, C=33.038 mS/cm and p=6000 dbar, $u_c(R_t)=5\times10^{-4}$ and $u_c(S)=0.0019$, so that with the correlations terms, $u_c(R_t)=1.4\times10^{-5}$ and $u_c(S)=0.0005$! The uncertainties on practical salinity computations take advantage of the ratio expression of R_t which reduces the effect of the uncertainties on each input variables.

With the correlation coefficients given previously, relation (26) can be simplified to give:

$$u_c(R_t) = R_t\left[\left(\frac{u_R}{R} - \frac{u_{r_t}}{r_t}\right)^2 + \frac{u_{R_p}}{R_p}\left(\frac{u_{R_p}}{R_p} + 0.88\frac{u_R}{R} - \frac{u_{r_t}}{r_t}\right)\right]^{1/2} \tag{27}$$

In fact, it is the standard uncertainty on the PSS-78 relations fits, given in Perkin and Lewis (1980), which increases significantly the uncertainty on S, particularly in the case when R_p is different of 1: u_{PSS} is then equal to 0.0015.

Then, in the case of CTD measurements, the expanded uncertainty on salinity computations can be assessed by the relation:

$$U_S = 2\sqrt{u_c(S)^2 + u_{PSS}^2} \qquad (28)$$

where $u_c(S)$ can be calculated with relations (13) and (26) or (27).

Table 4 shows the expanded uncertainties on practical salinities calculated from relation (28) and with the Monte Carlo method. The two methods give equivalent results (U_S=0.0034 on average), which are superior of about 0.0014 to the 0.002 expected by the WOCE program.

More, this uncertainty assessment is valid only in areas where temperature and salinity gradients are low. When measurements are made in areas of strong temperature and (or) salinity gradients, the major errors on practical salinity measurements come from the ability to align the response times of temperature and conductivity sensors, even when data are corrected with manufacturers correction algorithms, as shown by Mensah et al. (2009) recently. Errors up to 0.017, on average, still persist for some measurements in strong salinity gradients and increase as much the uncertainty on practical salinity if they can't be detected and corrected.

Lastly, one must not forget that practical salinity is only a way to approach the absolute salinity of seawater which is the real quantity to access thermodynamic properties of the ocean and ocean – atmosphere interactions. Therefore, non-electrolytes components are not detected by conductivity sensors and that leads an uncertainty of 0.16 ppt even at S=35, as estimated by Jackett et al. (2006). Then, the expanded uncertainty of 0.0034 on S, as obtained with relation (28), can be considered as largely sufficient and even inconsiderable in the assessment of the absolute salinity.

5 Conclusions

The uncertainties of practical salinity calculations have been assessed by two standardized independent methods: the GUM and the Monte Carlo one's, in the case of

salinities obtained with laboratory salinometers and in the case of CTD measurements after laboratory calibration of conductivity cells. The two methods give coherent and very similar results. The 0.002 psu required initially by the WOCE program are hardly hold, even in the case of laboratory salinometers. But, in the error budget, the part due to the PSS-78 relations fits is sometimes as much significant as the instruments one's. This is particularly the case with CTD measurements where correlations between the R_t variables contribute to decrease largely the uncertainty on S, even when the expanded uncertainties on conductivity cells calibrations are largely up of 0.002 mS/cm. The relations given in this publication and obtained with the normalized GUM method, allow a real analysis of the uncertainties sources and they can be used in a general way to assess the uncertainty on conductivity cells calibrations or practical salinity calculation made with data from instruments having different specifications than the examples taken in Tables 1 to 4.

Appendix A

PSS 78 algorithm as defined in Fofonoff et al. (1983)

p is expressed in dbar, t in°C and C in S/m

$a_1=0.0080$, $a_2=-0.1692$, $a_3=25.3851$, $a_4=14.0941$, $a_5=-7.0261$, $a_6=2.7081$

$b_1=0.0005$, $b_2=-0.0056$, $b_3=-0.0066$, $b_4=-0.0375$, $b_5=0.0636$, $b_6=-0.0144$

$c_1=0.676697$, $c_2=2.00564E-2$, $c_3=1.104259E-4$, $c_4=-6.9698E-7$, $c_5=1.0031E-9$

$d_1=3.426E-2$, $d_2=4.464E-4$, $d_3=0.4215$, $d_4=-3.107E-3$

$e_1=2.070E-5$, $e_2=-6.370E-10$, $e_3=3.989E-15$

Probe:

$R=C/4.2914$

$R_1=c_1+(c_2+(c_3+(c_4+c_5\times t)\times t)\times t)\times t$

$R_P=1+((e_1+(e_2+e_3\times p)\times p)\times p)/(1+(d_1+d_2\times t)\times t+(d_3+d_4\times t)\times R)$

$R_t=R/R_1/R_P$

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Table 1. Parameters of the input quantities used to compute the expanded uncertainty of Guildline Portasal salinometer for $S=35$, by the GUM and the Monte Carlo (M.C.) methods.

Input quantities	Unit	Pdf	Value for $S=35$	GUM Standard measurement uncertainty	Contribution to R_t	Mean value by M.C.	Standard deviation by M.C.
t	°C	Normal	24	0,0010			
r_t	No one	Normal	**1.212266**	**0.000024**	3.987E-10		
K_{15}	No one	Normal	0.99984	5.00E-06	2.500E-11		
G_{s_t}	mS/cm	Right-angled triangle	52.0153	1.72E-04	0.000E+00		
G	mS/cm	Right-angled triangle	52.0153	1.72E-04	0.000E+00		
$\delta_{k_{cell}}$	No one	Normal	1.21229	−8.51E-07	4.931E-13		
R_t	No one	Normal	**0.999862**	**0.000021**		**0.999848**	**0.000022**
S	No one	Normal	**34.9950**	**0.00081**		**34.9940**	**0.00085**
Linearity correction	No one	Normal	0.0000	0.0001			
Salinity value of the bottles	No one	Right-angled triangle	0.0000	0.00024			
PSS-78 fits	No one	Normal	0.0000	0.0007			
				GUM expanded uncertainty:		**0.0022**	
				Monte Carlo expanded uncertainty:			**0.0022**

Table 2. standard uncertainties of R_t and S, and expanded uncertainty on the corrected value of S, calculated by the two methods for three different salinities. These values don't take into account possible long term variations in KCl standard solutions used to adjust standard seawater bottles.

Method	G.U.M.			Monte Carlo		
Output quantity	$u_c(R_t)$	$u_c(S)$	U_S	$u_c(R_t)$	$u_c(S)$	U_S
$S=10$	7.0E-6	0.00023	0.0016	8.0E-6	0.00024	0.0016
$S=35$	0.000021	0.00081	0.0022	0.000022	0.00085	0.0022
$S=40$	0.000024	0.00099	0.0025	0.000027	0.0011	0.0024

Table 3. Standard combined uncertainties on reference conductivities ($u_{C_{ref}}$), computed for different values of temperature, conductivity and for S=35, and expanded uncertainty on conductivity values measured with linearized sensors (U_C). U_C and $u_{C_{ref}}$ have been assessed with the GUM and the Monte Carlo Method (M.C.).

Temperature (°C)	Conductivity (mS/cm)	$u_{C_{ref}}$ (mS/cm) GUM	$u_{C_{ref}}$ (mS/cm) M.C.	U_C (mS/cm) GUM	U_C (mS/cm) M.C.
0	29.0360	0.0011	0.0012	0.0024	0.0025
5	33.4554	0.0013	0.0013	0.0027	0.0028
10	38.0897	0.0014	0.0015	0.0030	0.0030
15	42.9175	0.0016	0.0016	0.0032	0.0032
20	47.9180	0.0017	0.0017	0.0035	0.0036
25	53.0710	0.0019	0.0019	0.0038	0.0039
30	58.3570	0.0020	0.0020	0.0041	0.0042
35	63.7569	0.0022	0.0021	0.0044	0.0044
40	69.2527	0.0023	0.0024	0.0047	0.0048

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Table 4. Expanded combined uncertainties on salinity, computed with representative values of temperature, conductivity and pressure and their combined standard uncertainties. Conductivity combined standard uncertainties u_C correspond to the values found in Table 3 and for temperature, the standard uncertainty correspond to the best case when $u_t = 0.001°C$. Idem for u_p.

| Temperature (°C)	Conductivity (mS/cm)	Pressure (dBar)	u_t (°C)	u_C (mS/cm)	u_p (dbar)	S	U_S (GUM)	U_S (M.C.)
15	13.7031	0	0.001	0.0012	0.29	10.000	0.0033	0.0033
0	29.0360	0	0.001	0.0012	0.29	35.000	0.0032	0.0032
35	71.7249	0	0.001	0.0025	0.29	40.000	0.0034	0.0034
40	69.2527	0	0.001	0.0024	0.29	35.000	0.0034	0.0034
15	42.9175	0	0.001	0.0016	0.29	35.000	0.0032	0.0033
12	40.2209	500	0.001	0.0016	0.30	35.000	0.0033	0.0033
10	38.5295	1000	0.001	0.0015	0.31	35.000	0.0032	0.0033
5	34,3185	2000	0.001	0.0014	0.34	35.000	0.0032	0.0032
4	34.1673	4000	0.001	0.0014	0.43	35.000	0.0032	0.0033
3	33.6111	5000	0.001	0.0013	0.48	35.000	0.0032	0.0032
2	33.0378	6000	0.001	0.0013	0.53	35.000	0.0032	0.0032
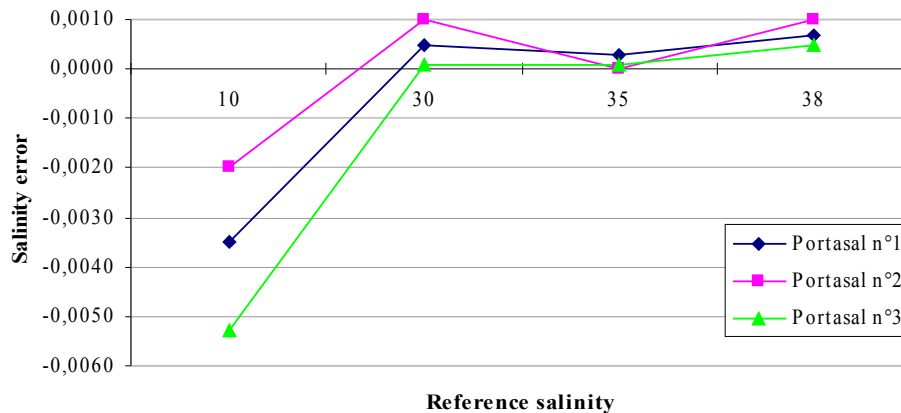
Fig. 1. Examples of linearity errors measured on three Portasal salinometers after calibration with standard seawater bottles.

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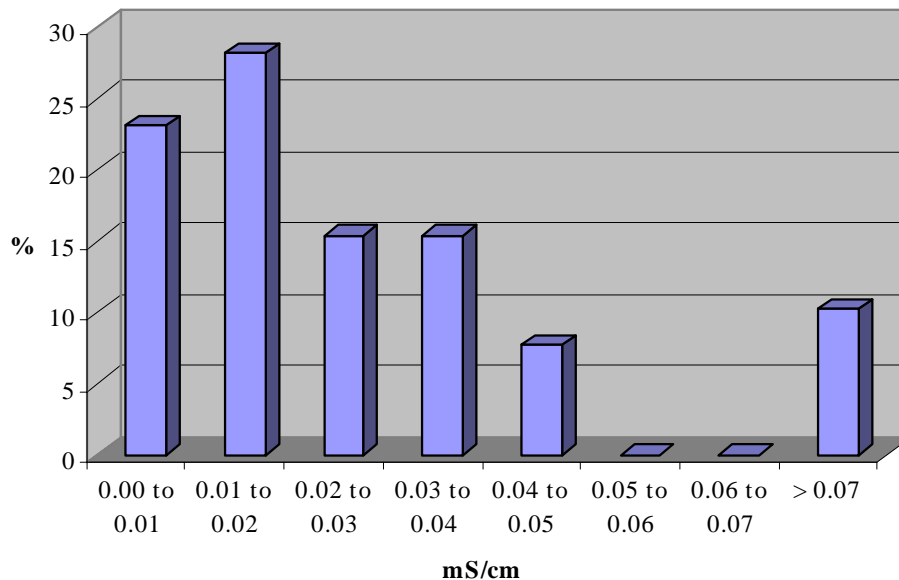
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Fig. 2. Statistics of the annual drifts of the 32 thermosalinographs SBE 21 of the French operational oceanography project Coriolis. Only 23% of them show annual shifts less than 0.01 mS/cm but 51% have annual shifts less than 0.02 mS/cm. It shows possible drifts of conductivity cells submitted to strong environmental conditions.