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RESEARCH ARTICLE **OPEN ACCESS**

Absolute salinity determination by oscillation-type densimetry and refractometry

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Abstract. The determination of salinity values from SI traceable densimetry and refractometry measurement results enable SI traceability of the former. In this work, a short study of the metrological compatibility of salinity determinations via these two methods for sodium chloride in ultrapure water solutions and two different standard seawaters (OSIL and ERM) solutions, in the [35.0; 215.0] g kg^{-1} interval, is presented. It evidenced the metrological compatibility of the salinity determinations in the referred interval. The largest salinity values enabled to test the matrix effect upon the determinations and concluded the preferable use of densimetry technique, when occurring.

Keywords: Absolute salinity / densimetry / refractometry / metrological compatibility

1 Introduction

The mass of dissolved salts found in seawater, brackish water, brine, or other saline solution, divided by the mass of the solution, defines salinity, S, usually expressed in SI units of grams per kilogram (symbol: g kg^{-1}), or expressed without the units given explicitly. Salinity values range from below a few g kg^{-1}, for rivers and lakes, to 35 g kg^{-1}, for seawater, 200 g kg^{-1} for the Dead Sea up to brine salinity values as high as around 260 g kg^{-1}.

As a matter of fact, two main kinds of salinity can be defined. Absolute salinity, S_A, essentially represents the total dissolved salts, whereas practical salinity, S, is only calculated from the conductive components. The former, S_A, offers several advantages over the latter, S, for oceanographic purposes, for example.

As seawater relative chemical composition is roughly uniform around the world [1], it is allowed to treat seawater as an aqueous solution of a single salt concentration by using the absolute salinity, S_A [2]. However, mass fraction of dissolved salts in seawater or other natural water is not easy to measure directly due to the difficulty of drying the salts from these waters. Consequently, the salinity is usually calculated from other quantities, such as chlorinity or electrical conductivity [3]. Nevertheless, the magnitudes of the uncertainty of these two quantities are still not fit for oceanographic purposes. On the other hand, among the experimental techniques that enable a quantitative analysis of aqueous solutions, densimetry and refractometry have shown to be reliable and easy to use for sodium chloride aqueous solutions. For instance, the metrological compatibility of their measurement results for sodium chloride aqueous solutions, with mass fraction, X_m(NaCl), ranging from 7 cg g^{-1} to 24 cg g^{-1} (corresponding to the 70 g kg^{-1} to 240 g kg^{-1} salinity interval), had already been demonstrated [4–8]. Indeed, the assignment of metrological compatibility to the measurement results, as defined in the International Vocabulary of Metrology – VIM [9], enables to decide whether the measurement results refer to the same measurand, when obtained by different measuring mehods, which would then be commutable.

In order to determine salinity, and due to the complexity of measuring the contents of multi-components aqueous solutions, the mass fraction of one salt dissolved in water may be determined through the above-mentioned analytical techniques. As sodium chloride is the main dissolved component in seawater, sodium chloride aqueous solution is a good candidate to be a model of seawater. In this study, densimetry and refractometry were used with sodium chloride aqueous solutions to test the metrological compatibility [9] of salinity determinations in an overall interval of S_A [35; 215] g kg^{-1} similar to previous works, with different seawater types. The larger salinity values enabled interestingly to test the matrix effect, i.e., the possible influence of one or more components from the

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sample matrix on the measurement of the analyte concentration [10], and, consequently, on density and refractive index of the sample, by using two standard seawater samples from different suppliers: OSIL and ERM) (OSIL and ERM) as matrix and incrementing the salinity by addition of sodium chloride and comparing with those produced by simple aqueous solutions of this analyte.

2 Materials and methods

The present work was divided into two experimental parts. The first one consisted on studying the metrological compatibility of absolute salinity values obtained by two different measurement techniques: refractometry and densimetry. For this purpose, a set of sodium chloride in ultrapure water solutions, corresponding to a [35; 215] g kg^{-1} S_A interval, was prepared and tested at 20 °C. In a second part, two sets of solutions based on two standard seawaters (OSIL SSW and ERM SSW) were prepared, with the aim of studying the matrix effect, i.e., the different saline compositions, on the determined absolute salinity and compare them to the ones in ultrapure water solutions. OSIL SSW is an open-ocean Atlantic ocean sewater and ERM SSW consists on a acidified coastal surface sewater.

2.1 Preparation of test solutions

The NaCl (pellets, 99.7 % purity, PanReac) solutions were gravimetrically prepared to obtain absolute salinity values between 35 g kg^{-1} and 215 g kg^{-1}, by using a mass comparator of Mettler Toledo, PR 2004. The ultrapure water (type I) [11] used in the preparation of the solutions was produced by the Milli Q Advantage water system from Merck Millipore. Finally, to ensure good homogeneity and the absence of precipitates, all solutions were agitated on a stirring plate for at least 60 min.

2.2 Density measurements

Density, ρ, is a derived quantity defined by the quotient of the mass of a substance by its volume. The density measurements were performed with an oscillation-type density meter DMA 5000 from Anton Paar, with a [0.000; 3000.000] kg m^{-3} measuring interval, with SI traceability by calibration with certified reference materials for density from National Metrology Institutes (GUM – Poland; NIST – USA and PTB – Germany) and by accredited laboratories (H & D Fitzgerald), ensuring a 0.010 kg m^{-3} standard uncertainty. The SI traceability of temperature measurements performed by the reference density meter is guaranteed by indirect thermometry using certified liquids for various temperatures and direct thermometry by comparing the indication of the density meter with the 100 ohms platinum resistance thermometers, calibrated by the IPQ Temperature Laboratory, introduced into its measuring cell.

The working principle of an oscillation-type density meter is based on the Law of Harmonic Oscillation, in which a U-tube glass oscillator of mass m_0 on a spring of stiffness k, is displaced from its equilibrium position x_0, by an external force, subject to the linear elastic restoring force Fe, as a vector proportional to a sinusoidal displacement $x(t)$. This system will oscillate with a natural frequency ω_0 determined solely by its mass m and by the spring stiffness k (Fig. 1).

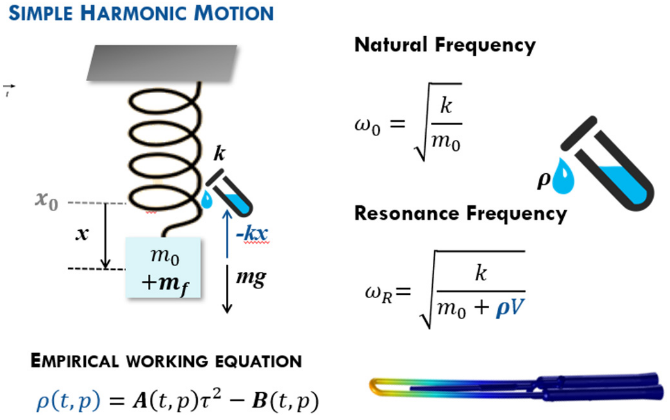

Fig. 1. Schematics and equations of the simple harmonic motion of the oscillation-type density meter cell filled with a fluid of density ρ (adapted from [7]).

When a fluid of density ρ is inserted inside the oscillator, results in an increase of system's mass of ρ times the inner volume V of the oscillator ($m_f = \rho \cdot V$), leading to a lower resonance frequency ω_R (Fig. 1). The density ρ of the sample can therefore be deduced from the measurement of period of oscillation τ. Most of these instruments use as measurement model a second order empirical relation between density and the squared vibration period, τ, represented by the equations in Figure 1, where A and B coefficients are physically meaningful parameters of the oscillator determined by calibration fluids with at least 2 fluids. However different types of mathematical models can be used.

2.3 Refractive index measurements

The refractive index, n, of a solution can vary with its composition, concentration, temperature, and the wavelength of the incident light. The relationship between the solution concentration and the refractive index has many applications including salt concentration measurement. The refractive index of the solution is deduced from angle measurement thanks to the Snell-Descartes law, that expresses the refractive index in terms of the propagation angle (Fig. 2).

The refractive indices of the samples were measured with a refractometer Abbemat 550 from Anton Paar, with a [1.300 000; 1.720 000] measuring interval, with SI traceability by calibration using certified reference materials for the refractive index from National Metrology Institutes (GUM – Poland; NIST – USA and PTB – Germany), ensuring a 0.000 010 refractive index standard uncertainty. Measurements of the Snell-Descartes law critical angle were performed by a charge coupled device (CCD) after refraction

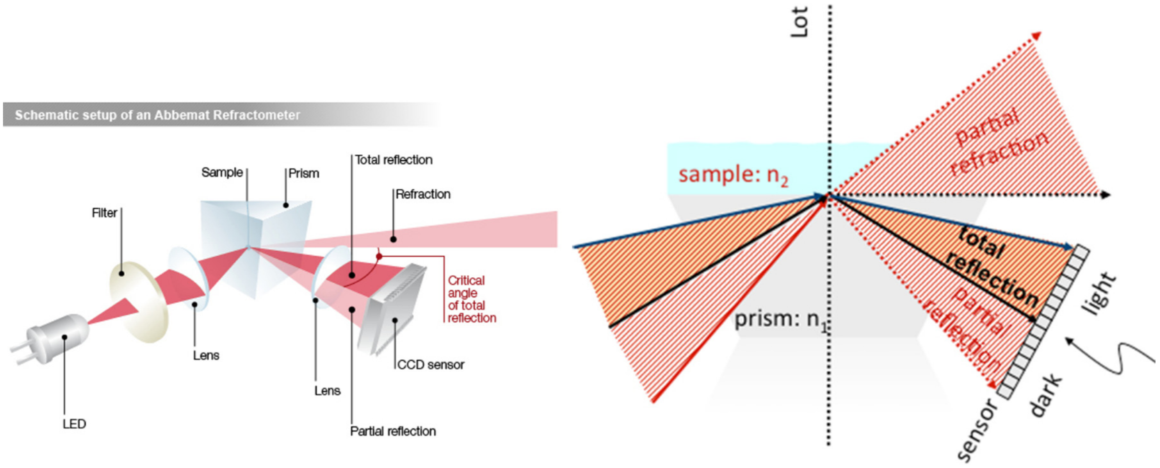

Fig. 2. Schematics setup of a refractometer [12].

in the solution located in an approximately 0.4 mL cell, maintained at 20.00 °C and illuminated by a light emitting diode (LED) at a 589.3 nm wavelength.

2.4 From density and refractive index to absolute salinity

The employed methodology to obtain the absolute salinity value of the test samples was similar to the one previously used [9,13]. Once the quantity of interest, the density, ρ, or the refractive index, n, was measured, internationally recognized reference tables were used to convert it into mass fraction, for the 20 °C reference temperature, as the quantities are temperature dependent. Linear interpolation in the intervals of the two successive tabled data were performed to deduce mass fraction value, as it provides a smaller corresponding uncertainty deduced value [14]. NaCl mass fractions were determined from density measurements, using density reference values published in 1985 [15], whereas for refractive index measurements, the reference values were published in 1966 [16] and that are still in use.

For instance, to obtain NaCl mass fraction value, $X_m(\rho)_p$ from the average between 5 and 7, N, density measurement values, at 20 °C, after correction based on certified reference materials (CRM), giving a density meter calibration function, with a C value according to:

$$\rho_p = \frac{\sum_{i=1}^{N} \rho i}{N} + C \tag{1}$$

an interpolation was done by using a set of pairs of values ($\rho_{(p\text{-}1)}$, $X_m(\rho)_{(p\text{-}1)}$) and ($\rho_{(p+1)}$, $X_m(\rho)_{(p+1)}$) from the reference values published by Söhnel and Novotny [15], following:

$$X_m(\rho)_p = \frac{\left[\rho_p - \rho_{(p-1)}\right]\left[X_m(\rho)_{(p-1)} - X_m(\rho)_{(p+1)}\right]}{\rho_{(p-1)} - \rho_{(p+1)}} + X_m(\rho)_{(p-1)} \tag{2}$$

From the interpolated value of the mass fraction in NaCl, $X_m(\rho)_p$, in cg g^{-1} (Eq. (2)), the value of absolute salinity was obtained by multiplication of a factor of 10, i.e. $S_\mathrm{A} = 10\ X_m(\rho)_p$, in g kg^{-1}.

The same methodology was applied to refractive index values by using the refractometer calibration curve and the respective set of pairs of values from the reference values published by Wolf [16].

2.5 Uncertainty budget of determination of the absolute salinity values from density and refractive index

The uncertainty budget associated to the salinity was calculated and expressed within the Guide to the Expression of Uncertainty in Measurement – GUM [17] framework. More specifically, the cause-effect diagram displayed in Figure 3 represents the different contributions to the standard uncertainty of the determination of absolute salinity, S_A ($S_\mathrm{A}(\rho)$ and $S_\mathrm{A}(n)$), from the different input quantities (density, ρ, and refractive index, n), as well the uncertainty due to the use of interpolation which is built with reference data. The uncertainty associated with each input quantity is a combination of three main sources: measurements repeatability, i.e., dispersion; correction of the input value due to the temperature of the sample; and component associated to the calibration of the measuring instruments (C). Concomitantly, the components of measurement uncertainty may be grouped into two categories, Type A and Type B, according to whether they were evaluated by statistical methods (Type A) or other methods (Type B).

The combined standard uncertainty, $u_\mathrm{c}(y)$, of the absolute salinity measured value S_A, i.e. $S_\mathrm{A}(\rho)$ and $S_\mathrm{A}(n)$ at 20 °C, is determined by taking the value of the square root of its variance deduced from the input quantities and from the influence quantities using the Law of propagation of the uncertainties of the GUM framework. This law consists of calculating the different uncertainty components $u_i(y) = |\frac{\partial y}{\partial x_i}|u(x_i)$ of y due the input quantities x_i, in which

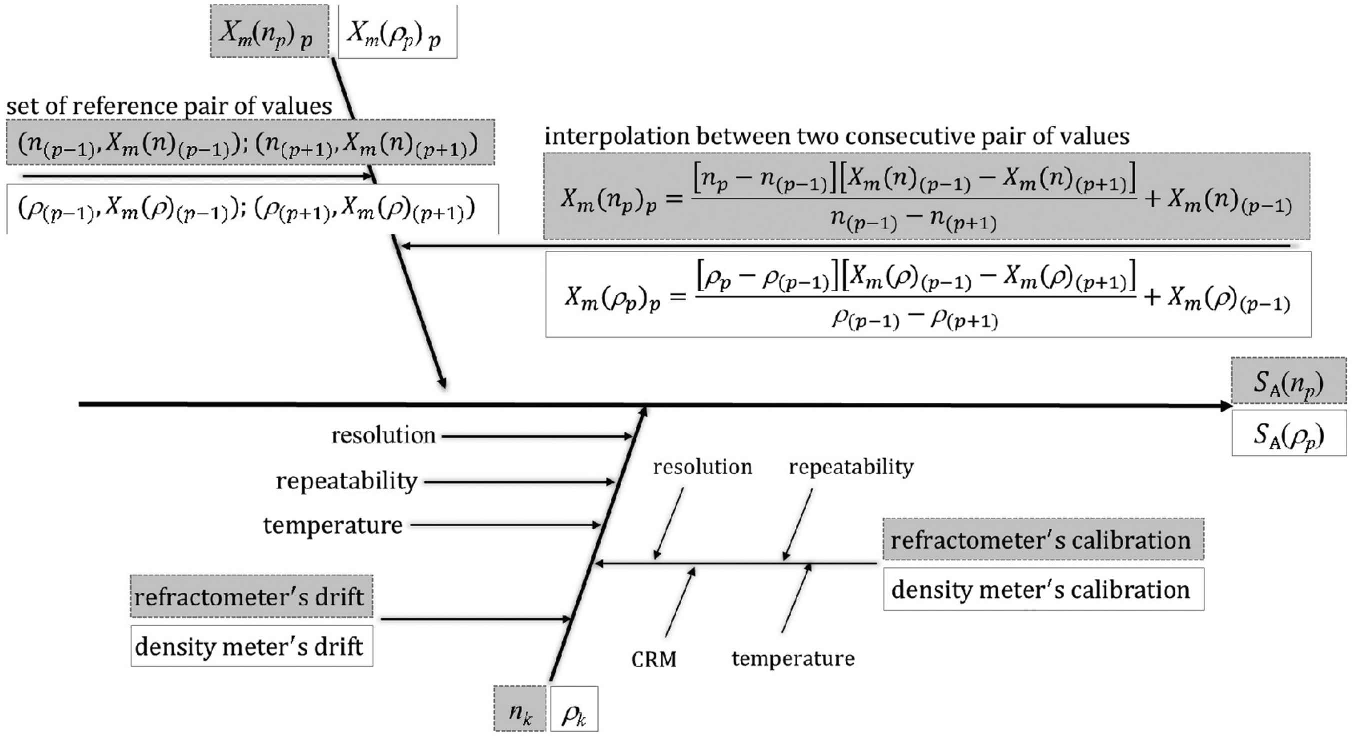

Fig. 3. Cause-and-effect diagram of the contributions to the standard uncertainty of the determination of the absolute salinity results, S_A, from the different input quantities: refractive index, n and density, ρ.

$u(x_i)$ represents the standard uncertainty of the input quantity x_i and $\frac{\partial y}{\partial x_i}$ are the sensitivity coefficients. The number of effective degrees of freedom, ν_{ef}, was calculated according to the Welch-Satterthwaite formula, given by:

$$\nu_{ef} = \frac{u_c^4(y)}{\sum_N^{i=1} \frac{u_i{}^4(y)}{\nu_i}} \tag{3}$$

The calculation of the expanded uncertainty, U, evaluates a confidence interval where the “true” value of the measurand is expected to lie. The expanded uncertainty is obtained by multiplying the combined uncertainty value, $u_c(y)$, by a coverage factor, k, assuming a normal distribution, i.e., $U = k\ u_c(y)$. Then, the measurement result lies in the interval $[y - U;\ y + U]$.

The uncertainty budget of the absolute salinity, S_A, results obtained via density, $S_A(\rho)$, and refractive index, $S_A(n)$, measurements at 20 °C, is given on Table 1.

2.6 Study of the metrological compatibility of the absolute salinity values

According to the VIM, the metrological compatibility is a property of a set of measurement results for a specified measurand, such that the “absolute value of the difference of any pair of measured quantity values from two different measurement results is smaller than some chosen multiple of the standard measurement uncertainty of that difference” [9].

The study of the metrological compatibility of the absolute salinity values obtained by densimetry and by refractometry in the [35; 215] g kg^{-1} interval of NaCl in ultrapure water solutions, prepared according to Section 2.1, began with the evaluation of the differences $\Delta S_{A,i} = S_A(n)_i - S_A(\rho)_i$.

Then, the evaluation of the standard measurement uncertainty of the differences of pairs of absolute salinity results $(S_A(n)_i;\ S_A(\rho)_i)$ was performed according to the GUM methodology [17], considering that the absolute salinity results by both densimetry and refractometry were uncorrelated. Indeed, the contribution of the temperature uncertainty component, which is present in expressions of uncertainties of all analytical techniques and is consequently the more likely to create a covariance term, is around 1000 times smaller than the greatest contribution of uncertainty components. This allows us to neglect any covariance term and correlation in the expression $u(\Delta S_{A,i}) = [u^2(S_A(n)_i - S_A(\rho)_i)]^{1/2}$ leading to:

$$u(\Delta S_{A,i}) = [u^2(S_A(n)_i) + u^2(S_A(\rho)_i)]^{1/2} \tag{4}$$

Finally, by choosing a multiple, q, of the standard measurement uncertainty of the difference $u(\Delta S_{A,i})$ equal to 2, for a given solution, a $\frac{\Delta S_A}{2u(\Delta S_A)}$ value less or equal to 1 or, equivalently, $\frac{\Delta S_A}{2u(\Delta S_A)} \in [-1; 1]$, corresponds to salinity measurement values obtained by densimetry and refractometry metrologically compatible.

Table 1. Uncertainty budget of the absolute salinity results, S_{A}, obtained via density, $S_{\mathrm{A}}(\rho)$, and refractive index, $S_{\mathrm{A}}(n)$, measurements at 20 °C.

Contribution	Measurement	Standard uncertainty	Method of evaluation	Distribution	Degrees of freedom
Instrument resolution	Density Refractive index	$\frac{10^{-3}}{\sqrt{12}}$ kg m^{-3} $\frac{10^{-6}}{\sqrt{12}}$	Type B	Rectangular	50
Instrument calibration (including drift)	Density Refractive index	10^{-2} kg m^{-3} 10^{-5}	Type B	Normal	50
Measurement repeatability	Density Refractive index	$\frac{\sigma}{\sqrt{N}}$	Type A	Normal	N-1
Temperature[1]	Density Refractive index	–	Type A	Normal	50
Interpolation (from ref. values[2,3])	Density Refractive index	6 10^{-3} kg m^{-3} 2 10^{-2}	Type B	Rectangular	50

Legend: σ – standard deviation of the N measurement values, following the 2.4 section; 1–the temperature uncertainty component is already taken into account in the uncertainty of the calibration of the measuring instrument; 2–according to [15], with a $U_{\rho} = (1\ 10^{-4})/(12)^{1/2}$ and $U_{Xm\mathrm{NaCl}} = (1\ 10^{-1})/(12)^{1/2}$ uncertainties; 3–according to [16], with a $U_n = (1\ 10^{-4})/(12)^{1/2}$ and $U_{Xm\mathrm{NaCl}} = (1\ 10^{-1})/(12)^{1/2}$ uncertainties.

3 Results and discussion

3.1 Evaluation of the metrological compatibility of the absolute salinity values obtained by densimetry and by refractometry

The absolute salinity results obtained from the measured values of density, $S_{\mathrm{A}}(\rho)$, and refractive index, $S_{\mathrm{A}}(n)$, at 20 °C and expanded uncertainties, U, of the different aqueous solutions of NaCl are given in Table 2; those of NaCl in OSIL SSW are presented in Table 3 and those of NaCl in ERM SSW in Table 4.

From Tables 2–4, it can be observed that, the expanded uncertainty $U(S_{\mathrm{A}}(n))$ is almost equal to $U(S_{\mathrm{A}}(\rho))$ for all solutions.

From Tables 2–4, not only can it be deduced that there is a seawater matrix effect on refractive index measurements, but also, for ERM SSW, this effect is stronger at low salinity values where lower matrix effect is expected. Indeed, ERM SSW is more acid than the other solutions, so ionic dissociation and consequently sedimentation are favored. In its turn, concentration gradient increases unstable refractive index measurements.

The results of the compatibility analysis of the absolute salinity values, S_{A}, obtained from the measured density ρ and refractive index values, n, at 20 °C, of the NaCl in ultrapure water solutions, of the NaCl in OSIL SSW solutions and those of the NaCl in ERM SSW solutions, are given in Tables 5–7. The differences $\Delta S_{\mathrm{A.i}}$ and corresponding 2 $u(\Delta S_{\mathrm{A.i}})$ values are also displayed, so that, as stated in 2.6, the ratios enable to evaluate the metrological compatibility of the S_{A} measurement results.

Following the methodology described in Section 2.6, it can be concluded that the absolute salinity values determined by refractometry and densimetry are metrologically compatible, since the condition $\frac{\Delta S_A}{2u((\Delta S_A))}\epsilon$ [-1; 1] is always fulfilled for the different studied NaCl solutions.

3.2 Study of the effect of the seawater matrix on the determination of salinity by refractometry and by densimetry

Figures 4 and 5 display the variation of the expanded uncertainty $U(S_{\mathrm{A}})$ values of the absolute salinity, S_{A}, obtained from the density, ρ, and the refractive index, n, measured values at 20 °C, in terms of the absolute salinity, S_{A}, nominal value of NaCl in ultrapure water (UPW), in OSIL SSW and ERM SSW solutions.

As expected from the analysis of Tables 2–4, the trends of $U(S_{\mathrm{A}}(\rho))$ or $U(S_{\mathrm{A}}(n))$ are very similar with respect to the kind of solution, being the uncertainties greater for lower nominal salinity values. As $U(S_{\mathrm{A}}(n))$ display greater values than $U(S_{\mathrm{A}}(\rho))$, it may be due to a matrix effect for the refractive index measurements.

By analyzing the ratios between the values of the absolute salinity obtained from the measured values of refractive index, $S_{\mathrm{A}}(n)$, and of density, $S_{\mathrm{A}}(\rho)$, at 20 °C, as

Table 2. Absolute salinity results of sodium chloride in ultrapure water solutions obtained from refractive index, $S_A(n)$, and density, $S_A(\rho)$, measured values and corresponding expanded uncertainties, U (k =2).

$S_{A,nom.}$ /(g kg^{-1})	$S_A(n)$ /(g kg^{-1})	$U(S_A(n))$ /(g kg^{-1})	$S_A(\rho)$ /(g kg^{-1})	$U(S_A(\rho))$ /(g kg^{-1})
35	34.74	0.86	34.96	0.82
50	49.66	0.86	49.63	0.82
74	73.59	0.89	73.86	0.84
98	98.4	1.0	97.86	0.94
144	143.9	1.0	143.99	0.95
166	166.39	0.91	166.40	0.87
188	188.20	0.87	188.37	0.83
197	196.97	1.04	196.91	0.99
214	214.48	0.93	214.16	0.89

Table 3. Absolute salinity results of sodium chloride in OSIL SSW solutions obtained from refractive index, $S_A(n)$, and density, $S_A(\rho)$, measured values and respective expanded uncertainties, U (k= 2).

$S_{A,nom.}$ /(g kg^{-1})	$S_A(n)$ /(g kg^{-1})	$U(S_A(n))$ /(g kg^{-1})	$S_A(\rho)$ /(g kg^{-1})	$U(S_A(\rho))$ /(g kg^{-1})
37.4	37.61	0.97	37.88	0.94
38.6	39.0	1.1	39.2	1.1
39.4	39.7	1.2	39.9	1.1
41.0	41.3	1.1	41.5	1.0
41.8	42.0	1.0	42.25	0.93
42.6	42.90	0.93	43.15	0.87
75.0	73.02	0.92	73.48	0.86
100	97.41	0.95	97.71	0.93
150	143.6	1.0	143.78	0.96
175	170.43	0.86	170.43	0.82
200	194.92	0.95	194.85	0.91

Table 4. Absolute salinity results of sodium chloride in ERM SSW solutions obtained from refractive index, $S_A(n)$, and density, $S_A(\rho)$, measured values and respective expanded uncertainties, U (k =2).

$S_{A,nom.}$ /(g kg^{-1})	$S_A(n)$ /(g kg^{-1})	$U(S_A(n))$ /(g kg^{-1})	$S_A(\rho)$ /(g kg^{-1})	$U(S_A(\rho))$ /(g kg^{-1})
36.2	36.01	0.88	35.49	0.82
37.4	37.29	0.94	36.72	0.87
38.2	38.1	1.0	37.51	0.92
39.8	39.7	1.2	39.1	1.1
40.6	41.4	1.1	39.9	1.2
50.0	49.1	1.1	48.8	1.0
75.0	73.39	0.90	72.97	0.88
100	97.57	0.96	97.00	0.88
150	145.73	0.93	144.96	0.92
175	170.47	0.86	169.82	0.82
200	194.78	0.95	193.89	0.88

Table 5. Assessment of the metrological compatibility from the relative differences between pairs of salinity values by densimetry and by refractometry ($S_\mathrm{A}(n)$; $S_\mathrm{A}(\rho)$), and the corresponding 2 $u(\Delta S_\mathrm{A})$ value, for NaCl in ultrapure water solution.

$S_\mathrm{A.nom.}$ /(g kg^{-1})	ΔS_A /(g kg^{-1})	$2u(\Delta S_\mathrm{A})$ /(g kg^{-1})	$\frac{\Delta S_A}{2u(\Delta S_A)}$
35	−0.22	1.2	−0.19
50	0.03	1.2	0.03
74	−0.27	1.2	−0.22
98	0.55	1.4	0.39
144	−0.13	1.4	−0.09
166	−0.01	1.3	−0.01
188	−0.17	1.2	−0.14
197	0.06	1.4	0.04
214	0.32	1.3	0.25

Table 6. Assessment of the metrological compatibility from the relative differences between pairs of salinity values by densimetry and by refractometry ($S_\mathrm{A}(n)$; $S_\mathrm{A}(\rho)$), and the corresponding 2 $u(\Delta S_\mathrm{A})$ value for NaCl in OSIL SSW solutions.

$S_\mathrm{A.nom.}$ /(g kg^{-1})	ΔS_A /(g kg^{-1})	2 $u(\Delta S_\mathrm{A})$ /(g kg^{-1})	$\frac{\Delta S_A}{2u(\Delta S_A)}$
37.4	−0.27	1.4	−0.20
38.6	−0.24	1.5	−0.16
39.4	−0.12	1.6	−0.07
41.0	−0.23	1.5	−0.16
41.8	−0.29	1.4	−0.21
42.6	−0.25	1.3	−0.20
75.0	−0.46	1.3	−0.37
100	−0.30	1.3	−0.23
150	−0.22	1.4	−0.16
175	0.00	1.2	0.00
200	0.07	1.3	0.05

a function of the nominal value of the absolute salinity, $S_{\mathrm{A,\ nom}}$, displayed in Figure 6, it is possible to conclude to the metrological compatibility of the two technique measurement results concerning the S_A measurement values, as it was evidenced in Section 3.1.

However, on one hand, Figure 6 enables to evidence a smaller ratio $\frac{\Delta S_A}{2u(\Delta S_A)}$ value for the OSIL SSW and UPW NaCl solutions than for the ERM SSW solutions, independently on the salinity value. The uncertainties estimated for the lower levels of S_A values are higher for the smaller absolute salinities. On the other hand, it is observed that $\frac{\Delta S_A}{2u(\Delta S_A)} > 0$, for ERM SSW solutions, whatever $S_{\mathrm{A,\ nom}}$ values, due to $S_\mathrm{A}(n)_i > S_\mathrm{A}(\rho)_i$, as it is evidenced by Table 7. This can be interpretated as a manifestation of matrix effect of ERM SSW solutions on refractive index measurements. Indeed, since this system is a more acidic medium than the others, the ionic dissociation of the species at small salinity values is favored, increasing the sedimentation, to which the refractive index measurement is sensitive.

4 Conclusion

The knowledge and characterization of the physical properties of the liquid matter are common objectives of the density laboratory and the refractometry laboratory. of IPQ, the National Metrology Institute of Portugal. Although each laboratory is specialized in a particular metrological area, knowledge intersects very often to better characterize a sample.

The main result of the present work regarding the determination of the salinity of NaCl aqueous solutions through both the density, ρ, and the refractive index, n, was

Table 7. Assessment of the metrological compatibility from the relative differences between pairs of salinity values by densimetry and by refractometry ($S_A(n)$; $S_A(\rho)$) and the corresponding 2 $u(\Delta S_A)$ value for NaCl in ERM SSW solutions.

$S_{\text{A.nom.}}$ /(g kg^{-1})	ΔS_A /(g kg^{-1})	2 $u(\Delta S_A)$ /(g kg^{-1})	$\frac{\Delta S_A}{2u(\Delta S_A)}$
36.2	0.52	1.2	0.43
37.4	0.57	1.3	0.45
38.2	0.58	1.4	0.42
39.8	0.61	1.6	0.39
40.6	1.51	1.6	0.97
50.0	0.30	1.5	0.20
75.0	0.42	1.3	0.33
100	0.57	1.3	0.44
150	0.77	1.3	0.59
175	0.65	1.2	0.55
200	0.89	1.3	0.69

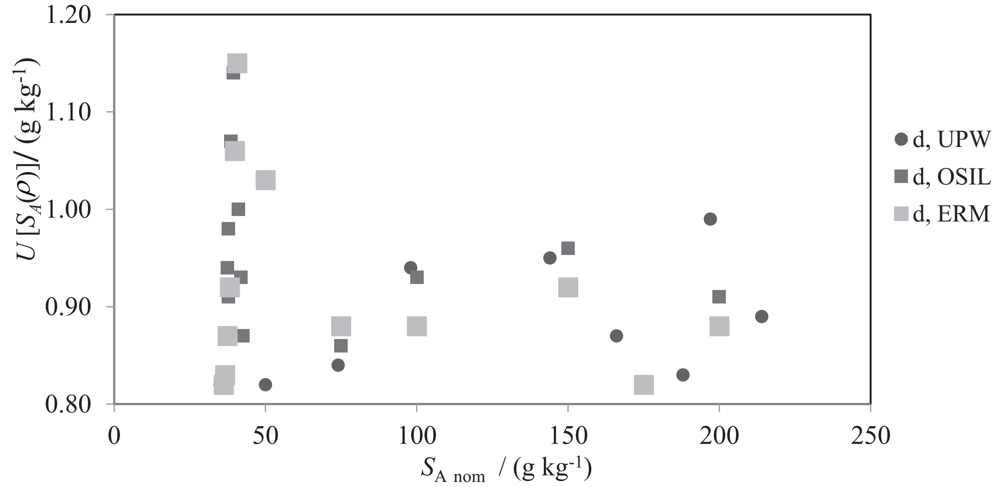

Fig. 4. Expanded uncertainty, $U(S_A(\rho))$, of the absolute salinity values, S_A obtained from the measured values of density, ρ, at 20 °C, for NaCl in ultrapure water (UPW), in OSIL SSW and in ERM SSW solutions.

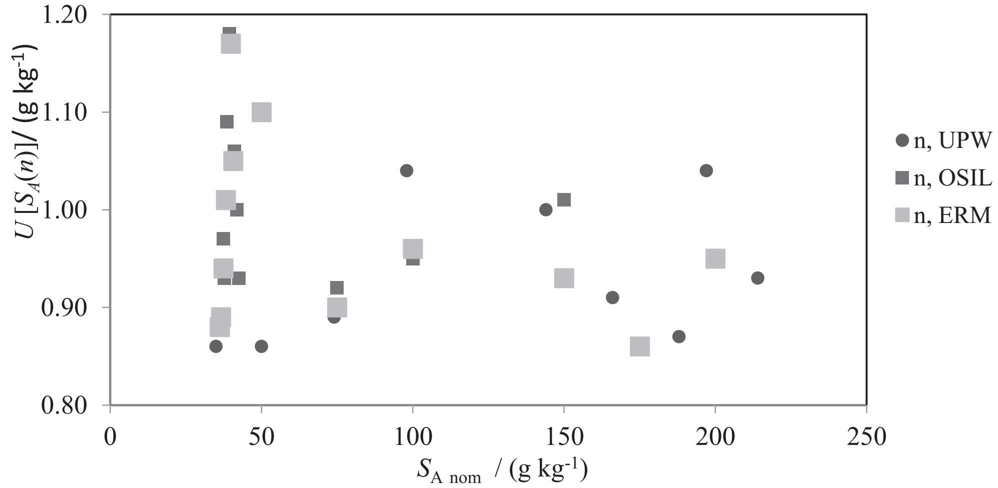

Fig. 5. Expanded uncertainty, $U(S_A(n))$, of the absolute salinity values, S_A obtained from the refractive index, n, at 20 °C, for NaCl in ultrapure water (UPW), in OSIL SSW and in ERM SSW solutions.

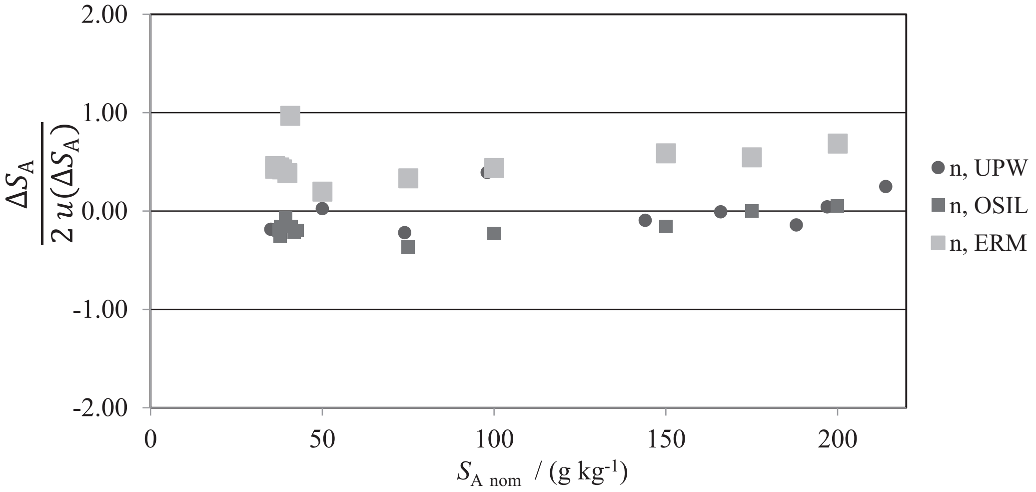

Fig. 6. Ratios $\frac{\Delta S_A}{2u(\Delta S_A)}$ between pairs of salinity values from refractometry and densimetry ($S_A(n)$; $S_A(\rho)$), as a function of the absolute salinity, $S_{\text{A nom}}$, for NaCl in ultrapure water (UPW), OSIL SSW and ERM SSW solutions.

to evidence metrological compatibility in the [35; 215] g kg^{-1} salinity interval. Indeed, whatever the kind of NaCl aqueous solution, ultrapure water (UPW), OSIL standard seawater (OSIL SSW) and ERM standard seawater (ERM SSW), the salinity uncertainties are very similar, even though, low salinity values favor measurement dispersion.

These results allow one to conclude that, in cases where matrix effects are expected, the use of the densimetry technique through the oscillation-tube density meter should be chosen. However, in the other cases, it is better to use refractometry, because it is a fast and cheap technique, which proved to provide salinity measurement results metrologically compatible with the previous one.

Due to the observed greater dispersion of the experimental values at the lower bound of the salinity interval, it may be challenging to extend the study of the metrological compatibility of density and refractive index measurement for the determination of smaller salinity values.

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