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Salinity determinations by refractometry and oscillation-type densimetry as compatible methods: from salinity to pH

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Abstract. The purpose of the present communication is to study the metrological compatibility of measurement results of mass fractions of sodium chloride in aqueous solutions, by different analytical techniques: refractometry and oscillation-type densimetry. In complement pH measurements were made in solutions of NaCl of 3,5 cg g⁻¹ and in a synthetic seawater standard (OSIL). Previously, metrological compatibility of measurement results with refractometer and oscillation-type density meter was showed for aqueous solutions of glucose, from 2 cg g⁻¹ to 42 cg g⁻¹. Due to its interest for the food science and health science, sodium chloride mass fraction in aqueous solution between 0,5 cg g⁻¹ and 7 cg g⁻¹ and for brine systems were also measured. Comparison was displayed between potentiometric pH and pH deduced by salinity experimental value.

1. Introduction

Despite of its high conceptual simplicity and importance for many human activity fields, the salinity, the amount of salt dissolved in water is not very easy to measure. Indeed, for seawater salinity, its biggest use, many compounds, like sodium chloride, magnesium sulphate, potassium nitrate, and sodium bicarbonate, have to be taken into account, due to the high capacity of water to dissolve ions. Seawater salinity also depends on the presence of dissolved molecules in water, due to the high solvation power of the water, and on quantities like temperature and pressure [1]. Whereas the salinity interval values for rivers and lakes are below a few g kg⁻¹, approximately 35 g kg⁻¹, and 200 g kg⁻¹ are typical salinity values for seawater and the Dead Sea, respectively and, at the end of the spectrum, brine salinity values can even be as high as around 260 g kg⁻¹. Among the experimental techniques that enable to quantitatively analyse the compounds in aqueous solutions, densitometry, refractometry and pH measurements are known to be reliable and easy to use. For instance, the metrological compatibility of the two former techniques measurement results for glucose aqueous solutions, between 3 cg g⁻¹ and 40 cg g⁻¹, and for sodium chloride aqueous solutions, between 7 cg g⁻¹ and 24 cg g⁻¹, has already been demonstrated [2], which potentiated interesting opportunities for various kinds of

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aqueous solutions, with the same techniques. To this purpose, 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 intended to be determined through the above mentioned analytical techniques. As it is the main dissolved component in seawater, sodium chloride in water is a good candidate to be a model of seawater. By the same token, information provided by pH measurements are also expected to provide useful information, as it is known to be of crucial role for a good knowledge of such systems, as it is the case for oceans [3]. Salinity and pH are relatively stable in seawater, whereas other natural parameters like temperature, dissolved oxygen and nutrients can vary significantly. The operational definition of potentiometric pH is based on standard buffers and does not yield a thermodynamic hydrogen ion activity. pH measurements in solutions with highly content of dissolved salts, such as seawater, may depart from the scale established with dilute buffers prepared with distilled water [4]. In fact, this means that the pH measured in such a media will not correspond exactly to the formal operational definition in the Electrometric approaches but will include an additive offset whose magnitude depends on the value of the electrometric amplitude that largely depends on the salinity, temperature and pressure of seawater sample [5]. However, studies of seawater salinities, S , evidenced empirical mathematical function between pH and S [6], enabling to deduce the former from the latter. It may then be interesting to use the pH measurements in order to corroborate the S value, i.e. the NaCl mass fraction in the appropriate range values, determined by refractometry and densimetry.

2. Materials and Methods

PanReac 99.5 % purity NaCl pellets were dissolved in water, in order to obtain 3.5 cg g⁻¹ to 26.0 cg g⁻¹ mass fractions solutions, through a weighing scale, insuring SI traceability of the mass measurements, with comparator Metler Toledo PR 2004, leading to mass fractions standard uncertainty values of around 0.1 cg g⁻¹. The type I water (ISO 3696) used in the solutions was produced by a Merck Millipore Milli Q Advantage to a Milli-RX 20 system. It was used an Anton Paar Abbemat 550 refractometer, with a [1.300 000; 1.720 000] measuring interval, with SI traceability by calibration using GUM, NIST and PTB reference standards, ensuring a 0,000 01 refractive index standard uncertainty. Measurements at the Snell-Descartes Law critical angle were performed by a charge coupled device after refraction in the solution located in an approximately 0.4 mL cell, maintained at 20.00 °C and illuminated by a light emitting diode at a 589,3 nm wavelength. The density meter was an Anton Paar DMA 5000, with a [0.000; 3000.000] kg m⁻³ measuring interval, with SI traceability by calibration using PTB reference standards, ensuring a 0,001 kg m⁻³ standard uncertainty. The operating principle of this oscillation-type density meter is based on the law of harmonic oscillation in which a U-shaped tube filled with the test sample is submitted to an electromagnetic force and the measuring cell, maintained at 20.000 °C, vibration period enables to determinate the density of the sample. For the potentiometric measurements of pH, a Metrohm 692 pH meter, with a glass electrode and reference electrode from Metrohm, and Radiometer meter lab PHM 250 ion analyser, with a glass electrode and a reference electrode (inner electrolyte 4 M KCl) and the Metrohm AG buffer solution were used. Within the [1.000; 14.000] measuring interval, with SI traceability by calibration using NIST and PTB reference standards, pH 0.02 standard uncertainties were ensured. The determination of NaCl mass fraction from refractometry and densimetry is very similar, as previously displayed [2]. Once the quantity of interest, either the refractive index or the density, is measured, uses are made of internationally recognized reference tables 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 are performed to deduce mass fraction value, as it provide a smaller uncertainty deduced value [6]. NaCl mass fractions were determined from refractive index measurements, using reference values published in 1966 [7] and they are still quoted since then, whereas the density reference values were published in 1985 [8].

As previously displayed for a smaller measurement interval [2], by comparing the absolute value of the difference of any pair of mass fraction values, determined by refractometry or densimetry, $X_{m, \text{refr.}}$ and $X_{m, \text{dens.}}$, respectively, to a chosen multiple of the standard measurement uncertainty of that

difference, namely $[u^2(X_{m, \text{refr.}}) + u^2(X_{m, \text{dens.}})]^{1/2}$, it is decided whether the results are metrologically compatible [9]. The calculation of the standard uncertainty of the differences of pair of mass fraction results are performed according to the GUM methodology [10], considering that the mass fraction results $u^2(X_{m, i.})$ by both refractometry and densitometry are uncorrelated. As a matter of fact, the temperature uncertainty component is present in expressions of uncertainties of all analytical techniques. But its contribution is around 1000 times smaller than the greatest contribution uncertainty component, which allowed us to neglect the respective covariance term in the expression $[u^2(X_{m, \text{refr.}}) + u^2(X_{m, \text{dens.}})]^{1/2}$. Finally, using the mathematical expression of seawater pH in function of salinity, S , by Millero *et al.* [6], we intend to compare the measured pH to the one deduced by the Millero's formula, as a way to validate the NaCl mass fraction values determined by refractometry and densitometry.

3. Results and Discussion

3.1. Mass fraction results from refractive index and density

The obtained results for the mass fraction sodium chloride in water at 20 °C by refractometry, $X_{m(n)}$, and densimetry, $X_{m(\rho)}$, are presented in Table 1. Following the methodology adopted previously [2], it can be concluded that the NaCl mass fractions determined by the refractometry and densimetry measurement results are metrologically compatible, as the ratio between the difference of the NaCl mass fraction determined by the two analytical techniques and the corresponding expanded uncertainty (taking the coverage factor $k=2$, for a 95 % confidence level), displayed in the last column of Table 1, is smaller than 1, whatever the mass fraction value.

Table 1. Results of NaCl solutions mass fraction at 20 °C by refractometry, $X_{m(n)}$ and densimetry, $X_{m(\rho)}$.

NaCl mass fraction at 20 °C				$\Delta X_m = X_{m(n)} - X_{m(\rho)} $	$\frac{\Delta X_m}{\sqrt{U^2_{Xm(n)} + U^2_{Xm(\rho)}}}$
Refractometry		Densimetry			
$X_{m(n)} / \text{cg}\cdot\text{g}^{-1}$	$U_{Xm(n)} / \text{cg}\cdot\text{g}^{-1}$	$X_{m(\rho)} / \text{cg}\cdot\text{g}^{-1}$	$U_{Xm(\rho)} / \text{cg}\cdot\text{g}^{-1}$		
3.73	0.02	3.74	0.010	0.01	0.38
3.51	0.02	3.50	0.010	0.01	0.32
20.13	0.05	20.09	0.010	0.03	0.64
21.14	0.06	21.09	0.010	0.05	0.88
23.16	0.08	23.08	0.010	0.07	0.91
26.21	0.16	26.11	0.010	0.11	0.66

3.2. Salinity results from refractive index and density and comparison with pH potentiometric values

Using Millero's *et al.* [6] empirical equation of seawater pH in function of salinity, S , and temperature, T , it is possible to deduce the pH values from NaCl mass fraction values, that is considered as the salinity of the considered solutions, as NaCl is the only dissolved salt compound, i.e. $X_{m\text{NaCl}} \cdot 10 = S$. The salinity results ($S_{(n)}$ and $S_{(\rho)}$) and expected pH values ($\text{pH}_{(S(n))}$ and $\text{pH}_{(S(\rho))}$) of OSIL and a NaCl aqueous solution with a 35 g kg⁻¹ nominal value, at 20 °C, obtained by refractometry and by densimetry, respectively, are presented in Table 2. The presented pH values resulted from the arithmetic average of pK_1 and pK_2 values, given by the expressions (22) and (23) of quoted work [6]. The expanded uncertainties are calculated by using the law of propagation of uncertainties of the GUM [10] to the Millero *et al.* empirical expressions (22) and (23), considering the respective salinity measurement uncertainties with the appropriate analytical technique. The pH values ($S_{(n)}$ and $S_{(\rho)}$) and the expected pH values ($\text{pH}_{(S(n))}$ and $\text{pH}_{(S(\rho))}$) of the OSIL sample and a sodium chloride aqueous solution of nominal salinity of 35, at 20 °C, by obtained by refractometry and by densimetry, respectively, are compared with potentiometric pH measured values and presented in Table 3. Although out-of-compatibility values are evidenced, due to the rough approximation of considering only one compound for the salinity calculation, encouraging results seem to be observed.

Table 2. Salinity results, $S_{(n)}$ and $S_{(\rho)}$, and expected pH values, $pH_{(S(n))}$ and $pH_{(S(\rho))}$, of OSIL and a NaCl aqueous solution with a 35 g kg^{-1} nominal S_{35} , at 20°C , obtained by refractometry and by densimetry, respectively.

Sample	Salinity at 20°C				Expected pH at 20°C			
	Refractometry		Densimetry		From $S_{(n)}$		From $S_{(\rho)}$	
	$S_{(n)} / \text{g}\cdot\text{kg}^{-1}$	$U_{S_{(n)}} / \text{g}\cdot\text{kg}^{-1}$	$S_{(\rho)} / \text{g}\cdot\text{kg}^{-1}$	$U_{S_{(\rho)}} / \text{g}\cdot\text{kg}^{-1}$	$pH_{(S(n))}$	$U_{pH_{(S(n))}}$	$pH_{(S(\rho))}$	$U_{pH_{(S(\rho))}}$
OSIL	37.29	0.24	37.39	0.06	7.441	0.048	7.440	0.012
S_{35}	35.10	0.24	35.01	0.06	7.454	0.051	7.455	0.013

Table 3. Comparison of potentiometric pH values (pH_{pot}) and empirical pH values (pH_{emp}) obtained from salinity results ($S_{(n)}$ and $S_{(\rho)}$) using [6] relations (22) and (23), of OSIL and a sodium chloride aqueous solution of nominal salinity of 35, at 20°C , by obtained by refractometry and by densimetry, respectively.

pH values				$\Delta pH = pH_{\text{pot}} - pH_{\text{emp}} $	$\frac{\Delta pH}{\sqrt{U^2_{pH_{\text{pot}}} + U^2_{pH_{\text{emp}}}}}$
pH_{pot}	$U_{pH_{\text{pot}}}$	pH_{emp}	$U_{pH_{\text{emp}}}$		
8.06	0.02	7.44	0.05	0.62	12.41
6.21	0.02	7.45	0.05	-1.24	-23.46

4. Conclusions

Following previous work in glucose aqueous solutions, metrological compatibility has been evidenced for salinity determination from refractometry and densimetry measurements, in a wide measurement interval. Of particular interest, it has been evidenced for seawater solutions and brine solutions. A comparison has been made with potentiometric pH measurements, using Millero *et al.* empirical function for seawater-like systems that seems to be encouraging for future studies in this direction.

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