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OPTICAL INSTRUMENTATION

Determination of Seawater Salinity by Measurements of the Refractive Index

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Abstract—Methods for measuring the salinity of sea water are considered. The results of an experimental study of samples of common and sea salt solutions with different salinity poured into a hollow trihedral optical glass prism are presented. The light refraction angles are measured with a goniometric system by use of which the minimum deviation method possessing a high accuracy of determining the refractive index is implemented. Using dispersion analysis of experimental results, it is proved that the refractive index of water does not depend on its salt composition. An equation describing the dependence of the refractive index on salinity and temperature for a fixed wavelength is proposed.

Keywords: salinity scale, seawater salinity, salinity measurement, refractive index, refractometry, prism method, goniometric system

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INTRODUCTION

Salinity (S, ‰) is the total mass of dissolved substances contained in 1 kg of water. The mass is expressed in grams. Water salinity in oceanography is the most important characteristic determining the biological productivity of seas and oceans and the distribution of marine organisms in them [1].

Most salts are present in water in the form of ions. The principal ions whose concentration in sea water exceeds 99.98% of total salinity include Cl^-, SO_4^{2-}, HCO_3^-, Br^-, CO_3^{2-}, F^- anions and Na^+, Mg^{2+}, Ca^{2+}, K^+, and Sr^{2+} cations. The average water salinity of the World Ocean varies from 33 to 37‰ with the average value of 34.7‰. The exception is the areas adjacent to river mouths, desalinization basins (for example, the Azov, Black, and Baltic Seas), where the salinity is considerably lower, and salinization basins (for example, the Mediterranean and Red Seas), where it exceeds 38‰ [1].

Regardless of the absolute concentration, quantitative relationships between concentrations of the principal ions remain almost unchanged [2]. This property of sea water was called Dittmar's principle in honor of the English chemist who proved it in 1884. However, the constancy of the salt composition is valid only for open parts of the oceans and is not satisfied in water areas with hampered water exchange.

The aim of this work is to describe a method for determining sea water salinity by measurements of the refractive index, the results of which do not depend on the salt composition.

METHODS FOR SALINITY MEASUREMENTS

Water salinity can be measured by different methods: chemical analysis, evaporation and determination of the solid residual mass, and measurements of electrical conductivity, specific density, or refractive index.

Due to the complex composition of sea water, certain problems arise when salinity is measured by chemical analysis. Determination of salinity by water evaporation is very hard due to hygroscopicity of the obtained solid substances, and their heating and drying lead to degradation and volatilization of some components. To provide constancy of the solid residual mass, Knudsen and Sørensen [3] developed a method in which hydrochloric acid was added to sea water, the water was evaporated to a small volume, treated by chlorine water to remove iodides and bromides by chlorine, and dried to a constant mass at a temperature of 480°C. However, such a technique for salinity determination is too complex and is not used in practice.

In [4], it was recommended to determine sea water salinity by argentometric titration and by the electrometric method.

More than half of all components dissolved in sea water (about 55%) are chlorine ions; therefore, taking into account Dittmar's principle, one can calculate the total concentration of salts (salinity) by measurements of chlorine (chlorinity) in a sample of sea water. Here, chlorinity (Cl, ‰) means the total mass of halides (chlorides, bromides, and iodides, with the exception of fluorides) expressed in grams and contained in 1 kg of sea water with reference to the equivalent content of chlorides [4]. The principle of chlorinity determination is the base of the argentometric titration method. For this purpose, a solution of silver nitrate $AgNO_3$ is added to the sea water sample till complete precipitation of all halides but fluorides. Quantitatively, the value of chlorinity is determined from the relationship

$$\mathrm{Cl} = (0.3285234\mathrm{Ag})‰, \qquad (1)$$

where Ag is the mass of chemically pure silver in grams necessary for precipitation of all halides contained in 1 kg of sea water.

The dependence between salinity and chlorine content was determined in the end of the 19th century by the special commission of the International Conference for the Exploration of the Sea in the form

$$S = (0.030 + 1.805\mathrm{Cl})‰. \qquad (2)$$

Equation (2) is usually called the Knudsen formula [3], in the name of the commission chairman. Argentometric titration and the Knudsen formula were taken as a standard for measurements of salinity by oceanologists all over the world until 1963 when the Joint Panel on the Equation of State of Sea Water proposed a new relationship between salinity and chlorinity (the R. Cox scale):

$$S = (1.80655\mathrm{Cl})‰, \qquad (3)$$

according to which the salinity is exactly equal to 35.0001‰ at Cl = 19.374‰ and does not go beyond the error limits of ±0.004‰ as compared to formula (1) when S varies from 30 to 40‰, i.e., for almost whole World Ocean, with the exception of desalinization and salinization basins [5].

The main standard solution for measurements of salinity is normal sea water [6], i.e., filtered oceanic water the chlorinity of which is close to 19.38‰; this corresponds to a salinity of 35.00‰, i.e., the average salinity of ocean water.

The argentometric method provides the measurement error of up to ±0.02‰, which meets the requirements of most oceanological problems. However, it is not free from certain shortcomings. The main reagent used (silver nitrate) is a very expensive consumable material. In addition, this method can reliably determine only the salinity of waters in open parts of seas and oceans. For seas with a hampered water exchange, reference tables [7] are used due to the difference in the salt composition of waters in these seas and oceanic waters. However, the main disadvantage lies in the complexity and duration of measurement procedures, calculations, and introduction of corrections; for this reason, this method often cannot provide the speed and mass character of the measurements.

In contrast to the argentometric method, the electrometric method is based on the ability of sea water to conduct electric current because sea water is qualified as a weak electrolyte. Electrical conductivity of water varies in proportion to salinity because it depends on the content of ions which are free carriers of electric charges. Measurements of electrical conductivity of sea water with respect to normal water, the conductivity of which is taken to be 1.0 using an induction type salinometer [4], allows one to determine salinity by international oceanographic tables with an error of not more than ±0.03‰.

The development of the new method for the determination of water salinity by electrical conductivity of water entailed in 1978 the introduction of the new Practical Salinity Scale (PSS-78). The scale acts within the variation ranges of salinity, temperature, and pressure peculiar for the World Ocean and interior seas [8]. The practical salinity S_P by this scale is determined as the ratio of electrical conductivity of the sea water sample to electrical conductivity of the standard potassium chloride solution; the ratio is determined at a temperature of 15°C and pressure of 1013 hPa. Thus, practical salinity is a dimensionless quantity and, instead of permille (‰), it is measured in practical salinity units (PSU). The practical salinity scale is based on the empirical dependence of electrical conductivity of the standard solution, not natural water; therefore, the question arises about the reliability of salinity measurements by electrometric methods due to the influence of variability of the salt composition on the electrical conductivity of sea water [9].

In 2010, oceanologists took a new standard—the International Thermodynamic Equation of Seawater – 2010 (TEOS-10)—in which practical salinity is replaced by absolute salinity S_A [10]. The new equation was developed based on the Gibbs thermodynamic function (potential) which is a function of absolute salinity, temperature, and pressure. In spite of the fact that such an approach requires using complex calculations, it provides a more accurate description of the thermodynamic state of fresh and sea water, ice, and moist air. TEOS-10 has software tools with prepared equations for calculating the absolute salinity which make it possible to considerably increase the calculation accuracy as compared to PSS-78. To determine water salinity by the new standard, it is necessary to know the coordinates and depth of the samples by which the value of the correction for measurement results obtained by the electrometric salinometer is calculated.

At present, creators of TEOS-10 give recommendations for calculating corrections to salinity depending on the latitude, longitude, and hydrostatic pressure; for this purpose, water samples were collected in basins of all oceans and their practical salinity was determined using laboratory salinometers. The corrections were calculated according to results of measurements of volume density of the samples with a vibration densimeter and calculation of S_A by the TEOS-10 equation depending on density, temperature, and pressure [11]. In doing this, it was assumed that values of S_A calculated from the density corresponded to absolute salinity of the samples under study.

There are known refractometric methods of salinity measurements [12–16] based on the dependence of the refractive index of water n on the content of salts. Since the refractive index of water is directly related to its density according to the Lorentz–Lorenz law [17] and the density at a fixed temperature and atmospheric pressure is related to the content of salts [18], the refractometry methods based on measurements of n can provide measurements of water salinity regardless of its composition.

Refractometric methods are notable for simplicity, versatility, and high accuracy [19] but relatively low sensitivity to changes in water salinity. The typical value of sensitivity of the refractive index to salinity is $dn/dS \sim 0.0002‰^{-1}$; therefore, to obtain the error $\Delta S \sim \pm 0.03‰$ similar to the error of the electrometric method, it is necessary to carry out measurements with an absolute error Δn at a level of $\pm 6 \times 10^{-6}$ provided that the temperature is controlled with an accuracy of ±0.01°C, which is achievable only with the use of standard machines [20]. However, one can measure the refractive index relatively simply with an error of about $\pm 2 \times 10^{-5}$ using goniometric methods [21], which provides $\Delta S \sim \pm 0.1‰$. At the same time, these methods do not require complex measurement procedures and calculations, scheduled calibration, expensive reagents, presence of standard sea water, etc.

To measure the refractive index by goniometric methods, prism methods are widely used [22], in particular, the most wide-spread minimum deviation method. Its essence is to determine the minimum possible deviation angle $\varepsilon_{\min}$ of a light ray passing through a trihedral prism with a refraction angle α [23]. Sea water can be studied using a hollow prism with plane-parallel faces.

EXPERIMENTAL

To corroborate the possibility of determining the salinity regardless of the salt composition of water, solutions of sodium chloride and sea salt were studied using a goniometric system produced by OOO Inertekh [24]. The samples under study with concentrations from 10 to 40 g/kg were poured into a hollow trihedral prism at atmospheric pressure and the angle $\varepsilon_{\min}$ was measured many times. The refractive index is determined by this angle from Fresnel's formula

$$n = \frac{\sin[(\alpha + \varepsilon_{\min})/2]}{\sin(\alpha/2)}. \tag{4}$$

Then, average values of the refractive index for the solutions of sodium chloride (n_1) and sea salt (n_2) were calculated, as well as the standard deviations (SDs) σ_1 and σ_2 (Table 1).

Table 1. Measurement results for the mean value and SD of the refractive index of sodium chloride and sea salt solutions with different concentrations

Parameter	Concentration, g/kg			
	10	20	30	40
n_1	1.333182	1.334972	1.336698	1.338332
n_2	1.333171	1.334952	1.336705	1.338354
σ_1	0.000027	0.000025	0.000021	0.000018
σ_2	0.000023	0.000032	0.000025	0.000029
t, °C	19.5	19.8	20.3	21.8

To corroborate that the measurement results are independent of the admixture composition, the equality of average values of the samples n_1 and n_2 from Table 1 of the same concentration was estimated by methods of dispersion analysis with the use of the statistical T-criterion proceeding from the assumption that the results are not correlated and have a normal distribution (Table 2) [25]. The T-criterion is calculated by the formula

Table 2. Calculation results for the pooled estimate of the SD and statistical T-criterion for the measurement results for the refractive index of sodium chloride and sea salt solutions with different concentrations

Parameter	Concentration, g/kg			
	10	20	30	40
σ_{12}	0.000025	0.000029	0.000023	0.000024
T	1.39	1.65	0.96	1.57

$$T = \frac{\overline{n}_1 - \overline{n}_2}{\sigma_{12}\sqrt{\dfrac{1}{N_1} + \dfrac{1}{N_2}}}, \tag{5}$$

where $N_1 = N_2 = 20$ is the number of measurements and σ_{12} is the pooled SD estimate determined by the formula

$$\sigma_{12} = \sqrt{\frac{(N_1 - 1)\sigma_1^2 + (N_2 - 1)\sigma_2^2}{N_1 + N_2 - 2}}. \tag{6}$$

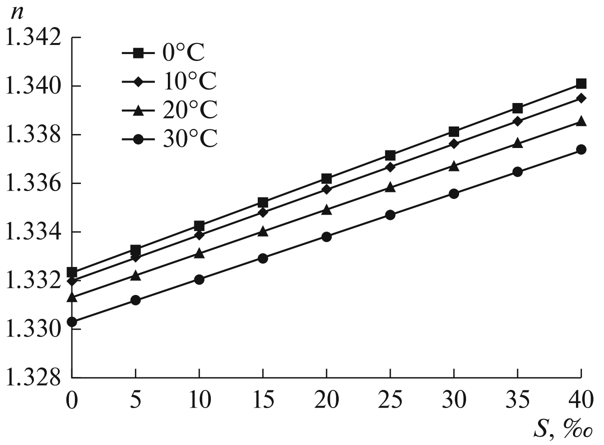

Fig. 1. Refractive index of water as a function of salinity at temperatures from 0 to 30°C at a wavelength of 650 nm according to [27].

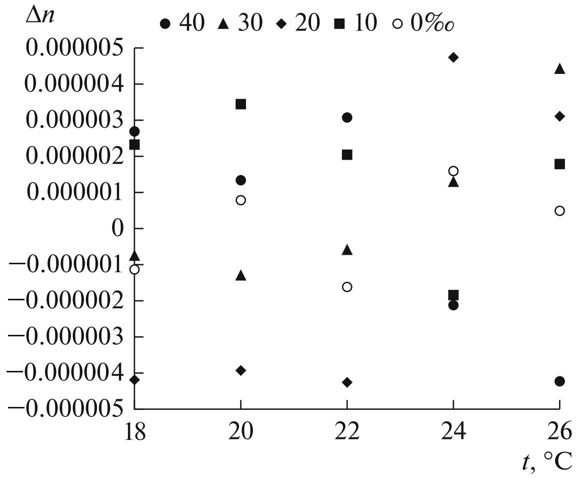

Fig. 2. Absolute approximation error of the experimental data presented in [27] using Eq. (8) in the temperature range from 18 to 26°C.

Since the calculated values of T are less than the critical value of the two-sided T-criterion with the number of degrees of freedom $N_1 + N_2 - 2$ ($t_{38;\,0.975} = 2.01$) at any concentration, the hypothesis about the equality of average values of the samples should be accepted at a significance level of 0.05.

Thus, the statistically significant difference between the average results is not observed, which proves the possibility of salinity measurements by the refractive index regardless of the salt composition of water.

MATHEMATICAL MODEL

To calculate salinity from results of measurements of $\varepsilon_{\min}$, it is necessary to obtain the mathematical model of the dependence of the refractive index of sea water on salinity and temperature at standard atmospheric pressure. In [26], an empirical equation for calculating the refractive index as a function of temperature t, salinity S, and radiation wavelength λ at standard atmospheric pressure was presented. It made it possible to obtain the approximation error Δn at a level of $\pm 3 \times 10^{-5}$. However, since the measurement of the refractive index is carried out at a fixed λ, it is desirable to find the dependence $n(S, t)$ for the wavelength of the radiation source of the goniometric system (~650 nm). Results of major studies from the technical report of the Scripps Institution of Oceanography [27] presented with an accuracy of 1×10^{-5} can be taken as initial data for constructing the model (Fig. 1).

As is seen in Fig. 1, the refractive index at a fixed temperature linearly depends on salinity:

$$n(S,t) = A_0(t) + A_1(t)S, \tag{7}$$

where the coefficients $A_0(t)$ and $A_1(t)$ nonlinearly depend on temperature. Since goniometric measurements are usually carried out in laboratory conditions, we choose a temperature range from 18 to 26°C. If the dependences of coefficients $A_0(t)$ and $A_1(t)$ on temperature in the aforesaid range are found from data of [27] and these functions are approximated using second order polynomials, then the mathematical model of the refractive index can be represented in the form

$$n(S,t) = B_2t^2 + B_1t + B_0 + (C_2t^2 + C_1t + C_0)S, \tag{8}$$

where $B_0 = 1.332336$; $B_1 = -15.879365 \times 10^{-6}$; $B_2 = -1.793651 \times 10^{-6}$; $C_0 = 1.423094 \times 10^{-6}$; $C_1 = 1.423094 \times 10^{-6}$; and $C_2 = 0.023214 \times 10^{-6}$.

A similar model provides the required approximation error Δn not larger than $\pm 5 \times 10^{-6}$ in the temperature range from 18 to 26°C (Fig. 2), which is less than the error in measurements of the refractive index by an order of magnitude.

Having measured the temperature and the refractive index at $\lambda = 650$ nm, one can determine the salinity by Eq. (8).

CONCLUSIONS

Thus, using dispersion analysis of experimental results, it has been proved that the refractive index of water does not depend on its salt composition. The equation presented in this paper describes the dependence $n(S, t)$ for a fixed wavelength and allows one to calculate water salinity from results of measurements of the refractive index in the temperature range from 18 to 26°C with an approximation error not larger than $\pm 5 \times 10^{-6}$. Similarly, using data of the Scripps Institution of Oceanography [27], one can find parameters of approximating polynomials for any other wavelength and temperature range. However, to reduce the error of salinity measurements to the level of ± 0.03‰ and lower, it is necessary to use precision refractometers and thermometers, as well as more exact initial data for constructing the mathematical model of the refractive index.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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