Light & Engineering
Vol. 26, No. 1, pp. 120-126, 2018

Svetotekhnika
No. 5, 2017, pp. 39–43

MEASURING THE SEA WATER ABSORPTION FACTOR USING INTEGRATING SPHERE

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ABSTRACT

Practical questions of quickly determining the sea water absorption factor using an integrating sphere are considered: measurement technique and data processing, as well as reference solution calibration. Numerical experiments using the Monte-Carlo method are performed to evaluate the influence of the device features (absence of spherical symmetry and the presence of a reflection specular component from the quartz shell) on the determination of the absorption factor considering scattering properties of the medium. Examples of how the results of the proposed technique can be used are given under the conditions of sea expeditions.

Keywords: light absorption, integrating sphere, Monte-Carlo method, sea water

1. INTRODUCTION

The absorption factor is a key parameter determining the propagation of light radiation in the water medium including weakening flux of solar radiation with the increasing depth, the observation conditions and visibility range of underwater objects under natural and artificial illumination [1, 2]. However, for today determining the spectral absorption factor in a low-absorbing light-scattering medium, which sea water is for the most part in the visible spectrum, is a complex problem, generally because of the need to take scattering into account [3].

During the last two decades, *ICAM* (Integrated Cavity Absorption Meter) technologies, in which the studied natural water is placed within an integrating sphere [4–6], are developing rapidly. Such an approach allows avoiding problems connected with light scattering and makes it possible to increase the sensitivity due to multiple light reflections inside the sphere. However, to determine absorption factor absolute values, the effective span of photons in their multiple reflections should be known.

The idea of the integrating sphere method emerged in the 1950s and was implemented under laboratory conditions [7]. In the 1970s, theoretical and experimental studies of integrating spheres fully filled with absorbing and light-scattering mediums were undertaken at the VNISI [8]. Experimental device specimens for the separate measurement of the absorption factor and of the turbid medium scattering were created.

Within this article, the problem of determining absolute values of sea water absorption factor is considered, taking into account features of the portable spectrophotometer *ICAM* developed at the Chair of biophysics of the Biological department of the MSU [9]. These features are the absence of spherical symmetry and availability of reflection specula component connected with the quartz shell. By means of this device, measurements were performed under expedition conditions performed on samples of sea water in Baltic, Norwegian and Barents seas.

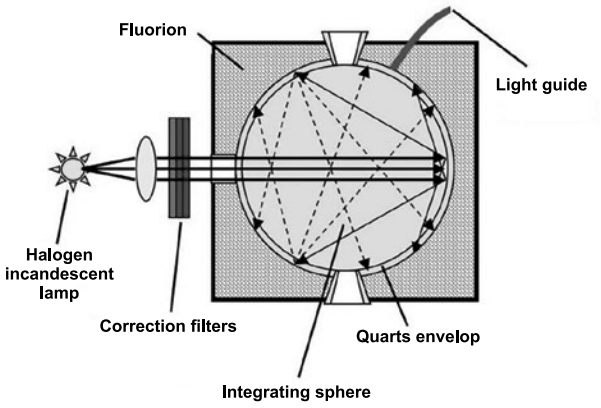

Fig. 1. Optical layout of the integrating sphere

The results of the application of the developed technique are reported in this article.

2. EQUIPMENT AND MEASUREMENT TECHNIQUE

2.1. *ICAM* spectrophotometer

An optical layout of the *ICAM* spectrophotometer is given in Fig. 1 [9]. The radiation source is a halogen incandescent lamp of 100 W stabilised by voltage. A collimated light beam passes through a combination of correcting colour light filters ПС-5, ПС-14 and СЗС-17, which partly level low luminous efficacy of the lamp in the blue and violet parts of the spectrum. After the light filters, the beam is directed to a spherical quartz envelope of 40 mm radius R and of 1.5 mm wall thickness placed into the integrating sphere made of fluorilon (*Fluorilon* 99-*W*™). The multiplied radiation scattered in the sphere goes out through a quartz light guide 600 μ in diameter to the *Ocean Optics USB4000* spectrometer. The light guide is built in the *ICAM* spectrophotometer housing at an angle of 110° relative to the axis of the specified light beam. Thus, the spectrometer records only multiple scattering undergone by the photons. Isotropy of multiple scattering allows avoiding its influence on the absorption level measurements (paragraph 3).

To determine the spectral absorption factor of sea water $a_{sw\lambda}$, values proportional to luminous fluxes leaving the sphere filled with sea water $I_{sw}(\lambda)$, empty sphere $I_s(\lambda)$, and sphere filled with distilled water I_d (λ) are measured (hereinafter, "*value*" refers to intensity spectral concentration (ISC).

A reproducibility error in the measurement has two main reasons: time drift of the lamp luminance and dark noise of the spectrometer. Irremovable dark noise of the *Ocean Optics USB4000* spectrometer does not exceed 50 ISC conventional units at maximum measured ISC units of 63999. The measurement cycle takes about 15 min. (Fig. 2). During this time, ISC of the operation mode lamp decreases by approximately 175 units. The random error of the measurement is about 0.35 %.

2.2. Calibration

To determine the parameter values necessary to calculate the absorption factor from the measurement data, a calibration by brilliant green solution was performed. Measurement data using the *SPECORD M400* dual-beam spectrometer in configuration with troughs were used as a reference. The wavelength operational spectral interval of this device is (185–900) nm, wavelength error is ±0.3 nm, and the photometric resolution is ±0.003 absorption units (ABS) at $ABS < 1$.

To prepare the solution, clear water obtained by inverse osmotic filtration was used. The concentration of the solution was selected so that sufficient dye absorption measurement accuracy would be provided on the one hand, and only one-fold scattering would occur, on the other hand. The measurements were carried out according to the dual-beam principle: a trough with clear water was placed into the reference channel. And into the re-

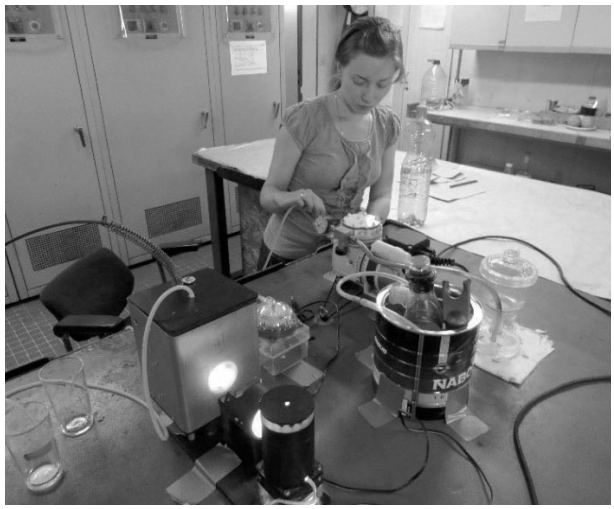

Fig. 2. Measurements of sea water absorption factor in a shipboard laboratory (a marine expedition, July, 2016); bottom left is the *ICAM* spectrophotometer, on the right is the filtration installation

ference channel, a trough with water was placed to obtain the baseline first, and then brilliant green solution was added. The water was allowed to settle for some time to allow gas bubbles, which could strengthen scattering, to escape. Brilliant green fluoresces at $\lambda_{max} \approx 660$ nm [10], which coincides with an abrupt decrease of absorption. Therefore fluorescence was not observed.

The absorption spectrum of brilliant green was calculated by the formula:

$$a_{gr\lambda} = \frac{1}{l}\left(ln\frac{I_0^{Sp}(\lambda)}{I_{gr}^{Sp}(\lambda)}\right), \quad (1)$$

where $a_{gr\lambda}$ is the spectral absorption factor of brilliant green, l = 0.05 m is the trough length, $I_0^{Sp}(\lambda)$ is ISC when measuring the baseline (when both troughs are filled with distilled water), $I_{gr}^{Sp}(\lambda)$ is ISC when measuring with the brilliant green calibration solution.

The measurements were performed by five spectra series, in two cycles; then the results were averaged. Optical concentration measurement error using the *SPECORD M400* spectrometer is 0.3 %, which taking into account the trough length, gives a measurement error $a_\lambda = 0.06$ m^{-1}.

3. SIMULATION OF LIGHT PROPAGATION IN THE INTEGRATING SPHERE BY MEANS OF THE MONTE-CARLO METHOD

The $I_{sw}(\lambda)/I_s(\lambda)$ relationship (paragraph 2.1) does not only depend on the spectral absorption factor a_λ but also on inner surface spectral reflection factors $\rho_{sw\lambda}$ and $\rho_{s\lambda}$. For the real *ICAM* device, these parameters depend on the sphere inner shell boundary refractive indices (sea water – quartz and quartz – fluorilon), on the thickness of the quartz envelope wall, on the outlet diameter and position, as well as on the reflective properties of the fluorilon. To evaluate the influence of these parameters, a simulation of light propagation in the *ICAM* was performed using the Monte-Carlo method. Direct (analogue) simulation, which is the simplest version of this method, was used [11, 12].

For each photon, processes of absorption and scattering in the medium, refraction and reflection on the boundaries quartz – sphere interior and quartz – fluorilon, absorption in fluorilon, and output from the sphere through the light guide were simulated.

3.1. Numerical experiments and interpolation formula

Simulation calculations with different values of the listed *ICAM* parameters under the condition $a_\lambda R \leq 0.1$, showed that in all cases results for the relationship $f(a_\lambda) = I(\lambda)/I_o(\lambda)$, where and input and output ISCs obtained by the Monte-Carlo method with good accuracy are approximated by the formula:

$$f(a_\lambda) = k/(1+ua_\lambda)^v, \quad (2)$$

where $k = f(0)$, as well as u and v parameters are customised in accordance with the calculation results by the least square method. Previously, a similar formula with small differences was used in work [13].

For all performed calculations, the root-mean-square error according to formula (2) did not exceed the Monte-Carlo method error. The performed calculations showed that their relative error was about 10^{-3}.

3.1.1. Effect of medium scattering properties

One of the most important questions is how far the assumption of the independence of the (a_λ) function from the scattering properties of the medium filling the sphere can be applied. As shown in studies [4, 5], for a spherically symmetric system with Lambert wall reflection, this assumption is used with good levels of accuracy. Strictly speaking, the system in our case is not spherically symmetric, and reflection from the surface with a quartz shell is not quite Lambert, even if we take the reflection from the fluorilon to be Lambert. For this purpose, simulating calculations were performed for an integrating sphere without a quartz shell under the assumption that the inner surface reflection contains a specula component, and the medium filling the sphere is scattering.

For the scattering simulation, the Henyey-Greenstein indicatrix and scattering factor of the studied medium (see below) were used. The surface reflection was simulated using the function:

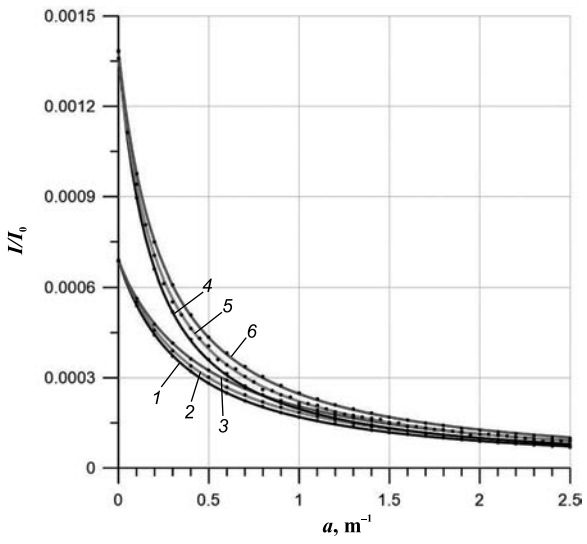

Fig. 3. Comparison of the calculated results with various reflection factor and relative refractive index values of fluorilon:
1, 2, 3 – ρ_s = 0.98; *4, 5, 6* – ρ_s = 0.99; *1,4* – $n_w = n_f = n_q$; *2, 5* – n_w = 1.34, n_q = 1.45, n_f = *1.35*; *3, 6* – n_w = 1.34, $n_q = n_f$ = 1.45. Solid lines show the calculation according to formula (1), points show the calculation according to the Monte-Carlo method

$$r(\mu_r,\phi_r;\mu_i,\phi_i) = \\ = \rho_s\left\{p\delta(\mu_i+\mu_r)\delta(\phi_r-\phi_i)+(1-p)\mu_i/\pi\right\}, \quad (3)$$

where μ_i and μ_r are cosines of zenith angles of incident and reflected rays, φ_i and φ_r are correspondent azimuthal angles, δ is Dirac function, p is a relative part of the specula component. The first expression in the curly brackets describes specula reflection, and the second relates to Lambert. The simulation was carried out in a wide parameter interval: the scattering factor is 0 and 5 m^{-1}, average scattering angle cosine is 0 and 0.9 and the absorption factor is from 0 to 2.5 m^{-1}.

The calculation for p = 0.1 showed a negligible influence of the medium scattering properties; scattering influence becomes significant only for $p \geq 0.5$.

To check the assumption of the $f(a_\lambda)$ function's independence on the medium's scattering properties, calculations were made for an integrating sphere with a quartz shell 1.5 mm in thickness (paragraph 2.1).

The calculation results showed that the contribution of the specula component when reflecting at the boundaries is not significant, and the assumption that the results of the absorption factor measurement are independent from the scattering parameters can be considered to be reasonable.

3.1.2. Influence of Freshnel refraction and reflection

Let's consider the possibility of simply taking accounting for Fresnel refraction and reflection from the sphere inner surface (the studied medium is quartz and quartz – fluorilon), and its influence on the measurement results using the *ICAM* spectrophotometer. In other words, whether is it possible for each set of permissible refractive indices to introduce a concept of a surface effective reflection factor so that formula (2) would essentially become one-parametric.

The dependences of the calculated result on relative refractive indices (RRI) of water, quartz and fluorilon are shown in Fig. 3.

It can be seen from Fig. 3 that the dependence of the $f(a_\lambda)$ function, namely u and v parameters in formula (2), on the *RRI* is considerable. Parameter k, i.e. $f(0)$, only depends on spectral reflection factor of the fluorilon $\rho_{s\lambda}$, whereas at $a_\lambda > 1$, refraction influence can be more essential than fluorilon reflection.

3.2. Calculation formulas

The spectral dependence of the absorption factor for the studied liquid is obtained by transforming formula (1): $a_\lambda = \left\{\left[kI_0(\lambda)/I(\lambda)\right]^{1/v} - 1\right\}/u$, contains an input ISC $I_o(\lambda)$. In order to exclude this value, measurements were taken with the empty sphere, for which equality $I_s(\lambda) = k_s I_o(\lambda)$ is correct. It follows here from:

$$a_\lambda = \left\{\left[\left(k/k_s\right)I_s(\lambda)/I(\lambda)\right]^{1/v} - 1\right\}/u, \quad (4)$$

where I is spectral dependence of the signal for the studied water solution (in particular, sea water), k is the coefficient for a liquid with water's refractive index.

Another calibration method of the *ICAM* spectrophotometer is based on using a water solution with the same refractive index as sea water and with a known absorption factor. For example, one

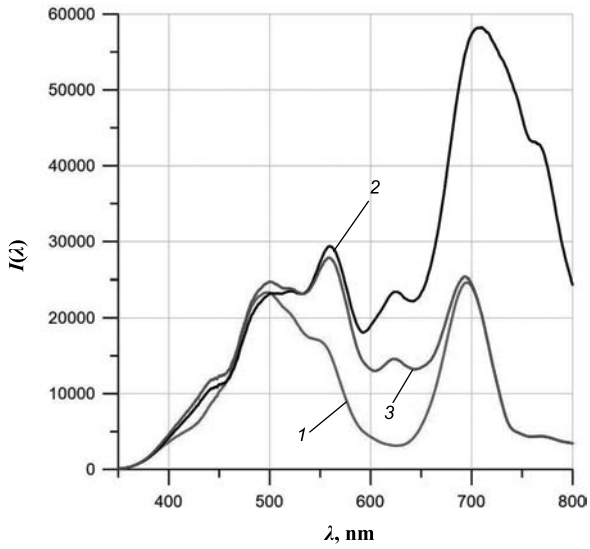

Fig. 4. Experimental results with the dye solution (1), empty sphere (2), and distillate (3)

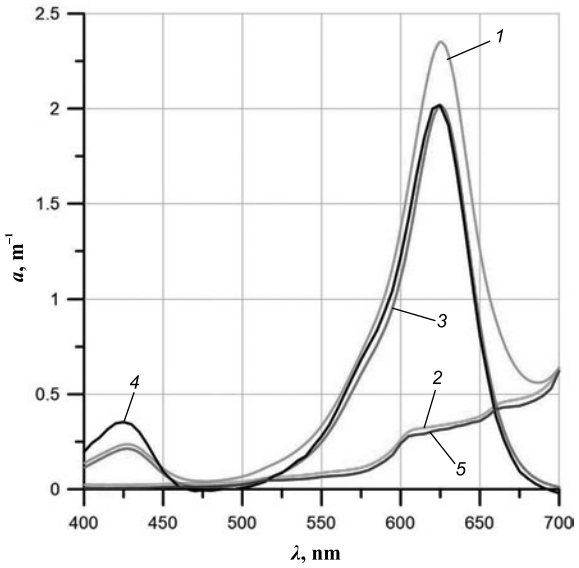

Fig. 5. Absorption spectra computed according to the experiment data with the dye:
1 – dye solution; *2* – distillate; *3* – dye (according to the *ICAM* indications); *4* – dye (according to the *SPECORD* indications); *5* – clear water according to data [13]

can use clear (pure) water, for which spectral dependence $a_{d\lambda}$ is known [14].

In this case k is not a part of the calculation formula:

$$a_{sw\lambda} = \left\{\left[I_d(\lambda) / I_{sw}(\lambda)\right]^{1/v} \times \left(1 + u a_{d\lambda}\right) - 1\right\} / u, \qquad (5)$$

where (paragraph 2.1) $I_d(\lambda)$ is the ISC measured in the experiment with a reference solution (distillate).

3.2.1. An experiment with brilliant green dye

Parameters k, k_s, u, and v in formulas (4) and (5) can be calculated using the Monte-Carlo method, if *ICAM* parameters are known. However, not all these parameters are known, especially in respect to the fluorilon reflection factor and refractive index. To customise these parameters, an experiment with brilliant green and a *SPECORD* device (paragraph 2.2) was performed.

In the brilliant green experiment, $a_{gr\lambda}$ are known. These are the dye's spectral absorption factors measured by the *SPECORD* device. $I_{gr}(\lambda))$, $I_d(\lambda))$ and $I_s(\lambda))$ are ISCs in the experiments with the dye solution, distillate and empty sphere respectively (Fig. 4).

To calibrate the device, k parameters were computed ($0.76 \cdot 10^{-3}$), *u (1.911)* and *v (1.27)* assuming that RRI values are $n_w = 1{,}34$, $n_q = 1{,}45$ and $n_f = 1{,}45$.

The value of parameter k_s is selected to be $0.66 \cdot 10^{-3}$ from the condition that a_λ values computed according to (4) coincide with the values measured by the *SPECORD* device, and a_λ of the distillate ($a_{d\lambda}$) is positive and differs from the work [13] data inessential.

Values $a_{gr\lambda}$ and $a_{d\lambda}$ were calculated by formula (4), and in doing so, $a_{gr\lambda} = a_{sol\lambda} - a_{d\lambda}$, where $a_{sol\lambda}$ is a_λ of the dye solution. The calculation results are presented in Fig. 5.

Absolute error of a_λ according to our evaluations is 0.05–0.06 m^{-1} and depends mainly on the measurement errors.

4. RESULTS OF EXPERIMENTAL MEASUREMENTS

Measurements of sea water a_λ ($a_{sw\lambda}$ were performed using the *ICAM* spectrophotometer during a trip of the Academician Mstislav Keldysh research vessel from Kaliningrad to Arkhangelsk between June 29 and July 9 2016. The obtained results are presented in Fig. 6. As it can be seen, at the research posts in the Baltic Sea, absorption factor values are significantly higher than in the Norwegian and Barents seas. In Fig. 6b, examples are given of the measured a_λ of the particles suspended in water, which are calculated as a difference of the measured $a_{sw\lambda}$ values before and after sea water filtration using a filter with a pore size of 0.4 μ.

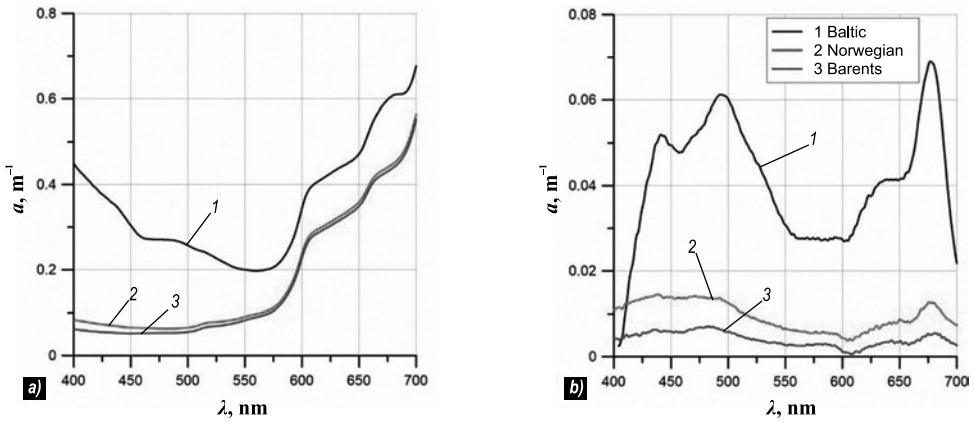

Fig. 6. Absorption spectra of sea water (a) and of particles (b) (Baltic, Norwegian and Barents seas, June and July 2016)

Curve $a_{sw\lambda}$ for the Baltic Sea is of interest due to the fact that blossoming blue-green algae (cyanobacteria) are visible. This presents as a peak corresponding to absorption in a wide band with λ_{max} of about 620 nm, which is of phycocyanin – the pigment marker of cyanobacteria, and λ_{max} of about 675 nm corresponds to the absorption band for chlorophyll *a*, which is a photosynthesizing pigment. These results are consistent with direct tests for phytoplankton species composition performed later in the laboratory. Such results are absent from the absorption spectra in the Norwegian and Barents seas.

5. CONCLUSION

The proposed technique allows to quickly determine the absorption spectra of sea water ($a_{sw\lambda}$) by means of an *ICAM* spectrophotometer under marine expedition conditions. Two measurements are needed: with a sphere filled with sea water, and with an empty sphere.

Prior to the measurement, a single calibration of the device using a reference water solution should be performed.

The Monte-Carlo method calculations carried out showed that despite the lack of spherical symmetry in the used device and the presence of a specula component due to the quartz shell, the independence of $a_{sw\lambda}$ results from the medium scattering properties remains when changing the scattering factor from 0 to 5 m^{-1}.

The study was undertaken with support of the RSF (project #14–17–00800) provided via the Institute of Oceanology of P.P. Shirshov of the RAS.

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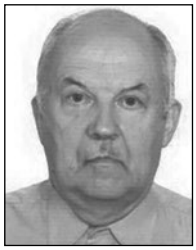

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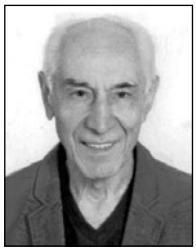

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