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Original article

A New Differential Method for Determining the Light Spectral Absorption by Suspended and Dissolved Organic Matter Directly in Seawater

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Abstract
Purpose. The purpose of the study is to introduce a new method for measuring the spectral absorption of light using suspended and dissolved organic matter directly in seawater, without its prior concentration or filtration onto a substrate.
Methods and Results. A new method is proposed for determining light absorption by impurities in seawater. It is based on the application of two reflective double-walled conical cuvettes of large length (connected at the input to an integrating sphere) and assembled according to the optical scheme of a two-beam differential spectrophotometer. The cuvettes are identical thin-walled quartz cones coaxially inserted inside the same outer cones, the latter having a mirror coating. When seawater is placed in the measuring channel and the deionized water is placed in the reference channel for comparison, only the total absorption by suspended matter and colored dissolved organic matter will be defined. It is necessary to pour the filtrate of the same seawater that was passed through the 0.2 μm-pore filter into the reference cuvette to determine only the light absorption by suspended matter in seawater. The seawater filtrate placed in the measuring channel and compared to the optically pure water in the reference channel permits determination of the spectrum of dissolved organic matter absorption in the original seawater.
Conclusions. For the first time, the spectral characteristics of light absorption by suspended matter in an aqueous medium are being defined directly in its natural state. This is being achieved by significantly increasing sensitivity, provided that all the scattered rays are collected completely by the receiving device. This is made possible by a method that uses double-walled conical quartz glass cuvettes, which increase the reflection angle by the value of the cone apex with each subsequent reflection. Therefore, the combination of conical cuvettes in the optical scheme of a two-beam differential photometer with an integrating sphere allows to obtain accurate data that require no more corrections for the influence of scattered rays. The principle of a two-beam differential spectrophotometer proposed and applied in the study makes it possible to perform spectral analyses of the absorption characteristics of various suspended matter components separately from all other substances and the properties of the seawater in which they are present.

Keywords: suspended particles, dissolved organic matter, light absorption, scattering medium, total internal reflection, double-walled cone cuvette, scattering angle

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Introduction

The propagation of natural sunlight in the ocean is determined by the patterns of its penetration into the aquatic environment and depends primarily on the aggregate properties of spectral absorption and scattering by the water itself, as well as on suspended particles and dissolved organic matter (DOM). For this reason, the optical properties of suspended particles and impurities in seawater significantly impact the transformation of the light field and its spectral properties as light penetrates deeper into the ocean. The selective spectral absorption of light by suspended particles and DOM also triggers photosynthesis in the ocean, which impacts the global carbon dioxide cycle and the ecological state of aquatic areas. The optical properties of water impurities provide important information about the taxonomic composition and size distribution of phytoplankton communities, as well as the influence of pigments in algal cells on photosynthesis and heat transfer [1–3]. Precise quantitative data on the spectral absorption and scattering of light by suspended particles and DOM are necessary for parametric representation of radiative transfer equations in bio-optical ecological models of the ocean [4].

Suspended particles in seawater are subdivided into suspended particles, consisting primarily of cells of various phytoplankton species, and sinking particles, composed of mineral solids and detritus. The spectral absorption features of phytoplankton pigments are of particular interest among all the optical properties of suspended matter because they exert a decisive influence on primary production and the life activities of marine organisms, making them important for studying many oceanographic, biological, and biogeochemical processes in the ocean [5]. The sinking component of suspended matter, consisting of non-algal solid particles, participates in the exchange between surface waters and the deep ocean. This component includes non-living organic and mineral particles, as well as heterotrophic microorganisms. The microbial populations responsible for remineralizing sinking particles are likely free-living in the water column. During the slow settling process in seawater, these populations deliver the necessary substances for the life activities of organisms inhabiting the depths [6].

Colored dissolved organic matter (CDOM), also known as the yellow substance, is a complex of substances that strongly absorb the short-wavelength part of light in water. This class of substances includes all impurities in seawater passing through a 0.2 μm filter. Their proportion in the ocean is ~ 10–90% [7]. The selective strong absorption of ultraviolet and blue radiation by CDOM promotes aquatic photochemistry, which has important consequences for biogeochemical processes that influence the carbon cycle. One can also infer the composition and variability in concentration of DOM based on its characteristic spectral absorption signatures. Knowing the precise shape of the spectral absorption curve is necessary for modeling the role of DOM in many of these processes. In semi-analytical ocean color models, light absorption by phytoplankton and other suspended particles is determined by extrapolating DOM absorption from the blue region into the rest of the visible spectrum [8].

The optical properties of light absorption in natural waters are highly variable. This necessitates regular comprehensive interdisciplinary research in the fields of ocean optics, biophysics, and biogeochemistry during marine expeditions on research vessels, oceanographic platforms, and other floating craft. Global studies using satellite data are now possible because the spectral characteristics of upwelling radiation from the ocean – observed as ocean color – depend on the presence of light-absorbing impurities in the water. This upwelling radiation can be used for remote sensing of the surface layer of aquatic environments and provides information on the global distribution of suspended matter components and CDOM from ocean color satellite images [9, 10]. In order to verify data from spaceborne ocean color scanners, subsatellite determinations of the spectral absorption coefficient of various suspended matter components – especially phytoplankton and cyanobacterial cells – should be carried out with the highest possible accuracy and spectral resolution at the ocean surface level. The isolation of absorption by planktonic cells is justified by the unique spectral features of pigments in phytoplankton, in contrast to the simple, monotonous decrease in absorption spectra of mineral particles and DOM with increasing wavelength. Further advances in the bio-optics and optical oceanography of the upper ocean layer could significantly benefit from fundamentally new approaches to accurately determining light absorption by suspended matter and DOM in seawater, which is essential for improving light radiation transfer models in the sea.

The aim of the present study is to demonstrate a novel method for determining the spectral absorption of light by seawater impurities and to substantiate its high accuracy.

Materials and methods for determining light absorption by seawater impurities

Direct determinations of the spectral absorption coefficients for total absorption by suspended matter and CDOM are conducted based on seawater sample measurements collected from various ocean depths. This methodology has several advantages: it ensures environmental stability, allows for the preliminary preparation of concentrated seawater suspensions with specified characteristics, and increases particle concentration on the filter substrate through filtration. The main drawback of this methodology, however, lies in the inability to study the fine structure of the spatial and vertical distributions of the optical properties of seawater due to the discreteness of the samples.

The most common method for determining the spectral absorption of light by suspended particles is to filter a seawater sample through a paper filter, which acts as a substrate, to deposit solid particles onto it. Then, absorption is measured using a spectrophotometer. This method is called the filter pad method or the quantitative filter technique. There are three configurations: transmission of directed light through the filter [11]; illumination of the filter with direct light and measurement of its reflection [12]; and placement of the filter inside an integrating sphere, where it is illuminated by direct and diffuse light [13]. The transmission configuration is the simplest to apply, but the obtained results are significantly distorted due to losses of scattered rays. Consequently, this approach does not allow for quantitative assessment of significant errors in determining light absorption by suspended matter. The transmission-reflection configuration largely circumvents these limitations, but this method is more labor-intensive and is therefore rarely used in routine practice. The configuration involving the irradiation of the filter substrate inside an integrating sphere is the most preferable, as it avoids errors in measurements resulting from losses of scattered radiation [14].

In addition to determining the total absorption by all organic suspended particles, the quantitative filter technique provides the possibility for the experimental determination of absorption by phytoplankton cells and detrital particles separately. Typically, this separation is carried out by treating the filter sample with an organic solvent or bleaching agent to extract or bleach the pigments present in phytoplankton cells [15, 16].

As measurement technology improves and methods employing integrating spheres are adopted, the drawbacks of the quantitative filter technique are mitigated by eliminating uncertainties in absorption measurements caused by methodology. Although the method of measuring spectral light absorption on a filter inside an integrating sphere yields superior results, the data obtained using this method still require correction for the influence of multiple light scattering paths through the suspended particles. Though it has some limitations, it has been shown that this method is practically independent of strong scattering by suspended solid particles and provides acceptable sensitivity. One limitation is the sufficiently complex and labor-intensive measurement procedure, as well as the inability to separate absorption by phytoplankton cells, detritus, and mineral particles [17].

Methods for determining the spectral absorption characteristics of seawater have proven more promising. In these methods, seawater is collected from different depths in the studied areas without preliminary preparation and poured into a spherical quartz flask, which is lined over its entire external surface with diffusely reflecting Fluorilon (Fluorilon 99-W™) possessing a very high reflectance. A careful analysis showed that, with the appropriate calibration using a reference aqueous solution, this method can yield satisfactory data on the absorption spectra of seawater. According to the method, light absorption by particles suspended in water is calculated as the difference between the measured spectral absorption coefficients of the seawater and the water after its filtration through a 0.4 μm pore size filter [18].

The primary sources of error in all light absorption determination methods are the pathlength amplification factor for scattered rays and the zero baseline offset. The pathlength amplification factor is associated with the increase in the distance photons travel through a filter containing suspended particles, resulting in an overestimation of the measured absorption coefficient. Most studies aimed at determining corrections for these factors were conducted using the light transmission method through a filter-substrate on a standard spectrophotometer. However, the pathlength amplification factor proved inconsistent across studies and depended on the sample type [19, 20]. For this reason, to obtain quantitative absorption values, data must be corrected by applying a predetermined pathlength amplification factor for scattered rays, which is defined as the ratio of the optical pathlength to the geometric pathlength [21].

The correction for the pathlength amplification factor is usually derived from experiments with algal cultures. It is calculated as the ratio of the optical density of the filter containing suspended particles to the optical density of the same suspension in a dilute solution. This establishes a functional relationship that can be subsequently applied to field samples [22].

Nevertheless, a comprehensive analysis of various experimental and analytical methods conducted to obtain reliable estimates of errors in determining absorption by suspended particles revealed significant variability between different approaches for different water types [23]. In this regard, existing methods for determining absorption by suspended matter and phytoplankton pigments currently do not allow for the unambiguous selection of a single method for applications in optical oceanography.

A new method for determining light absorption by impurities directly in seawater

Seawater is a weakly absorbing scattering medium with concentrations of suspended matter and impurities that allow light beams to travel significant distances through single scattering. Single scattering, which requires that scattering particles are not too close to each other and are separated by at least three times their radius, is the primary necessary condition for correctly determining the optical properties of a scattering medium [24]. This condition means that the optical properties of suspensions and impurities in seawater must be determined in their natural state, without any concentration or thickening procedures. Currently employed methods for determining absorption in suspensions and filter substrates do not meet the single scattering condition, necessitating unreliable corrections to the obtained data. Therefore, these methods cannot fully satisfy the modern requirements of solving a wide range of bio-optical problems in oceanography and limnology. Completely different approaches to determining light absorption by suspended matter and DOM are needed. These approaches must be free of the aforementioned drawbacks and must not require the introduction of theoretical and experimental numerical corrections into the final result. In order to measure light absorption directly in natural seawater without first thickening it into a suspension or concentrating it by filtration, the sensitivity would need to be increased by a factor of ten while simultaneously ensuring that all scattered rays are completely collected by the receiving device.

A new method has been proposed based on the use of previously developed reflective, double-walled, long-path cone cuvettes [25]. These cuvettes are connected to an integrating sphere and assembled according to the optical scheme of a dual-beam differential spectrophotometer. This method positions the measuring and reference conical reflecting cuvettes outside the integrating sphere, directly in front of its input apertures, ensuring that all rays exiting the cuvettes enter the sphere. The seawater under investigation is placed into the measuring cuvette, while the reference cuvette contains either ultrapure water with no impurities or filtered seawater with DOM. The new method uses elongated cone cuvettes with light beams that diverge at the cone angle to increase sensitivity, which may allow for the determination of spectral light absorption across a broader range of seawater transparencies. Additional sensitivity enhancement is achieved by significantly reducing instrumental error through the application of the dual-beam differential spectrophotometer optical scheme. Both cuvettes are identical and consist of coaxially nested thin-walled quartz cones that ultimately form unique double-walled cone cuvettes. The small air gap between the cuvette walls ensures total internal reflection on the inner wall. It also allows for the application of a stable, air-stable multilayer mirror coating with a very high reflection coefficient on the outer wall. Cone cuvettes are notable because the angle of reflection of rays from the walls increases by the value of the cone's apex angle with each reflection event. Using this property of cone cuvettes in the new method for determining the spectral absorption of light by suspended matter and DOM offers the following advantages and reveals new photometric properties:

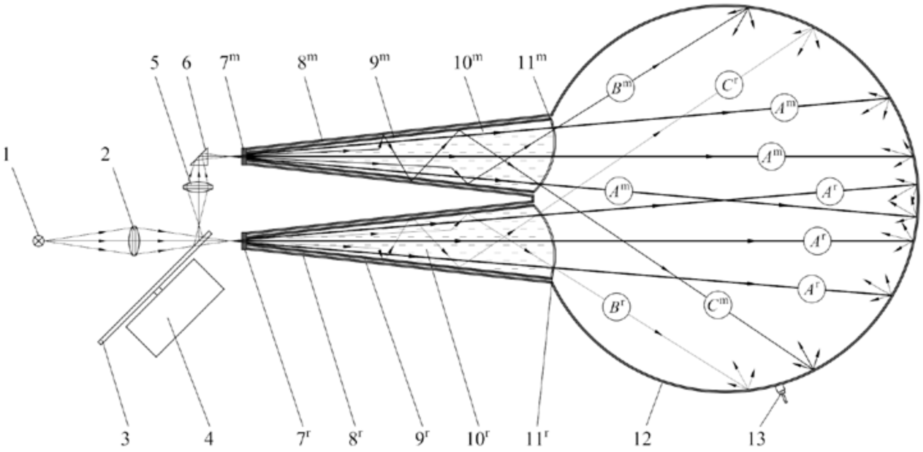
– substantial increase in sensitivity for determining spectral light absorption of impurities across a wide range of seawater transparencies;

– capability to perform spectral determination of light absorption by suspended matter in natural seawater without thickening it into suspensions or concentrating it by filtration;

– minimization of errors caused by the strong influence of scattering on the results of determining light absorption by impurities in seawater;

– elimination of the influence on the absorption magnitude caused by the mutual penetration of diffuse radiation from the sphere into the double-walled cone cuvette and back.

Fig. 1 shows the optical scheme of the dual-beam differential spectrophotometer used to determine light absorption by suspended matter and DOM directly in seawater in its natural state, without any concentration or thickening procedures. The dual-beam scheme consists of two channels: a measuring channel and a reference channel (subscripts $^{\mathrm{m}}$ and $^{\mathrm{r}}$ respectively). These channels are identical, and in Fig. 1, they both have the same numerical designations for the elements of the double-walled cone cuvettes and the same letter designations for the ray paths.



F i g. 1. Scheme for determining the light spectral absorption by suspended DOM in seawater: *1* – light source; *2* – light source lens; *3* – rotating mirror disk with notches; *4* – electric motor; *5* – measuring beam objective; *6* – rectangular prism; 7^{m}–7^{r} – entrance illuminators; 8^{m}–8^{r} – external conical reflectors with mirror coating; 9^{m}–9^{r} – conical quartz cuvettes providing total internal reflection of scattered rays in forward direction; 10^{m}–10^{r} – measuring and reference mediums; 11^{m}–11^{r} – output illuminators; *12* – integrating sphere, *13* – receiving light guide of spectrometer; A^{m}–A^{r} – direct rays that weakened as a result of absorption in the medium and passed through the measuring and reference cuvettes, B^{m}–B^{r} – rays scattered in the range of angles of total internal reflection of a quartz cuvette, C^{m}–C^{r} – rays scattered at large angles beyond the total internal reflection angles

The operation of the scheme proceeds as follows: light from source *1* is formed by lens *2* into a diverging beam at an angle matching that of the double-walled cuvettes’ cone. This beam is then directed to mirrored disk *3*, which has mirrored sectors that alternate with identical sectors containing cutouts. Therefore, as this disk rotates via electric motor *4*, the beam is sequentially switched between the measuring and reference channels. When a mirrored sector of disk *3* passes in front of the light beam from source *1*, the light reflected by lens *5* and rectangular prism *6* is directed to the double-walled cuvette of the measuring channel. Here, the beam passes sequentially through the input illuminator 7^{m}, the seawater sample under investigation 10^{m}, the output illuminator 11^{m}, and then enters the integrating sphere *12*. Inside the sphere, multiple reflections from the diffusely reflecting spherical surface transform the beam into isotropic light for the measuring channel. During the next phase, when a cutout in the disk is positioned in front of the light source, the beam passes through the cutout and is directed to the double-walled cuvette of the reference channel.

Similarly to the measuring channel, the beam passes sequentially through all elements of the reference channel, including the illuminator 7^{r}, the comparative aqueous medium 10^{r}, and the output illuminator 11^{r}. Inside sphere *12*, *the* beam forms isotropic light for the reference channel. The isotropic light fluxes formed by integrating sphere *12*, from the measuring and reference channels, sequentially pass through receiving light guide *13* to the input of a precision spectrometer with a data acquisition system based on a personal computer.

As evident from the ray paths shown in Fig. 1, the double-walled cuvettes in the measuring and reference channels very effectively redirect all light scattered within the aquatic environment towards the integrating sphere. This occurs because the reflecting cones increase the reflection angle by the value of the cone’s apex angle with each subsequent reflection. Consequently, inside the cone, rays of any direction reflecting multiple times from the cone walls gradually turn towards the cone’s axis. As a result, rays scattered at small angles (B^{m}–B^{r}) are efficiently redirected towards the sphere via total internal reflection within the conical quartz cuvettes (9^{m}–9^{r}), while those scattered at larger angles (C^{m}–C^{r}) are redirected via reflections from the outer mirrored wall (8^{m}–8^{r}). In the cone cuvettes, the number of reflections from the walls is drastically reduced. Rays are redirected from the point of light scattering to the input apertures of the integrating sphere along an expanding zigzag path with a gradually increasing step size. The reduction in reflections and straightening of scattered rays’ zigzag paths within conical cuvettes results in the beam traversing a much shorter path length than with existing methods. Thereby, this minimizes the error associated with the path length amplification factor. Within the inner cone cuvettes, the main light flux is dominated by rays that pass through the water without contacting the walls, as well as by rays that are scattered at small angles and experience one or a few reflections. Due to the elongation of the scattering phase function of seawater, ~ 93% of all scattered rays pass through the inner cuvettes and enter the integrating sphere [25]. This phenomenon is explained by the scattering phase function of seawater, which exhibits a pronounced peak at small angles (0–10°) [26].

A small fraction of C^{m}–C^{r} photons scattered at large angles that exit the cuvette into the air gap are reflected from the mirrored coating of the outer cone walls 8^{m}–8^{r}. These photons also follow a gradually straightening zigzag trajectory. After several reflections from the outer cones 8^{m}–8^{r}, the C^{m}–C^{r} rays scattered at large angles return to the cuvettes 9^{m}–9^{r} at the angle of total internal reflection.

They are then redirected towards the integrating sphere, along with the main flux of direct rays A^m–A^r and rays scattered at small angles B^m–B^r. Since the reflection and refraction of rays at the surface of the quartz cuvette occur with virtually no losses, all rays scattered at large angles (~ 6%) are redirected into the sphere. As a result, ~ 93% of rays from the small-angle scattering region and ~ 6% from the large-angle region are redirected from the double-walled cone cuvettes into the sphere for detection by the photodetector. In other words, more than 99% of all rays scattered in seawater are redirected [25]. Fewer than 1% of scattered rays are irretrievably lost due to minor absorption on the mirrored coating of the outer cones and on microscopic inhomogeneities of the quartz glass during total internal reflection. Therefore, combining cone cuvettes with an integrating sphere can overcome the challenges associated with the strong influence of scattering on determining light absorption by suspended matter and DOM. This is achieved by the receiving device simultaneously registering both the direct rays transmitted through the medium without absorption and all photons scattered along this path. Consequently, only the rays absorbed within the medium fail to reach the sphere, while all rays scattered along the length of the cuvette and the direct rays not absorbed throughout the cuvette end up inside the integrating sphere. However, it should be noted that diffuse radiation from the sphere returning into the measuring cone cuvette would cause an unknown change in absorption. In a dual-beam scheme, though, this change is compensated for by normalization relative to the reference channel. Once inside the integrating sphere, all these rays create uniform illumination throughout its internal volume after multiple diffuse reflections. The spectral absorption of light in the studied marine environment governs this illumination in both the measuring and reference channels.

The use of the optical scheme of a dual-beam differential spectrophotometer in the proposed new method enables the spectral analysis of the optical absorption properties of various impurities in seawater. This is achieved by selecting the appropriate aqueous media for the measuring and reference channels. When seawater extracted from the study depth is placed in the measuring channel and ultrapure water is placed in the reference channel, the total absorption by suspended matter and CDOM can be determined. To determine light absorption by suspended matter alone in seawater, it is necessary to fill the reference cuvette with a filtrate of the same seawater that has been passed through a 0.2 μm pore filter. Placing seawater filtrate in the measuring channel and comparing it with ultrapure water in the reference channel allows for determining the absorption spectrum of DOM in the original seawater.

Theoretical analysis of using double-walled cone cuvettes with an integrating sphere

Within the double-walled cone cuvettes, we distinguish three light beams directed toward the entrance of the integrating sphere. These beams are shown in Fig. 1 by lines of different thickness, which correspond to the light ray intensities. The beams are direct light, light scattered at small angles or reflected from the cone wall without energy loss, and scattered light that has lost energy through one or several reflections from the mirrored coating.

In the single-scattering approximation, the measured signal can be represented as follows:

$$I = I_0\left(1+\frac{bL_0}{4\pi}\int_0^{\Omega_1} p(\theta)d\Omega+\frac{bL_0}{4\pi}\int_{\Omega_1}^{\Omega_2} R^n \exp\left[-\left(a+b\right)\Delta L\right]p(\theta)d\Omega\right)\cdot\exp\left[-\left(a+b\right)L_0\right], \tag{1}$$

where I_0 is the intensity generated by the light source; b is the scattering coefficient; L_0 is the measurement path length; Ω_1 is the solid angle within which a ray enters the integrating sphere entrance after total internal reflection or without reflection from the cone wall; $L(\theta)$ is the phase function of angle θ; R is the reflection coefficient of the cone cuvette wall; Ω_2 is the solid angle within which rays can enter the integrating sphere entrance after multiple reflections from the wall of the cone reflector and the quartz cuvette; n is the number of reflections; a is the absorption coefficient; ΔL is the additional path length of the ray in water depending on the scattering angle.

For small values of optical thickness $\left(a+b\right)L_0$, it is more convenient to rewrite expression (1) in the following form:

$$I = I_0 \exp\left[-\left(a+\Delta b\right)L_0\right], \tag{2}$$

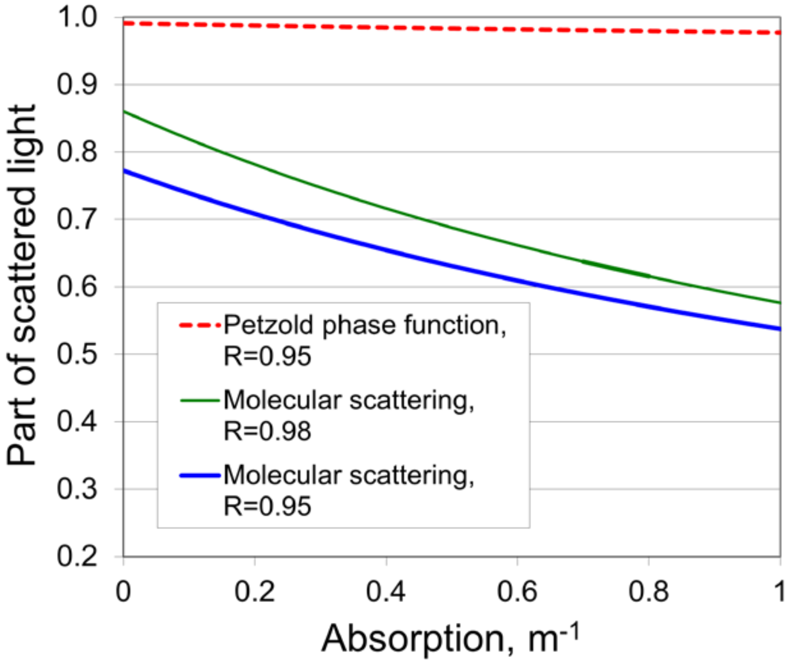
where $\Delta b = \frac{b}{4\pi}\int_{\Omega_3}^{4\pi} p(\theta)d\Omega$ is a quantity determining light loss due to scattering. The Ω_3 angle is smaller than Ω_2 and depends on the R reflection coefficient. Using the calculation algorithm presented in [27, 28], the average path length of light in the $L(\theta)$ cuvette and the amount of light incident on the entrance of the $I(\theta)$ integrating sphere were computed as a function of the given θ angle for the following parameters: measurement path length – 250 mm; apex angle – 8° of the outer cone reflector and quartz cuvette; input diameter of the cone cuvette – 5 mm; output diameter – 40 mm; combined thickness of the glass and air gap – 2 mm; reflection coefficient of the mirrored coating of the outer cone reflector – 0.95. Integration over the angle, taking into account the scattering phase function, shows what fraction of the scattered rays can be collected by the optical scheme under consideration. If the path length of a ray in the medium increases due to scattering, additional excess absorption will occur. For a given phase function $p(\theta)$ and the calculated function $I(\theta)$, the integral was computed:

$$\frac{1}{4\pi I_0}\int_{4\pi} I(\theta)p(\theta)\exp\left[-a\Delta L(\theta)\right]\sin\theta d\theta d\varphi, \tag{3}$$

where $\Delta L(\theta) = L(\theta) - L_0$.

According to the conducted estimates, with low absorption and a mirror coating reflection coefficient $R_m = 0.95$, using the Petzold phase function [29], light loss after scattering will be 0.91%, while with the molecular phase function it will be 22.8%. In calculations using the Petzold phase function, this value decreases from 0.99 at $a = 0$ to 0.977 at $a = 1$ m^{-1}. In reality, the asymmetry of the scattering phase function in the Black Sea is higher than the Petzold phase function. Therefore, the influence of scattering on absorption measurement in the long-wavelength region will be less. Moreover, the improvement in the mirror coating quality has a diminishing effect as absorption increases. This pattern is explained by the elongation of the ray path in water upon multiple reflections from the wall of the cone reflector. Thus, the scattered light reaching the integrating sphere travels a path whose length depends on the scattering phase function. For molecular scattering and $a = 1$ m^{-1}, approximately half of the scattered light is lost. It should be noted that purely molecular scattering does not occur in natural water (for example, in the clearest waters of the World Ocean, the light scattering coefficient minus molecular scattering at a wavelength of 515 nm is 0.023 m^{-1} [30], which is almost three times higher than the theoretical value of molecular scattering at a wavelength of 400 nm). In seawater, the higher the absorption in a given spectral interval, the smaller the contribution molecules make to scattering.

Fig. 2 shows how the fraction of scattered light detected by the photometer changes with increasing water absorption.



F i g. 2. Relative amount of scattered light leaving a cone cuvette depending on the water absorption coefficient for molecular scattering (reflectance coefficients of the mirror coating of a cone wall are 0.95 and 0.98), and for highly anisotropic light scattering in water with the Petzold phase function (reflectance coefficient of the mirror coating is 0.95)

Calculations demonstrated that the average path length of scattered light in seawater with the Petzold phase function is $\overline{L}_{\text{p}} = 1.027L_0$, where L_0 is the measurement path length, while for molecular scattering it is $\overline{L}_{\text{m}} = 1.6L_0$.

Let us express the intensity of light incident on the entrance of the integrating sphere as

$$I = I_0 \exp[-a\overline{L}_0 - \delta_p b_p \overline{L}_p - \delta_m b_m \overline{L}_m], \quad (4)$$

where δ_p, δ_m are the fractions of light loss due to scattering by particles and water molecules, respectively; b_p, b_m are the light scattering coefficients for particles and water molecules. $\overline{L}_0$ is close to the measurement path length, since a significant portion of the total intensity consists of direct light. In calculations using formula (4), the main uncertainty is introduced by δ_p, δ_m, as they significantly depend on the actual reflection coefficient of the cuvette walls. At the same time, the δ_m multiplier is responsible for the strong spectral dependence of the measurement error and depends more strongly on the reflection coefficient of the mirror coating, which also depends on the wavelength. Note that if the I_0 reference intensity is the intensity obtained by measuring a sample of filtered seawater or purified freshwater, then the molecular component will be compensated. Instead of expression (4), taking into account the path length estimates, we obtain

$$I = I_0 \exp[-(a + 1.027\delta_p \Delta b_p) L_0], \quad (5)$$

where Δb_p is the difference between the light scattering coefficients by hydrosol particles in the measured sample and in the reference water. Henceforth, we will assume that the error in determining absorption is 1% of the scattering coefficient by hydrosol particles.

The next problem in determining the intensity of the optical signal arises due to the strong spatial non-uniformity of the light field exiting the measurement volume. According to expression $\exp(-cL_0)$ the main light energy is contained in the direct beam. The remaining part is also distributed non-uniformly due to the anisotropy of scattering and reflection from the cuvette wall. In the proposed scheme, the integrating sphere, performing the function of an ideal collector, is used to measure the intensity of the light flux, which has a spatial-angular non-uniformity of brightness distribution. After multiple reflections from the spherical wall, the uniform distribution of light throughout the volume of the sphere leads to an increase in its intensity and to the fact that part of the light rays is redirected back towards the conical cuvette from the sphere. Due to the high reflectivity of the conical cuvette wall and the property of the cone to redirect rays towards its apex, part of the light energy will return to the sphere, while another part will be absorbed by the medium or the mirror coating of the conical reflector. As the ray propagates in the conical cuvette, a sufficient number of reflections and a distance in the medium exceeding the length of the cuvette are required for it to be redirected back towards the sphere. Because of this, uncertainty arises in calculating the main characteristic of the photometric sphere – its gain coefficient.

Let us substantiate this conclusion with analytical expressions. Let $\bar{a}$ be the average albedo of the sphere surface, a_c – the albedo of the double-walled conical cuvette when illuminated from its wide end, and δ – the fraction of the sphere surface occupied by the cone insert. The gain coefficient is equal to the sum of the geometric progression $\bar{a} + \bar{a}^2 + \bar{a}^3 + \ldots = \frac{\bar{a}}{1-\bar{a}}$. For a perfectly reflecting surface

$$\bar{a} = \frac{1}{4\pi \cdot r^2} \int_S a(s)ds = 1 - \delta(1 - a_c)\,, \tag{6}$$

$$K = \frac{1 - \delta(1 - a_c)}{\delta(1 - a_c)}\,. \tag{7}$$

Since the light flux entering from the conical cuvette is proportional to $\exp\left(-a\bar{L}\right)$, where $\bar{L} \approx L_0$, determining absorption in transparent water requires specifying the gain coefficient with high accuracy, which depends on a_c. The albedo of the double-walled cone cuvette for rays entering the cuvette at different angles will be a function of the angle, as it depends on the number of reflections from the walls of the outer cone with the mirror coating and on the attenuation of the ray along the path traveled in the water from the sphere into the cuvette and back. The estimation formula for the albedo of the double-walled cone cuvette will include n – the average number of reflections, l_{avg} – the average path length of rays reflected from the walls and exiting back into the sphere, as well as a_w – the light absorption coefficient of water:

$$a_c = r^n \exp(-a_w \cdot l_{\text{avg}})\,. \tag{8}$$

The estimative nature of the formula does not imply precise determination of the albedo of the double-walled cone cuvette. From formulas (7) and (8), it is evident that the gain coefficient fundamentally depends on the optical properties of the water sample. This dependence, as well as the insufficient accuracy in determining the gain coefficient, is eliminated by normalization relative to the reference channel. Here, the property that each ray entering the sphere is amplified equally is used. Then, by dividing the measured isotropic light flux by the value in the reference channel, we obtain the expression $\exp\left(-a_w \bar{L}\right)$ equal to the attenuation of light due to its absorption by water in the cuvette.

Let us consider and analyze three methods for determining light absorption in seawater.

1. The method for determining absorption based on the use of a double-walled cone cuvette connected to an integrating sphere and a reference channel via an air path [27].

2. The method for studying the spectral absorption properties of seawater by sequentially determining the absorption of reference water and a sample using this

approach. The reference can be either ultrapure freshwater obtained by various means or filtered seawater.

3. The method under consideration, based on the use of two long conical cuvettes connected to an integrating sphere in a differential spectrophotometer scheme, for determining light absorption by suspended matter and CDOM directly in seawater.

In the first case, the total light absorption by seawater will be measured. Then to obtain the light absorption by suspended matter and dissolved substances, the absorption of pure water should be subtracted. It is known from the literature that laboratory experiments have failed to obtain values of the spectral absorption of pure water that are closely matched with high accuracy. In the short-wavelength region (according to [31]), the absorption values are strongly influenced by the degree of water purification, while in the long-wavelength region, where the influence of impurities is significantly less (according to [32]), a noticeable spread in the values of the light absorption coefficient of pure water is observed. The long-wavelength region of the visible spectrum is most susceptible to errors in determining absorption by impurities, because besides methodological errors, random measurement errors will also have an influence. Fig. 3 shows the difference between two absorption spectra of pure water according to the data from [31] and [32], compared to the absorption of yellow substance in the central part of the Black Sea. The data on the yellow substance absorption are taken from the work [1].

It is evident from Fig. 3 that the error from using tabulated values from the cited works can exceed light absorption by DOM. Furthermore, the non-monotonic nature of the error could be misinterpreted as a phytoplankton pigment absorption peak in measurements.

Using the second method, two sequential measurements are performed, resulting in two signals proportional to $\exp(-a_\mathrm{w}\overline{L})$ and $\exp(-a_\mathrm{r}\overline{L})$, where a_r is the light absorption in the reference water. Logarithm of the ratio of the two signals, divided by the average path length $\overline{L}$, is precisely the absorption by those particles and molecules not present in the reference water ($a_\mathrm{w}-a_\mathrm{r}$). The advantage of determining the analyzed sample and the reference water using this method lies in the compensation of systematic error and the reduction of errors caused by differences in spectral resolution. However, this method is sensitive to random errors in measurements, since they are performed at different times, which requires high stability of the photodetector and the power supply voltage.

In the third method, continuous comparison is achieved through the use of a differential dual-beam scheme with two rapidly switching sequential signals. Since these signals are proportional to $\exp(-a_\mathrm{w}\overline{L})$ and $\exp(-a_\mathrm{r}\overline{L})$, the light absorption by suspended matter in seawater can be easily calculated continuously via the logarithm of the ratio of the measuring and reference signals, divided by the average path length $\overline{L}$.

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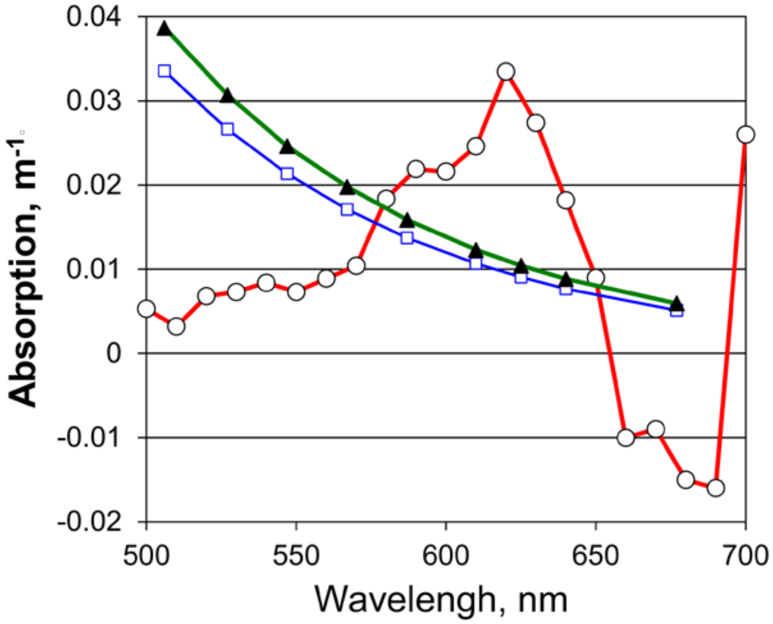
[1] Mankovsky, V.I., Soloviev, M.V. and Mankovskaya, E.V., 2009. *Hydro-Optical Characteristics of the Black Sea. Reference Book.* Sevastopol: ECOSI-Gidrofizika, 90 p. (in Russian).



F i g. 3. Difference in the coefficients of pure water light absorption based on the data of two experiments, and the values of light absorption by CDOM in the central part of the Black Sea. ○ – difference between the coefficients of pure water light absorption given in [31] and [32]; ■ – typical values of CDOM absorption [1] for low values of beam attenuation (c = 0.28 м$^{-1}$); ▲ – CDOM absorption for high values of beam attenuation (c = 0.60 м$^{-1}$)

As we see, the third method does not differ mathematically in its formulas from the previous one, but due to the application of the differential dual-beam scheme, it achieves two orders of magnitude higher measurement accuracy.

Conclusion

The primary condition for correctly determining the optical properties of a scattering medium is single scattering, where scattering particles are not too close to each other and are separated by a distance greater than three times their radius. For seawater, this condition implies that the spectral absorption properties of suspended phytoplankton cells, detritus, and mineral particles must be determined in their natural state, without any preliminary procedures such as depositing particles on a filter or concentrating samples extracted from the sea. Currently, in none of the methods for determining light absorption by suspended matter satisfy the single scattering condition. Since seawater is a weakly absorbing medium dominated by scattering, directly measuring light absorption by suspended matter in an aqueous medium would require increasing sensitivity by tens of times while simultaneously ensuring complete collection of all scattered rays by the receiving device. It has been demonstrated for the first time that this can be achieved using the method proposed in this work. This method is based on the use of double-walled cone cuvettes made of quartz glass connected to an integrating sphere.

Integrating these elements into the optical scheme of a differential dual-beam photometer also facilitated this process. Consequently, the new method enables spectral analysis of the optical absorption properties of all impurities collectively and of each component separately, independently of the other substances in the mixture and the properties of the seawater in which they are present.

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