ISSN 1573-160X, *PHYSICAL OCEANOGRAPHY*, Vol. 31, Iss. 2, pp. 178-193 (2024)
Original Russian Text © M. E. Lee, E. B. Shybanov, 2024,
published in *Morskoy Gidrofizicheskiy Zhurnal*, 2024, Vol. 40, Iss. 2, pp. 198–214

Original article

New Method for Determining Spectral Absorption of Light in the Sea

M. E. Lee ✉, E. B. Shybanov

Marine Hydrophysical Institute of RAS, Sevastopol, Russian Federation
✉ *michael.lee.mhi@gmail.com*

Abstract
Purpose. The study is purposed at presenting and analyzing a new method for determining light absorption in the sea which for the first time made it possible to redirect almost all the scattered rays from the studied light beam to the photodetector along the path of its propagation in a weakly absorbing medium, as well as at showing that application of a new method providing such an efficient collection of the scattered rays, permits not only to avoid significant errors from a strong influence of scattering upon the results of determining light absorption, but also to give up the necessity in correcting the data by theoretical modeling.
Methods and Results. It is known that sea water is a weakly absorbing light-scattering medium where light propagation is accompanied by its attenuation that is many times stronger due to scattering than due to absorption. Therefore, the determination of light absorption by sea water at a receiving device requires collection of not only the light that has traveled a certain distance in the absorption medium, but also all the light scattered along this path. Previously, a method was proposed for measuring the light absorption in a cylindrical mirror cuvette with a light source at the input and a collector with a photodetector at the output (reflective-tube absorption meter). Somewhat later, a similar method based on the phenomenon of total internal reflection was applied. Since these methods do not provide a complete collection of scattered rays, the data are to be corrected by theoretical modeling. The authors propose a new method for determining spectral absorption of light in a quartz cone cuvette with an external mirror cone. It is shown that the cone cuvette permits to collect most of the scattered rays in the beam passing through the water medium by means of more efficient redirection of these rays from the place of light scattering to the receiver. The rest of the scattered rays that have left the cuvette reach the receiver in the air space between the cuvette and the cone mirror due to multiple reflections from it. As a result, the new method makes it possible to redirect almost all of the scattered light to the receiver and thus to minimize the errors in determining light absorption in a weakly absorbing medium. To quantify the advantages of the new method, the authors have calculated geometric parameters of the scattered light propagation for a quartz cone cuvette in air and for the same cuvette placed inside the external cone mirror.
Conclusions. The combination of a quartz cone cuvette and an external mirror cone in the new method made it possible to collect all the rays scattered in a weakly absorbing medium in the receiver. Thus, it permitted not only to exclude their strong influence upon determining light absorption in the sea, but also to give up correcting the data by theoretical modeling.

Keywords: light absorption, scattering medium, total internal reflection, quartz cone cuvette, cone mirror, scattering angle, ray path

Acknowledgments: The work was carried out within the framework of state assignment FNNN-2024-0012.

For citation: Lee, M.E. and Shybanov, E.B., 2024. New Method for Determining Spectral Absorption of Light in the Sea. *Physical Oceanography*, 31(2), pp. 178-193.

Introduction

Sea water absorption is one of the most important hydro-optical characteristics that determine propagation of light radiation in the sea. The absorption coefficient spectrum contains information about mineral and organic suspended matter, phytoplankton cells and dissolved organic matter in sea water. Light absorption and scattering by these impurities form an underwater light field of the open waters of most seas and oceans and, thus, affect the solar radiation spectrum penetrating into the depths and rising from the sea. Such spectral changes provide information about the ocean color that with the help of space color scanners can be used for systematic monitoring of global spatiotemporal changes in the surface vital layer throughout the World Ocean [1]. In all models of light radiation transfer in the marine environment, the inherent optical properties, which include absorption and scattering, are either necessary input parameters or, in the case of inverse problems, output data of calculations. In this regard, measurements of the absorption value are of great practical importance, especially for verification of satellite scanners of sea color closely related to the environmental monitoring of its condition.

The currently applied natural methods for determining the spectral coefficient of light absorption make it impossible to obtain reliable data due to insufficient measurement accuracy. For example, in the blue region of the spectrum, where the main absorption bands of phytoplankton pigments and dissolved organic substances are located, the amount of light absorption in highly transparent sea water is so insignificant that it can hardly be recorded by modern photometers.

An even more significant difficulty in light absorption measurement in the sea is due to the fact that sea water is a weakly absorbing light-scattering medium where light propagation is accompanied by many times stronger attenuation from scattering than from absorption. Consequently, when measuring light absorption by sea water, it is necessary to collect at the receiving device not only the light that has traveled a certain distance in the medium after absorption, but also all the light scattered along this path. This feature leads to mutually contradictory requirements when developing methods for measuring light absorption in the sea. On the one hand, to ensure the method sensitivity, it is necessary to measure weakened due to absorption light along as much of its path as possible in a medium longer than the measuring base length. On the other hand, the larger length of the base makes it very difficult to redirect all the light scattered along this path towards the collector to be collected in the light receiving device.

For relatively transparent sea water, the difficulties of collecting scattered rays increase many times as scattering predominates over absorption in the sea. For this reason, the existing methods for determining light absorption do not provide reliable data suitable for use in modeling and in problems of retrieving impurities based on sea color. Based on the range of sea radiance factor variability in the spectral interval, where pure water absorption can be neglected and also using the data on the characteristic values of the asymmetry parameter of scattering indicatrices [2], it can be estimated that the ratio between light attenuation from scattering and its attenuation from absorption can reach values of 20 and higher with intensive blossom of coccolithophores.

It should be borne in mind that in this case we are talking specifically about relatively pure waters and not about ideally pure waters or especially pure ocean waters prepared in the laboratory because direct light absorption determination methods are not applicable to them due to impossibility of collecting all scattered light from measuring bases up to 10 meters long on the receiving device. To determine the spectral absorption of light for such ideally pure waters is possible only indirectly with the help of a method based on the use of characteristics of the natural underwater light field in the purest waters of certain World Ocean areas [3, 4].

To determine spectral absorption characteristics of pure water, the integrating cavity absorption meter (ICAM) method [5] has been proposed. It involved using two integrating cavities located one inside another: an internal one, filled with water, and an external one, creating isotropic radiance in the internal cavity, independent of any scattering effects. A rigorous theoretical justification of the ICAM method, working equations for taking into account the influence of scattering particles on the determination of spectral absorption of especially pure water and methods of absolute calibration are considered in [6]. Due to isotropic radiation and very high diffuse reflectivity of integrating cavities, ICAM enables us to measure very low optical absorption values, practically independent of scattering effects in a sample.

A method [7] was proposed to determine spectral absorption of light in very turbid sea water. It involved placing of the studied suspension of algal cultures not inside the integrating sphere, but outside it at different distances from the entrance to take into account scattering by cells. The use of this method is justified only in rare environmental situations, when in certain water area conditions of rapid growth of microalgae are realized and extremely high concentrations of phytoplankton are observed in sea water. It is shown that true absorption spectra, practically independent of the influence of scattering, are determined based on light attenuation measurements at different distances from the integrating sphere.

Light absorption spectra determinations under the conditions of sea expeditions can be carried out in a vessel laboratory using a portable spectrophotometer with an integrating sphere filled with sea water [8]. In this spectrophotometer, the sea water sampled in the studied water areas from different horizons is poured without preliminary preparation into a spherical quartz flask, lined over the entire outer surface with a diffusely reflective material – fluorilon (*Fluorilon* 99-*W*™). In this method, the sea water-filled integrating sphere cannot provide spherical symmetry due to radiance by the collimated beam and the presence of a specular reflection component associated with the quartz shell. Nevertheless, a thorough analysis carried out in [9] showed that with appropriate calibration of the spectrophotometer against a standard aqueous solution, it is possible to obtain quite satisfactory data on the light absorption spectra of sea water.

Method for determining light absorption in a reflective-tube absorption meter

Currently, a reflective-tube absorption meter has become widespread in hydrooptics [10, 11]. Having ideal specular reflection, such an absorption meter could redirect all light scattered into the front hemisphere to the receiving collector and thereby provide a qualitative determination of its absorption in the sea. In fact, to prevent direct contact with aggressive sea water, a mirror coating on the outer wall of a thin glass tube with a reflectivity of < 95% was used. This was not enough to achieve the minimum acceptable error in determining light absorption in weakly absorbing aquatic media. Due to the low specular reflection factor of such a tube absorption meter, the rays scattered towards the walls were lost because of losses during multiple reflections. As a result, only part of the forward-scattered light reached the collector, and with an elongated path through the medium. The influence of these scattered rays that did not reach the receiving device had to be taken into account through theoretical modeling with subsequent correction of the values [12]. Such correction allowed to obtain data with an acceptable error for turbid lake water, but for sea water only estimates were obtained.

In the 90s of the past century, a measurement scheme with a cylindrical quartz cuvette without a mirror coating was proposed. To redirect the rays scattered inside the cuvette to the collector, the phenomenon of total internal reflection from the quartz-air interface was used [13, 14]. An ideally smooth, well-polished cylindrical surface of a quartz cuvette reflects all photons incident on it at an angle greater than the critical one $\arcsin(1/n_w) \approx 48.5°$ (where n_w is the refractive index of sea water), since the photons will experience total internal reflection. Therefore, all photons scattered in the angular range of 0–41.5° will reach the receiving collector without loss, either directly without touching the wall or through several reflections. Due to the fact that the scattering indicatrix of natural sea waters has a strong peak in the forward direction [15, 16], in this case it is possible to redirect most of the forward scattered rays and thus preserve them in the beam passing through the aquatic medium. However, using this method, it is not possible to avoid the loss of some rays scattered at large angles, since they exit the cuvette into the air and do not reach the receiving collector. The elimination of these scattered rays from the main light beam is the main source of errors in the method for determining light absorption in a cylindrical quartz cuvette [11]. Thus, the disadvantages of this method, which is widely used in commercial devices [17], include the loss of scattered rays at angles in the 41.5–90° range.

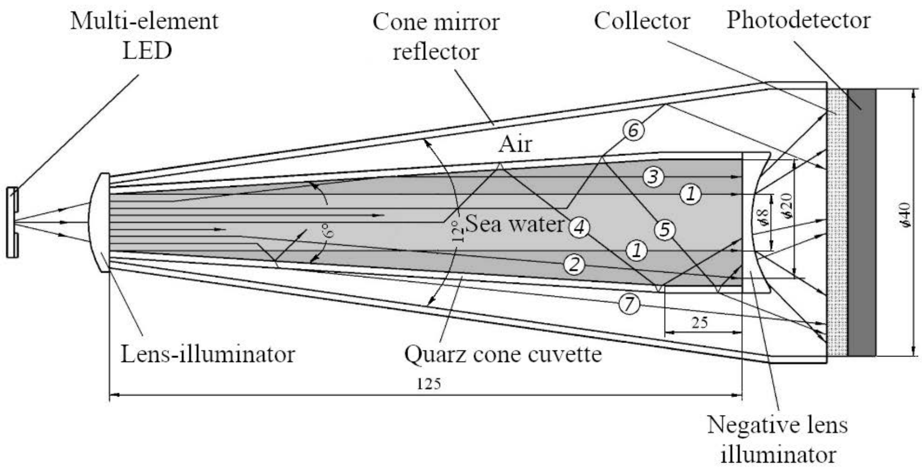
Another disadvantage of the method analyzed is lengthening of the path of scattered rays from the source to the collector, propagating in a zigzag pattern inside the cuvette. Due to these downsides, as when using a method based on the operation of reflective-tube absorption meter, it is necessary to resort to the obtained data correction through theoretical modeling [18, 19]. The results showed that the relative absorption error is always positive and increases linearly with increasing scattering to absorption ratio. The error increases with decreasing the cylindrical surface reflectivity of the cuvette.

Aspects of a new approach to determining light absorption properties in the sea

In the present paper, it is proposed to minimize errors by using a new method for determining spectral absorption of light, allowing to redirect almost all the light scattered in a weakly absorbing aquatic medium to the collector. To achieve the best results, it is necessary to redirect all scattered rays in the range of 0–180° to the receiving collector. Taking into account the fact that only 1–2% of photons are scattered in the opposite direction in sea water, it is quite acceptable to limit to intercepting rays scattered into the front hemisphere in the range of 0–90°. To solve this problem, we propose to determine light absorption in a **quartz cone cuvette** placed coaxially inside an external mirror cone (Fig. 1).

As shown in Fig. 1, instead of the currently commonly used cylindrical cuvette, the cone cuvette is made of quartz glass in the form of a thin-walled cone, which ends in a cylindrical part only in a short section in front of the receiving collector. This shape permits to redirect photons scattered in the aquatic environment and experiencing total internal reflection at the quartz-air interface to the collector more and more efficiently.

The rays scattered at large angles enter the air space between the cone cuvette and the mirror cone. These rays are not lost, as in currently used methods, but are collected by an outer mirror cone in a beam of light directed at the collector. Thus, determining light absorption in a cone cuvette combined with a cone mirror reflector allows to eliminate the above-mentioned disadvantages of existing methods, since almost all rays scattered into the front hemisphere are redirected to the receiving collector.



F i g. 1. Diagram of a new method to determine light absorption in sea water with the examples of ray paths from a source to a collector. The rays ending in water indicate the absorbed part of light in a beam: *1* – the rays which passed through the whole cuvette without attenuation; *2*, *3* – the scattered rays at small angles which reached the collector without touching its wall and also redirected after their reflection from the cuvette wall; *4* – the scattered rays which experienced total internal reflection and reached the collector by means of the repeated additional reflections from one part of the cuvette wall to the opposite one; *5*, *6* – the scattered rays partially reflected by the wall inward and exited after refraction into the air space between the cuvette and the mirror cone; *7* – the scattered rays which left the cuvette and reached the collector without touching the mirror cone reflector

Restrictive geometric parameter of the new approach is the length of the measuring base, which cannot exceed 0.1–0.15 m due to the cone shape of the cuvette and the mirror reflector. The main factor limiting the length of the measuring base is the cone cuvette angle. Note that a cylindrical cuvette is the limiting case of a cone cuvette with the 0° angle. Therefore, it is necessary to calculate the optimal angle of the cone cuvette satisfying many conflicting factors, such as measuring base length, diameter of the collimated light beam, diameter of the collector, etc. As a result, the following were chosen as the optimal geometric parameters for determining light absorption in the sea using the new approach:

– measuring base length – 0.125 m;
– diameter of the collimated light beam – 0.008 m;
– angle of quartz cuvette cone – 6°;
– angle of external mirror reflector cone – 12°;
– diameter of receiving collector – 0.04 m.

A powerful multi-element LED with a collimator can be used as a light source, providing determination of light absorption in different parts of the spectrum in the range of 390–630 nm. The multi-element LED has an important advantage over traditionally used incandescent lamps due to its much higher light output. A comparative analysis shows that LEDs are tens and hundreds of times more powerful in terms of luminous flux in the selected spectral range than incandescent lamps. The spectral ranges of LEDs are relatively narrow (10–20 nm), so their radiation can be considered quasi-monochromatic. Multi-element multi-colored LEDs also allow for fast electronic scanning across the spectrum, as opposed to mechanical switching of a set of narrow-band interference filters.

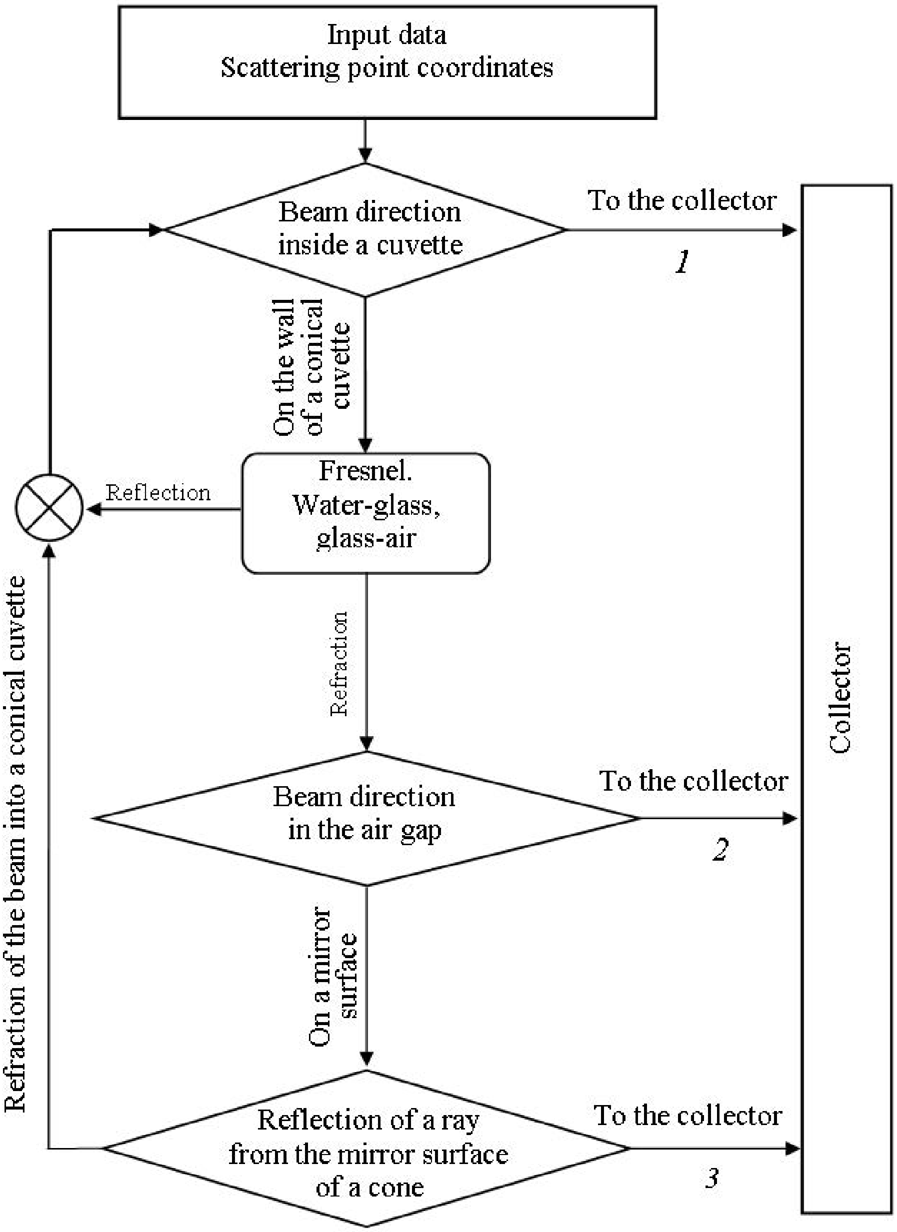
A plate made of milk glass is most often used as a receiving collector. Its optical characteristics and geometric parameters are selected to ensure uniform redistribution of the incident light throughout its entire thickness. Rays fall onto the receiving collector from a variety of directions, unevenly illuminating the surface, and their intensity varies significantly. Therefore, the main function of the collector is to generate uniform total radiation at the output. In reality, it is not possible to achieve complete uniformity of the radiation coming out of the collector, therefore, for better matching, it is necessary to use light radiation receivers with a large photosensitive area comparable to the collector size.

The path of rays in a cone cuvette is characterized by the fact that for a light flux directly passing through an aquatic medium, everything happens in the same way as in a cylindrical cuvette. However, in a quartz cone cuvette, significantly more photons scattered at small angles reach the collector without contacting the walls. Due to this, the cuvette wall influence on determining light absorption in the sea is reduced, since in natural waters scattering occurs mainly in small angles and almost all of them are redirected to the collector without interacting with the walls.

Calculations of the ray path in a quartz cone cuvette

In the described method for determining light absorption in the sea, it is very important to take into account the variety of features of reflection, refraction and absorption of scattered rays when interacting with the walls of a quartz cuvette and an external cone mirror reflector to minimize errors in their impact on the final result. For that, the corresponding calculations of geometric parameters of scattered light propagation were carried out, first separately for a quartz cone cuvette in the air, and then for the same cuvette placed inside an external cone mirror reflector.

Figure 2 shows a block diagram of the algorithm for calculating the effective reflection coefficient and geometric parameters of the path of rays scattered by a weakly absorbing aquatic medium in a quartz cone cuvette in the air.

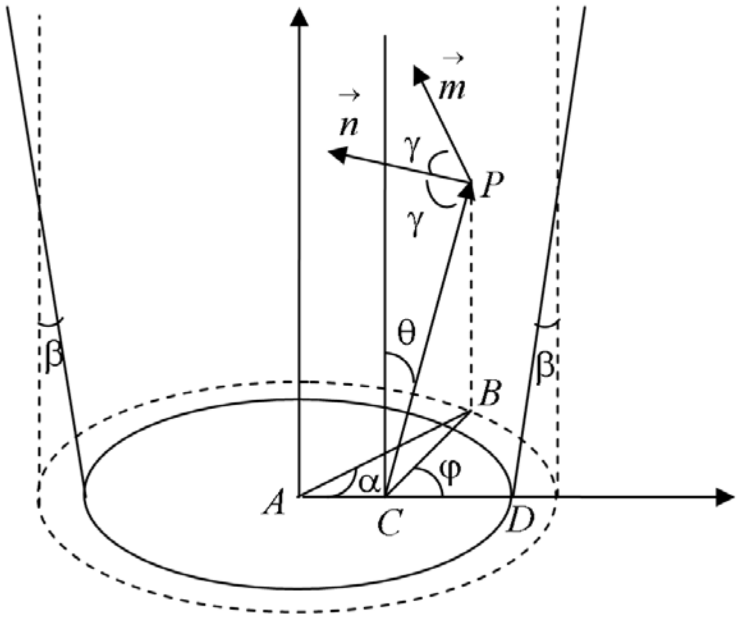


F i g. 2. Block diagram for calculating the ray paths in a cone cuvette with a mirror cone

The input parameters are the position of the initial point of light scattering in the medium, as well as the azimuthal and zenith angle. The ray can reach the collector in three ways: *1* – through a cone cuvette immediately or after several reflections from the walls; *2* – along the air gap between the cone cuvette and the mirror coating after refraction at the glass-air interface; *3* – along the air gap after reflection from the mirror coating. Thus, a ray can travel part of its path through the air, reducing its absorption probability. However, this applies to those rays that are scattered at angles > 44.5°. For such angles in the standard diagram, the path length increases significantly, which raises additional questions when calculating absorption.

To avoid multiple duplication of low-intensity rays, it was assumed that light reflected in the direction of a quartz cone cuvette penetrates the medium with a transmittance equal to unity. The relative error of this simplification is estimated at 5%. Further calculation of the Fresnel coefficients for such rays was carried out according to a simplified scheme, namely: a ray of greater intensity was selected from the reflected and refracted ray. The corresponding Fresnel coefficient was set to unity. For a given scattering angle, integration over two spatial coordinates and azimuth was carried out. Light losses in this scheme can only be associated with the ray reflection in the direction of the light source and with the absorption of light during specular reflection from the external cone mirror reflector.

For a narrow beam, initial geometric conditions are determined by the distance from the illuminator and the angle between the cone axis and the scattering direction. When calculating the path of wide beam rays, it is necessary to specify the distance from the cone axis to the scattering point, as well as the azimuthal angle.



F i g. 3. Diagram of a scattered ray propagation in a cone cuvette used for calculating path length, reflection angles and their number

Let us consider the reflection geometry inside a quartz cone cuvette. Figure 3 shows a diagram of the scattered ray propagation in a cone cuvette with an opening angle of 2β. The cone axis is directed upward. The horizontal section of the cone forms a circle with r_1 radius and a center at point *A*. The cone is filled with sea water illuminated from below by a parallel beam. Let the direct light be scattered at point *C* in a certain direction determined by zenith angle θ and azimuthal angle φ. The scattered ray intersects with the surface of the cone at height z at point P where the ray is reflected back into the medium. A horizontal section of a cone drawn through point P forms a circle with radius $r(z) = r_1 + z \cdot \mathrm{tg}\beta$, where $z = |BP|$. The circle projection is shown by a dashed line in Fig. 3.

Let us denote by x the $|AC|$ distance from the cone center. From the equations for ABC and BCP triangles, the BC segment length is determined

$$|BC| = \sqrt{(r_1 + x \cdot \mathrm{tg}\,\beta / \mathrm{tg}\,\theta)^2 - x^2 \sin^2 \varphi} - x \cdot \cos\varphi \tag{1}$$

and its corresponding height $z = |BC / \mathrm{tg}\,\theta|$. The path length of a light ray $|CP|$ to the reflection point is calculated using the Pythagorean Theorem.

The intersection of a ray with a cone is possible if the inequality is satisfied

$$(x \cdot \cos\varphi \cdot \mathrm{tg}\,\theta - r_1 \cdot \mathrm{tg}\,\beta)^2 \geq (x^2 - r_1^{\,2})(\mathrm{tg}^2\,\theta - \mathrm{tg}^2\,\beta). \tag{2}$$

Condition (2) will be checked for cases where point C is outside the cone. Azimuth α relative to the center for the reflection point P satisfies the equation

$$\cos\alpha = \frac{|AC|}{r(z)} \cdot \sin^2 \varphi + \cos\varphi \sqrt{1 - \frac{|AC|^2}{r^2(z)} \sin^2 \varphi} \,. \tag{3}$$

The unit vector in the scattering direction has Cartesian coordinates

$$\vec{e}_s = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta), \tag{4}$$

and the normal to the surface $\vec{n}$ at the reflection point is

$$\vec{n} = (-\cos\beta\cos\alpha, -\cos\beta\sin\alpha, \sin\beta). \tag{5}$$

Cosine of reflection angle γ_r calculated through the scalar product

$$\cos\gamma_r = -(\vec{e}_s \cdot \vec{n}), \tag{6}$$

is used in determining Fresnel coefficients. The direction of reflected ray $\vec{e}_r$ is given by the expression as follows

$$\vec{e}_r = \vec{e}_s - 2(\vec{e}_s \cdot \vec{n})\,\vec{n} = \vec{e}_s + 2\cos\gamma_r \cdot \vec{n}\,. \tag{7}$$

According to Snell's law $m_1 \sin\gamma_s = m_2 \sin\gamma_t$, the direction of the refracted ray $\vec{e}_t$ is found from the following expression

$$\vec{e}_t = \frac{m_1}{m_2}\vec{e}_s + \left(\cos\gamma_t - \frac{m_1}{m_2}\cos\gamma_r\right)\vec{n}\,, \tag{8}$$

where m_1 is the refractive index of the medium under study; m_2 is the refractive index of the medium outside the cone.

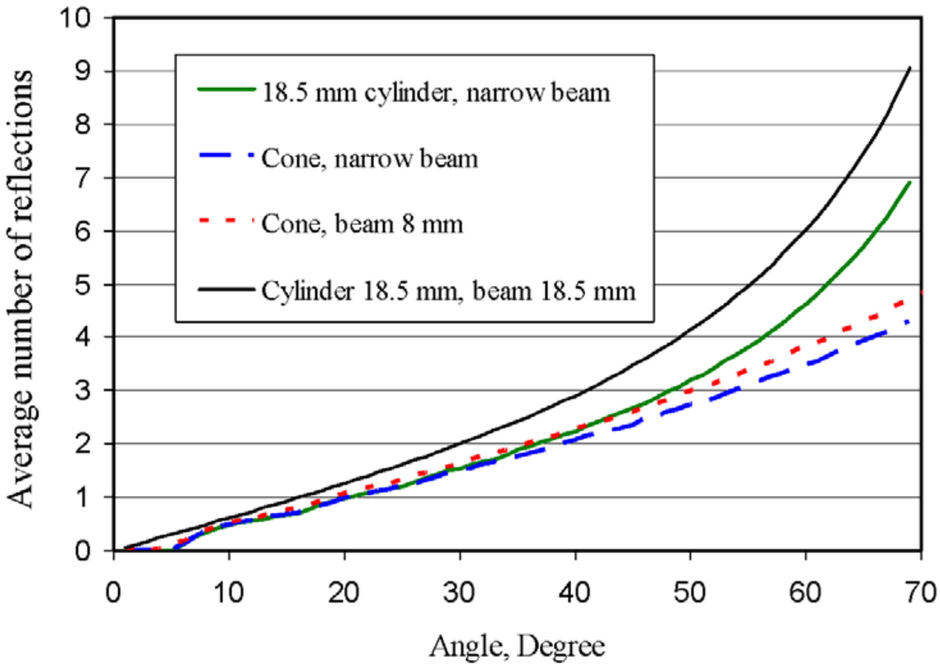
Vector $\vec{e_r}$ specifies the new direction of ray propagation at the next height z. Iterations are carried out until the ray leaves the cone. In this case, the number of reflections is summed up, the total path length and reflection losses are determined for any scattering angles. Integration is carried out over azimuthal angle φ, the full cross-section of the light beam and the entire length of the cone.

To demonstrate the advantages of using a cone cuvette compared to absorption measurement methods using a cylindrical cuvette [10–14], calculations using a simplified algorithm were carried out. In this case, refracted rays are not taken into account and calculations are reduced to determining the ray intersection point with the cone boundaries, as well as calculating the reflected ray direction (formulas (1) – (7)). Since the Fresnel reflection coefficient sharply decreases, starting from the angle of total internal reflection θ_f, the actual gain in saved energy is estimated through the integral of the indicatrix from the angle $90 - \theta_f$ to $90 - \theta_f + \beta$. Calculations show that the main advantage of measuring light absorption method using a cone cuvette is the reduction in the number of reflections and the reduction in path length variation depending on the scattering angle. The calculations were carried out for the following parameters: cone length $z_{\max} = 100$ mm, opening angle $2\beta = 6°$, light beam circle radius equals to the minimum cone radius $r_0 = 4$ mm. The simplest case of a central ray does not require integration over two variables. The calculations for a cylindrical cuvette (a special case of a cone with a zero opening angle) with radii of 4 and 9.25 mm were also carried out.

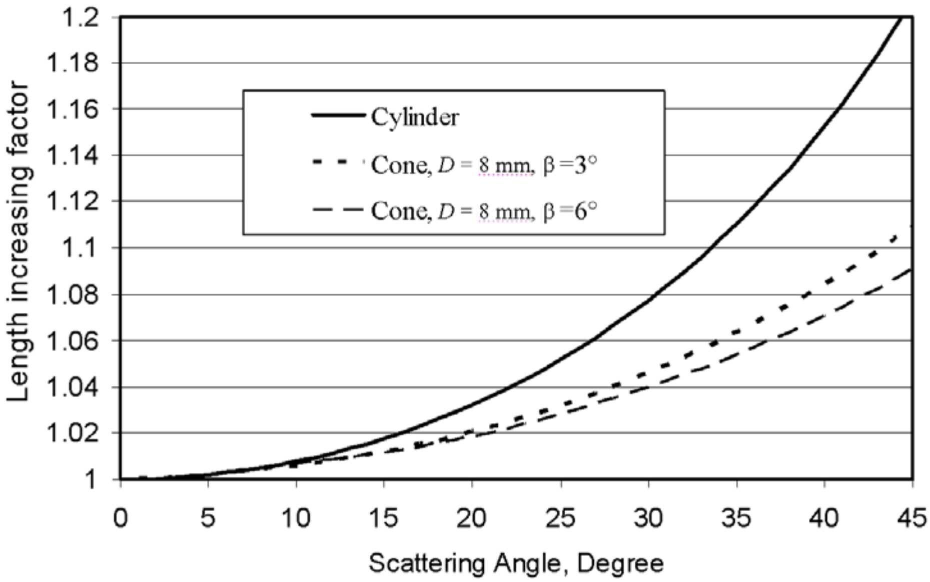
Results and discussion

The calculations of the path of scattered rays made it possible to determine that when they propagate in a cone cuvette, half the number of reflections from the cuvette walls occurs than in a cylindrical cuvette (Fig. 4).

Reduction in the number of reflections results in the new approach permitting to weaken the effect of lengthening the path of scattered rays on the spectral absorption of light by straightening the zigzag propagation of light in the cuvette (Fig. 5).



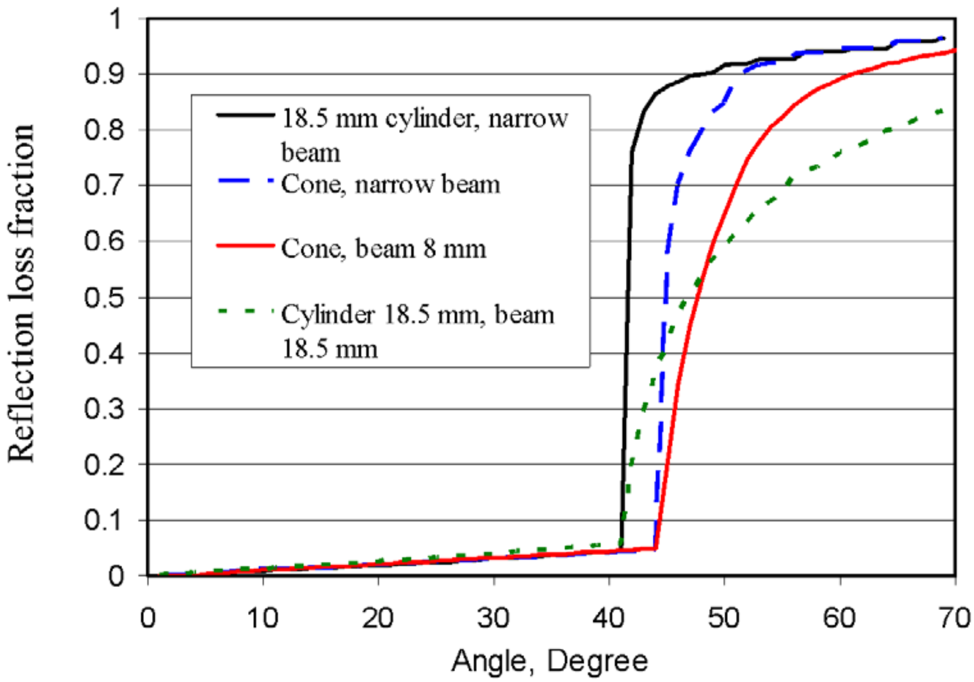
F i g. 4. Average number of reflections experienced by a beam as a function of the scattering angle



F i g. 5. Coefficient of a path length increase depending on the scattering angle for the cuvettes in the form of a cylinder and cones with the angles 6° and 12°

In a quartz cone cuvette, the region of angles where total internal reflection of scattered rays takes place becomes wider by half the cone angle, i.e., at $\beta = 3°$ in the range of 0–44.5°. According to the estimates, the proportion of scattered rays redirected to the receiving collector will increase by almost 1% for scattering indicatrices characteristic of sea water.

If the processes of reflection, refraction and transmission of light in a thin layer of quartz are neglected, then it can be argued that near the receiving collector such redirection occurs mainly as a result of a single reflection from the cuvette wall. The rays arriving at the collector after double reflection from one part of the wall to the opposite have lower intensity due to strong anisotropy of the scattering indicatrix. From the cuvette entrance to the collector, scattered rays will propagate along a zigzag path from one part of the wall to the opposite by repeated reflection along its entire length. The redirection of scattered rays as a result of single and double reflections in a cylindrical and cone cuvette occurs approximately in the same way, while for multiple reflections there is a significant difference. In a cylindrical cuvette, the propagation of scattered rays as a result of multiple reflection occurs along a uniform zigzag path with the same step. For large scattering angles, the zigzag path becomes so rapid that all rays that reached the cylindrical cuvette interface and did not experience total internal reflection eventually exit the cuvette into the air and are irretrievably lost. In a cone cuvette, the propagation of scattered rays as a result of multiple reflections from the walls occurs along an expanding zigzag path with a gradually increasing step. Accordingly, the scattered rays experience fewer reflections and therefore fewer photons are lost during interactions with the walls of the cone cuvette, as the calculation data in Fig. 6 show.



F i g. 6. Proportion of light losses in different forms of a quartz cuvette and a light beam. Calculations were carried out for the case of total internal reflection from the water – air interface, provided that another 2% of light energy is lost during reflection

According to the figure, we can see that a fraction of the energy leaving the measuring system has a characteristic step-like appearance in a device with a central narrow beam. This is explained by a sharp decrease in the Fresnel reflection coefficient after passing through the angle of total internal reflection. A strong dependence of the reflection angle on the azimuth appears in a device with a wide beam. Thus, for example, with zenith and azimuthal scattering angles equal to 90° and when the scattering point approaches the cuvette surface, the scattered light will propagate in a direction close to the tangent to the surface, which leads to specular reflection of light. Therefore, light loss as a result of ray refraction on the cuvette walls and exiting the measurement area increases more slowly. Apparently, the authors of [19] did not take into account the azimuthal dependence of the reflection angle, as evidenced by a comparison of Fig. 6 with the results of the calculations given in this study.

Consequently, a cone cuvette allows to collect more scattered rays on the receiving collector compared to a cylindrical one due to more efficient redirection of these rays from the place of light scattering in the medium to the collector. When calculating with the help of Petzold [1] indicatrices for scattered rays in the range of angles 0–44.5°, this fraction varies within the range of 88–95% with an average value of 93%.

The remaining rays with scattering angles in the range of 44.5–90° at the outer quartz–air interface are divided into two streams. In accordance with Fresnel's law, part of the scattered rays enters the space between the cuvette and the mirror cone and another, reflected from the wall, returns back to the medium. As noted above, in currently used methods (reflective-tube absorption meter), these rays are irretrievably lost and their losses have to be taken into account by introducing a correction using theoretical modeling. Although the total share of these rays is relatively small and amounts to 5–12% of the total light scattering, failure to take them into account can lead in some cases to large errors in determining absorption of light in the sea. Therefore, it is important that the scattered rays leaving the cuvette, as well as the rays propagating inside the cuvette, reach the collector as far as possible without loss. Scattered rays emerging from the aquatic media propagate in the air space between the quartz cone cuvette and the cone mirror reflector. The redirection of these rays to the collector occurs either because the light from the quartz cuvette enters the air at a greater angle than in water, or because of its repeated reflection from the external mirror cone.

Conclusion

When light propagates in the sea, its scattering processes significantly prevail over absorption in high transparency waters in the spectral window, which ensures

[1] Petzold, T.J., 1972. *Volume Scattering Functions for Selected Ocean Waters: Final Report.* Warminster, Pennsylvania: Naval Air Development Center, 82 p. doi:10.21236/ad0753474

maximum light penetration into the thickness. This indicates that sea water is a weakly absorbing light-scattering medium, where the determination of light absorption depends mainly on how effectively the receiving device collects not only the light that has traveled a certain distance in the medium after absorption, but also all the light scattered along this path. A solution to this problem has been proposed by using a new approach for determining spectral absorption of light in a quartz cone cuvette placed coaxially inside an external mirror cuvette. Calculations of the ray path geometry show that a cone cuvette permits to collect up to 90% of the scattered rays on the receiving collector due to their more efficient redirection from the light scattering place in the medium to the collector. Another ~ 8% of the rays scattered at large angles can be collected at the receiving collector due to redirection through the air by an external mirror cone reflector. The combination of a quartz cone cuvette and an external mirror cone in a new approach made it possible to collect almost all the rays scattered in a weakly absorbing medium in the receiver (while in a cylindrical medium – only 75–85%) and thereby not only eliminate their strong influence on the light absorption determination in the sea, but also to abandon the need to correct data through theoretical modeling.

REFERENCES

1. Gordon, H.R. and Morel, A.Y., 1983. *Remote Assessment of Ocean Color for Interpretation of Satellite Visible Imagery. A Review*. Coastal and Estuarine Studies. Coastal, vol. 4. New York: Springer, 114 p. https://doi.org/10.1007/978-1-4684-6280-7

2. Levin, I.M. and Kopelevich, O.V., 2007. Correlations between the Inherent Hydrooptical Characteristics in the Spectral Range Close to 550 nm. *Oceanology*, 47(3), pp. 344-349. https://doi.org/10.1134/S000143700703006X

3. Smith, R.C. and Baker, K.S., 1981. Optical Properties of the Clearest Natural Waters (200–800 nm). *Applied Optics*, 20(2), pp. 177-184. https://doi.org/10.1364/AO.20.000177

4. Lee, Z., Wei, J., Voss, K., Lewis, M., Bricaud, A. and Huot, Y., 2015. Hyperspectral Absorption Coefficient of "Pure" Seawater in the Range of 350–550 nm Inverted from Remote Sensing Reflectance. *Applied Optics*, 54(3), pp. 546-558. https://doi.org/10.1364/AO.54.000546

5. Pope, R.M. and Fry, E.S., 1997. Absorption Spectrum (380–700 nm) of Pure Water. II. Integrating Cavity Measurements. *Applied Optics*, 36(33), pp. 8710-8723. https://doi.org/10.1364/AO.36.008710

6. Fry, E.S., Kattavar, G.W. and Pope, R.M., 1992. Integrating Cavity Absorption Meter. *Applied Optics*, 31(12), pp. 2055-2065. https://doi.org/10.1364/AO.31.002055

7. Merzlyak, M.N. and Naqvi, K.R., 2000. On Recording the True Absorption Spectrum and the Scattering Spectrum of a Turbid Sample: Application to Cell Suspensions of the Cyanobacterium Anabaena Variabilis. *Journal of Photochemistry and Photobiology B: Biology*, 58(2-3), pp. 123-129. https://doi.org/10.1016/S1011-1344(00)00114-7

8. Pogosyan, S.I., Durgaryan, A.M., Konyukhov, I.V., Chivkunova, O.B. and Merzlyak, M.N., 2009. Absorption Spectroscopy of Microalgae, Cyanobacteria, and Dissolved Organic Matter:

Measurements in an Integrating Sphere Cavity. *Oceanology*, 49(6), pp. 866-871. https://doi.org/10.1134/S0001437009060125

9. Glukhovets, D.I., Sheberstov, S.V., Kopelevich, O.V., Zaitseva, A.F. and Poghosyan, S.I., 2018. Measuring the Sea Water Absorption Factor Using Integrating Sphere. *Light & Engineering*, 26(1), pp. 120-126. https://doi.org/10.33383/2016-079

10. Clarke, G.L. and James, H.R., 1939. Laboratory Analysis of the Selective Absorption of Light by Sea Water. *Journal of the Optical Society of America*, 29(2), pp. 43-55. https://doi.org/10.1364/JOSA.29.000043

11. Zaneveld, J.R.V. and Bartz, R., 1984. Beam Attenuation and Absorption Meters. In: M. A. Blizard, ed., 1984. *Proceedings SPIE*. SPIE. Vol. 0489: Ocean Optics VII, pp. 318-324. https://doi.org/10.1117/12.943318

12. Zaneveld, J.R.V., Kitchen, J.C. and Moore, C.C., 1994. Scattering Error Correction of Reflecting-Tube Absorption Meters. In: J. S. Jaffe, ed., 1994. *Proceedings SPIE*. SPIE. Vol. 2258: Ocean Optics XII, pp. 44-55. https://doi.org/10.1117/12.190095

13. Zaneveld, J.R.V., Bartz, R. and Kitchen, J.C., 1990. Reflective-Tube Absorption Meter. In: R. W. Spinrad, ed., 1990. *Proceedings SPIE*. SPIE. Vol. 1302: Ocean Optics X, pp. 124-136. https://doi.org/10.1117/12.21439

14. Zaneveld, J.R.V., Kitchen, J.C., Bricaud, A. and Moore, C.C., 1992. Analysis of in-Situ Spectral Absorption Meter Data. In: G. D. Gilbert, ed., 1992. *Proceedings SPIE*. SPIE. Vol. 1750: Ocean Optics XI, pp. 187-200. https://doi.org/10.1117/12.140649

15. Jonasz, M. and Fournier, G.R., 2007. *Light Scattering by Particles in Water. Theoretical and Experimental Foundations*. Amsterdam: Academic Press, 704 p. https://doi.org/10.1016/B978-0-12-388751-1.X5000-5

16. Mankovsky, V.I. and Mankovskaya, E.V., 2020. Spatial Variability of Water Optical Characteristics in the Southern Mediterranean Sea in Spring (May, 1998). *Physical Oceanography*, 27(1), pp. 48-59. https://doi.org/10.22449/1573-160X-2020-1-48-59

17. Moore, C.C., Bruce, E.J., Pegau, W.S. and Weidemann, A.D., 1997. WET Labs AC-9: Field Calibration Protocol, Deployment Techniques, Data Processing, and Design Improvements. In: S. G. Ackleson and R. J. Frouin, eds., 1997. *Proceedings SPIE*. SPIE. Vol. 2963: Ocean Optics XIII, pp. 725-730. https://doi.org/10.1117/12.266391

18. Röttgers, R., McKee, D. and Woźniak, S.B., 2013. Evaluation of Scatter Corrections for AC-9 Absorption Measurements in Coastal Water. *Methods in Oceanography*, 7, pp. 21-39. https://doi.org/10.1016/j.mio.2013.11.001

19. McKee, D., Piskozub, J., Röttgers, R. and Reynolds, R.A., 2013. Evaluation and Improvement of an Iterative Scattering Correction Scheme for in Situ Absorption and Attenuation Measurements. *Journal of Atmospheric and Oceanic Technology*, 30(7), pp. 1527-1541. https://doi.org/10.1175/JTECH-D-12-00150.1

Submitted 05.06.2023; approved after review 26.12.2023;
accepted for publication 18.01.2024.

About the authors:

Mikhail E. Lee, Chief Researcher, Marine Hydrophysical Institute of RAS (2 Kapitanskaya Str., Sevastopol, 299011, Russian Federation), DSc (Phys.-Maths), Professor, **ORCID ID: 0000-0002-2292-1877**, **ResearcherID (WOS): R-4344-2018**, **Scopus Author ID: 56142710400**, michael.lee.mhi@gmail.com

Evgeniy B. Shybanov, Leading Researcher, Marine Hydrophysical Institute of RAS (2 Kapitanskaya Str., Sevastopol, 299011, Russian Federation), DSc (Phys.-Maths), **ORCID ID: 0000-0001-7943-305X**, **ResearcherID: ABB-9097-2021**, **Scopus Author ID: 6507075380**, shybanov@mail.ru

Contribution of the co-authors:
Mikhail E. Lee – basic concept, text writing, analysis of results

Evgeniy B. Shybanov – algorithm and calculation program, analysis of results, description of the calculation method, proposals for improving the design of the device

The authors have read and approved the final manuscript.
The authors declare that they have no conflict of interest.