Laboratory and flow-through optical spectral probes to measure water quality and content

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ABSTRACT

A new set of two optical spectral probes developed to measure content of organic and inorganic constituencies suspended and dissolved in natural water is proposed. The set is capable to measure spectral attenuation and absorption coefficients of light, total amounts of organic and terrigenic hydrosoles suspended in water, and amount of organic matter dissolved in natural water. It can be used to monitor water quality and measure optically active ingredients in oceans, lakes and other natural water basins.

Keywords: Optical probe, natural water, dissolved matter, suspended matter, hydrosole, dissolved carbon, beam attenuation, absorption, water quality.

1. INTRODUCTION

This paper describes a new set of optical spectral probes (SOSP) developed to measure content of organic and inorganic constituencies suspended and dissolved in natural water. The SOSP is capable to measure total amounts of organic and terrigenic hydrosoles suspended in water, and amount of organic matter dissolved in natural water. It can be used to monitor water quality and measure optically active ingredients in ocean, lake and other natural waters. The probes utilize optical spectra of absorption and luminescence of natural waters to measure amounts of optically active ingredients. They were tested in situ in Sevastopol Bay and the results of measurements are compared with the data obtained with other independent optical probes.

This paper displays results of extensive measurements of water quality and water content made with the SOSP. The presented results show that these probes could successfully monitor amounts of organic and inorganic hydrosoles and dissolved organic matter in natural waters. The presentation also shows how proposed new set of probes can be utilized to verify and calibrate optical remote sensing data measured from airborne and spaceborne carriers.
2. SCHEMATICS AND THE WORK OF THE OSP PROBES

We describe here two optical probes that differ in their goals, but based on the same principle. The goal to the first device OSP-IPO is to measure beam attenuation coefficient of natural water. The goal of the second device is to measure absorption coefficient of natural water. The main idea of both probes is to employ a double-pass measurements, measurements that are identical but differ only by the attenuation path, and to estimate beam attenuation coefficient by the ratio of these two measurements. This approach eliminates the need to correct results on refraction coefficients of a cell and parasitic Fresnel reflections from the cell and illuminator surfaces. The device based on this approach does not require calibration with pure water.

2.1. Optical Spectral Probe OSP-IPO

The Optical Spectral Probe OSP-IPO [1] is designed to measure spectral attenuation of directed light (see Fig. 1). The OSP probe consists of an optical-mechanical module, a double-path cell, a differential monochromator, a photo-receiver FEU-100, a high-voltage power source, and a control and processing module. The light stream emitted by a halogen lamp is splitted into two parallel streams by a system of flat mirrors, and, passing through iris and mechanical shutter falls on collimated lenses. Two collimated light streams reflected by the system of two flat mirrors enter a double-pass cell, and, reflected from another two mirrors, focus on an input slot of a monochromator. The monochromator, made of a flat diffraction array, splits light stream into spectral components in the range of 390 - 700 nm. Registration of output spectral stream is accomplished by a photoreceiver FEU-100. The analog output from a photoreceiver is converted to a digital one by the processing module.

When a probe cell is filled with water, the resulting signal is proportional to the spectral clarity of the water. The use of a double-pass cell allows us to measure spectral clarity directly without corrections on refractive indices and Fresnel reflections in the cell. The use of a double-pass cell with the adjustment of anode sensitivity of a photoreceiver allows us to increase dynamic range of measurements to 10-20 1/m without sacrificing precision of measurements in the whole range of 0.01 to 20 1/m.

If we have two passes, \( l_1 > l_2 \), then the light streams from these passes would be:

\[
E_1 = q E_0 e^{-c l_1}, \quad E_2 = q E_0 e^{-c l_2},
\]

(1)

here \( E_0 \) is a light stream from the source, and coefficient \( q \) is determined by refractive indices and internal Fresnel reflections. By taking a natural logarithm of the ratio of these streams, we have the following equation that determines beam attenuation \( c \):

Fig. 1. External view of the Optical Spectral Probe (OSP-IPO) to measure spectral beam attenuation coefficient of natural water.
Fig. 2. Schematics of the Optical Spectral Probe (OSP-II) to measure spectral absorption of natural water.

Measurements of spectral attenuation coefficient $c$ are based on measurements of spectral energies of two monochromatic light beams with different paths in water.

### 2.2. Optical Spectral Probe OSP-II

The Optical Spectral Probe OSP-II is designed to measure spectral absorption of directed light (see Fig. 2). It consists of an optical-mechanical spectral unit, a photometric sphere with enclosed two-pass flow-through cell, photomultiplier FEU-114, a high voltage power supply, and an electronic module. Optical-mechanical spectral unit consists of a light source, scanning monochromator with a spherical diffraction array (1200 lines/mm), a collimating lens, a mirror modulator and mirrors, that form light fluxes on input surfaces of two optical glass cells of different length. The light source, which consists of a halogen lamp KGMN-27-17, a lens, and a spherical mirror, forms light flux on an input slot of scanning monochromator. The width of the input slot (1 mm) determines required light energy.

A monochromator with a spherical diffraction array has the most optimal linear dispersion, spectral resolution, and aperture ratio. A concave monochromator array accepts parallel beam of light created by a collimative spherical mirror. In order to achieve minimal aberration the center of spectrogramm is placed near the normal to the array. Linear dispersion of monochromator, that is manufactured according to Wordsworth scheme with spherical array, depends on the following array properties [2]: radius of an array, $r$; order of a diffraction spectrum, $k$; number of lines on a length unit, $N$; and property of the optical schematics, striking angle of the light beam, $\varphi$:

$$\frac{d\lambda}{dL} = \frac{(1 + \cos \varphi)}{(r k N)} = \frac{(1 = \cos 25^\circ)}{(250 \cdot 1 \cdot 600)} = 1271 \text{nm/mm},$$

(3)
Consequently, for the spectral resolution of 5 and 10 nm, the width of the input slot should be 0.39 and 0.79 millimeters, respectively.

Monochromatic light flux exiting monochromator slot is directed to the splitting unit. The splitting unit divides the light flux into two identical fluxes directed to the short and long optical cells. At the same time the mirror modulator modulates both fluxes with opposite phases. The optical paths for long and short cells are identical, because the illumination unit and monochromator are the same for both fluxes, and spectral properties of mirror modulator and deflecting mirror are identical. The illuminators of long and short cell are also identical.

Light fluxes that pass through the long and short cells are absorbed and scattered. The scattered light radiance is integrated by a photometric sphere and returned to the cells. As a consequence, the attenuation of light directed to a cell placed in a photometric sphere is due only to absorption, so we can write similar to (1) equations where the attenuation coefficient $c$ is replaced by the absorption coefficient $a$:

$$E_{o1} = q_o E_{o0} e^{-a l_1}, \quad E_{o2} = q_o E_{o0} e^{-a l_2}.$$ (4)

here $E_{o0}$ is a light stream from the source, and coefficient $q_o$ is determined by refractive indices and internal Fresnel reflections in cells placed into photometric sphere. By taking the natural logarithm of the ratio of these streams, we have the following equation that determines absorption coefficient $a$:

$$a = \frac{1}{(l_1 - l_2)} \ln \left( \frac{E_{o2}}{E_{o1}} \right).$$ (5)

The interior of a photometric sphere, that contains two similar but unequal flow-through cells, is coated with a diffuse scattering white layer. The established light regime inside this sphere depends on an absorption of light in long and short cells. The inegrated light energy is registered by a photoreceiving unit which is built around a photomultiplier FEU-114. The power supply to a photoreceiving unit can control its sensitivity of the probe by varying anode voltage on a photomultiplier. This method allows us to drastically increase the range of measurements of absorption coefficient. The spectrum scanning unit consists of a rotating cylinder with a forward and backward moving slot. The electronic control unit monitors and controls all operations of this probe. The feature of consecutive time strobing for both optically modulated fluxes allows to integrate both channels separately during the spectral scan.

A method of double optical base, applied to the absorption coefficient measurements, has the same advantages as a double-base method of measurements of attenuation coefficient: direct measurements, absence of influences by external conditions and spectral properties of optical elements and photometric sphere, expansion of dynamic range of measurements with the same calibration coefficients.

The technical characteristics of both probes are given in Table 1 [1, 3].

### 3. EXAMPLES OF MEASUREMENTS

The results of spectral measurements of beam attenuation coefficient in different coastal areas of World Ocean with high concentrations of suspended and dissolved ingredients are shown in Fig. 3.
Table 1. Technical specifications of SOSP probes.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Probe</th>
<th>OSP-IPO</th>
<th>OSP-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range of Measurements, 1/m</td>
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<td>0.01 - 5</td>
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<td>Errors of measurements, %</td>
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<td>5</td>
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<td>Output Signal</td>
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<td>Specral range, nm</td>
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<td>Spectral resolution, nm</td>
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<td>5, 10</td>
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Fig. 3. Examples of spectral measurements of beam attenuation coefficient
The numbers in Fig. 3 denotes: (1) - Estuary of La Plata river in Atlantic Ocean; (2) - Southern Ocean (close to the Antarctic UK station Faraday); (3, 4) Sevastopol Bay on the Black sea; (5) - Aegean sea; (6) - Marmara sea. The systematic measurements of spectral attenuation and absorption coefficients [4,5] in Sevastopol Bay allow us to determine concentrations of suspended and dissolved matter, organic carbon, and pollutants (see Figures 4-7) and estimate factors that influence water content.

Fig. 4. Concentration of suspended matter in a Sevastopol Bay, in mg/l.

Fig. 5. Concentration of dissolved organic matter in a Sevastopol Bay, in mg/l.

Fig. 6. Concentration of dissolved carbon in a Sevastopol Bay, in relative units.

Fig. 7. Concentration of pollutants in a Sevastopol Bay, in relative units.
CONCLUSION

The proposed set of spectral attenuation and absorption probes can be used with the submersible probes [6] and phase function measurement devices [7] to obtain a full set of spectral inherent optical properties and concentrations of suspended and dissolved matter [4]. This allows us to estimate visibility and properties of laser light propagation in seawater, as well as water quality itself.

ACKNOWLEDGMENTS

One of the authors (VIH) thanks continuing support at the Naval Research Laboratory (NRL) through the Hyperspectral Signatures 73-8028-B2 program. This article represents a NRL contribution PP7330—02—61.

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Ocean Remote Sensing and Applications

Robert J. Frouin
Yeli Yuan
Hiroshi Kawamura
Chairs/Editors

24-26 October 2002
Hangzhou, China

Sponsored by
CSO—Chinese Society of Oceanography (China)
SPIE—The International Society for Optical Engineering