

Experimental study of the light absorption in sea water by thermal lens spectroscopy

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Abstract. Thermal lens spectroscopy is well known as highly sensitive technique enabling measurements of low absorption and concentration determination of various compounds. The optical absorption coefficients of doubly distilled water and samples of water from different places of the open Ocean and different coastal regions have been measured at 532.8 nm wavelength using this technique. The method enables sensitive, rapid and reproducible determination of small variations of the absorption coefficient which are related with small trace contaminations in sea water.

1. Introduction

Nowadays, the optical properties of liquid water are the basic building blocks on which hydrologic optics is built. To understand the optical properties of the Oceans we must understand the optical properties of the liquid water, which is its major component. The optical properties of both pure liquid water (distilled) and salt waters have been investigated by numerous authors [1-4]. Most early absorption measurements were made by employing conventional absorption spectrophotometer techniques. These techniques require careful evaluation of the optical characteristics of the transmission cell and the preparation of water free from contaminants scattering and absorbing materials. Additionally, due to their low sensitivity require the use of long path cells. The present investigation involves the thermal lens technique that avoids many of the experimental problems associated with the earlier methods [5].

The thermal lens spectroscopy (TLS) is a photothermal technique that has been widely used with high sensitivity and versatility for determination of the absorption coefficient of nearly transparent materials [6-8]. In recent years there has been growing concern about environmental pollution and speciation of trace metals and has received particular attention. Rapid population growth combined with industrialization, urbanization and agricultural intensification has resulted in an increased consumption of natural resources and energy, massive waste production, and steadily growing environmental pollution. The purpose of the present investigation was to measure the absorption coefficient for specimens of sea water from various typical areas of the open Ocean and to analyze different effects of dissolved and suspended materials in the waters of several regions, including



measurements on coastal waters located near to the industries and human populated areas. Furthermore, we compare our absorption values with measurements in doubly distilled water to ascertain in what particulates the sea water differs from distilled water in its optical properties. Information would thus be gained as to whether the salts in solution or any other contaminant exert an appreciable effect on the general transparency, and particularly whether they have any selective action on the absorption coefficient.

A further important object of the present undertaking was to determine to what degree the differences in transparency of various Ocean waters could also be correlated with measurements obtained by other conventional physicochemical methods frequently used in Oceanography.

2. Materials and methods

2.1. Collection of water samples

The locations from which water samples were collected (see Figure 1) were chosen so as to cover the entire range of transparencies or contaminations currently found in the Ocean and coastal areas.



Figure 1. Locations from where water samples were obtained

2.2. Experimental method

The dual-beam thermal lens experimental set-up (see figure 2) is composed of two blocks as follows:

Probe beam and recording block. The He–Ne laser (632.8 nm, 10 mW, Spectra Physics) generates the probe beam. This beam passes through a 10 cm L_1 and 30 cm L_2 focal-length lenses, resulting in a 4 mm width near collimated probe beam. This beam is reflected by mirrors E_1 and E_2 , passes through the dichroic beam combiner $Div.D$, and the sample M (contained in a 1 cm quartz cuvette). The dichroic mirror $E.D$ then reflects the beam towards the 0.5 mm pinhole A and the photodetector D (model DET 110/M, Thorlabs). The output signal of the photodetector is then transformed by the current pre-amplifier Amp (model SR570, Stanford Research Systems) and introduced into the digital oscilloscope Osc (model TDS 3052, Tektronix), where the signal is

digitized, saved, and processed statistically. The radiant flux of the probe beam at the sample surface is 0.5 mW .

Excitation beam block. The second harmonic of a diode pumped Neodymium Yttrium Aluminum Garnet (Nd:Yag) CW laser (model GSF32–200, 532.8 nm , 200 mW , Intelite) delivers the excitation beam through the shutter T (model 846, Newport Corporation), the beam splitter $Div.D$, and the 180 mm focal length lens L_3 to the beam combiner $Div.D$, which reflects it to the sample M . The excitation beam passes from the left to the right through the sample cell. The dichroic mirror $E.D$ block the excitation beam preventing it from reaching the pinhole A and the photodetector. The beam transmitted through the beam splitter $E.D$ is sensed by the photodetector Ref (model DET 110/M, Thorlabs), which transforms the incident radiant flux into a synchronization signal for the oscilloscope.

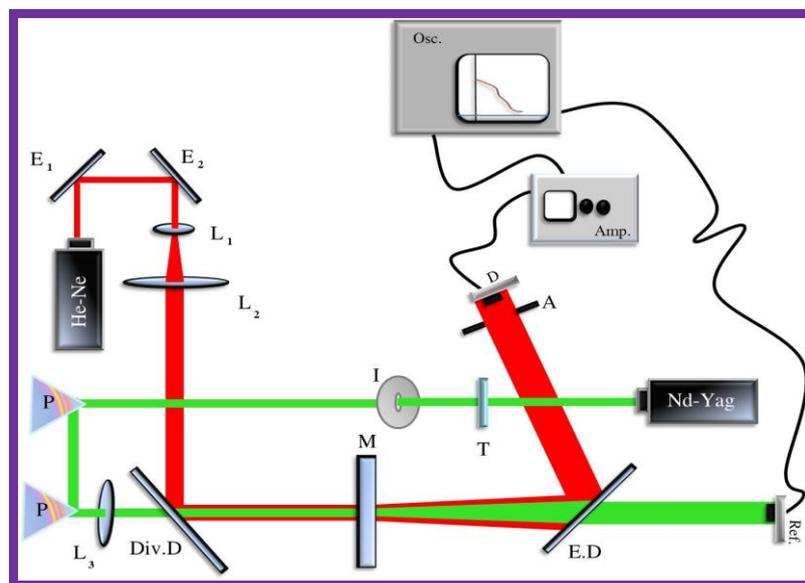


Figure 2. Dual beam TL experimental setup for absorption measurements. E_1 , E_2 mirrors; L_1 , L_2 lenses; $Div.D$ dichroic mirror; M sample; $E.D$ dichroic mirror; A pinhole; D photodetector; Amp current preamplifier; Osc oscilloscope; T shutter; I beam expander; P prism, L_3 lens, Ref reference photodetector.

Measurements were taken according to the following procedure: the shutter T modulates the beam with a period of 10 s , and for each sample the signal was obtained from the average of 128 recordings at the digital oscilloscope. Then the experimental TL signal can be measured as [8]

$$S(z,t) = \frac{T(z,t) - T_0}{T_0} \quad (1)$$

where T_0 is the probe light's transmittance through an aperture with no excitation beam present and $T(z,t)$ is the probe beam's aperture transmittance in the presence of the excitation beam. As we showed before, in a stationary situation, the TL signal is related to the photothermal parameters of the sample by the following expression [8]

$$S(z,t) = \frac{\pi P_e \alpha l}{2 \lambda_p k} \frac{dn}{dT} \quad (2)$$

where P_e is the total excitation light power, α , l , k and dn/dT are the sample's absorption coefficient, thickness, thermal conductivity, and temperature coefficient of the refractive index, respectively. z is the sample's position with respect to the waist of the excitation beam radius, t is the time and λ_p is the probe beam wavelength. Finally the absorption coefficient can be obtained as

$$\alpha = \frac{S2\lambda_p k}{\pi P_e l dn/dT} \quad (3)$$

Therefore, the measurement methodology can be resumed as follows: the experimental TL signal $S(z,t)$ is measured from the experimental data using equation (1), then the corresponding absorption coefficient is calculated using equation (3) with the rest of the photothermal parameters of water very well known, $dn/dT = 0.8 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$, $k = 5.95 \times 10^{-3} \text{ Wcm}^{-1} \text{ } ^\circ\text{C}^{-1}$ and fixed experimental values $l = 1 \text{ cm}$, $\lambda_p = 632.8 \text{ nm}$ and $P_e = 57 \text{ mW}$.

3. Results and discussion

3.1. Absorption measurements

In figure 3 the nonprocessed signal obtained at the digital oscilloscope for the sample number 10 is shown. In the figure we indicate the values of the nonperturbed probe light aperture's transmission T_0 and the probe light's aperture transmission $T(z,t)$ in the presence of the excitation beam. The excitation power used in this experiment is 57 mW , the TL signal is then calculated with equation (1) ($S = -0.017$) and the absorption coefficient for this sample was calculated with equation (3) as $\alpha = 8.90 \times 10^{-4} \text{ cm}^{-1}$. Additionally, the absorption coefficient for the double distilled water sample was measured as $\alpha = 4.5 \times 10^{-4} \text{ cm}^{-1}$.

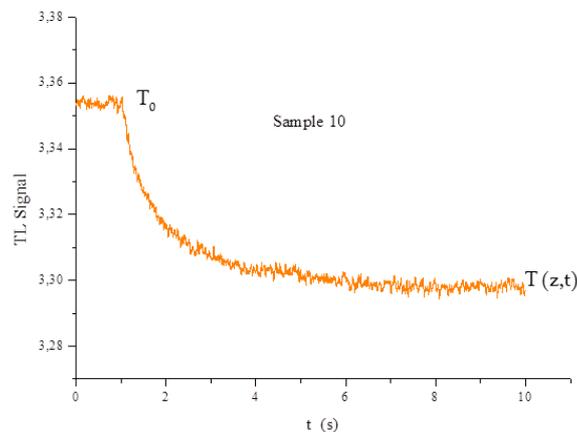


Figure 3. Nonprocessed TL signal for sample number 10 as a function of time for an excitation power of 57 mW . The values of the probe beam aperture's transmission in the absence (T_0) and in the presence $T(z,t)$ of the excitation beam are indicated.

We have also performed similar thermal lens measurements for the rest of collected samples and the results are shown in Table 1. Absorption coefficients shown in Table 1 represent the mean value of at least three observations in all cases, what means three samples from the same place and three measurements in each sample.

Table 1. Absorption coefficient values for water samples.

Sample	α (cm ⁻¹)
1	4.73 x 10 ⁻⁴
2	5.30 x 10 ⁻⁴
3	6.30 x 10 ⁻⁴
4	8.09 x 10 ⁻⁴
5	7.20 x 10 ⁻⁴
6	8.40x 10 ⁻⁴
7	6.80 x 10 ⁻⁴
8	7.35 x 10 ⁻⁴
9	9.25 x 10 ⁻⁴
10	8.90x 10 ⁻⁴
11	8.40 x 10 ⁻⁴

3.2. Physicochemical analysis

Physicochemical parameters of water samples were determined using a multiparametric sound Horiba and the results are shown in Table 2.

Table 2. Physicochemical parameters of water samples.

Sample	pH	Electrical Conductivity (S m ⁻¹)	Temperature (°C)	Salinity (PSU)	Disolved Solids (g L ⁻¹)
1	8.11	5.63	31.2	37	35
2	8.02	5.5	30.1	36.6	35.3
3	8.07	5.48	29.9	36	35,6
4	7.95	5.6	30.0	37	37
5	7.85	5.67	30.6	38	36
6	7.92	5.57	30.96	37	36
7	7.86	5.73	30.96	38	37
8	7.87	5.74	30.93	38	37
9	7.86	5.73	30.86	38	38
10	7.99	5.46	30.53	36	38
11	8.02	5.52	30.93	37	36

3.3. Discussion

The absorption measurements of the water sample collected from the open Ocean (sample 1) differs little ($\alpha = 4.73 \times 10^{-4} \text{ cm}^{-1}$) compared to the absorption value of the doubly distilled water ($\alpha = 4.1 \times 10^{-4} \text{ cm}^{-1}$ [8] and $\alpha = 4.5 \times 10^{-4} \text{ cm}^{-1}$ in the present work); however α increases as one goes from the open Ocean toward the coastal region (see sample 2 and 3), this is due to the higher contamination in this region related with the anthropological activity (note that the sample 3 located near to the beach area presents greater absorption coefficient that the sample 2 which is located far away from the beach).

The absorption of those samples collected close to industrial and populated areas (samples 4, 5, 6, 7, 8, 9, 10, 11) is even higher but the higher value is observed for the sample 9 that was collected in the vicinity of an industrial waste dump. Note that, samples 7 and 8 collected from the same region of the sample 9 have lower value of the absorption. This result may be associated with the fact that the zone where the sample 7 and 8 were collected is very rich in mangrove plants which would also contribute to the purification of some contaminant elements in this region. In general the term mangrove refers to salt-tolerant species of tree or shrub which grow on sheltered shores and in estuaries in the tropics and some sub-tropical regions. They are outstandingly adapted to growing in sea water, which they desalinate by an ultrafiltration process. Mangroves are affected by the freshwater and nutrient supply which they receive from their catchment area, and on the other hand have a strong influence on the adjoining coastal waters and associated ecosystems, therefore we hypothesize that in this zone there is an increased activity of filtering and trapping of water-borne pollutants by mangroves. On the other hand, the sample 6 was not collected from a place located near to any population but presents high absorption because is located near a pier with high contamination activity.

The effect of salinity on absorption must be known to interpret the measured absorption values. Not accounting for the change in the absorption coefficient with salinity could lead to errors in the measurement of absorption by colored dissolved organic matter. Measurements of other optical properties, such as remotely sensed reflectance, which depends on the inherent optical properties of water, must also account for the possible effects of salinity. However, there has been little research done in studying the role of salinity on the optical properties of water at visible wavelengths [9]. The addition of ions to water causes larger, more tightly bound clusters, in which the ions are surrounded by a loose outer shell of water molecules [10]. Therefore, the salinity is expected to affect the molecular structure of water, which in terms affects its absorption properties. Changes in the scattering coefficient with increasing salinity can also influence measurements. However, the reference water used in this study has a salinity of 0 PSU, and sea water samples typically have a salinity of 35 PSU (37 PSU in the present research). In our specific measurements (see Table 2) the salinity is not significantly different from sample to sample and on the other hand the electrical conductivity, that depends on the ionic species and dissolved solids, correlated well with salinity having similar tendencies. Additionally, the absorption by particulate material or scattering absorption was also neglected because the TLM method is free of scattering. Consequently, samples collected from the open Ocean (1, 2, 3) were affected by the absorption of dissolved organic materials and these collected from the coastal zone (4, 5, 6, 7, 8, 9, 10, 11) by the organic materials but also by the waste residues of industries with additional metals and inorganic traces. Generally, the pH of open Ocean waters oscillates between 8.1 and 8.3, taking their lowest values near to the coastal areas indicating some degree of photosynthesis or organic contamination. These tendencies are similar in our measurements in which the sample of the zone I has a pH 8.11 and for coastal samples the pH decreases.

Finally, TLS is a non-specific detection technique and therefore requires prior separation of analytes species for a quantitative analysis such as metal speciation. Metal speciation refers to the identification and quantification of chelated, organometallic or free metal ions or is very important to efficiently separate their oxidation states in a particular sample. Ion chromatography (IC) [11] has become one of the most widely used analytical method for the speciation of these elements due to its potentialities. The main advantages of IC are the capability for speciation and, furthermore, on-line matrix elimination and sample preconcentration is possible using an appropriate column, which can lower the detection limits. One of the detection methods to improve the detection limits in IC is TLS. The combination of TLS and IC is a good option for quantitatively account the degree of contamination in natural and sea waters.

4. Conclusions

In this paper, a TLS method was applied for measuring the absorption in water samples obtained from different places of the open Ocean and the coastal region of the Caribbean Sea to qualitatively account for a degree of contamination due to the anthropological action of humans. Collectively, our results suggest that there is an increased degree of contamination in the coastal zone with high industrial and human activity. The accuracy of the applied method does not depend on the water salinity indicating that it is possible to account for the influence of organic, inorganic or heavy metal species. This work confirms the applicability of TLS qualitative detection of trace contaminants in water samples and the possibility of quantitative determination if combined with other separation methods.

Acknowledgments

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