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Light absorption by aquatic particles in the near-infrared spectral region

Abstract—In this study, we used a special measurement geometry with samples placed inside the integrating sphere to address whether significant absorption by aquatic particles exists in the near-infrared (near-IR) spectral region from about 700 to 850 nm. Our tests with inorganic dyes and $MgCO_3$ particles showed that placing a small sample (1 cm cuvette) inside a relatively large integrating sphere (15 cm diameter) reduced the scattering error to a negligible level with no adverse effect on the absorption measurement. Our measurements of absorption by various particle suspensions suggest that absorption is generally negligible in the near-IR regardless of the type of particles. We examined four species of phytoplankton, phytodetritus derived from phytoplankton cultures, three samples of natural assemblages of mineral particles that show distinct reddish or brownish color, and three samples of aquatic particles from coastal and inland waters that have varying proportions of organic and inorganic particles.

The spectral absorption coefficient of aquatic particles, $a_p(\lambda)$, can be determined from measurements with laboratory spectrophotometers and in situ instruments such as ac-9 (WetLabs, Inc.) and a-βeta (HobiLabs, Inc). When particle concentration is high enough, a laboratory spectrophotometer can be used to measure the particle suspension directly in a small cuvette of 1 cm pathlength. In these measurements, the sample is placed as close as possible to the detector, usually either in a scattered transmission accessory (Bricaud et al. 1983) or at the entrance port of an integrating sphere (Kirk 1994). Typically, the concentration of particles in natural seawater is relatively low, which requires a different approach to routine measurements of $a_p(\lambda)$. One approach is to concentrate water samples by collecting particles on glass fiber filters, which are then measured with a conventional bench-top spectrophotometer (Yentsch 1962; Mitchell 1990). Another approach is to make a measurement in situ with an instrument whose pathlength is of the order of 10 cm or more (e.g., Zaneveld et al. 1990).

Not all of the scattered light is detected in these absorption measurements, which is a source of error. This scattering error has been a major obstacle for resolving the question of whether significant absorption by aquatic particles exists in the near-infrared (near-IR) spectral region, specifically within the wavelength (λ) range from about 700 to 850 nm. Absorption measurements with the various techniques generally yield significant positive values in this range. In many studies, these values have been assumed to entirely represent scattering error (e.g., Roesler et al. 1989; Nelson and Robertson 1993; Zaneveld et al. 1994; Bowers et al. 1996). One simple way of correcting for this error has involved the subtraction of a null-point signal measured at some near-IR wavelength (typically, 715, 750, or 800 nm) from all other spectral values.

Although the null near-IR absorption by phytoplankton is generally accepted (e.g., Bricaud and Stramski 1990), no sufficient evidence exists that would allow rejection of the hypothesis that other marine particles absorb in the near-IR (e.g., Prieur and Sathyendranath 1981; Bricaud and Stramski 1990; Bukata et al. 1991). In coastal marine environments, the optical properties of water are often dominated by various nonliving particles (minerals, organic detritus), which are characterized by high scattering-to-absorption ratios. The accurate determination of absorption by such particles is especially difficult. In a recent study of European coastal waters, Babin et al. (in press) showed that a_p at 750 nm can represent up to 35% of $a_p(443)$. Because they used the T-R technique that is supposed to be free of scattering error (Tassan and Ferrari 1995), this result suggests that particles exhibited significant absorption in the near-IR.

In this study, we present laboratory measurements of absorption by different types of particles encountered in aquatic environments. We used a special measurement geometry with samples placed inside the integrating sphere, which allowed us to minimize the scattering error and to determine whether significant absorption exists in the near-IR.

Tests of the integrating sphere—Measurements of absorption by various samples were performed using a dual-beam spectrophotometer (Perkin Elmer, Lambda 18) equipped with a 15-cm Spectralon integrating sphere (Labsphere, RSA-PE-18). We tested the performance of the integrating sphere with two types of samples to ensure that the geometry accurately measured absorption. The first type of test sample was characterized by significant absorption with no (or negligible) scattering. These samples included aqueous solutions of different inorganic dyes ($CuSO_4$, $KMnO_4$, K_2CrO_4, and $Fe_4[Fe(CN)_6]_3$) and a solution of tea (Trader Joe's, Earl Grey Tea). The objective of the tests with these solutions was to verify that placing the sample inside the integrating sphere produced no adverse effects on the measurement of absorption. The second type of test sample was a suspension of $MgCO_3$ particles characterized by significant scattering with negligible absorption. This sample was used to verify that placement of the sample inside the sphere reduces the scattering error to a negligible level.

Prior to test measurements, the dye and tea solutions, as well as the reference pure water (Barnstead, B-Pure), were filtered through a 0.1-μm filter (Pall, Acrodisc). Absorbance measurements were made from 200 to 850 nm at 1-nm intervals using a 2-nm slit. Samples and reference water were put into a 1-cm quartz cuvette. Two measurements were made for each sample. In one measurement, the cuvette was placed outside the integrating sphere, that is, at the entrance port of the sphere. In the second measurement the cuvette was placed in a special holder (Labsphere) inside the integrating sphere, that is, at the center of the sphere. On the one hand, the geometry of the outside-sphere measurement implies much greater loss of photons due to scattering than the inside-sphere measurement. However, because the dye solutions have negligible scattering, we expect true absorption to be measured.

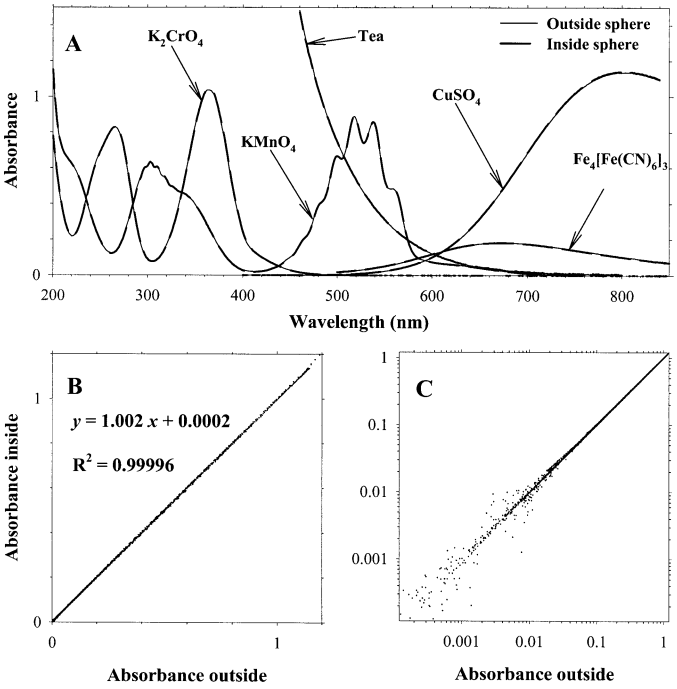

Fig. 1. (A) Absorbance spectra of various dyes measured outside and inside the integrating sphere. Two additional replicate scans were made to verify reproducibility, which is very good. Such replicates were also made for all spectra in all remaining figures. (B) Absorbance measured inside the integrating sphere as a function of absorbance measured outside the sphere. Data for all dyes and all wavelengths are shown. The regression line, the formula of the best fit, and the squared correlation coefficient are also shown. (C) As in B but on a log-log scale.

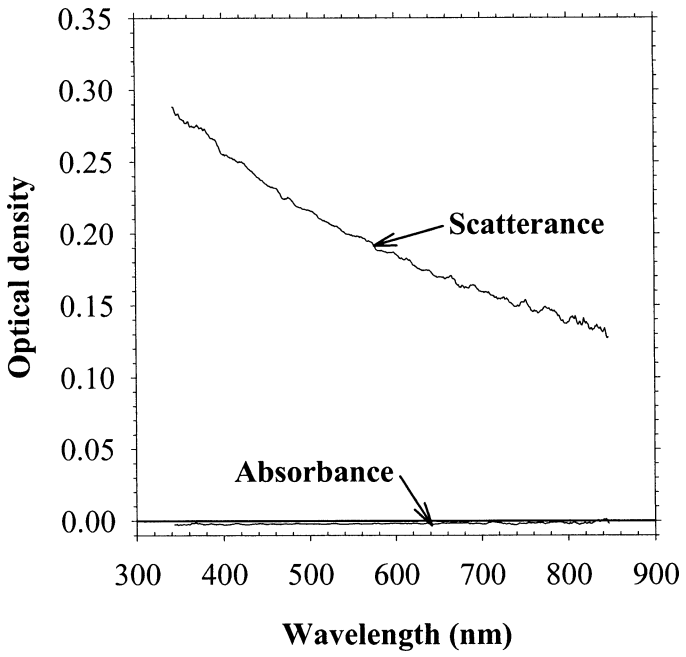

Fig. 2. Absorbance and scatterance (the scattering equivalent of absorbance) spectra of a suspension of $MgCO_3$ particles. The $MgCO_3$ particles were suspended in absolute acetone. The straight line indicates null optical density.

In fact, Rayleigh scattering is present, but it is very weak and assumed to be the same for the sample and the reference. On the other hand, it was suggested that the geometry of the inside-sphere measurement may yield amplified absorption values due to photons reentering the cuvette after reflection inside the sphere (Nelson and Prézelin 1993).

Our measurements clearly showed that absorption amplification was negligible for our geometry of inside-sphere measurement (Fig. 1A). For each dye, the spectral curves obtained from inside-sphere and outside-sphere measurements were nearly identical. The difference between these curves was so small that it can hardly be noticed in the figure. Note that these measurements cover a broad range of absorbance values, and absorption bands occur in different parts of the spectrum. When all the inside-sphere data from Fig. 1A are plotted against the outside-sphere data, a nearly perfect 1 : 1 relationship is obtained (Fig. 1B), although some noise was present at low absorbance values <0.01 (Fig. 1C). These tests led to the conclusion that the presence of a cuvette and its holder inside the integrating sphere produced negligible amplification effect and negligible perturbation to the light field within the sphere, with no adverse effect on the absorption measurement.

In contrast to our results, Nelson and Prézelin (1993) reported a nonlinear relationship between the inside-sphere and outside-sphere absorption data and generally higher values inside the sphere than outside the sphere. They used a smaller integrating sphere (76 mm diameter), which could have been more susceptible to artifacts because of the presence of a sample inside the sphere. Also, as opposed to our samples of nonfluorescent dyes, they used a chlorophyll *a* (Chl *a*) solution in acetone, which shows significant fluorescence (Rabinowitch and Govindjee 1969). This fluorescence may be partly responsible for the nonlinearity shown by Nelson and Prézelin (1993, *see* fig. 3C).

In the test measurements of the $MgCO_3$ particle suspension, the most desirable result would be a zero-absorbance signal when the sample is placed inside the integrating sphere. This sample, in a 1-cm cuvette, showed a visual effect of significant turbidity and colorless (white) appearance. With the assumption that the sample scatters light but does not absorb light, the zero-absorbance values inside the sphere would mean that the scattering error was reduced to a negligible level (i.e., nearly all scattered light was captured by the detector and only a negligible amount of scattered light escaped from the sphere through openings for sample beam and reference beam). The result of our inside-sphere measurement of the $MgCO_3$ sample confirms that the scattering error is indeed minimal for such measurement geometry (Fig. 2). The measured absorbance values were nearly zero across the examined spectrum. In fact, these values were slightly negative. This is likely because photons escape from the sphere through the sample beam port by back-reflection from cuvette walls (especially the quartz–air interface). The negative values are obtained because more reflected photons escape from the sphere in the measurement of the reference nonscattering (particle-free) medium than in the measurement of the scattering suspension of particles.

To demonstrate the scattering properties of the $MgCO_3$ suspension, we also measured the scatterance (defined here as the scattering equivalent of absorbance) of the same sample. The cuvette was placed outside the sphere at a significant distance from it. Three apertures were aligned along the beam path; two apertures between the light source and the cuvette and one aperture between the cuvette and the entrance port of the integrating sphere (which essentially acts as a detector). These apertures ensured that the effective angle of acceptance for detecting photons was only about 0.8°. This system provided an approximate measure of total scattering by the sample because only primary unscattered beam and a fraction of light scattered at extremely small angles was detected. Figure 2 shows the scatterance spectrum of the $MgCO_3$ sample, with values varying from about 0.13 to 0.29 across the spectrum. We emphasize again that this relatively strong scattering was efficiently eliminated in the absorption measurement when the $MgCO_3$ sample was inside the integrating sphere.

Measurements of absorption by various types of particles—We examined four different categories of particles, which include phytoplankton (four species), phytodetritus derived from phytoplankton (four samples), natural assemblages of mineral particles (three samples), and assemblages of aquatic particles collected in coastal and inland waters that have different proportions of organic and minerogenic particles (three samples).

Three phytoplankton species, *Chroomonas salina, Thalassiosira weissflogii,* and *Gymnodinium sanguineum,* were grown under moderate light in batch cultures in F/2 plus Si medium, and one species, *Prochlorococcus* sp., was grown in batch culture in PRO99 medium (modified from Chisholm et al. 1992). A suspension of healthy cells was used for absorption measurements. The phytodetritus samples were produced using the phytoplankton cultures mentioned above, except that *Pyrocystis fusiformis* was used in place of *C. salina.* The cultures were exposed to two freeze–thaw cycles. Between the cycles, the cultures were subject to strong ultrasound treatment and were stored in the dark for several days. Prior to absorbance measurements, the *P. fusiformis* phytodetritus was passed through a 20-μm nylon filter (Spectrum Laboratories, Spectra/Mesh) to remove large particles.

The three samples of natural assemblages of mineral particles included in this study represent different environments. The Saharan dust sample was collected in Villefranche-sur-Mer, France, in November 1996 during a strong ''red-rain'' event. Such events containing very high loads of Saharan dust are common in this region (e.g., Chester et al. 1997). To obtain dry particulate matter, the collected sample of rainfall water was evaporated at ambient temperature. The second sample represents minerogenic particles derived from glacier erosion in the north polar environment. This sample was obtained from a small block of ice floating at the sea surface in Kongsfjord (western Spitsbergen) in July 1998. The sample was collected relatively close (<2 km) to the front of major glaciers, Kongsvagen and Kronebreen, where surface waters show distinct reddish color due to significant glacial discharge of meltwater and minerogenic sediments (Beszczynska-Möller et al. 1997). The pockets within the ice block contained significant amounts of particulate matter, which was dark red in color. This particulate matter was dried at ambient temperature. The third sample was reddish soil, which was collected at the cliff shore near Palm Beach north of Sydney, Australia, in December 2000. This shore is subject to substantial erosion by the action of ocean waves.

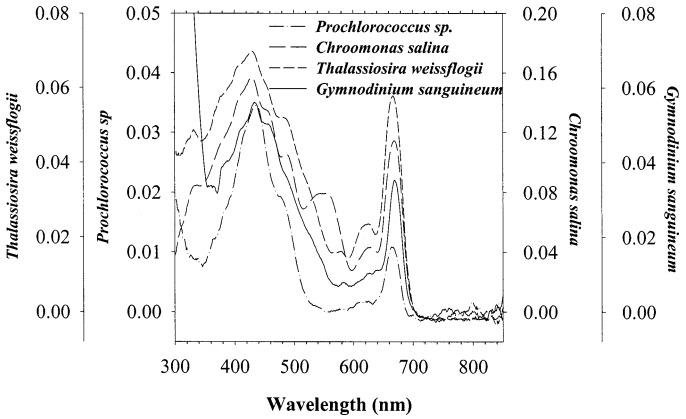

Fig. 3. Absorbance spectra of four phytoplankton species grown in batch cultures.

Prior to absorption measurements of these samples, the particles were suspended in pure deionized water, exposed to ultrasound for a few seconds, and then allowed to settle in a small beaker for about 5 min to remove large particles from the suspension. The particulate fraction that was still in suspension after the settling period was used for absorbance measurements.

The final category of samples included natural water samples that were collected at three sites in the San Diego region of Southern California: first, in San Dieguito River about 200 m from its end into Pacific Ocean; second, in Mission Bay; and third, at the pier of the Scripps Institution of Oceanography in La Jolla. These samples were concentrated by filtration of water onto 47-mm polycarbonate 0.2-μm filters (Whatman, Nuclepore) and resuspension of collected particles in a small volume of water. Ultrasound was applied to facilitate resuspension.

Absorption measurements of all samples were made on particle suspensions contained in a 1-cm quartz cuvette that was placed inside the integrating sphere. For each sample, three replicate scans of absorbance were made between 300 and 850 nm. In each case, this result was corrected for the appropriate reference. For example, in the case of phytoplankton the reference scans were made on the culture medium that was filtered through a 0.2-μm filter (Pall, Acrodisc). Similar filtration of suspension media was made for other samples to obtain the reference. All measurements were made on optically thin suspensions to avoid multiple particle–photon interactions within the cuvette. This was verified with phytodetritus and mineral particle assemblages by making measurements on samples that were diluted. These measurements showed a linear dependence of absorbance on the dilution factor within the examined range of absorbance values.

Figure 3 shows the absorbance spectra of phytoplankton species, which exhibit typical absorption bands of Chl *a* and accessory pigments. As expected, absorbance signal above 720 nm becomes null or, in fact, slightly negative. Phytodetritus spectra are characterized by enhanced absorption in

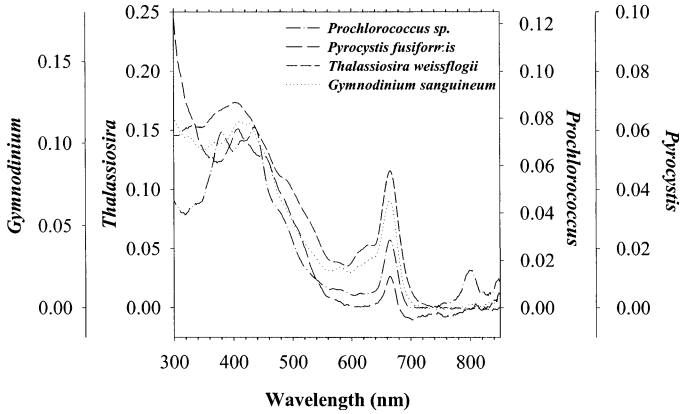

Fig. 4. Absorbance spectra of phytodetritus derived from phytoplankton cultures.

the near-UV compared with healthy phytoplankton cultures, although pigment signatures are still strong (Fig. 4). The spectral shapes are similar to those reported previously (Nelson and Robertson 1993). For phytodetritus derived from *T. weissflogii* and *G. sanguineum*, absorbance becomes null near 730 nm. Absorbance of phytodetritus derived from *Prochlorococcus* sp. is also reduced to values near zero around 730 nm but then exhibits a small absorption band of unknown origin around 800 nm. In the case of *P. fusiformis* phytodetritus, we measured slightly negative values at 700 nm and a slow increase to zero at longer wavelengths. For an unknown reason, some other samples also showed a small increase of the signal above 800 nm, but it is important to note that these changes are comparable with the level of noise observed at these extremely small absorbance values.

The absorbance spectra of natural assemblages of mineral particles all exhibit increasing values toward UV (Fig. 5). In the near-IR, the spectra are nearly flat with values close to zero above 750 nm. We emphasize that this result was observed despite these particle assemblages showing very distinct reddish or brownish color. The remaining three samples from the San Diego region exhibited a similar pattern in the near-IR (Fig. 6). In these samples, the absorption bands of Chl *a* are more or less pronounced. This result suggests that proportions of phytoplankton and nonphytoplankton particles varied between these samples. The largest relative contribution of phytoplankton is seen in the coastal ocean water from the Scripps pier and the smallest contribution in the sample from the San Dieguito River.

Our experiments suggest that absorption measurements of samples with a small pathlength (1 cm cuvette) placed inside a relatively large integrating sphere (15 cm diameter) reduce the scattering error to a negligible level. In contrast, this error is usually significant when using other techniques (e.g., sample outside the integrating sphere or reflecting tube technique). This error is illustrated in Fig. 7, which compares absorbance spectra of our Saharan dust sample measured outside and inside the sphere. The increase in the absorbance signal outside the sphere can be attributed to scattering error.

We also conclude that various samples, including phytoplankton, nonliving organic particles, mineral particles, and mixtures of organic and inorganic particles, all exhibit similar

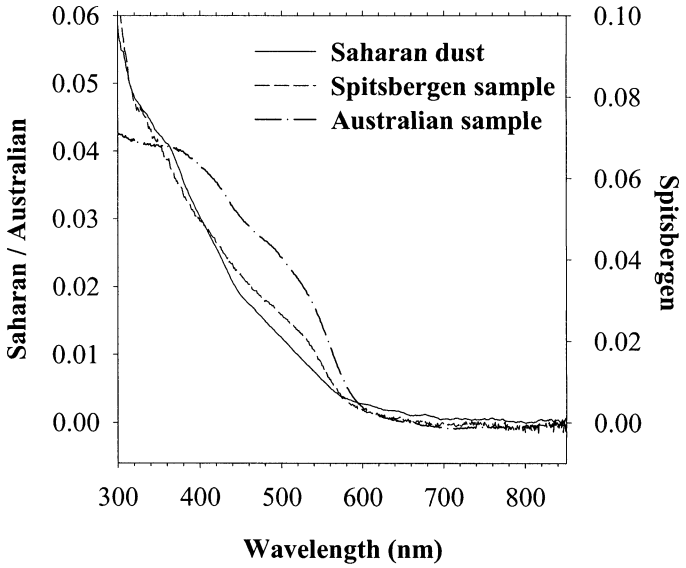

Fig. 5. Absorbance spectra of natural assemblages of mineral particles from three different environments.

absorbance pattern in the near-IR spectral region above 700 nm, that is, a nearly flat spectrum with values very close to zero. The only exception was phytodetritus derived from *Prochlorococcus* sp., which showed a small but significant absorption band of unknown origin around 800 nm. The measured absorbance in the near-IR was slightly negative for most samples, including phytoplankton that are not expected to absorb in this spectral region. These negative values are also consistent with our test made on the nonabsorbing suspension of $MgCO_3$ particles. This effect is likely attributable to differences between the sample and reference in terms of light that is reflected back by cuvette walls. Regardless of this effect and some noise observed at very small absorbance values in the

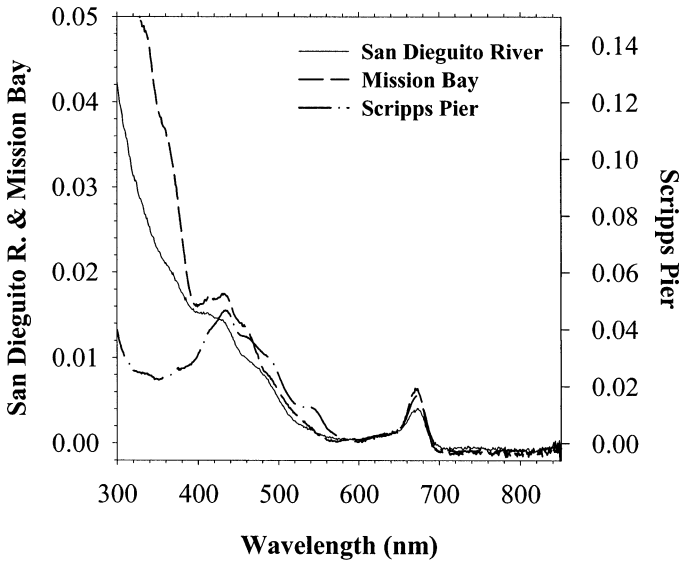

Fig. 6. Absorbance spectra of natural assemblages of aquatic particles from three locations in the San Diego region in Southern California.

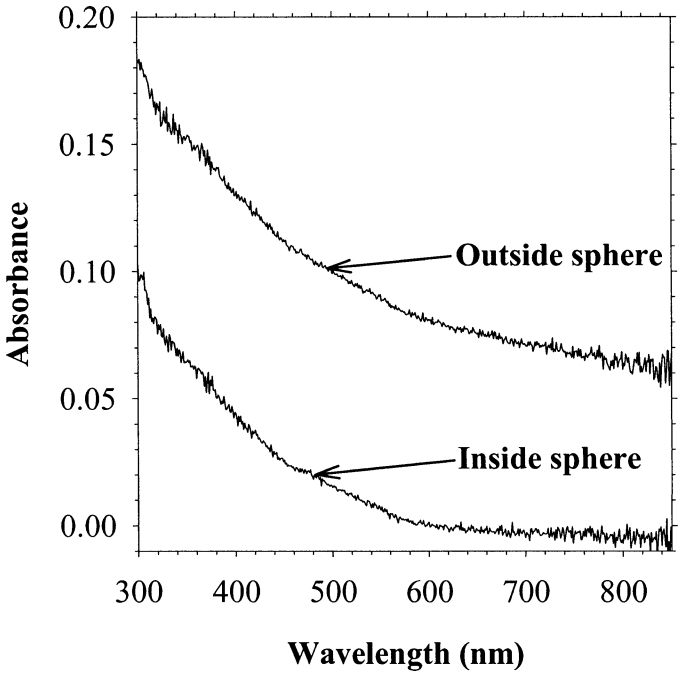

Fig. 7. Absorbance spectra of Saharan dust sample measured outside and inside the integrating sphere.

near-IR, our results suggest that absorption by various aquatic particles in this spectral region is generally negligible.

This negligible near-IR absorption supports the main assumption of the correction for scattering error that occurs in absorption measurements with commonly used instruments such as ac-9 or bench-top spectrophotometers with samples placed outside the integrating sphere or at some distance from the detector. Note, however, that our data provide no insight regarding the question of possible wavelength dependency of the scattering error in such measurements.

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