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For particulate absorption, the locations of absorption peaks were offset up to 5 nm in the integrating cavity spectra due to the use of interference filters for determining wavelength. The filter wheel has bands centered every 10 nm, while the spectrophotometer has a monochromator with 1 nm spectral resolution. Modification of the integrating cavity, presently in progress, will include replacement of the filter wheel with a monochromator.

Particulate absorption measured with the integrating cavity was similar to that measured with the glass fiber filters through a portion (500 to 700 nm) of the visible spectrum. However, from 400 to 500 nm, absorption measured on glass fiber filters. For example, at 400 nm, cavity values were only 45 to 83% of the glass fiber filter values. Possible causes of this difference are discussed.

Absorption spectra for dissolved materials measured in the integrating cavity were similar to those measured in the spectrophotometer.

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Spectral absorption coefficients measured with an integrating cavity absorption meter

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ABSTRACT

Absorption spectra (400 to 700 nm) measured with a new instrument, the integrating cavity absorption meter, were compared to those measured with standard techniques for particles (collected on glass fiber filters) or solutions (in long pathlength cuvettes). The integrating cavity absorption meter has two advantages over previously used methods: 1) low absorption signals can easily be measured due to the long effective pathlength created by the highly reflective walls of the cavity, and 2) scattering averages to zero because of the isotropic light source.

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Absorption spectra for dissolved materials measured in the integrating cavity were similar to those measured in the spectrophotometer.

2. INTRODUCTION

An understanding of the spatial and temporal variability of light absorption in the ocean is required in order to understand

the variability of attenuation, since attenuation is caused by the processes of absorption and scattering. Accurate measurements of absorption are needed for refining predictive and closure models of the optical properties of the ocean. Field measurements of total absorption and phytoplanktonic absorption are also useful for modelling rates of primary production. However, in order to measure these required absorption values for oceanic samples, two problems must be circumvented. First, the absorption by either particles or dissolved organics at natural concentrations is difficult to measure because it is low compared to the absorption by water. The absorption signal must be increased by concentrating the samples or by measuring absorption over a long pathlength. Second, suspended particles scatter light and a conventional spectrophotometer cannot distinguish scattering from absorption. Several approaches have been developed to solve these two problems. A layer of light-diffusing opal glass between the sample and light sensor decreases loss of scattered light[1]. Particles in field samples can be concentrated onto a filter[2], but a correction for pathlength amplification by scattering within the filter must be applied[3]. For dissolved materials, the absorption signal can be increased by measuring in a long pathlength cuvette[4].

A new instrument, the integrating cavity absorption meter[5,6], solves these two problems in a unique manner. The absorption signal is increased by the long effective pathlength, which is provided by the highly reflective surface of the integrating cavity. Second, scattering corrections are unnecessary because the isotropic light source makes the measurements inherently independent of scattering[6]. In this paper, we present absorption spectra measured with the integrating cavity and compare these spectra to those measured with the glass fiber filter technique (particles) and the long pathlength cuvette (dissolved).

3. METHODS

Phytoplankton cultures were grown at 20°C under a 12/12 light/dark cycle at 33 μmol photons m^{-2} s^{-1}, provided by cool-white fluorescent lamps. The culture medium was sterile-filtered artificial seawater[7] enriched with IMR nutrients[8].

Field samples were obtained in the Gulf of Mexico (30°05.09 N, 88°53.98 W) on 23 Aug. 1989 from a Naval Construction Battalion (SeaBee) hydrographic survey launch. Water was sampled using 10 l Niskin bottles. Samples were stored in plastic cubitainers (cleaned with Micro) in the dark at ambient temperature and returned to the shore laboratory. Processing occurred about four hours after sampling.

3.1. Spectrophotometer absorption

Absorption spectra for suspended particulates were measured using the technique described by Mitchell and Kiefer (1988). An aliquot (10 to 500 ml for laboratory samples; 100 to 200 ml for field samples) was filtered through a Whatman GF/F glass fiber filter (nominal pore size 0.7 μm) using low vacuum. A wet GF/F filter was used as a blank and optical density [$OD_{part}(\lambda)$] was measured by scanning from 750 to 400 nm in a dual-beam spectrophotometer (Kontron Uvikon 860). The correction for pathlength amplification [$\beta(\lambda)$] due to scattering within the glass fiber filter[9,10,3] has been determined specifically for this instrument and resembles published results[3]. Optical density at 750 nm [$OD_{part}(\lambda)$] was subtracted as a scattering correction and absorption was calculated:

$$a_{part}(\lambda) = \frac{2.303\ [OD_{part}(\lambda) - OD_{part}(750)]}{X\ \beta(\lambda)}\ , \qquad (1)$$

where X is the volume filtered (in m^3) divided by the area of the filter (in m^2).

Absorption by dissolved organics [$a_{diss}(\lambda)$] was measured for the field samples only. Wetting agents were removed from the filters (Whatman GF/C prefilter and Millipore filter, pore size 0.22 μm) by rinsing with approximately 200 ml filtered seawater. Following the rinse, 1 l of sample was filtered and the filtrate was collected. Optical density [$OD_{diss}(\lambda)$] of the filtrate was measured from 700 to 400 nm in 10 cm quartz cuvettes, with distilled water as a blank. Optical density was converted to absorption:

$$a_{diss}(\lambda) = \frac{2.303\ OD_{diss}(\lambda)}{l}\ , \qquad (2)$$

where l is the pathlength (in m).

3.2. Integrating cavity absorption

The integrating cavity absorption meter consists of a two-layer cavity with walls made from a white plastic (Spectralon, Labsphere) with high diffuse reflectivity[6] (Fig. 1). Light is introduced into the outer cavity (containing air) via six plastic optical fibers; the light reflects many times off the two Spectralon surfaces and diffuses through the inner wall of Spectralon into the sample cavity, illuminating the sample isotropically. The waveband is selected from a wheel containing 31-10 nm bandpass interference filters, centered at 10 nm intervals from 400 to 700 nm. Three fiber optics, each connected to a photomultiplier tube, monitor irradiance levels within the

system (Fig. 1). Sensors S1 and S2 monitor incoming irradiance while sensor S0 measures irradiance from within the sample cavity, i.e., net irradiance after passing through the sample. Irradiance ratios (S1/S0 or S2/S0) are proportional to the light absorbed by the sample. Two different measurements of absorption (channels 1 and 2) can be determined using these two ratios. The absorption of a standard solution is measured in the spectrophotometer and used to calibrate these irradiance ratios. Pope et al. (this volume) describe the instrument and calibration procedure in greater detail.

Data presented here were obtained with the model II (120 ml sample volume) integrating cavity[6]. The cavity was calibrated with a single concentration of irgalan black (5 mg l^{-1}; Ciba-Geigy Corp.) and the empty cavity, which was interpreted as zero absorption. Spectrophotometer values represent absorption by irgalan black only, since distilled water is used as a blank, while cavity values represent absorption by irgalan black plus water. To compensate for this difference, assumed values for absorption by water[11] were added to the spectrophotometer absorption values. Calibration coefficients at each wavelength were obtained from the slopes between the points for the irgalan black standard (with water absorption added) and the empty cavity. This calibration process has been modified for later measurements[6].

The integrating cavity measures absorption by all the absorbing components [$a_{total}(\lambda)$], including water, dissolved materials, and particles, while the glass fiber filter method measures absorption by the particles alone. Absorption spectra for particles [$a_{part}(\lambda)$] and dissolved materials [$a_{diss}(\lambda)$] can be calculated if absorption spectra for the filtrate [$a_{filt}(\lambda)$] and distilled water [$a_{water}(\lambda)$] are also measured.

$$a_{part}(\lambda) = a_{total}(\lambda) - a_{filt}(\lambda) \quad (3)$$

$$a_{diss}(\lambda) = a_{filt}(\lambda) - a_{water}(\lambda) \quad (4)$$

Fig. 2 illustrates this for a sample from the Gulf of Mexico.

4. RESULTS AND DISCUSSION

Absorption spectra measured with the integrating cavity and the glass fiber filters are shown for the diatom Chaetoceros gracilis (Fig. 3), the chlorophyte Dunaliella tertiolecta (Fig. 4), the prasinophyte Micromonas pusilla (Fig. 5), and two samples from the Gulf of Mexico (0 and 11 m; Figs. 6 and 7). For all samples, the two methods measured similar absorption values from 500 to 700 nm. However, two differences were apparent. First, the locations of absorption peaks were offset. For example, the red chlorophyll a peak occurred at 673 nm in the glass fiber filter spectrum for C. gracilis while it occurred at

680 nm in the integrating cavity spectrum (Fig. 3). The filter wheel used to determine wavebands in the integrating cavity aliased the absorption peaks. The interference filters are centered every 10 nm on the 10 nm; no band is centered at the red chlorophyll a absorption peak. The spectrophotometer has a monochromator with 1 nm spectral resolution and the absorption peaks are found at the expected wavelengths. This problem of peak offset will be solved by replacing the filter wheel with a monochromator.

Absorption measured in the cavity was lower than that measured on the glass fiber filters from 400 to 500 nm (Figs. 3 to 7). At 400 nm, cavity absorption was only 45 to 83% of glass fiber filter absorption (Table 1). The cause of this difference is uncertain but several hypotheses have been considered. The first hypothesis is that a wavelength-dependent scattering artifact, caused by a precipitate present in the culture medium (note the high absorption in the blue part of the spectrum for M. pusilla, Fig. 5), created an apparent increase in absorption on the glass fiber filters. This scattering artifact was ruled out as a possible explanation when a similar difference was seen in the blue region of the spectrum for dissolved food coloring (Fig. 8). Second, detrital particles[12,13,14] and bacteria[15] have high absorption in the blue, similar in shape to the difference between glass fiber filter and cavity spectra. However, if present, unidentified absorbers would have been in both the integrating cavity and on the glass fiber filters and would contribute to absorption as measured by both methods. Unidentified absorbers cannot explain the observed difference. A third explanation is that fluorescence by the sample produced light in the cavity. Fluorescence, if detected in the integrating cavity but not in the spectrophotometer, would cause an apparent decrease in absorption. However, for phytoplankton, the quantum yield of fluorescence is only 3%[16] while the observed differences in absorption are as high as 50% (Table 1). Fluorescence cannot account for the observed difference. A fourth possibility is that a calibration artifact caused the observed difference in the blue. The calibration process utilizes a measurement of irradiance ratios (S1/S0 and S2/S0) with the cavity empty as zero absorption; this process assumes that the optical properties of the cavity do not change when it contains air instead of water. This last suggestion remains to be tested. Unfortunately, this step of the calibration cannot be replaced with a water baseline (as suggested by Pope et al., this volume) unless very clean, organic-free water, with an unchanging absorption spectrum and magnitude less than that of clear oligotrophic ocean water, is available for use in the calibration process.

One advantage expected from the integrating cavity is an ability to measure low absorption signals without concentrating the sample. In order to examine this in the laboratory,

M. pusilla was diluted with culture medium to a chlorophyll a concentration of 0.44 mg m^{-3}. This concentration is similar to that found in oligotrophic oceans. The results for this dilute culture of M. pusilla followed the pattern previously described: absorption peaks were offset due to the filter wheel; the two methods gave similar results from 500 to 700 nm; and cavity values were lower than glass fiber filter values in the blue region (Fig. 5). In addition, the cavity spectra were not as smooth as the glass fiber filter spectra. For example, there was a small spike at 460 nm (Fig. 5). These spikes probably resulted from small calibration errors and can be eliminated with a regression that includes more standard concentrations than used in these preliminary measurements. This modification of the calibration process has been used for later work[6]. Despite these differences, the agreement between results from 500 to 700 nm at low chlorophyll a concentration and low absorption magnitudes suggests that the integrating cavity is capable of measuring samples typical of the oligotrophic ocean.

The spectra for dissolved organics (Gulf of Mexico samples; Fig. 9) exhibited the expected exponential decrease with increasing wavelength, with similar magnitudes for cavity and spectrophotometer results. Spectra for both 0 and 11 m are shown together due to their similarity. For oligotrophic ocean samples, $a_{diss}(\lambda)$ will be much lower (e.g., 0.01 to 0.09 m^{-1} at 440 nm[17]) than observed for these Gulf of Mexico samples; a field test at a lower absorption value needs to be performed.

5. CONCLUSION

Absorption measured with the new integrating cavity absorption meter compared well with standard techniques for both particles (from 500 to 700 nm) and dissolved materials (throughout the visible spectrum). The observed discrepancy in peak location can be solved by replacing the filter wheel with a monochromator. The underestimate of absorption by the cavity in the blue region of the spectrum requires further investigation. The integrating cavity absorption meter solves the problems of low signal and scattering in a unique way and promises to improve our ability to accurately measure absorption in the ocean.

6. ACKNOWLEDGEMENTS

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Table 1: Absorption (m^{-1}) at 400 nm measured in the integrating cavity [$a_{cav}(400)$] and the spectrophotometer [$a_{spec}(400)$] and the ratio of cavity to spectrophotometer values.

Sample	$a_{cav}(400)$	$a_{spec}(400)$	ratio
C. gracilis	1.730	2.091	0.83
D. tertiolecta	0.659	0.928	0.71
M. pusilla	0.017	0.038	0.45
Gulf 0 m	0.244	0.456	0.54
Gulf 11 m	0.428	0.587	0.73
Food color	0.290	0.485	0.60

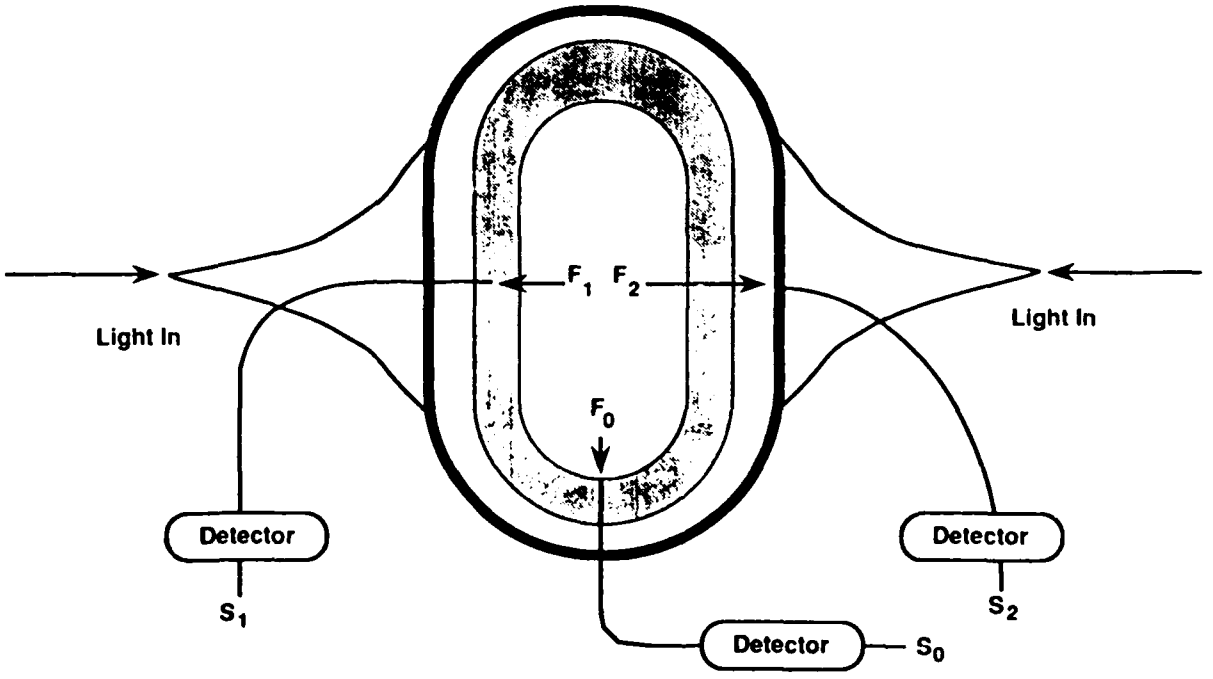

Fig. 1. Schematic of the integrating cavity absorption meter. F0, F1, and F2 indicate the three fiber optics leading from the cavity to the photomultiplier tubes, S0, S1, and S2.

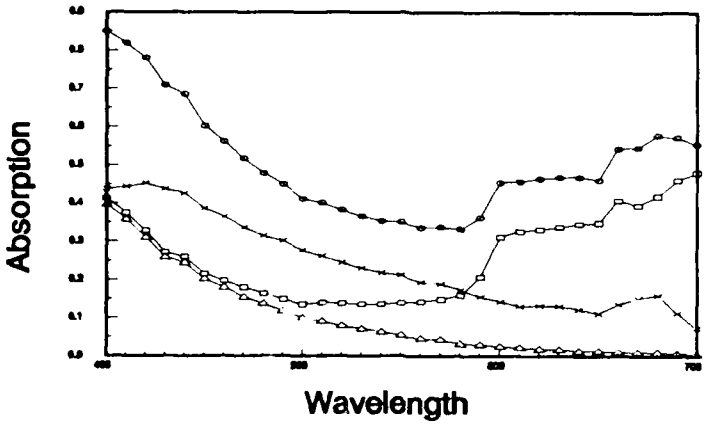

Fig. 2. Absorption (m^{-1}), measured in the integrating cavity, for the whole sample (circles), filtrate (squares), particles (x; equation 3), and dissolved organics (triangles; equation 4) for a sample from the Gulf of Mexico, 11 m.

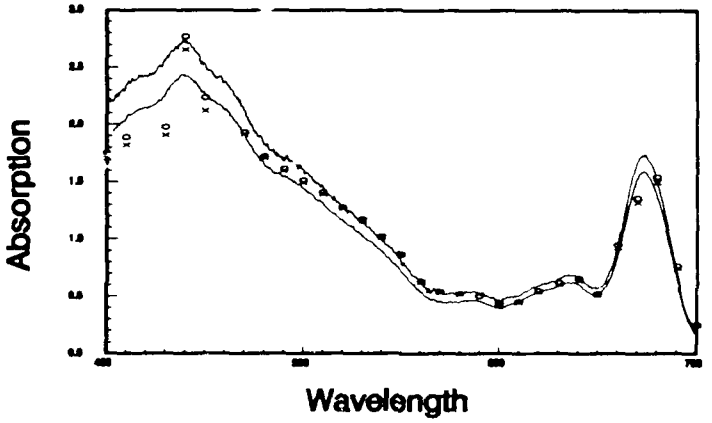

Fig. 3. Absorption spectra (m^{-1}) for Chaetoceros gracilis. Solid lines represent spectrophotometer data. Circles (channel 1) and x's (channel 2) represent integrating cavity data.

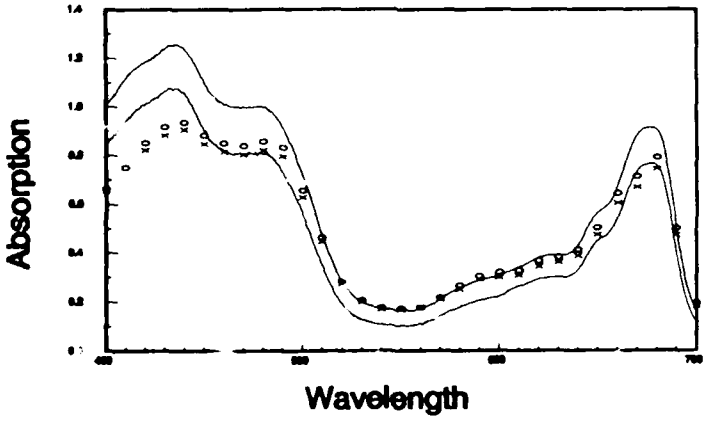

Fig. 4. Absorption spectra (m^{-1}) for Dunaliella tertiolecta. Symbols as in Fig. 3.

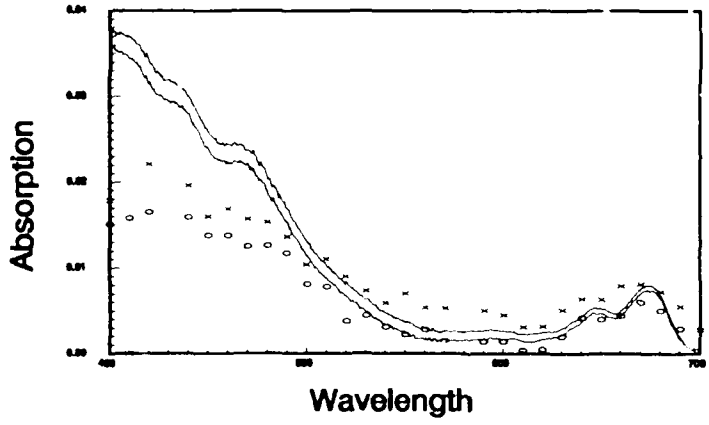

Fig. 5. Absorption spectra (m^{-1}) for Micromonas pusilla. Symbols as in Fig. 3.

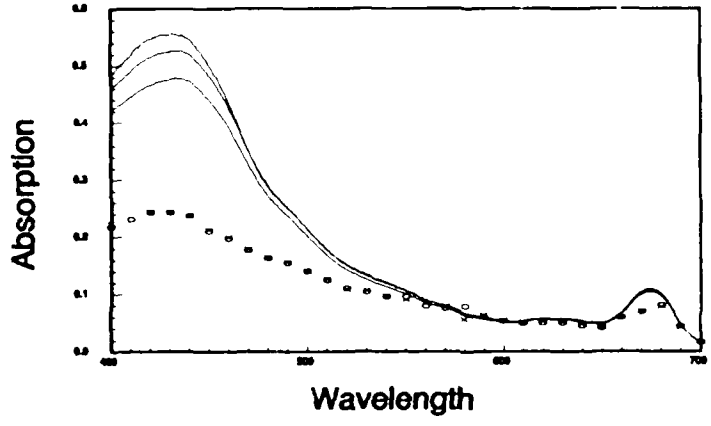

Fig. 6. Absorption spectra (m^{-1}) for particles from the Gulf of Mexico, 0 m. Symbols as in Fig. 3.

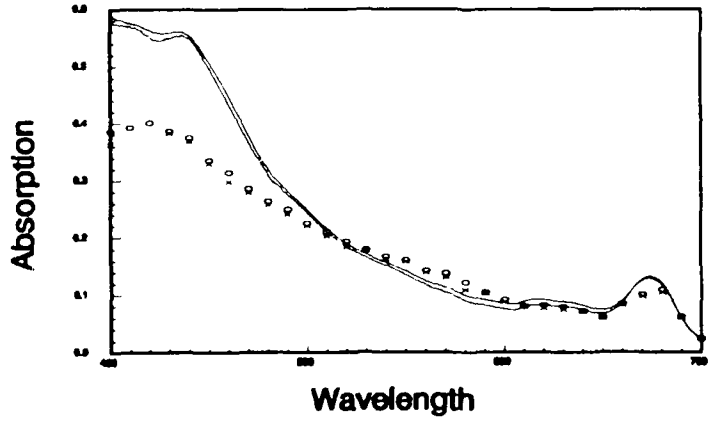

Fig. 7. Absorption spectra (m^{-1}) for particles from the Gulf of Mexico, 11 m. Symbols as in Fig. 3.

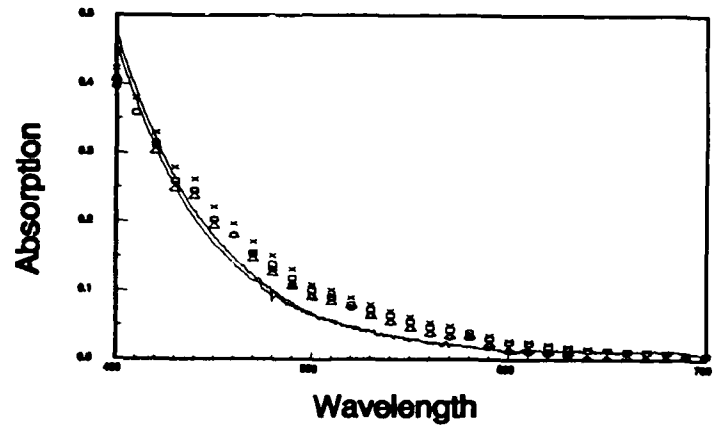

Fig. 8. Absorption spectra (m^{-1}) for dissolved organics from the Gulf of Mexico. Solid lines represent spectrophotometer data; integrating cavity data are represented by circles and x's for 0 m and by squares and triangles for 11 m.

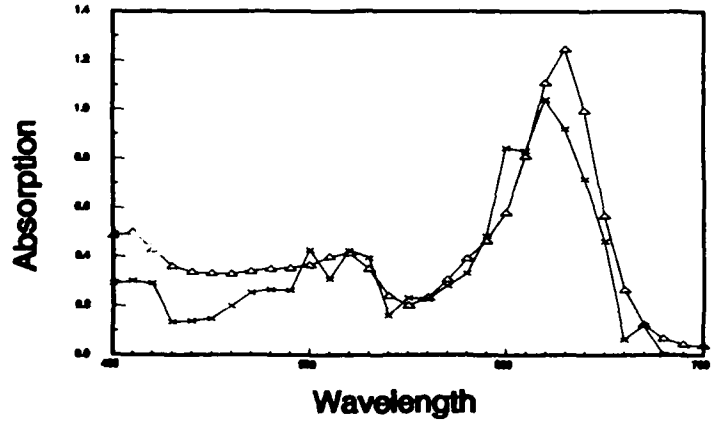

Fig. 9. Absorption spectra (m^{-1}) for a test solution of food coloring measured in the spectrophotometer (solid line) and integrating cavity (circles).