

30 JAN. 1968

KONINKLIJK NEDERLANDS
METEOROLOGISCH INSTITUUT

Wetenschappelijk Rapport W.R. 67-002 (IV-5)

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transmittance of Sargasso Sea water in the visible
and near infrared part of the spectrum

De Bilt, 1967

Kon. Ned. Meteor. Inst.
De Bilt

VIII. c. 281.

This report will also be published in the series
"Technical Reports" of the NATO-Subcommittee on
Oceanographic Research (Technical Report No.39).

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Acknowledgement

The author participated in the oceanographic expedition of the Danish research vessel DANA to the Sargasso Sea in February-March 1966 under the leadership of Prof. N.G. Jerlov, University of Copenhagen. This expedition was sponsored by NATO at the proposal of its Subcommittee on Oceanographic Research. This report only presents the results of measurements for which the author was responsible, together with a preliminary discussion.

1. Introduction

During an international expedition in the Sargasso Sea in February-March 1966 a large number of optical measurements, most of them in situ, were made near and also south of Bermuda. In addition transmittance of sea water samples was measured on board in order to obtain an impression of the transmittance curve of the sea water over the whole of the visible spectrum and also over the near infrared spectrum. These measurements are presented in this report. They supplement results of in situ beam attenuation measurements.

2. Experimental

A Beckman model DU spectrophotometer (manufacturer: Beckman, München, Germany) with a Beckman power supply, was used for the measurements. Originally this spectrophotometer was equipped for use with small cuvettes (light path 10, 20, 50 or 100 mm) of which two or, for the smallest type, even four can be used in the sample room of the instrument at the same time. Also a big cuvette can be used in which a water column of 250 mm is traversed twice by the light beam (the volume of this cuvette is about 280 cm³).

Of this big type of cuvette one can be placed in the sample room, and measurements - either with "standard" water or with an unknown sample - are made by comparing the transmittance through the cuvette with the transmittance of a light path in air. The axis of the light pencil traversing the samples is always in a horizontal direction.

The light source is a tungsten lamp of high quality. Wavelength range of the monochromator is 200 - 2000 nm, light of short wave lengths ($\lambda \leq 600$ nm) being detected by a photo-multiplier tube, and that of long wavelengths ($\lambda \geq 600$ nm) by a lead sulphide cell. However, as in general a photo-multiplier cannot be used for very short wavelengths without special precautions, the lower wavelength limit for our measurements has been chosen as 380 nm, being one of the standard wavelengths of the (in situ) beam attenuation meter during the cruise. Maximum wavelength is about 1200 nm for our measurements.

Most of the observations described here were made using bucket samples at room temperature (20-30°C).

Looking at the Beckman meter one might ask what is actually measured, absorption factor or beam attenuation? For one thing, the light beam, traversing the water samples, is not a parallel one, especially if the big cuvette is used. In addition,

a part of the scattered light (roughly that scattered between 45° and 135°) escapes from the cuvettes (fig. 1) whereas the light scattered under small angles still reaches the cell.

The following simple consideration may elucidate this point. Let us assume a water-filled, thin-walled cylinder of glass, placed in air, the axis of which is traversed by a pencil of light. At a certain point a small element of unit volume of water irradiated by the pencil scatters light. We also assume that the light scattering function $\beta(\theta)$ equals β^* (arbitrary units) independent of θ and that reflection on the glass-water interface is negligible compared with that of the air-glass interface. The total amount of light scattered over the whole solid angle of 4π equals.

$$I = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \beta^* \sin \theta \, d\theta \, d\phi = 4\pi \beta^*$$

We assume that light scattered in direction θ between 0° and 45° and between 135° and 180° cannot escape from the cylinder, owing to total reflection at the glass-air interface, and that light scattered in direction θ between 45° and 135° can escape except for a 5% reflection at that interface. Then the amount of scattered light, trapped in the cylinder will be

$$I' = \int_{\phi=0}^{2\pi} \left(\int_{\theta=0}^{\pi/4} \beta^* \sin \theta \, d\theta + \int_{3\pi/4}^{\pi} \beta^* \sin \theta \, d\theta \right) d\phi + 0.05 \int_{\phi=0}^{2\pi} \int_{\pi/4}^{3\pi/4} \beta^* \sin \theta \, d\theta \, d\phi = 0.4 \times I$$

Of course, an average reflection coefficient of 5% is an underestimate since for scattering angles from 90° to 45° and from 90° to 135° its amount will gradually increase from 5% to 100%. On the other hand, influences from multiple reflections and skew rays have been neglected.

However, this approximation gives us a rough impression of the order of magnitude of the amount of scattered light that can be expected to be trapped in this cuvette.

Actually, most of the scattered light is scattered in a forward direction, so we can state that only a much smaller fraction of it can escape from the cuvette which fraction will still be different for different sizes of cuvette.

Therefore, in the following we shall assume that 1 minus the transmittance approximately equals the absorption factor and we shall speak of absorption coefficient a (based on natural logarithms, unit m^{-1}) instead of beam attenuation coefficient.

It is not the first time that this type of apparatus has been used at sea (Burt, 1958; Holmes and Linn, 1962). No special arrangements were made for the work on board a ship but certain minor precautions were observed, e.g. desiccators were frequently refilled and the big cuvette was fastened during heavy weather.

3. Calibration

Since it is only possible to make relative measurements, especially when using the big cuvette, a reference standard has to be used, for which both filtered Sargasso surface water and unfiltered Sargasso deep water were chosen. Sargasso surface water being extremely pure concerning dissolved substances contains particles that must be removed before it can be used as a standard. Occasionally a sample of deep water (several hundred meters) was available for which Tyndall-measurements showed that the particle content was very low. It can be stated that the absorption characteristics of these two "types" of water are sufficiently similar to those of pure water for the purpose of this investigation (Jerlov, 1951). Some series of measurements with either one or the other of these standards were averaged to obtain a mean standard value.

Also, distilled water (from stock on board) turned out to be useful as a standard for the spectral region 600-900 nm, as in this region the absorption of distilled water is fairly equal to that of "pure" water; absorption by dissolved impurities plays a minor role; so one has only to take care that the particle content of the distilled water is negligible small.

In the near infrared, ($\lambda > 900$ nm) where a higher absorption factor occurs, "absolute" measurements over 80 mm path length are obtained by using two cuvettes of different length, 20 and 100 mm, and by comparing the transmittances. A set of 10 mm cuvettes was also used in this spectral region; in this case a correction has to be applied for reflectance at the interfaces.

The results of Clarke and James (1939 resp. James and Birge) and of Curcio and Petty (1951) were used for the absolute values of the absorption coefficient of pure water.

4. Accuracy of the data

Apart from the influences mentioned below (section 5) the accuracy of the measurements appeared to be highly dependent on the ship's motion. In the harbour or during very calm weather, as to the visible part of the spectrum where transmittances are close to unity, r.m.s. deviations are found of 0.005-0.01 transmittance per $\frac{1}{2}$ m path length for a single reading. Multiplied by $2 \times \sqrt{2}$ this amounts to a deviation of about 0.02-0.05 in transmittance per metre path length relative to "standard". It may well be imagined that the accuracy will be even less when conditions are less favourable.

With regard to the values obtained for the absorption coefficient, the following remarks are relevant: if it is assumed that an accuracy (r.m.s. error) of ± 0.005 transmittance can be reached over the whole range (0-1) for a single measurement with any type of cuvette, then for different path lengths and different measured transmittance values we have an accuracy in \underline{a} as given in the graph (fig. 2): for a certain value of measured transmittance \underline{a} always the same relative accuracy $\Delta \underline{a}/\underline{a}$ is found, but the value of the absorption coefficient \underline{a} to which this applies depends on the path length used. So it is clear from fig. 2 that for the interval $\underline{a} = 0.3 - 250 \text{ m}^{-1}$ a relative accuracy of ± 0.02 or more in absorption coefficient can be attained for a single measurement. As measurements are always relative, this value must be multiplied by $\sqrt{2}$, for a true estimate of the accuracy, viz. ± 0.03 .

Generally speaking, accuracy is only moderate, but it is doubtful whether it is possible to get better results when working at sea with this apparatus (see, e.g., the remarks by Burt (1958)).

5. Time dependency of measurements

As Clarke and James (1939) already pointed out, measured light absorption depends on the time delay between taking the sample and making the measurements. To get an idea of this effect, some measurements have been made on this phenomenon on different samples, filtered and unfiltered, at two wavelengths, 655 nm and 380 nm, being the wavelengths used in the in situ beam attenuation meter.

Results are given in figure 3 which shows transmittance versus time for three different "water types", viz. filtered Sargasso water, unfiltered Sargasso water and unfiltered water from St. Georges Harbour. It is thought that the initial increase in transmittance of some of the unfiltered samples during the first one or two hours is brought about by disintegration and settling down of

particles. The decrease of transmittance that follows is attributed to the activity of bacteria or other living material. It is obvious that changes occur from the very moment of sampling, or at least from the moment that the sample is enclosed in the cuvette. As all other measurements were always made with the shortest possible delay after the sample was taken (about 1 to 2 hours), figure 3 at the same time illustrates the inevitable error involved. Here the advantage of in situ measurements as compared with laboratory measurements is clearly shown. Details of fig. 3 will be discussed briefly below.

Filtered Sargasso water

Transmittance for violet light starts at about the maximum value that can be expected, having the same value as that for pure water as stated in the foregoing. Apart from a few irregularities, transmittance gradually decreases to a low value while, at the same time, the value for red light remains more or less constant and - for this sample - only slightly below the value to be expected for pure water. After about ten hours transmittance for red light tends to decrease. It may be concluded that the number of particles is very small and nearly constant so that their sinking rate must be very slow; in fact, pore size of filter used was 0.6 - 1.0 μ m. But at the same time certain processes take place: probably "yellow substance" is produced which decreases transmittance for the violet.

Unfiltered Sargasso water

Transmittances for both violet and red light are lower than the corresponding ones for the filtered water. However, in general the same trends are observed. The transmittance for violet decreases very rapidly during the first few hours but the rate of change gradually becomes slower. For one sample it was established that an initial increase occurred, undoubtedly due to settling of particles, but after one hour this increase is obviously balanced by the decrease caused by the production of violet absorbing material.

Absorptance in the red has been measured on two samples, one of which had a nearly constant transmittance. The other sample showed an initial increase in transmittance, probably as a result of settling of particles, then a slow decrease.

Unfiltered water from St. George's Harbour

It can be expected that water from St. George's Harbour is quite different from Sargasso Sea water because of the different characteristics of the two areas. St. George's Harbour is a relatively shallow inlet on the north eastern part of Bermuda. Its water although very clear to the eye, contains a lot of particles of the coral of the island while the abundance of fish points to a large amount of nutrients in the water. The inlet has a few relatively narrow connections with the ocean. Owing to the large number of particles, transmittance in both red and violet initially are very low but immediately start to increase, obviously due to the settling of particles. It seems that after about 24 hours the transmittance for red has reached its maximum value, indicating that all particles have settled, from which it may be concluded that the particles are rather large.

For spherical particles with radii 0.5-2 μ m and a density of 2-3 times that of water one finds, applying Stokes' law, settling velocities between 2 and 60 mm per hour, which is enough to allow for complete settling within 24 hours in our cuvette, which has a diameter of several centimetres.

The absorption factor in the violet which persists with time points to the production of either material or to very small particles with diameters small compared to the wavelength of the light or both. However, some measurements of filtered St. George's Harbour water give transmittance values for both red and violet that are very close to the values for very clear water. Therefore it may be concluded that the failure of transmittance for violet of unfiltered harbour water to reach the value for pure water (as the transmittance for red does) is a result of production of violet-absorbing material "yellow substance".

It is interesting to plot the values of the absorption coefficient a found for these water samples with respect to those of pure water as has been done in fig. 4, taking for pure water $a_{w,red} = 0.30 \text{ m}^{-1}$ and $a_{w,violet} = 0.04 \text{ m}^{-1}$, according to Clarke and James (1939). The latter value is perhaps a little too high as it is not clear whether (or not) total beam attenuation or only absorption was measured by these authors, but the value seems to be in accordance with Hulburt (1945), who gives values of the absorption coefficient down to 400 nm. Now it is found in fig. 4 that the values for the unfiltered St. George's Harbour water fit closely to a straight line intersecting the violet axis at $a - a_w = 0.26$. This suggests a gradual increase of "yellow substance" concentration during 24 hours, since for the filtered harbour water the increase in $a - a_w$ appears to be only 0.10 for violet light over the same time.

6. Measurements in the range 380-900 nm (big cuvette)

These measurements are made in two sub-ranges one "blue" ($\lambda \leq 600 \text{ nm}$) with the photo-multiplier, and one "red" ($\lambda \geq 600 \text{ nm}$) with the lead sulphide cell, with a certain "overlap" between these two sub-ranges. For some unknown reason a discrepancy occurs in this intermediate area, as shown in fig. 5 to 13. From the foregoing it will be clear that especially in the region of very high transmittance (around 500 nm) the relative accuracy of the absorption coefficient is low, which is a direct result of the method of observation, see fig. 2, extreme left part. Results are shown in figures 5 to 14. Station numbers and their positions are given in fig. 15. These transmittance measurements were not made at every station as standardization of the big cuvette and other measurements described in this report are rather time-consuming. As has been shown in the foregoing, it is especially in water of St. George's Harbour (fig. 5) that settling of particles plays an important rôle, so that measurements have to be completed in as short a time after sampling as possible. As this figure shows, on February 27 a check series gives higher transmittance (upper curve) than the initial one (lower curve) a result that gave reason to start the series of measurements given in fig. 3.

On station 2, a few miles off the south-eastern coast conditions change already (fig. 6), as here violet transmittance decreases with time. Although the initial transmittance curve equals those of the true Sargasso water as given in the next figures, the influence of the island can still be recognized by the considerable decrease of violet transmittance after 12 hours, compared to the smaller effect found on pure Sargasso sea water (compare fig. 3).

Inside and outside St. George's Harbour exit, (fig. 7,8) samples taken only a few hundred meters apart, there seems to be no big difference. Transmittance is much higher than in the harbour itself, but it still does not reach the values found in the Sargasso Sea which are given in figs. 9-14. In these figures some measuring points do not seem to be reliable; they are marked by a question mark. Also on some occasions, fig. 12 and 13, so as to gain at least some information about the influence of settling particles, the transmittance at a number of key-wavelengths, viz. 380, 488, 550 and 655 nm was measured as soon as possible after sampling, and

afterwards as soon as possible, the whole series of measurements was made. These "first" observations are indicated by an arrow, pointing to the later obtained decisive ones. Particles, but perhaps also small air bubbles may play a rôle in it.

By taking the average of the values (over the range 380-800 nm) of surface samples from the "Sargasso Sea" stations, viz. 2, underway, 3, 5, 9, 10 and 13, we obtain the transmittance curve shown in figure 16. This curve agrees well with the one obtained by Clarke and James (1939) for samples 200 miles northwest of Bermuda.

7. Measurements in the range 700-1200 nm (small cuvettes)

The best-known values of the absorption of pure water in the near infrared are those obtained by Curcio and Petty (1951) but as far as the author knows until now no measurements have been made with sea-water for this wavelength range. However, it is generally assumed that transparency in this wavelength range is the same for seawater and for fresh water, see Joseph (1952), this assumption being apparently based on some unpublished results. Two slightly different methods, used for the measurements in the near infrared are described here.

Method I. Two cuvettes were used (of length 20.0 and 100.0 mm).

These were filled with water from the same sample and with the 20 mm cuvette as standard; the reading with the 100 mm cuvette gives the transmittance over 80 mm path length in the liquid. This method was used for filtered Sargasso Sea water, and as a check also for distilled water both filtered and unfiltered.

Method II. Cuvettes of 10.0 mm path length were used, filled with water from different samples. This method has the advantage that various samples can be measured simultaneously and since the path length is small, the measurements can be extended to higher absorption values (near 1200 nm); however, accuracy is too low in the region of low absorption ($\lambda < 900$ nm). This method was used for water from St. George's Harbour as well as for distilled water, both unfiltered. An empty, clean and dry cuvette must be used for standardization, and corrections for interfaces must be applied as follows.

The output signal obtained when using no cuvette at all is adopted as the reference value ($T = 1.00$). Next the empty cuvette is measured, giving a transmittance of, say, p ($p < 1.00$). It is well-known that the transmittance of four air-glass interfaces is given by $(1-r)/(1+3r)$, where r is the reflectance of one interface. Thus r can be calculated; it is about 0.04. For a glass-water interface, the reflection is much smaller and it is sufficiently accurate to calculate the reflection of one interface according to Fresnel's formula for perpendicular incidence of the light beam, taking 1.45 and 1.33 for the refractive indices of glass and water respectively. This gives a reflection loss of 0.002 for one glass-water interface which value must be doubled in the case of 2 interfaces. Then to correct the measured transmittance of the samples (two air-glass and two glass-water interfaces) it is sufficient to simply add $2r + 0.004$. This correction amounts to 0.07 - 0.08, the exact value depending somewhat on λ .

Results of both methods have been plotted in fig. 17 in the form of a (m^{-1}) vs λ (nm). There is fair agreement with the values given by Curcio and Petty for pure water. This, of course, does not mean that the differences between the absorption coefficients for pure water and seawater (filtered or not) for this wavelength region are absolutely negligible since the high absorption of water itself makes the use of relatively small cuvettes necessary, with a consequent loss in sensitivity (see figure 2, extreme right part; a relative error $\Delta \frac{a}{a} = 0.03$ for $a = 100 m^{-1}$ means an absolute error $\Delta a = 3 m^{-1}$).

8. Scattering measurements

Scatterance of light in some of the water samples was also measured, using the well-known Tyndall meter described by Jerlov (1958). Measurements were made using white light and a scattering angle of 45° ; for some samples an angle of 90° was also taken. The scatterance of a piece of plexiglass was used as a reference; thus all scatterance values are relative values.

For all samples of distilled water of filtered surface water (even that from St. George's Harbour) and of Sargasso Sea deep water, ratios of 0.5 to 0.7 were found.

For unfiltered surface water the Tyndall values could be much higher as can be seen from Table I which gives the results of some simultaneous measurements with the Tyndall meter and the spectrophotometer. Attempts to correlate these Tyndall values with the measured absorption values for red and violet light (fig. 18) give a rather disappointing result. Values for red light suggest an approximately linear relationship giving for the arbitrary Tyndall value τ :

$$\underline{a} = 0.30 + 0.07 \tau$$

taking $\underline{a} = 0.30 \text{ m}^{-1}$ and $\tau = 0$ for pure water, though τ for pure water strictly speaking, will have a value somewhere between 0 and 0.5. But for violet light there seems to be no simple relation. This may be due to the inaccuracy of the measurements, both of \underline{a} and τ , or may partly arise from the fundamental difficulty connected with the interpretation of the transmittance measurements, mentioned in the beginning of this report, viz. the uncertainty as to the amount of scattered light measured by the cell. More measurements are needed than the few discussed here, to clear up this point.

TABLE I

Date	STATION (unfiltered surface w.)	TYNDALL		a(m ⁻¹)	
		45°	90°	red(655 nm)	violet(380 nm)
27-2-1966	2 southern coast	.7		.40	.25
28-2-1966	underway	1.3		.41	.26
1-3-1966	3	1.1	.7	.39	.17
5-3-1966	St.George's Harbour	6.0	8.0	.70-.78	.83-.88
8-3-1966	inside harbour				
	exit	3.3	2.2	.44	.39
	outside harbour				
	exit	2.0	1.4	.43	.43
	5	.9	.5	.43	.19
13-3-1966	9	1.5		.43	.10-.21
15-3-1966	10	2.5		.46	.17

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Summary

Measurements were made in the visible and in the near infrared part of the spectrum on water samples, using a Beckman DU spectrophotometer. Both Sargasso Sea deep water and filtered Sargasso Sea surface water are used as "Standard" in the visible range.

The values found for the transmittance in the visible region on Sargasso Sea water agree with those found by Clarke and James and in the near infrared no difference could be established between distilled water and seawater, even for water from St. George's Harbour (Bermuda).

Some measurements were made on the time dependency of the light transmittance due to the settling of particles in the cuvette and to chemical and biological processes. Some simultaneous measurements on Tyndall scattering are reported.

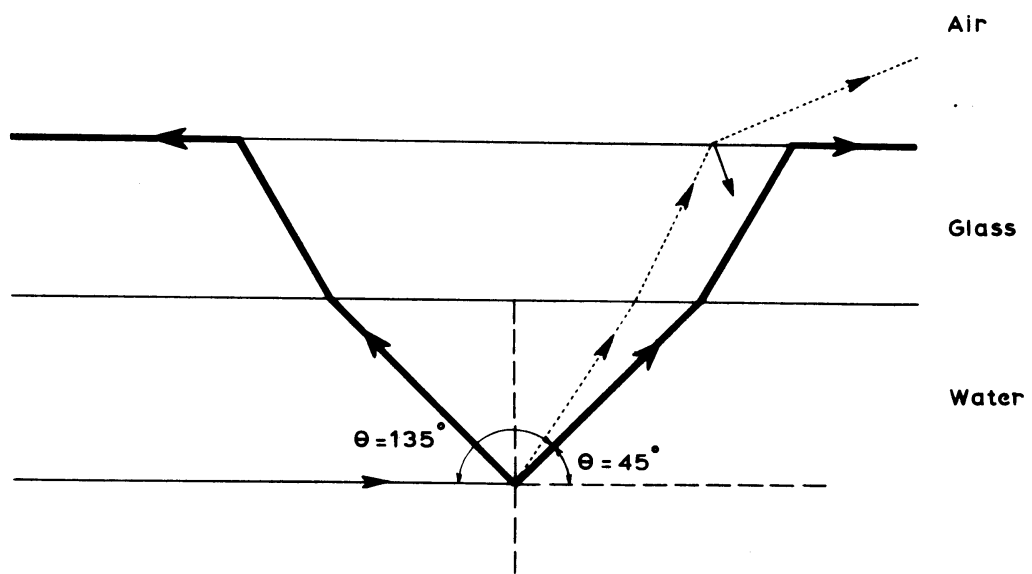


Fig. 1

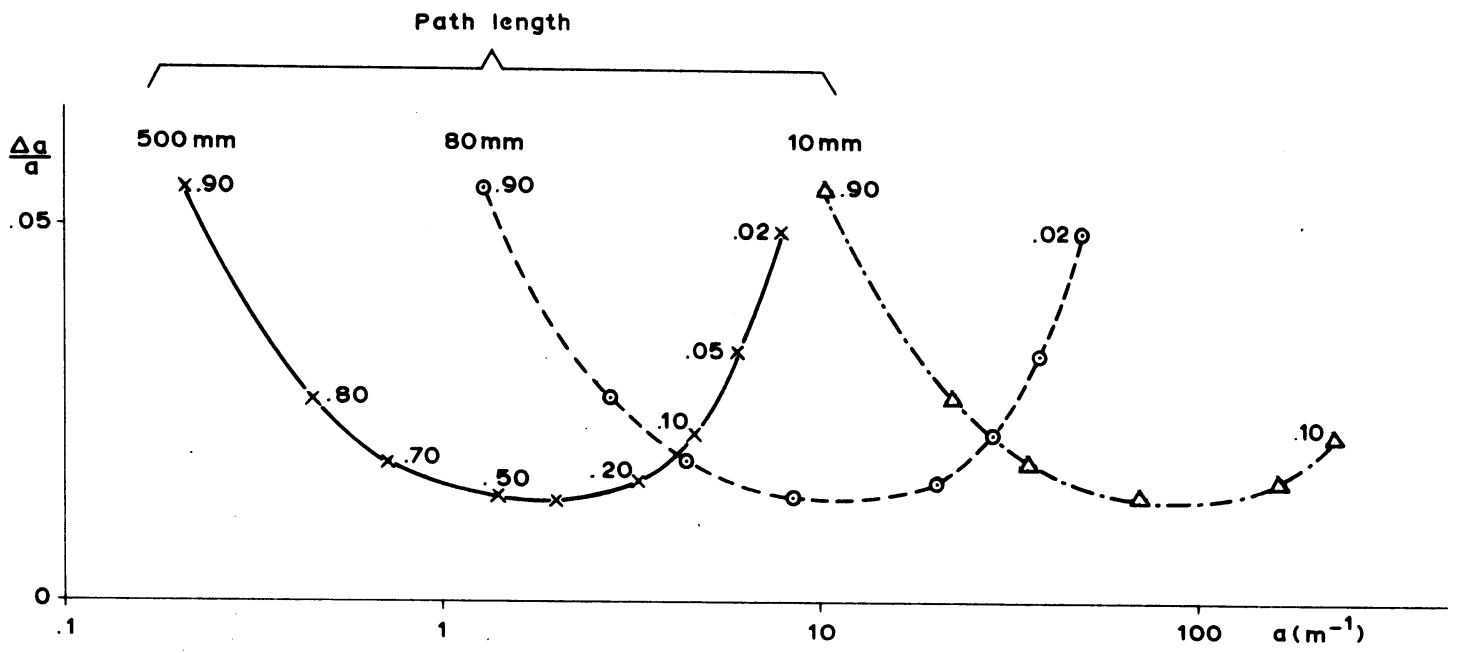


Fig. 2

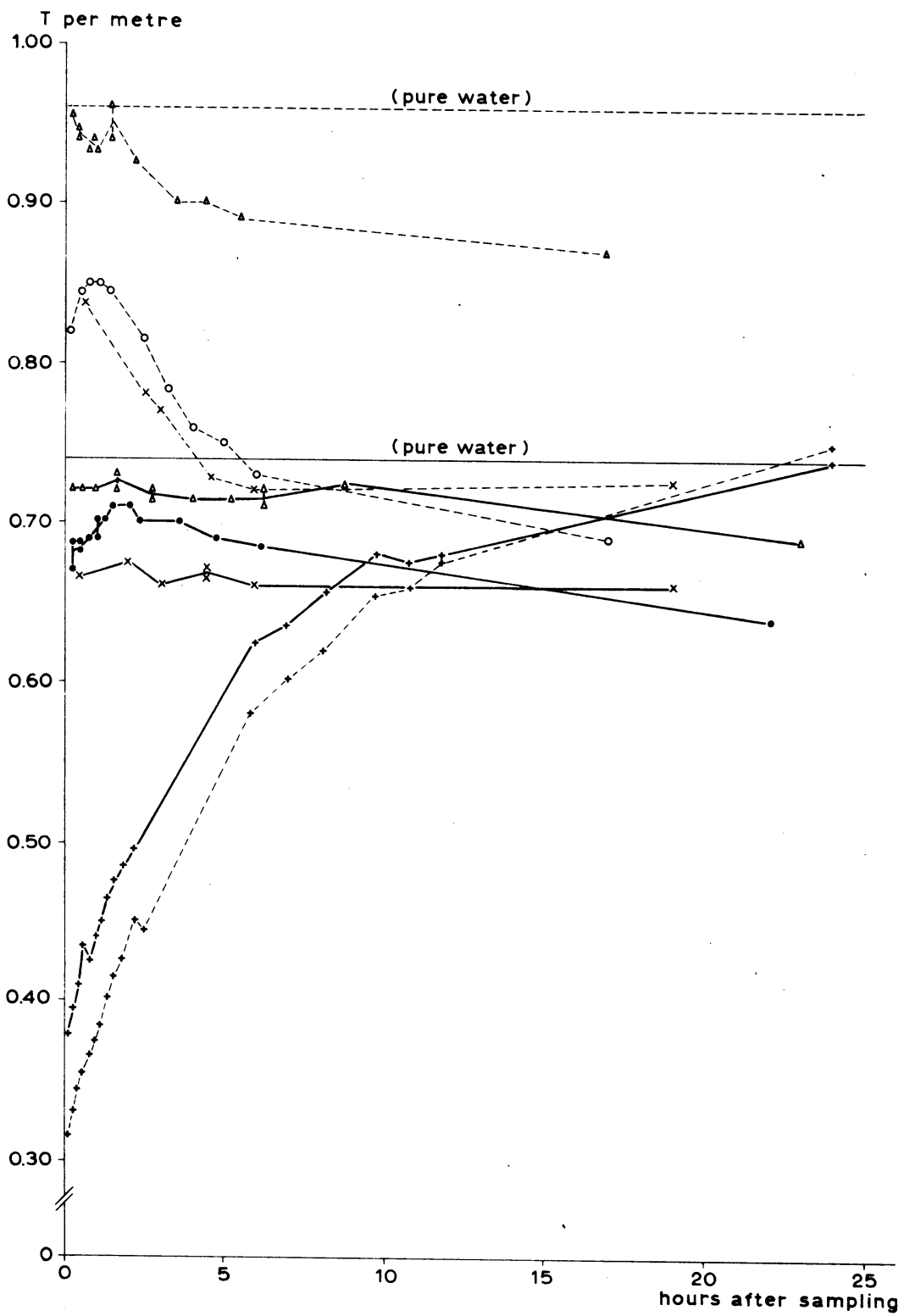


Fig. 3

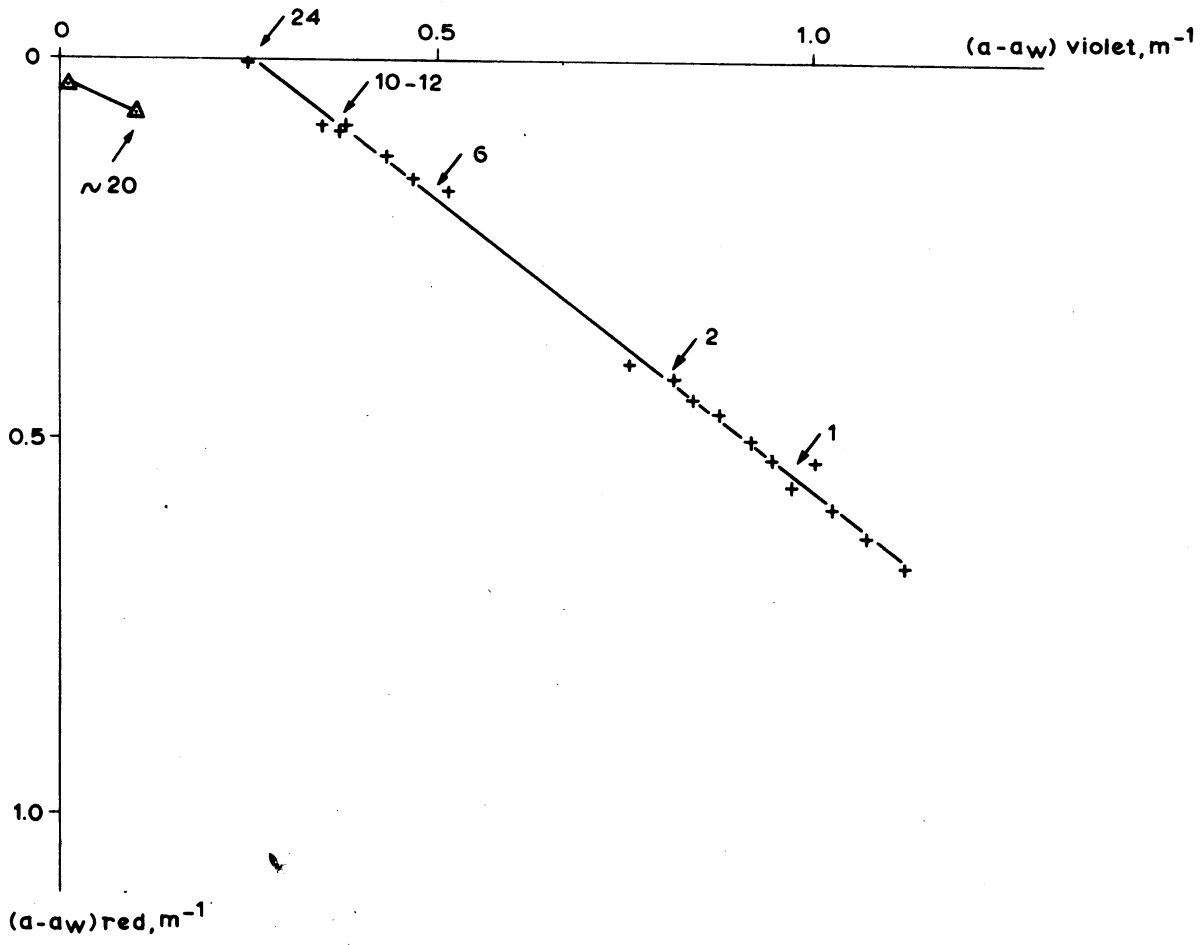
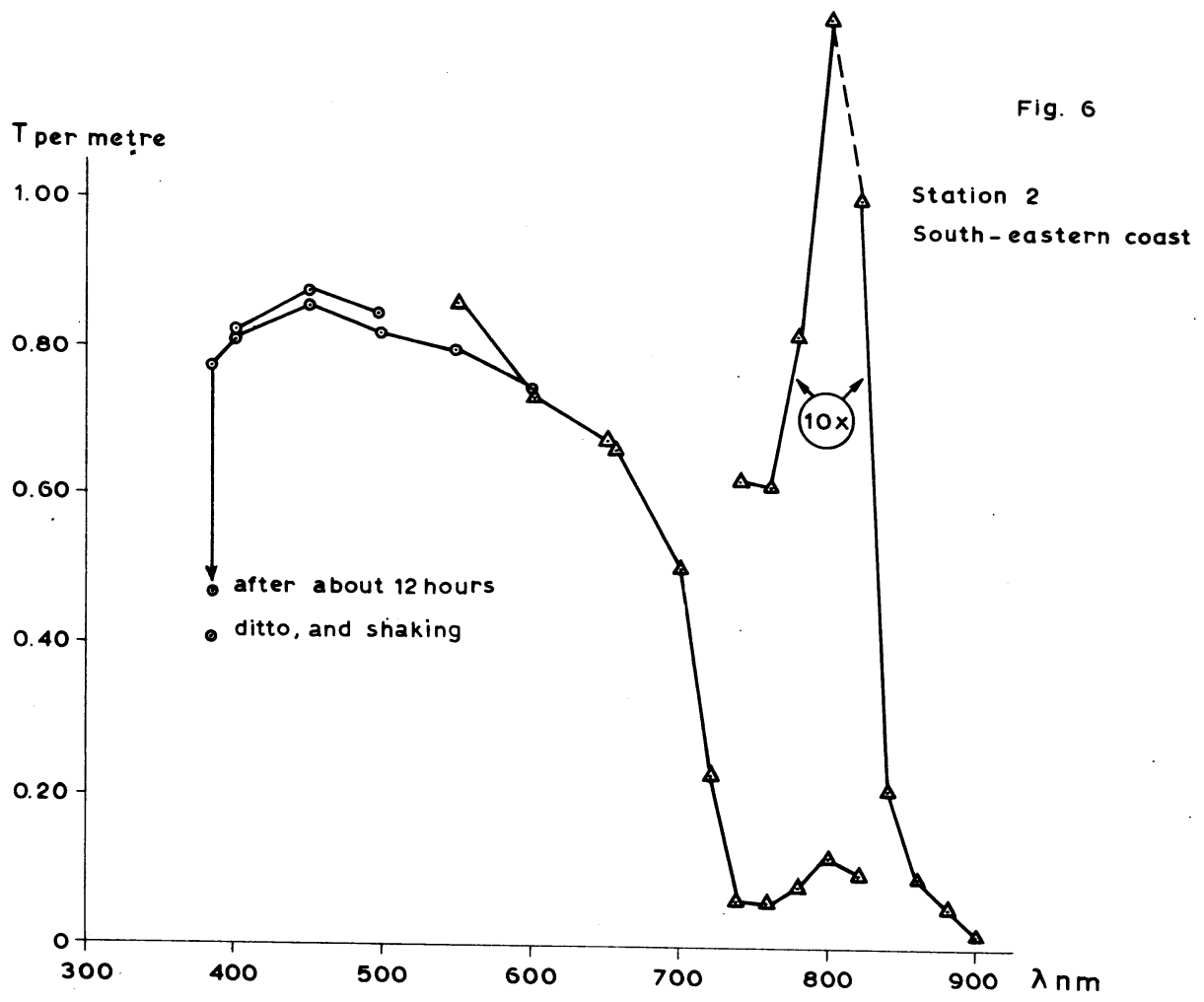
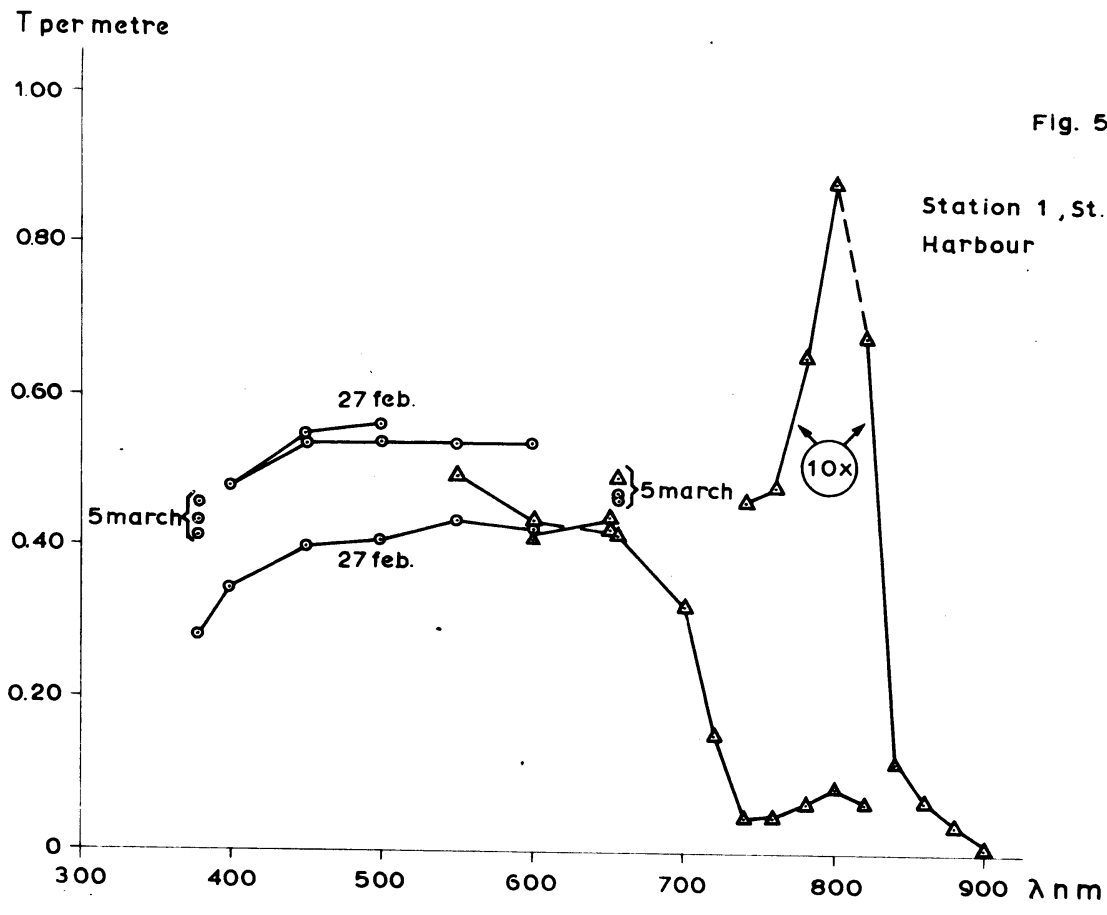


Fig. 4.



T per metre

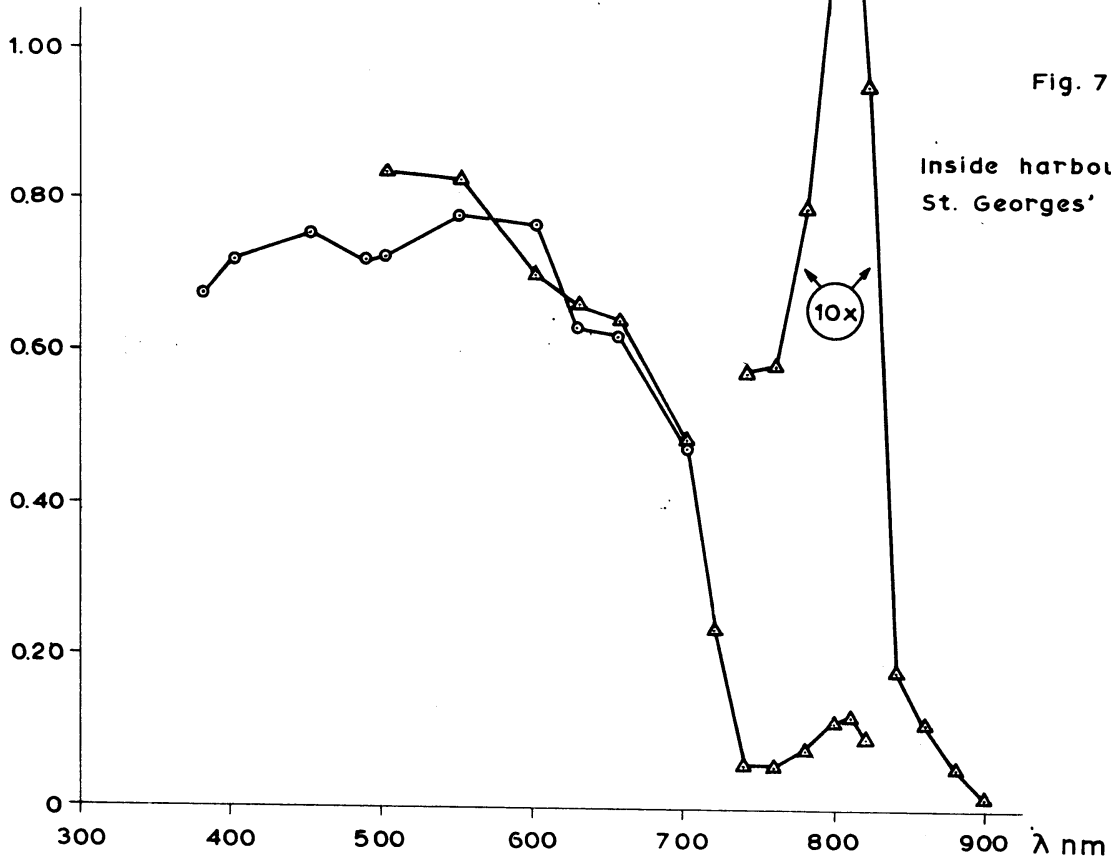


Fig. 7

Inside harbour exit
St. Georges'

10x

T per metre

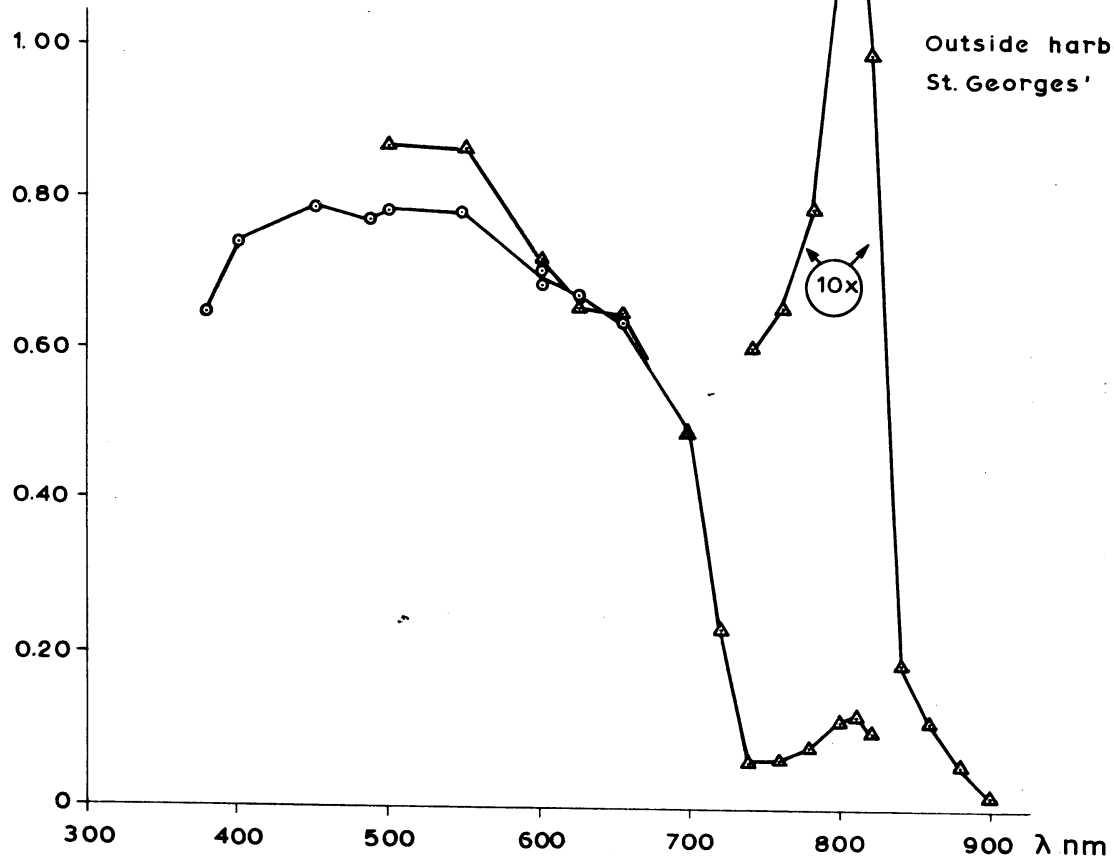
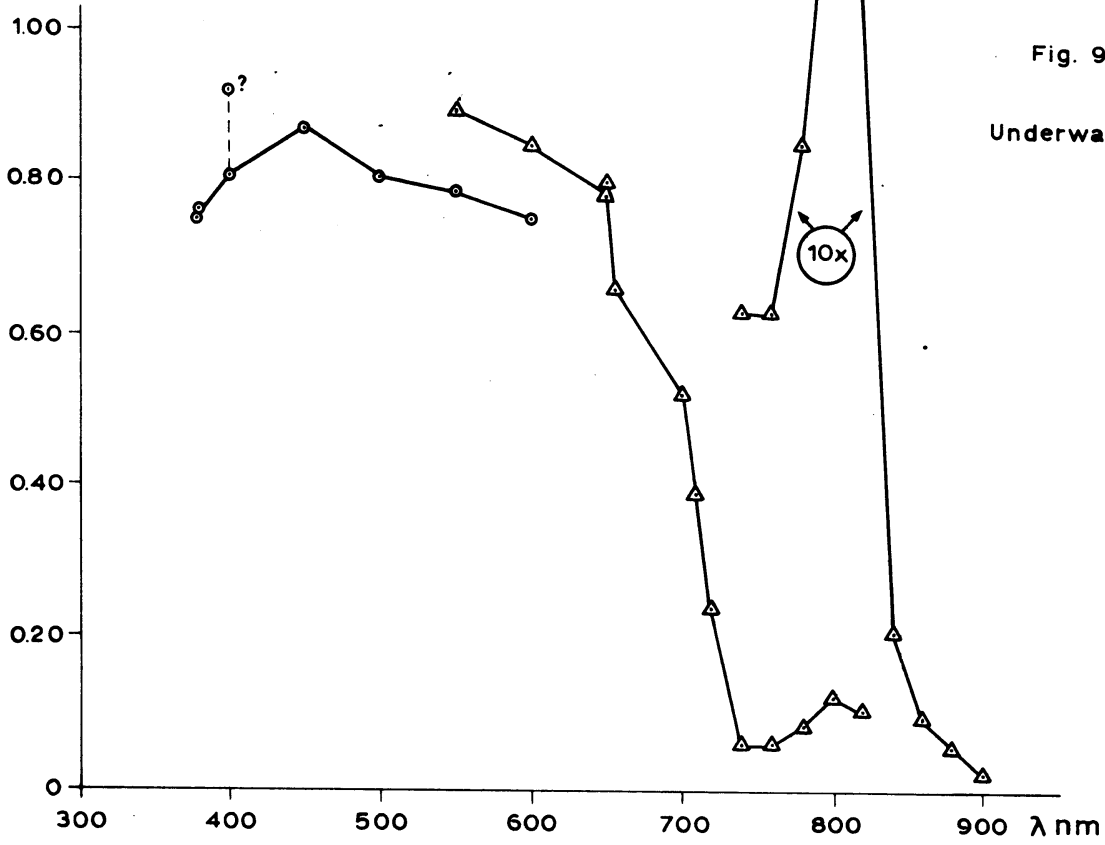


Fig. 8

Outside harbour exit
St. Georges'

10x

T per metre



T per metre

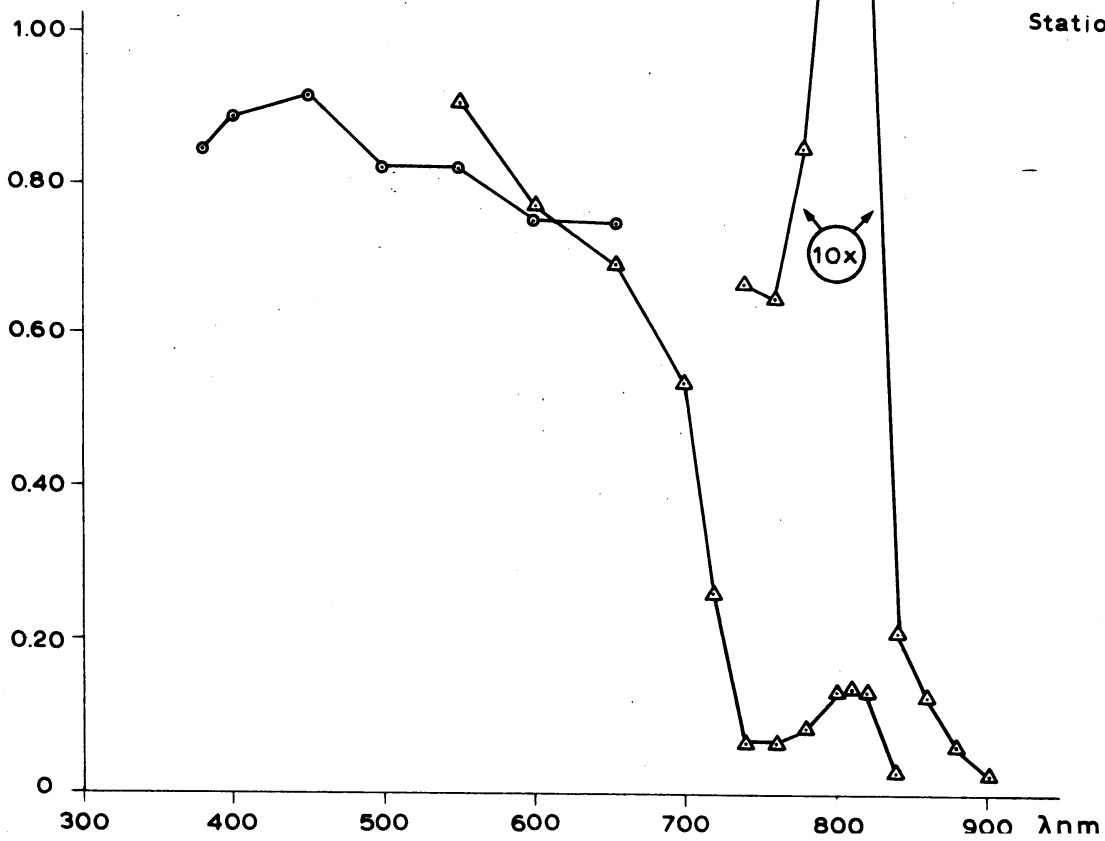


Fig. 11

Station 5

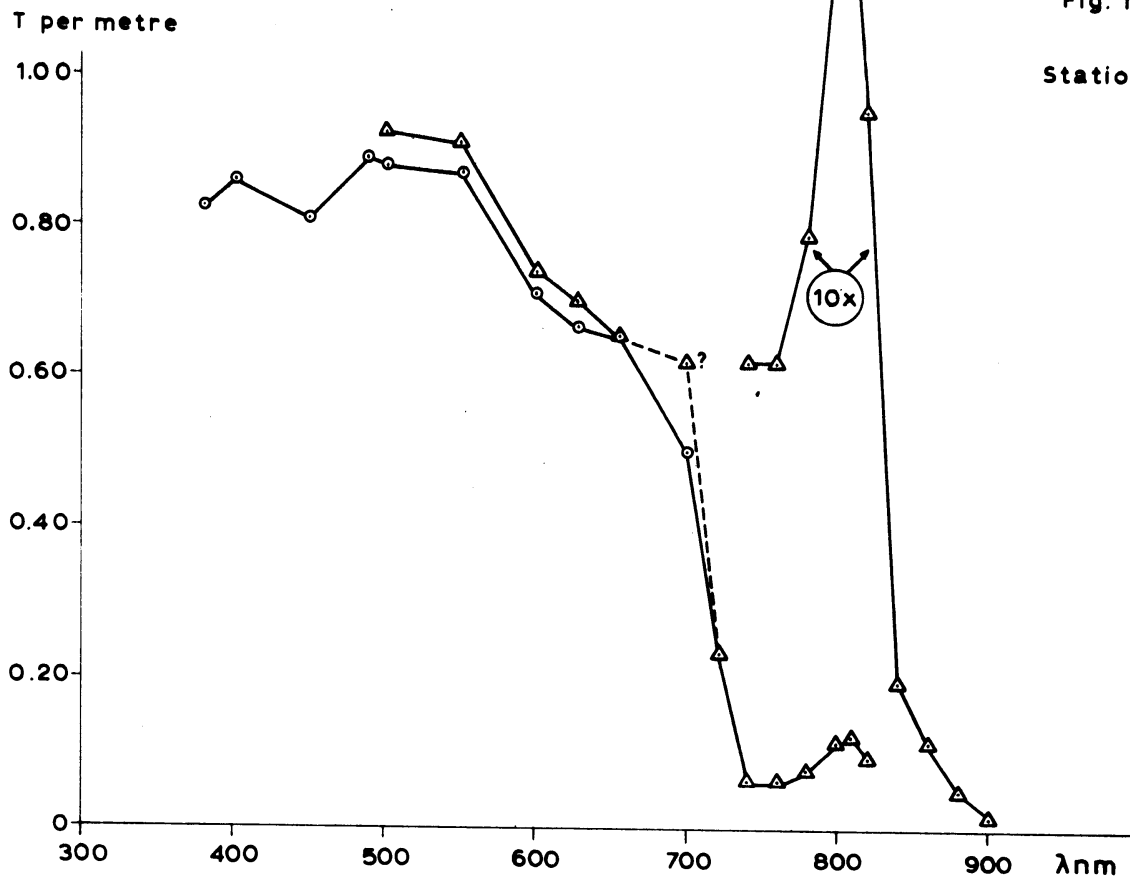
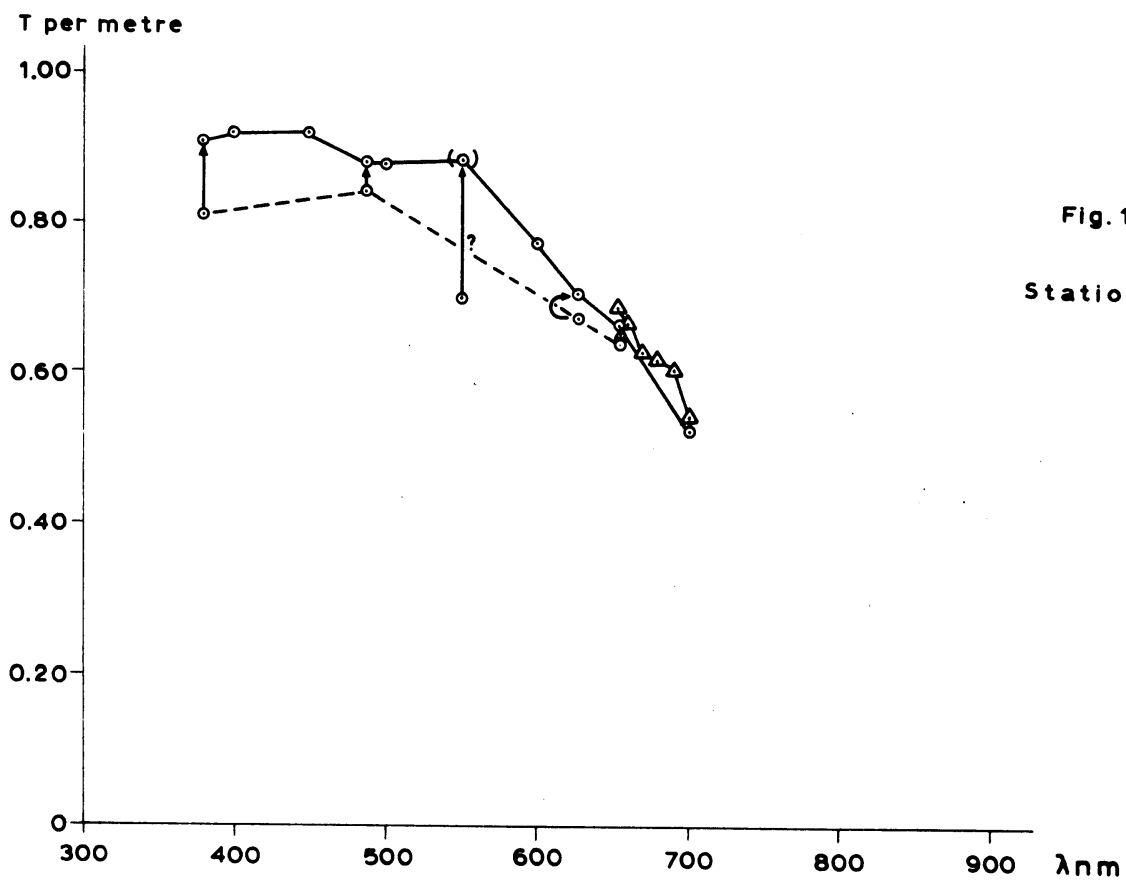
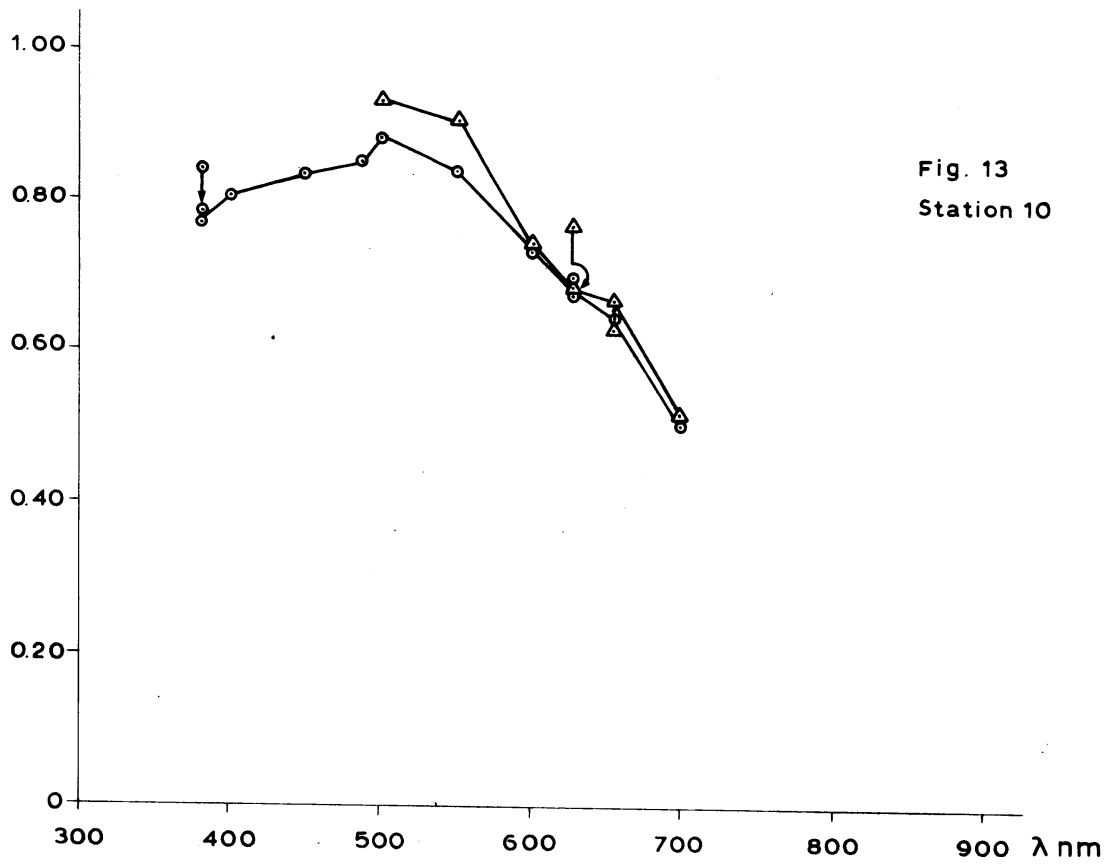


Fig. 12

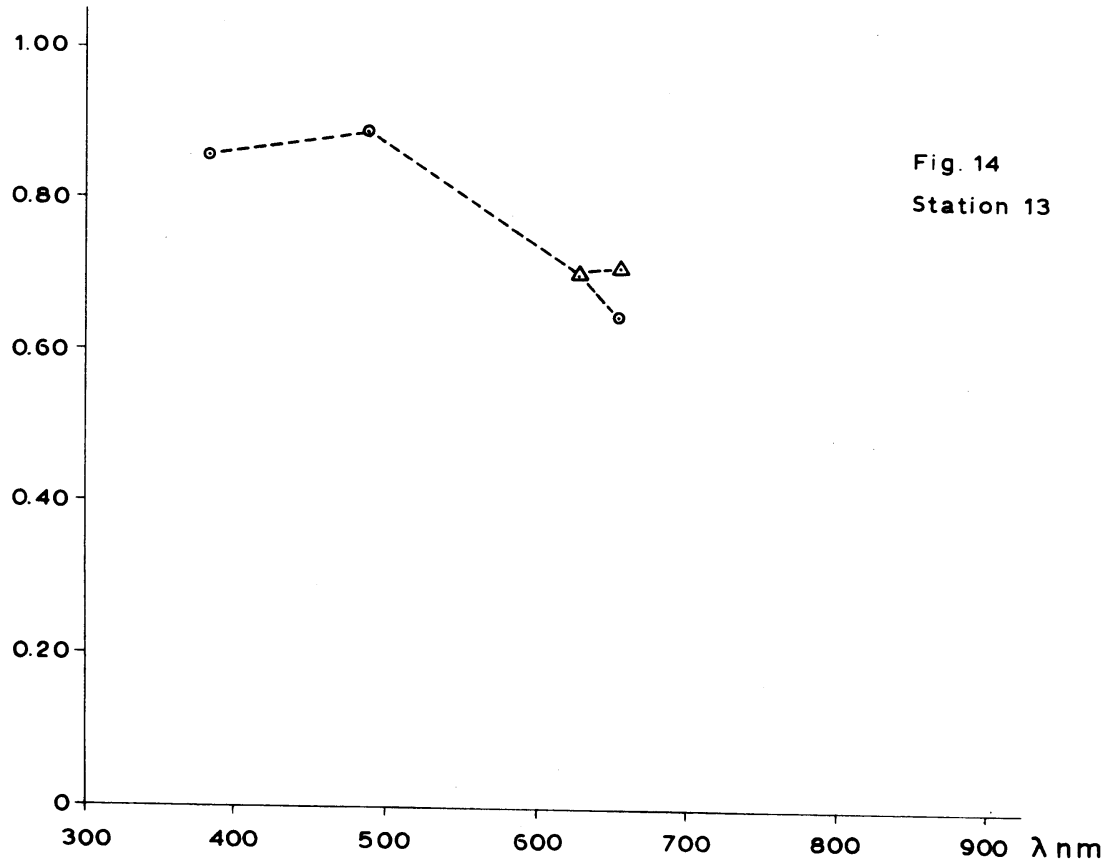
Station 9



T per metre



T per metre



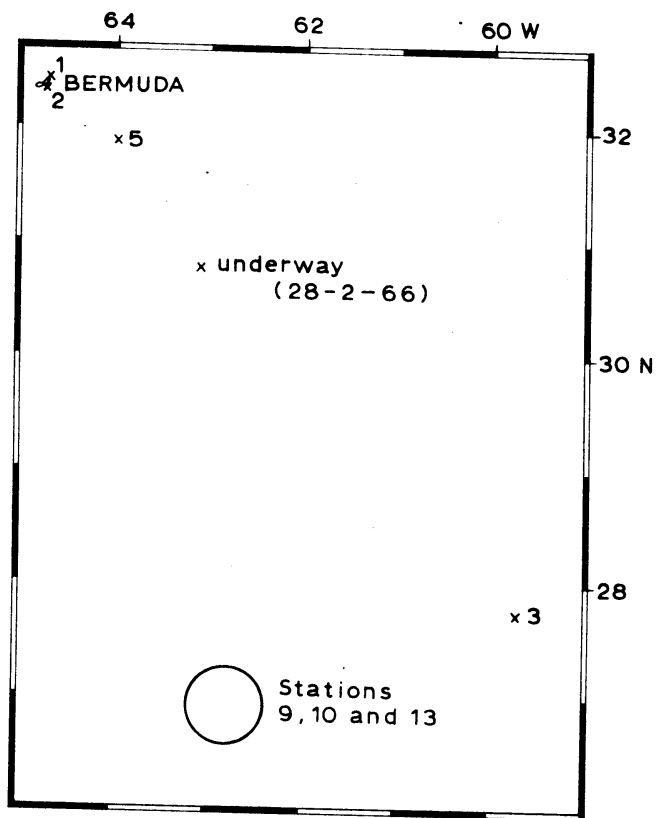


Fig. 15

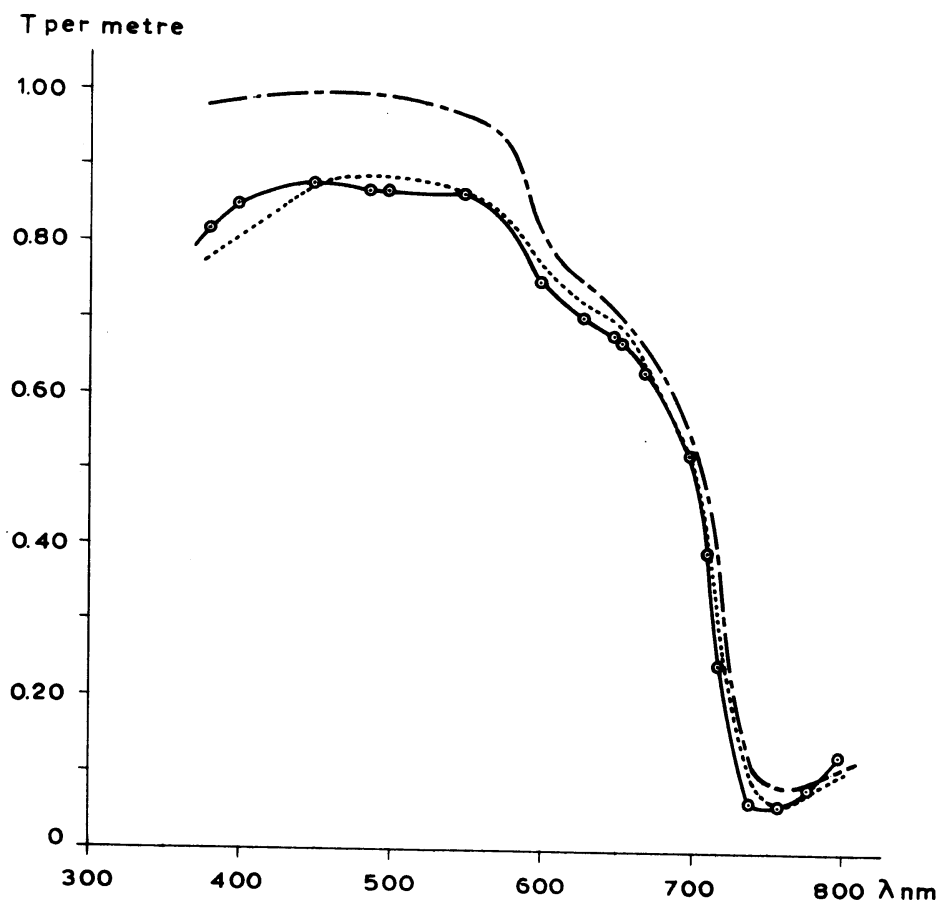


Fig. 16

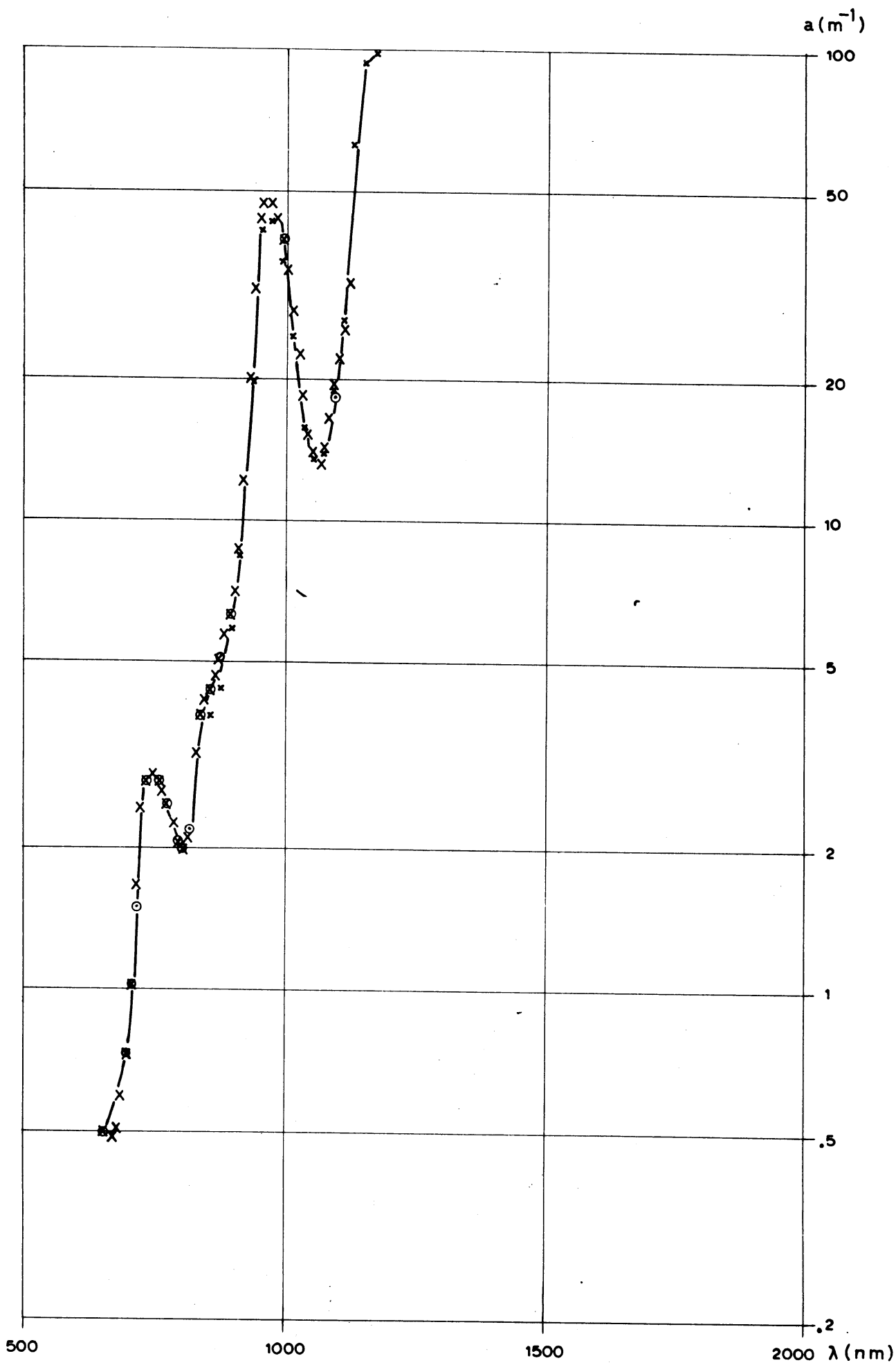


Fig. 17

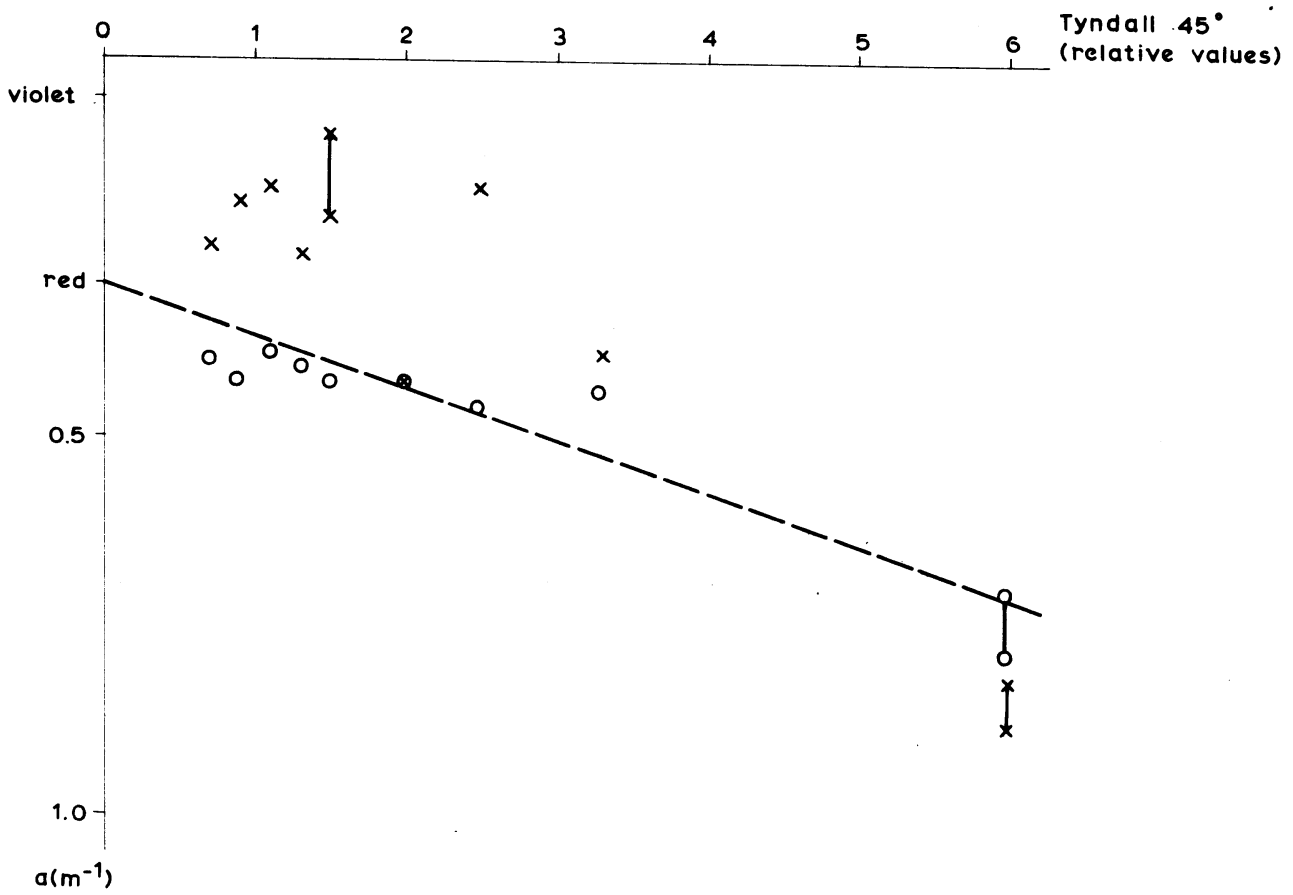


Fig. 18