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**MEASUREMENT OF ULTRAVIOLET-VISIBLE SCATTERING
OF POLYMERIC FILMS**

Key Words: UV/Vis Spectroscopy, Scattering, Polymeric film, Polyethylene, Regenerated Cellulose.

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ABSTRACT

A method for measuring scattered radiation using a UV/Vis Spectrophotometer without accessory as integrating sphere is described in this paper. This method can detect the scattered radiation because the spectrophotometer has two sample positions and the detector subtends a different solid angle at each position.

In this way, it is possible to obtain some measure of the scatter of a sample by observing the difference in absorbance readings. As example it was applied to polymeric films (regenerated cellulose and polyethylene).

INTRODUCTION

Scattering of the incident radiation is observed when light from a spectrophotometer pass through a sample. This effect is illustrated in Figure 1, where I_o represents the incident radiation, I_s represents the scattering radiation and I_t represents the transmitted light that has not been scattered.

The scattered transmittance of light through a sample can be measured with a UV/Vis spectrophotometer with an accessory which is designed to measure the amount of turbidity rather than the absorbance. The accessory consists of an integrating sphere with a built-in photomultiplier detector. The sphere's internal surface is coated with a white diffusing material ¹.

The purpose of the present investigation was to develop other procedure to measure scattered transmittance.

In a normal spectrophotometer arrangement, the detector may be some distance from the sample, making the light-collection efficiency very low ². But when the detector is nearer the scattering matrix a greater proportion of scattered radiation is collected.

We have used a spectrophotometer with two sample positions. In the primary sample position only a small proportion of scattered radiation is received by the detector. If the sample is placed in the secondary

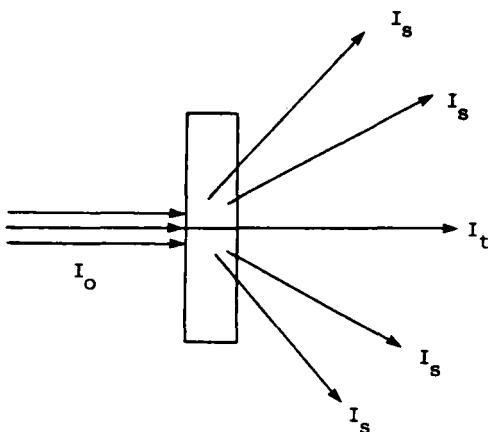


FIG. 1. Scattered transmittance of light through a sample. I_o represents the incident radiation, I_s represents the scattered transmittance, and I_t represents the transmitted radiation that is not scattered.

sample position more scattered radiation will reach the detector.

The loss of light by scattering causes an apparently greater absorbance with the sample in the primary sample position.

INSTRUMENTATION

The spectra were recorded by a Pye-Unicam SP-1800 UV/Vis Spectrophotometer, over the range of 210 - 700 nm, with a 0.5 mm slit width.

METHOD

The detector presents a greater solid angle at the nearby secondary sample position than at the primary sample position because the distance separating the sample and the detector is 17 cm and 1.3 cm respectively. Assuming that the scattered radiation is uniformly distributed and reaches the detector by direct routes only, in the primary sample position 0.5 per cent reaches the detector, whereas 15 per cent reaches it from the secondary position ³.

If A_1 and A_2 are the measured absorbance with the sample placed at primary and secondary position respectively, these values represent:

$$A_1 = \log \left\{ I_0 / (I_t + \varsigma I_s) \right\} \quad (1)$$

$$A_2 = \log \left\{ I_0 / (I_t + \varsigma I_s + \Delta I_s) \right\} \quad (2)$$

where $\varsigma \approx 0.005$ and $\Delta \approx 0.145$ in the used device.

The difference between the obtained results in the two different sample positions are related to the intensity of scattered radiation by the expression:

$$A_1 - A_2 = \log \left(1 + \frac{\Delta I_s}{I_t + \varsigma I_s} \right) \quad (3)$$

Thus the relationship between scattered radiation and the difference of absorbances is:

$$\frac{I_s}{I_t} \approx (10^{(A_1 - A_2)} - 1) / 0.145 \quad (4)$$

In this way it is possible to obtain a measure of the scatter (I_s/I_t) of a sample by observing the difference in absorbance readings when the sample is placed consecutively in the two sampling positions.

The approximation that simplifies equation (3) to equation (4) and so simplifies the I_s/I_t calculation has an error that increases with the increasing $A_1 - A_2$ difference, as table 1 summarizes.

TABLE 1

Differences of absorbance ($A_1 - A_2$), calculated scattering (I_s/I_t) approximately by equation (4) and exactly by expression (3), and committed error.

$A_1 - A_2$	(I_s/I_t) ap.	(I_s/I_t) ex.	Error, %
0.0	0	0	0
0.1	1.79	1.80	0.6
0.2	4.03	4.12	2.2
0.3	6.86	7.11	3.5
0.4	10.43	11.00	5.1
0.5	14.91	16.11	7.4
0.6	20.56	22.91	10.3
0.7	27.67	32.11	13.8

EXPERIMENTAL

The study of difference between obtained absorbances in the two different sampling positions has been applied to turbid solutions, as dilute whole blood, skimmed milk ³ or beer ⁴. In this paper we show the obtained values for two different kinds of commercially available extruded polymeric films: regenerated cellulose and polyethylene. We have chosen these samples because of their industrial significance.

In these films, scattered radiation intensity is principally related to irregularities on the surface and to inhomogeneities in the structure resulting from the different refractive indexes of the crystalline and noncrystalline regions ^{5,6}.

Figures 2 and 3 show the obtained absorbances in the two sample positions, for regenerated cellulose film (thickness of 30 μm) and for polyethylene film (thickness of 50 μm) respectively, between 210 and 700 nm. The spectra were measured point for point, each 10 nm, adjusting the zero control to zero the display, with the aim of obtain more accurate results.

In each case, the lower curve was obtained with the sample in the secondary sample position and this is because the spectrum corresponds more closely to the true spectrum, as described previously. However, for the cellulose film the two spectra are more similar than for the polyethylene film.

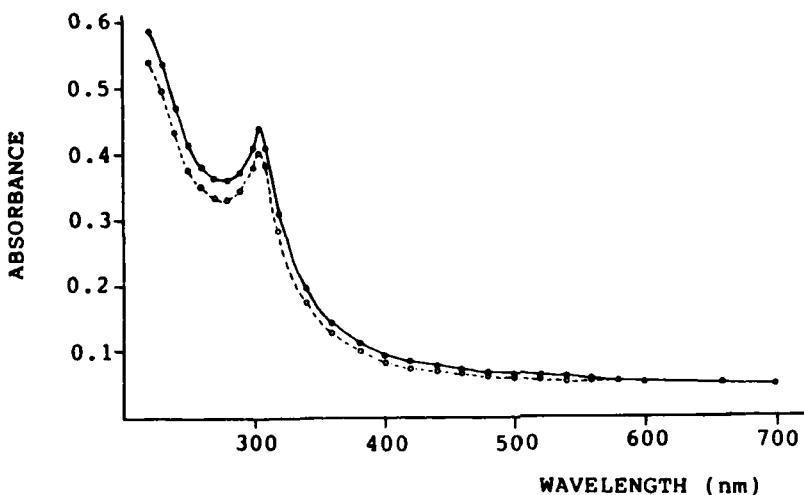


FIG. 2. UV/Vis absorption spectrum of a regenerated cellulose film (thickness of 30 μm). Primary sample position (—●—) and secondary sample position (---●---).

RESULTS AND CONCLUSIONS

From referred measures before, it is possible to obtain the scattered radiation intensities values (I_s/I_t) by applying equation (4), and so, we have obtained the represented values in figures 4 and 5.

As illustrated in these figures, the scattered radiation intensity decrease with the increasing wavelength. Figures 4 and 5 are similar in form although measured scattering for cellulose film is much lower than those observed for polyethylene film. This is justified because, by far, the greater proportion of scattered light by these kind of films occurs at irreg-

ularities on the surface (more abundant on polyethylene) of the film, being caused by melt flow phenomena, and the contribution made by crystallisation effects is usually negligible.

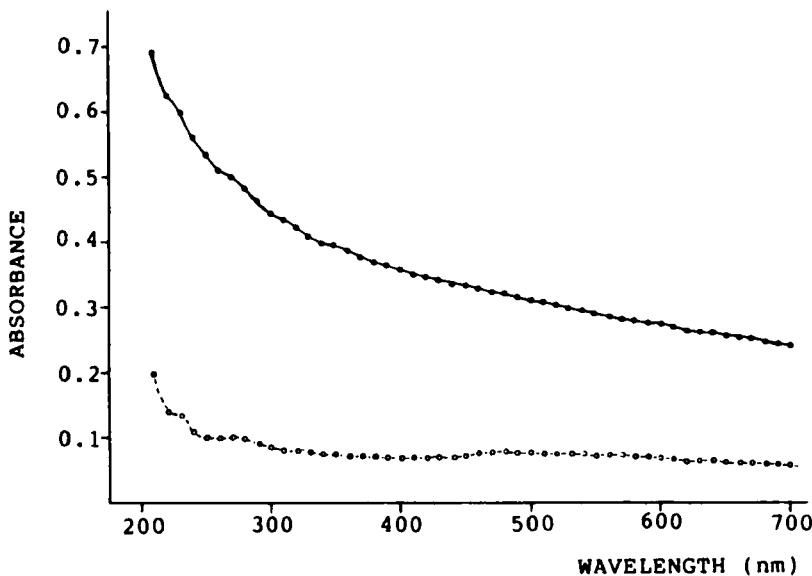


FIG. 3. UV/Vis absorption spectrum of a polyethylene film (thickness of 50 μm). Primary sample position (—●—) and secondary sample position (---○---).

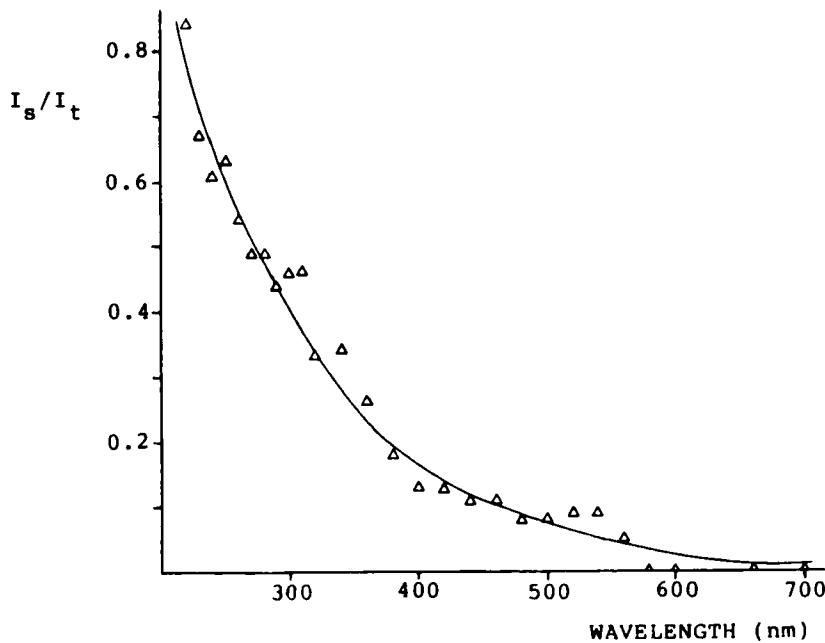


FIG. 4. Relationship between scattered transmittance divided by transmitted radiation and wavelength of a regenerated cellulose film (thickness of 30 μ m).

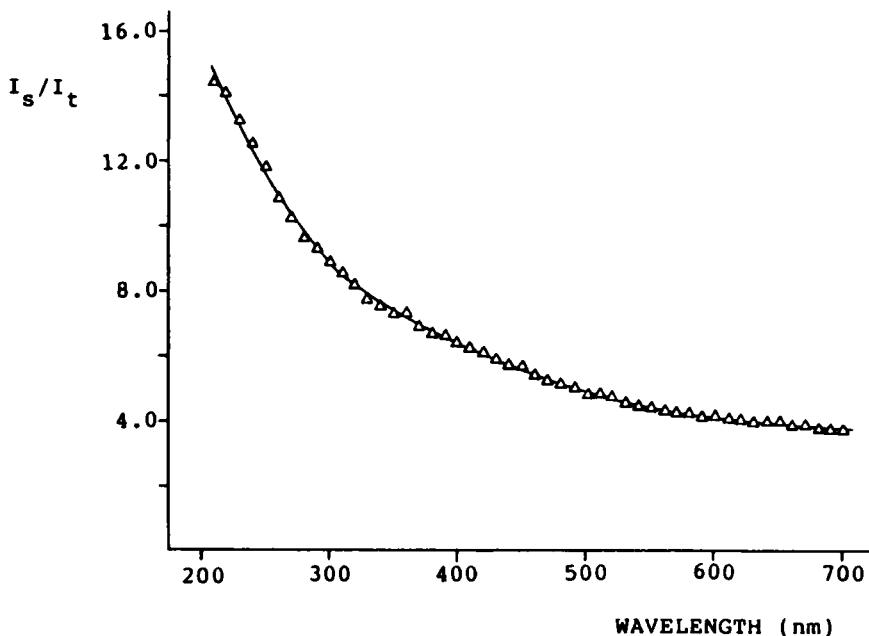


FIG. 5. Relationship between scattered transmittance divided by transmitted radiation and wavelength of a polyethylene film (thickness of 50 μm).

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