A Multiplication Method for the measurement of the absorption of light in thin layers.

By **Dr. L. Honty**, Praha.

(Received November 2, 1936.)

The diminution of light by absorption, when travelling through a thin film of some absorbing substance, is, as a rule, only measurable when the extinction coefficient is fairly high. In the case of weak absorption it becomes necessary to use sensitive photo-electric methods, which have of recent years been developed to a high degree of efficiency, so that by their use it is possible to determine the dimming or extinction of light to one tenth of one per cent (e. g. in the measurement of absorption in thin crystals by Gudden and his pupils). However even these sensitive methods are often insufficient, and frequently it is necessary to determine the absorption by some quite distinct method for other reasons. This is the case when the absorption is required to be measured directly in a thin layer, and it is not possible to get the absorbing substance into the form of a thicker layer, more suitable to the experimental measurement, as, for example, in the case of only a small quantity of the absorbent being available, such as a finished and mounted thin filter, etc. Besides, even when the substance is obtainable in thicker layers, it may be necessary to determine the absorption of light in a thin layer, for which the physical and physico-chemical (colloidal) properties are characteristic, and different from those shown by thicker layers.

It is possible to obtain increased absorption during the passage through a thin layer by prolonging the path of the measured ray within the layer concerned (illumination along the layer is, for the most part, experimentally impracticable) by means similar to those used in the Lummer-Gehrcke interference-film spectroscope, i. e. by ensuring that the ray incident on the boundary of the thin layer never emerges from it, but by repeated reflection within the critical angle continues within the layer till its final emergence to the measuring apparatus. The application of this principle to absorption measurements is as follows (Fig. 1).

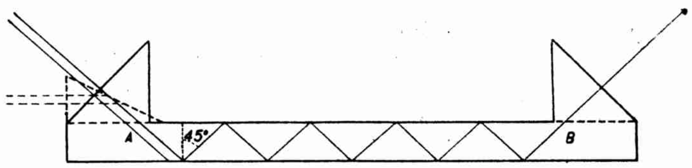


Fig. 1.

The thin layer, either alone or else cemented to a glass plate, is fixed in optical contact (by the use of glycerine, cedar-wood oil, etc.) with a small glass prism, say a right-angle glass prism as shown in the plate. The prism is best fixed flat on one of its right-angle sides, so that the incident light falls vertically on its hypothenuse, or else on the other right-angle side, according to the method of F. Twyman, for parallel incident light. A thin beam of parallel rays proceeding from a slit falls, through this prism, upon the lower side of the thin layer, at so great an angle that, by repeated total internal reflection, it traverses the entire length of the thin layer before finally emerging through a similarly placed exit prism to the measuring apparatus (photometer, polarimeter, or spectrograph). By this means the path of the ray in the absorbing material of the thin layer is prolonged to such a degree (about 200 times) that even an apparently colourless thin layer will visibly show its characteristic absorption tints.

The angle of incidence for total internal reflection at the lower surface of the layer is given by the well-known expression

$$\sin \beta \geqq \frac{n_1}{n_2} < 1,$$

where n_1 and n_2 stand for the absolute indices of refraction of the bounding medium and the layer respectively. For an average value of the relative index of refraction $n_2/n_1 = n = 1{,}5$, which corresponds to the mean value between the surrounding air and ordinary crown glass, we obtain for the critical angle almost 42° (41° 40′). If the narrow beam used for the measurement falls perpendicularly upon the hypotenuse face of the mounted right-angle prism, the angle of incidence on the lower surface of the layer will be exactly 45°, so that the condition for total internal reflection is fulfilled for a distinct pencil of rays of small divergent angle. In the case of the second modification, for parallel incidence of the light, the face of the prism in optical contact with the layer must be twice as long as that exposed to the incident light. Under these circumstances the ray strikes the hypotenuse face of the prism at an angle of less than 45° and is them totally reflected from the lower surface of the layer. Considering the fact that the angle of incidence usually differs sensibly from the angle of minimum deviation, and also considering that the index of refraction depends on the wave-length of the incident light, it is necessary to investigate the effects of these facts.

Deviations from the critical angle produce a double change: thus, a change in the angle of incidence from the critical angle within the layer alters the course, and hence the length of the optical path pursued by the ray within the layer. For an approximately constant distance between the initial entry to and final exit from the layer at the points where the prisms are homogeneously attached to it, and for a constant thickness of the layer, the length of the path traced out by the ray under repeated reflection within the layer is given by the expression

$$\frac{\overline{AB}}{2d \tan \beta} \cdot n \cdot \frac{2d}{\cos \beta} = n \cdot \frac{\overline{AB}}{\sin \beta}.$$

According to this, the length of the optical path traversed within the layer has no connection with the thickness of the layer; it is, however, connected with the angle of incidence, and with the distance between the points of entry and exit. That it is not connected with the thickness of the layer follows as a direct consequence of the fact that, in thinner layers the increased number of reflections offsets the longer path between each pair of reflections obtained in thicker layers, as is quite obvious from the above expression, in which $\frac{\overline{AB}}{2d \tan \beta}$ gives the number of reflections, while $n \frac{2d}{\cos \beta}$ gives the length of the optical path taken between each pair of successive reflections. For a layer 1 mm thick with an angle of incidence of 45°, we obtain 100 reflections at each surface of the layer, where the distance between the points of entrance and exit is 100 mm, and under these conditions the optical path is extended to n . 141 mm, as compared to n . 1 mm for direct passage of the ray through the layer.

The length of the optical path within the layer is indirectly proportional to the sine of the angle of incidence, and if the angle of incidence is decreased below the critical angle the length of this optical path increases, while at the same time the amount of light reflected simultaneously decreases. However, even a rough and approximate calculation is enough to make it clear that the decrease of the reflected light due to the decrease of the incident angle below the critical value far outweighs the simultaneous lengthening of the optical path, and the increase of absorption obtained thereby, so that the optimum results are obtained from the method when using the critical angle of incidence for the ray. According to the above expression, the length of the optical path for a decrease of 10′ and 1° below the critical value is diminished in the ratio, respectively of 0,707 : 0,705, and 0,707 : 0,695. The intensity of the reflected light decreases far more rapidly. According to the Fresnel's law, the intensity of the reflected light is given by the expression

$$J^r = J^r_{\parallel} + J^r_{\perp} - \tfrac{1}{2}J_0 \left[\frac{\sin^2(\alpha - \beta)}{\sin^2(\alpha - \beta)} + \frac{\tan^2(\alpha - \beta)}{\tan^2(\alpha - \beta)}\right],$$

where $J^r_{\parallel}$ and $J^v_{\perp}$ are the intensities of light polarised respectively in planes parallel and perpendicular to the plane of incidence, J_0 and J^r the total intensities of the incident and reflected light, and α and β the angles of incidence and refraction respectively, so that $\sin \alpha / \sin \beta = n$.

This expression, with the necessary modification of symbols, is also valid for the incidence of light in an optically dense medium upon the boundary of an optically less dense medium, since even in the case of the difference $\alpha - \beta$ having a negative value its square still remains positive. For total reflection, where $\alpha = 90°$, $J^r \doteq J_0$.

The numerical values of this equation have been worked out by Krüss, and for the case of light reflected within an optically denser medium, for index of refraction $n = 1{,}5$, for angles of incidence slightly smaller than the critical angle (i. e. 41° 81′) within a difference of 1° we get the following intensity ratios for the given differences in minutes of arc from the critical angle

n	critical angle	$\beta_m - 0$	$\beta_m - 1'$	$-5'$	$-10'$	$-20'$	$-30'$	$-40'$	$-50'$	$-60'$
1,5	41° 81′	1,000	0,860	0,723	0,634	0,530	0,462	0,412	0,375	0.343

According to this calculation compared with the small increases in the optical path got by lowering the angle of incidence 10′ and 1° below the critical value, the intensity of the reflected light for $n = 1{,}5$ decreases in the rations respectively of 1,000 : 0,634 and 1,000 : 0,343 respectively, compared to which the absorption increases in the ratio $e^{-0{,}707} : e^{-0{,}695}$ are inappreciable.

It is clearly shown, from the above, what serious losses in reflection, from the standpoint of absorption, are caused by even slight decreases of the angle of incidence below the critical value. Increase of the angle of incidence above the critical angle does not produce any loss on reflection. A similar calculation gives the course of reflection for the following large intervals of excess of the angle of incidence over the critical value

n	critical angle	0°	10°	20°	30°	40°	50°	60°
1,5	41° 81′	0,040	0,040	0,041	0,055	0,245	1,000	1,000

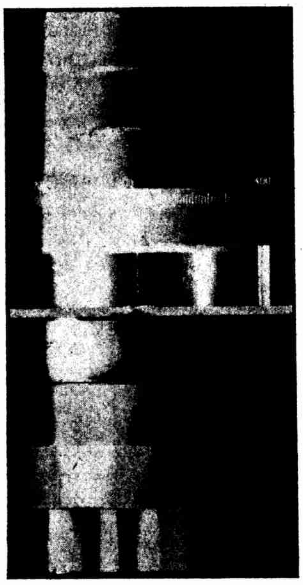
From these figures it is evident that even for an increase of 20° we get a constant value for the reflected light; at the same time, however, the length of the optical path in the layer is decreased in the ratio 0,707 : 0,342. In consequence, it is advisable to carry out measurements at an angle of incidence slightly greater than the critical value, with which it is certain that the whole spectral range is totally reflected (provided, of course, that strong anomalous dispersion does not take place).

In considering the above conditions the dimming of the light in its passage through the layer has been attributed entirely of absorption. At the boundaries of the layer, of the prisms, and of the optical joining medium, a minute reflection of light always occurs, which may be neglected. The same thing occurs during the normal entrance and exit of light at the prism faces. For the vertical incidence of light on the boundary between air and glass, we get light reflected in accordance with the expression

$$J^r = J_0 \left(\frac{n_2 - n_1}{n_2 + n_1}\right)^2.$$

For a mean index of refraction $n_2/n_1 = 1{,}5$ this reflection at the glass accounts for about 4% of the incident light. Over a range of indices of refraction from 1,40 to 1,99 the intensity of the reflected light for normal incidence increases in the ratio 2,78 : 10,96. From the point of absorption we may either take this reflection loss into account or else compensate for it experimentally. In the accurate determination of the conditions applicable to this experimental method attention must also be given to phenomena of anomalous dispersion taking place simultaneously with absorption, and to polarisation phenomena, especially during reflection (natural light is not changed by total reflection, and only plane polarised light is polarised elliptically thereby (at 45° to the plane of incidence it becomes circularly polarised after being twice totally reflected) however it is probable that even ordinary light becomes weakly polarised in the plane of incidence after multiple (× 50) reflection (see the photograph Fig. 2 of the Herotar screen). Further we must also consider interference phenomena in the case of passage through a very thin layer, with which is further connected the question of inequalities in the surfaces or homogeneity of the layer, as also the case of anisotropy.

By means of this method the spectral absorption of thin and apparently colourless layers of dyestuffs was determined, as also that of polarisation filters. Under experiment a thin layer (0,01 mm, placed between plates of thicker glass) of polarisation filter (periodide quinine sulphate) showed weak diffusion colours, characteristic for fluorescent quinine compounds, which even appeared as visible streaks in the region of total reflection.



Ordinary- non multiplication-method:

1. Eastman Pola-screen (filter cemented in glass),
2. Zeiss Herotar (filter cemented in glass),
3. a neutral glass (absorption 50%),
4. the white flame carbon arc. (Zeiss, 10 Amp.), direct,
5. the mercury vapour lamp Philips Philora.

Multiplication method:

1a. Pola-screen ⦶ ||,

2a. Herotar ⦶ ||,

2b. Herotar ⦸ 45°,

3a. the neutral glass.

Fig. 2. Photographs of the spectral absorption in the visible region taken on Kodak SS panchromatic films.

The Kodak „Polaroid" filter composed of small crystals combined togather by the Friedmann-Land method showed on examination a stronger blue-green colour than the yellower Zeiss „Herotar" made by the Bernauer method from a single large thin crystal. In the spectroscopic analysis of the absorption (see the annexed spectrum photograph) with the aid of the multiplication method described above, a dense purple filter showed chiefly light red light, an increase of absorption being accompanied by an increase of the polarisation of the emergent light. According to the direction in the layer of the ray of light traversing it, relative