

INDUSTRIAL PHOTOCHEMISTRY I: MEASUREMENT OF THE ABSORPTION PROFILE OF THE LIGHT IN A PHOTOCHEMICAL REACTOR

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Summary

Knowledge of the local distribution of the light energy in a photochemical reactor in the presence of an absorbing substance, leading to a reaction of which the rate is of an order different from first order with respect to the absorbed light intensity, is important to calculate the mean rate of reaction and the design of the reactor. We report a simple method for the determination of this profile as a function of the concentration of an absorbing substance and we compare the results obtained with the models of emission which have been published. A semiempirical model accounting for our experimental results is presented.

1. Introduction

The study of photochemical reactions has been the subject of a very large number of both laboratory and industrial works, in particular with regard to first-order reactions with respect to the absorbed light intensity (photonitrosation of cyclohexane for example [1]), or of order one-half, such as the chain reactions of photochlorination or of photooxidation [2 - 4].

In the cases where this order is equal to one, knowledge of the mean number of photons absorbed in the reactor per second is sufficient to account for the rate of reaction, and, moreover, often the design of the photoreactor is carried out from the phenomena of heat transfer. In contrast, when this order differs from 1 and when the chemical reaction implies other reactions between unstable species (excited electronic states, free radicals, ion radicals etc.), the existence of a concentration gradient of these species depends on the absorption profile of the light and on the rate of the microscopic and macroscopic homogenization processes of the medium (diffusion and stirring, functions of the mean lifetime of the unstable species (essentially radicals)). These can

be responsible at a given absorbed light intensity for a mean rate of reaction which is a function of this absorption profile [4] and which it becomes essential to determine.

With this as our aim, a bibliographic search has led us to the conclusion that, although researchers [5 - 22] are in agreement on the interest of such a determination, the majority of them have only carried out model calculations which are often very sophisticated. However, experimental works are rare and in general carried out in the absence of absorbing substances [7, 17, 21]. With the aim of obtaining access to better knowledge of the kinetics of photochemical reactions of oxidation and chlorination, which depend on the absorption profile of the light [2 - 4], we have been led to measure the absorption profile in an annular reactor in the absence and presence of a substance which absorbs the light, and to search for a simple model to express the experimental results. It is the assembly of these results which is summarized in the present paper.

2. Experimental set-up

2.1. Principle of the set-ups

In the numerous industrial or laboratory set-ups, between the lamp and the solution to be irradiated one or several filters are placed for selecting the active wavelengths emitted by the lamp [1] and to dissipate the thermal energy. Indeed, with the exception of lasers, instrumental devices of monochromatic emission are practically non-existent when it is often useful (if not necessary) to isolate a band of wavelengths for measurements of quantum yields in the laboratory or to eliminate the destructive wavelengths in industrial reactions (photochemical synthesis of caprolactam for example [1]).

This type of set-up, shown in Fig. 1, has the advantage of allowing the determination of the absorption profile of the light without, in principle, having to know the intensities of the different wavelengths emitted by the lamp, the molar extinction coefficients of the absorbing substance or finally the response of the photodetector used for the measurement. The measurement of the local light intensity in a photoreactor dictates the use of a photodetector of restricted dimensions, which shows large dynamics, in order to allow the measurement of the absorption profile at high optical densities. The photodetectors used so far, *e.g.* the microphotoreactors which contain a light-sensitive solution [21, 23] or the physical receptors of the photopile type, cannot be made sufficiently small. We have been forced to build another system of measurement capable of satisfying these two conditions. This system is described in the next section.

2.2. Proposed technique

2.2.1. The photodetector

We have used an optical fibre (Fort Company) of small diameter (0.2 mm) fixed onto a rigid support of small dimensions (a glass tube of 2 mm external

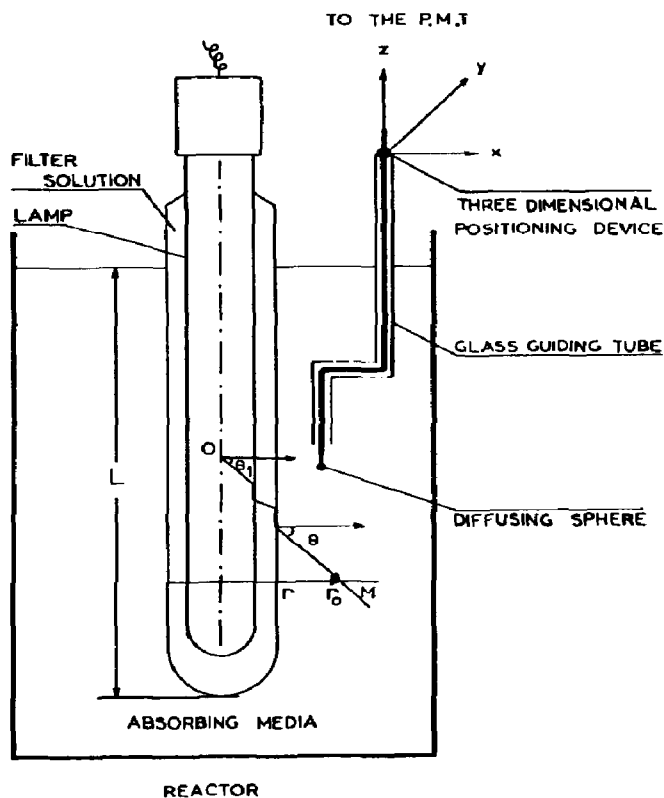


Fig. 1. A diagram of the set-up and the nomenclature used.

diameter) in order to alleviate all perturbations of the light profile to be studied. The optical fibre and rigid support assembly are jointly responsible for a three-dimensional system of reference. Obviously only the extremities of the optical fibre are stripped, as is shown in Fig. 1.

The end that is plunged into the reactor is covered by a diffusing sphere of gum of about 0.5 mm diameter; the other end penetrates the housing of a photomultiplier. The optical fibre is chosen to be long, *i.e.* several metres, to avoid modification of the transmission of the fibre by displacements of the rigid support in three dimensions. Thus we have built a system of measurement that is sensitive to radiation emitted in practically all space, *i.e.* 4π steradians. Having taken into account the large dynamics of the photomultiplier tube (PMT), the system of measurement thus formed obeys the conditions defined in Section 2.1.

This photodetector also possesses the advantage of allowing measurement of the light distribution in the photoreactor for the different wavelengths emitted by the lamp by removing the chemical filter placed between the lamp and the solution to be irradiated and introducing it between the fibre and the PMT. This type of set-up has not been used in the present work as it does not correspond to the conventional working conditions of photoreactors.

2.2.2. Reactor filter and absorbing solution

The photoreactor is a glass cylinder, diameter 120 mm and height 230 mm, the inside of which has been coated with black paint in order to suppress the stray reflections from the lamp and from the outside (non-filtered light) which considerably perturbed our first attempts in the search for an emission model (see Section 4). The light source is a low pressure mercury vapour lamp (Ultra Violet Products) of cylindrical form, from which we succeeded in selecting two radiation lines that were close in wavelength (404.7 and 435.8 nm) with the aid of a chemical filter $\text{CuSO}_4\text{-NH}_4\text{OH}$ [24].

The transmission curve of the filter is shown in Fig. 2(a). The necessity of using two emission radiation wavelengths has compelled us to search for a substance that is soluble in water and absorbs with practically the same molar extinction coefficient ϵ at 404.7 and 435.8 nm, in order to study the absorption profiles. We chose a dye (quinoline yellow) characterized by the absorption spectrum reproduced in Fig. 2(b) and which, moreover, shows a non-perturbing fluorescence emission.

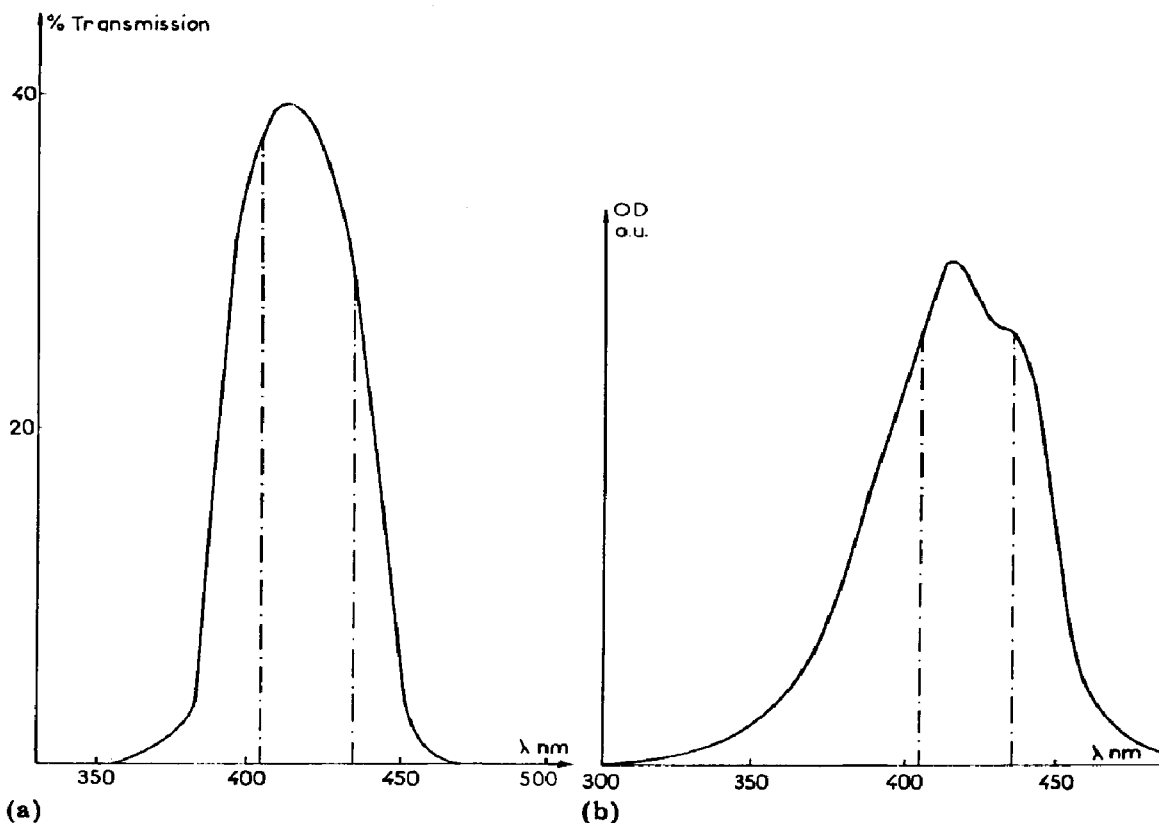


Fig. 2. (a) Transmission of the filter $\text{CuSO}_4\text{-NH}_4\text{OH}$; (b) the absorption spectrum of quinoline yellow in aqueous solution.

2.2.3. Control and limit of the set-up

A control of the experimental set-up has been carried out during a verification of the Beer-Lambert law on excitation with a parallel monochro-

matic beam of an absorbing solution contained in a plane reactor. This monochromatic beam was obtained with the aid of a xenon lamp and an H2O monochromator (Jobin and Yvon).

The precision of the measurements of light intensity is limited by the following phenomena: (1) the presence of non-filtered stray light; (2) a non-negligible volume of the diffusion sphere; (3) the difficulty in assigning a perfectly radial trajectory to the support of the optical fibre with respect to the lamp and low precision in locating the fibre in the vicinity of the filter (± 0.5 mm). In practice the experimental set-up enables measurements of transmitted light intensity to be made with good accuracy up to optical densities of about 3 for an optical path length of 1 cm.

3. Results of measurements

On addition of quinoline yellow to the solution present in the photoreactor, we carried out measurements of optical densities varying from 0 to 2.1 for an optical path length of 1 cm; optical densities were measured with the aid of a Cary 15 UV-visible spectrophotometer. The profiles obtained are shown in Figs. 3(a) and 3(b). The modelling of these curves will be outlined in Section 4.2.

4. Discussion

4.1. Different types of emission models

As the majority of industrial photoreactors are of the immersed lamp type, numerous researchers have tried to schematize the profile of the light distribution in an annular space. A certain number of theoretical models have thus been developed, with hypotheses based on the following.

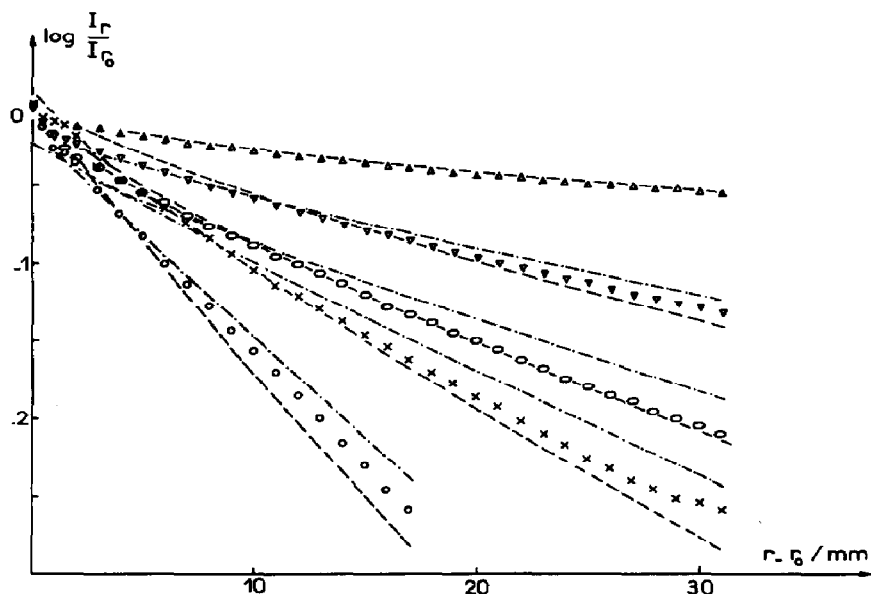
- (1) The light emitted by the source is assumed to be monochromatic.
- (2) The phenomena of reflection, refraction, diffusion and diffraction of the light are neglected.
- (3) The light source obeys the Lambert law or emits with the same probability in all directions of space.
- (4) The absorption coefficient of the liquid is assumed to be independent of the direction of propagation of the light rays (homogeneous and anisotropic fluid).

4.1.1. Radial model (line source with emission in parallel planes perpendicular to the lamp axis)

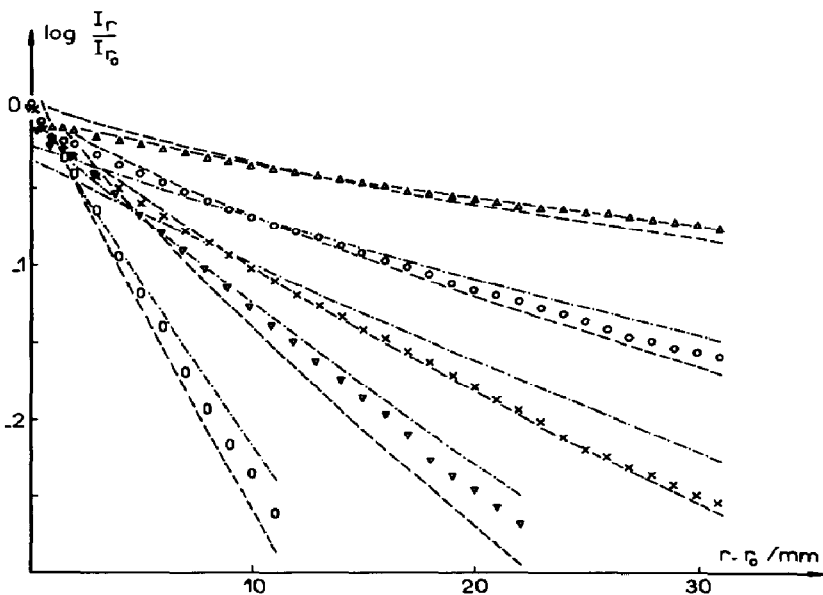
In this model we suppose that the lamp is of infinite length and that all the light rays are radial with respect to the lamp. At a distance r from the axis of the lamp the flux per unit length of the cylinder is

$$2\pi r I_r = 2\pi r_0 I_{r_0} \exp\{-\mu(r - r_0)\}$$

where μ represents the product of the concentration of absorbing substance and the molar extinction coefficient at the wavelength being considered. Thus



(a)



(b)

Fig. 3. Results of measurements of the distribution of the emitted light in the presence of quinoline yellow for the two-dimensional model (---) and the radial model (-·-·): (a) optical densities for an optical path length of 1 cm (Δ , 0; ∇ , 0.20; \circ , 0.40; \times , 0.605; \circ , 1.18); (b) optical densities for an optical path length of 1 cm (Δ , 0.068; \circ , 0.28; \times , 0.54; ∇ , 0.94; \circ , 2.10).

$$I_r = \frac{I_{r_0} r_0}{r} \exp\{-\mu(r - r_0)\} \quad (1)$$

This model is evidently very easily applied but gives little *a priori* explanation of physical reality.

4.1.2. Two-dimensional model

According to the type of photoreactor, several models of two-dimensional radiation have been developed. For a cylindrical reactor, several researchers [18, 19, 25] have supposed that the light rays are exclusively situated in a plane perpendicular to the axis of the reactor and that in this plane the wall emits in accordance with the Lambert law. For the design of annular reactors, Jacob and Dranoff [17] have considered the light source as a straight line each point of which emits light rays in all directions (line source (LS) model).

Under these conditions the law defining the absorption profile at the mid-depth of the reactor is written with the notation shown in Fig. 4.

$$I\left(r, \frac{L}{2}\right) = \frac{2I_{r_0} r_0}{\pi} \int_0^L \frac{\exp\{-\mu\rho(r - r_0)/r\}}{\rho^2} dz$$

with

$$\rho = (r^2 + z^2)^{1/2}$$

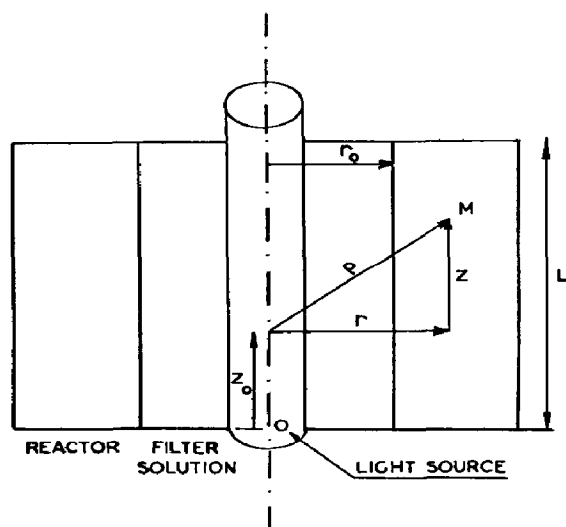


Fig. 4. The nomenclature used for the LS model.

4.1.3. Three-dimensional model (extended source model [15])

Whereas the preceding models simplify the geometry of the emission of the light source, on the contrary, the diffused three-dimensional model will take into account this geometry, with the following hypotheses.

(1) The emission of photons is distributed uniformly throughout the volume of the lamp.

(2) The emission of each element of volume is isotropic.

(3) The quantity of energy emitted by each element of volume is proportional to its volume.

(4) Each element of volume inside the lamp is transparent to the emission from the other elements of volume.

Although this model enables us to include a large number of parameters, it seems to be difficult to handle and leads to very complex calculations in the presence of an absorbing substance, so we have not tried to make use of it in the interpretation of our experimental results (this model has been tested by Cerda *et al.* [15] in the absence of an absorbing solution).

4.2. Simplified model

If we admit that the internal radius of the lamp is small compared with the distances at which the measurement of the profile is carried out ($r > r_0$) (see Fig. 1), we can (in principle) define the variations of $I(r)$ with r from the radial model or from the Dranoff model [17] (LS model).

The use of the three-dimensional model has been rejected for the following two important reasons: (1) the difficulty of calculation because there are too many parameters, in particular in the presence of an absorbing substance; (2) poor knowledge of the distribution of the emitted light. Indeed, even if the emission of photons is distributed uniformly throughout the volume of the lamp, the useful photons emitted first undergo refraction at the quartz interface, then are partially absorbed by the filter and escape and are refracted on the glass separating the filter from the reactor.

As a result there is a distribution $g(\theta)$ of the light in the reactor (even in the absence of absorption therein), which will depend on the angle θ_1 at which the photon has been emitted (see Fig. 1). The lack of knowledge of this law of variation eliminates the use of sophisticated models such as the two- and three-dimensional models.

However, as is shown by the results in Fig. 3, the use of the radial model does not enable us to explain exactly the $I(r)$ - r variations. We have then been led to search for a semiempirical representation of $I(r)$. In order to do this, we have first of all supposed that the radial model is satisfactory and have searched for the correction factor k which must be applied to μ so that the curve calculated from variations in $rI(r)/r_0I(r_0)$ with $\mu(r - r_0)$ gives the best fit to the experimental points. Then

$$\frac{I(r)}{I(r_0)} = \frac{r_0}{r} \exp\{-k\mu(r - r_0)\}$$

In Fig. 5 we have shown the logarithmic variations in $rI(r)/r_0I(r_0)$ with $\mu(r - r_0)$ for all our measurements. These results show that it is possible to find a

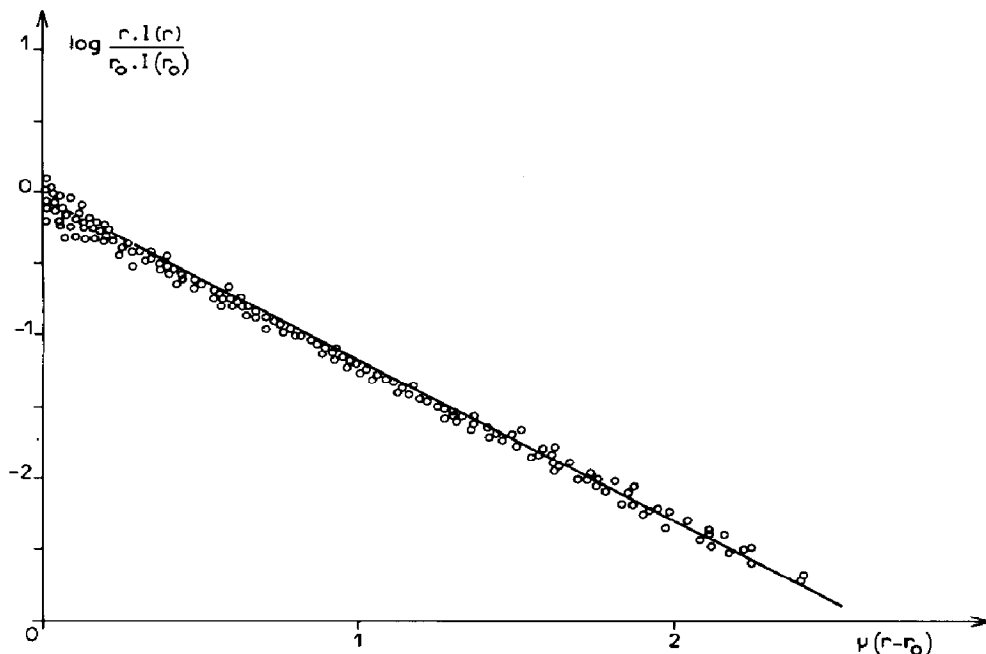


Fig. 5. A comparison of the two-dimensional analysis of the experimental results obtained with the simplified model.

satisfactory linear representation from which k is found to be approximately 1.14. A value of k greater than unity can be interpreted by taking into account that the non-radial rays ($\theta \neq 0$) have a longer optical path length than those corresponding to $\theta = 0$ and therefore have a larger probability of being absorbed. Thus it is as if the value of $\mu(r - r_0)$ were larger than it is in reality.

At high values of μ the non-radial radiations which have a larger optical path length to reach the collector have a high probability of being absorbed. Thus as soon as the region close to the filter is passed, practically only the nearby rays have the largest probability of crossing the solution. We can explain the curved form of the variations in $\log_{10}\{rI(r)/r_0I(r_0)\}$ versus $\mu(r - r_0)$ (see Fig. 5) in this manner.

However, we think that with the simplified analysis proposed here we may hope for better knowledge of the kinetics of photochemical reactions studied in the laboratory. In particular for large values of r we can describe our experimental results with the aid of the radial model put forward in Section 4.

5. Conclusions

The results of the present study indicate the partial influence of stray reflections and the predominant influence of stray absorptions of the exciting light by the filtering solution. The existence of these phenomena does not enable us to use the models of light emission published so far in order to interpret all our experimental results.

A semiempirical model has been developed in which we have tried to take these stray phenomena into account and has been compared satisfactorily with our experiments using the work presented here. Our results, however, show clearly that the description of the emission profile at high optical densities corresponds approximately to that of the radial model where we use a constant correction for the optical density of the substance absorbing the light. The kinetic analysis of reactions carried out in the laboratory, of which the rate is of an order different from first order with respect to the absorbed intensity and which depends on this absorption profile, can then be followed up and improved.

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