RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

July 1977

Translated from *Uspekhi Khimii*, **46**, 1153-1182 (1977)

U.D.C. 535.36; 543.42

The Application of the Spectroscopy of Light Scattering Media in Physicochemical Research

S.M.Baranov and N.M.Bazhin

The theoretical and applied aspects of the spectroscopy of light scattering media are examined and approximate methods for the solution of the radiative transfer equation are described. The data obtained with the aid of certain approximations are compared with the results of accurate calculations and certain experimental light scattering data are analysed. The bibliography includes 123 references.

CONTENTS

I.	Introduction	603
II.	Equation of radiative transfer. Notation	604
III.	The two-flux approximation method	605
IV.	The diffusion approximation	608
V.	The transport approximation	610
VI.	Other methods for the description of light scattering processes	611
VII.	The application of the spectroscopy of light scattering media to the interpretation of experimental data	612
VIII.	Conclusion	615

I. INTRODUCTION

In order to follow and investigate the mechanisms of a wide variety of chemical processes, optical spectroscopy is frequently used. However, its scope is most completely realised only for transparent (non-scattering) systems. On the other hand, many important chemical processes, for example catalytic, photochemical, polymerisation, etc. reactions, proceed in light-scattering media, where optical spectroscopy in its usual version developed for transparent media is inapplicable.

In a study of such processes, the optical spectroscopy of scattering media is a very important and sometimes the only physical method which can yield the required information about the course of the chemical reaction. However, despite the probable utility of the spectroscopy of light scattering media (SLM) in the solution of many physicochemical problems, it has not been adequately developed, particularly compared with the spectroscopy of transparent media. This is due to the following causes: firstly, the complexity of the mathematical description of the processes involving light transmission through scattering systems and the difficulties associated with the solution of the corresponding equations (thus the spectroscopy of transparent media involves only two parameters—optical density and the optical path length, while a light-scattering

layer is characterised, together with these parameters, also by the scattering coefficient, the angular distribution of the scattered light, and the refractive index of the layer. In real systems, the scattering coefficient and the angular structure of the scattered light may also depend on the direction of propagation of light); secondly, the lack of simple, reliable, and well founded experimental methods, which is related directly to the foregoing considerations.

In the spectroscopy of transparent media, one usually measures the optical density, which is related to the extinction coefficient and the concentration of the test substance by a simple linear expression. In SLM, the measured quantities are usually the integral reflectance (R) or transmittance (T) defined as the ratios of the amount of reflected radiation or radiation which has passed through the layer to the incident light flux. Furthermore, one can measure the angular dependence of the reflected and transmitted light as well as the angular dependence of the radiation within the medium.

Unfortunately, none of the experimentally measured quantities is linked by simple relations to the system parameters. In the general case, the measured quantity depends on the characteristics of the medium in a fairly complex manner, and this relation frequently cannot be expressed in an analytical form. Nevertheless, in terms of certain approximations, it is possible to put forward analytical relations whereby one can derive information from the experimental data about the characteristics of the medium and ultimately about the concentrations and extinction coefficients of the chemical compounds present in the scattering specimen.

There have been a number of extensive reviews and books on the theory of light scattering and its practical applications[1-13]. Some of these[1,2,11-13] are devoted mainly to the consideration of the theoretical problems of light scattering using a complex mathematical procedure. Other studies also deal with the analysis of the experimental data. However, we may note that, among these studies, only two[5,7] are specifically concerned with the application of SLM to physicochemical research, although some results of physicochemical experiments are given in the other investigations.

Analysis of the available studies[1-13] shows that there is a significant gap between the work of theoreticians and experimental chemists. Also the conditions under which particular approximate expression used in the interpretation of the experimental data are applicable are frequently not clearly defined in chemical literature.

The aim of the present review is, on the one hand, to give an account of various methods for the approximate description of light scattering processes, to indicate the limits of their applicability, and to compare the different approximate methods with one another, and, on the other hand, to demonstrate the possibility of applying these approximations to the solution of practical chemical problems.

II. EQUATION OF RADIATIVE TRANSFER. NOTATION

Processes involving the transmission of light through scattering media are described by the integrodifferential equation of the transmission of radiation[1-3,8,9]:

$$\mu \frac{\partial I(z, \mu, \varphi)}{\partial z} = -(\alpha+\sigma) I(z, \mu, \varphi) + \frac{\sigma}{4\pi} \int_{(4\pi)} I(z, \mu', \varphi') \chi(\mu, \varphi, \mu', \varphi') \, d\mu' \, d\varphi' + Q(z, \mu, \varphi), \quad (1)$$

where $I(z, \mu, \varphi)$ is the intensity of the light beam, z the coordinate, $\theta = \arccos\mu$ and φ are the polar and azimuth angles respectively, α and σ are the absorption and scattering coefficients of the volume element of the medium, the function χ specifies the angular distribution of the scattered light (the scattering indicatrix for the volume element), and the function Q characterises the internal sources of photons.

The equation of radiative transfer [Eqn.(1)] reflects the change in the intensity of the light beam during its passage through a volume element of the scattering medium[2,8]. The first term on the right-hand side of the equation takes into account the weakening of the intensity owing to absorption and scattering and the second represents the contribution of the light beams incident on the volume element from all sides (these beams are characterised by variable angular coordinates μ' and φ') and scattered with particular scattering indicatrix in the direction of the beam under consideration (μ and φ). Finally, the third term $Q(z, \mu, \varphi)$ takes into account the contribution of the internal sources of photons in the direction considered.

In the solution of practical problems, it is very important to determine from the known light fluxes the parameters of the medium: α, σ, and χ. Among all the parameters of the scattering medium, the absorption coefficient is of greatest interest in chemical research, since it is related to the concentration of the light absorbing substance c by the usual expression

$$\alpha = 2.3 \varepsilon c,$$

where ϵ is the molar extinction coefficient on the decadic scale.

In view of the complexity of Eqn.(1), the procedures used for its solution involve either certain simplifying assumptions or specific experimental conditions. In particular, a generally accepted method involves the consideration of a plane-parallel layer illuminated with monochromatic light at right angles to the layer ($\mu_0 = 1$ is the cosine of the angle of incidence of the light) or with diffuse light (diffuse light is light whose intensity is independent of angular variables[14]).

In view of the planar symmetry of the problem and the selected illumination conditions (light incident at right angles or diffuse light), the intensity depends only on two variables: the coordinate z at right angles to the bulk of the layer and reckoned from the upper boundary of the layer and the cosine of the angle μ between the direction of the light beam and the normal. With these assumptions, Eqn.(1) becomes[9,12]

$$\mu \frac{\partial I(z, \mu)}{\partial z} = -(\alpha+\sigma) I(z, \mu) + \frac{\sigma}{2} \int_{-1}^{1} I(z, \mu') \chi(\mu, \mu') \, d\mu' + Q(z, \mu). \quad (2)$$

A number of simplifying assumptions are usually introduced. In order to eliminate the edge effects, the dimensions of the layer and of the light source are assumed to be infinite in the z = const. plane. Next, it is postulated that the layer is uniform, i.e. the parameters α, σ, and χ are independent of the coordinates. To simplify the notation, we also assume that the layer is illuminated with a light flux having a single intensity both for light at normal incidence and for diffuse light. Finally we exclude from consideration polarisation effects, luminescence, and departure from steady-state conditions.

Although the media considered do not contain internal sources of radiation, in directional illumination one must regard the direct light quanta, i.e. quanta which penetrate

to a depth z without scattering, as such sources. In this case, the function Q is [1,9]

$$Q(z, \mu) = \frac{\sigma}{2} \chi(\mu) \exp[-(\alpha+\sigma)z]. \quad (3)$$

In diffuse illumination, the function Q is assumed to be zero and the incident radiation is taken into account in the boundary conditions. We may note that in Eqn. (2) the quantity $I(z, \mu)$ should be understood as the intensity of scattered light only.

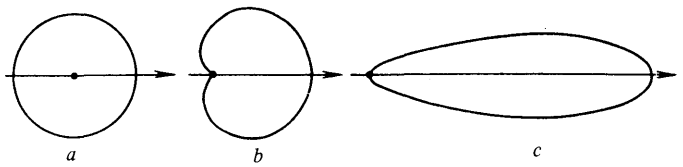


Figure 1. The scattering indicatrices of a volume element. The arrow indicates the direction of the light beam incident on the volume element (point): *a*) χ_1; *b*) χ_2; *c*) χ_3.

Fig. 1 illustrates certain scattering indicatrices of the volume element described by the following expressions:

$$\chi_1 = 1, \ \chi_2 = 1+\mu, \ \chi_3 = 0.21/(1.1-\mu)^2. \quad (4)$$

We may note that the scattering indicatrices are normalised:

$$\frac{1}{2}\int_{-1}^{1} \chi(\mu)\, d\mu = 1.$$

For the practical analysis of data obtained with the aid of SLM, it is necessary to define the relation between the experimental quantities R and T and the characteristics of the layer. The coefficients R and T are related to the light fluxes directed along the z axis $[F_1(z)]$ and in the opposite direction $[F_2(z)]$:

$$R = F_2(0), \ T = F_1(l), \quad (5)$$

where l is the thickness of the layer and the fluxes are defined as follows:

$$F_1(z) = \int_0^1 I(z, \mu)\mu\, d\mu, \quad F_2(z) = -\int_{-1}^0 I(z, \mu)\mu\, d\mu. \quad (6)$$

The minus sign of F_2 was chosen so that the flux should be positive. We may point out that Eqn. (5) for the coefficient T is valid only for diffuse illumination, while in directed illumination it must be supplemented by the term $\exp[-(\alpha+\sigma)z]$ taking into account the direct light which has passed through the layer. Thus, in order to relate the coefficients R and T to the parameters of the layer, it is necessary to know the light fluxes emerging from the layer, which may be found by solving Eqn. (2). However, this problem is mathematically very difficult and algorithms for its solution have been developed only in relatively simple cases and largely in a numerical form [1-3,8-12].

Approximate methods for the solution of the radiative transfer equation therefore play an important role and an advantage of some of them is the possibility of obtaining a solution in an analytical form. Physically reasonable postulates and agreement with the results of the accurate numerical solution of the radiative transfer equation should serve as the criteria of the accuracy of the approximate methods.

In conclusion, we may point out that the characteristics of the medium are sometimes formulated in the form of the following relations: the attenuation factor:

$$k = \alpha + \sigma,$$

the probability of the survival of a quantum in a single scattering step or the albedo of a single scattering step:

$$\Lambda = \sigma/(\alpha+\sigma),$$

the coefficient of the specific absorption of the layer:

$$\beta = \alpha/\sigma,$$

and the optical thickness of the layer

$$\tau_0 = \int_0^l (\alpha+\sigma)\, dz = k\, l.$$

In considering the instances of the illumination of the layer by diffuse light, we shall henceforth use the superscript (or subscript) d in all the expressions and the coefficients for layers with a refractive index N differing from unity will be formulated thus: $R(N)$ and $T(N)$.

III. THE TWO-FLUX APPROXIMATION METHOD

The two-flux approximation method is one of the simplest and most widely used approximation procedures, the main idea of which is as follows. One considers the light fluxes F_1 and F_2 [see Eqn. (6)], whereupon the radiative transfer equation is replaced by a system of differential equations, which is solved with certain additional postulates. We shall consider the principal features of the two-flux approximation method.

1. Diffuse Illumination of the Layer

Suppose that the layer is illuminated by diffuse light and $Q(z, \mu) = 0$. We integrate Eqn. (2) with respect to the upper and lower hemispheres, i.e. the integral is evaluated with respect to $d\mu$ from -1 to 0 and from 0 to 1. We obtain as a result a system of equations for the fluxes F_1 and F_2: [8,9]

$$\frac{dF_1(z)}{dz} = -\frac{\alpha+\sigma\psi_1(z)}{\nu_1(z)}F_1(z) + \frac{\sigma\psi_2(z)}{\nu_2(z)}F_2(z),$$
$$\frac{dF_2(z)}{dz} = \frac{\alpha+\sigma\psi_2(z)}{\nu_2(z)}F_2(z) - \frac{\sigma\psi_1(z)}{\nu_1(z)}F_1(z). \quad (7)$$

$$\nu_1(z) = \frac{\int_0^1 I(z, \mu)\mu\, d\mu}{\int_0^1 I(z, \mu)\, d\mu}, \quad \nu_2(z) = -\frac{\int_{-1}^0 I(z, \mu)\mu\, d\mu}{\int_{-1}^0 I(z, \mu)\, d\mu}. \quad (8)$$

The following notation has been introduced here: the average cosines of the angles of inclination of the light beams (the minus sign of ν_2 was chosen so that ν_2 is positive)

$$\psi_1(z) = \frac{1}{2}\frac{\int_0^1 I(z, \mu')\, d\mu' \int_{-1}^0 \chi(\mu, \mu')\, d\mu}{\int_0^1 I(z, \mu')\, d\mu'}, \quad (9)$$

$$\psi_2(z)=\frac{1}{2}\frac{\int_{-1}^{0} I(z,\mu')\,d\mu' \int_{0}^{1}\chi(\mu,\mu')\,d\mu}{\int_{-1}^{0} I(z,\mu')\,d\mu'}$$

are the components of the light flux scattered by an infinitessimal layer (for its illumination from above and below respectively) backwards in relation to the entire scattered light. We may note that, when the light intensity in the layer is diffuse, then $\nu_1=\nu_2=0.5$ and $\psi_1(z)=\psi_2(z)$.

All the numerous versions of the two-flux approximation reduce to the different selections of the functions $\nu_i(z)$ and $\psi_i(z)$ ($i=1$ or 2) and the solution of Eqns. (7) with the corresponding boundary conditions. This problem has already been discussed in detail [9]. However, in most cases in the interpretation of the experimental data one uses the two-parameter equation of the two-flux approximation (TFA) in which it is assumed *a priori* that the following conditions hold: $\nu_1=\nu_2=\nu$ and $\psi_1=\psi_2=\psi$. [3,9] We may note that such averaging of the quantities defined by Eqns. (8) and (9) with respect to the thickness of the layer is justified only when the bulk-phase conditions obtain and only far from the boundaries of the layer [9].

The boundary conditions for Eqn. (7) in TFA are chosen in the form [9] ($N=1$)

$$F_1(0)=1,\ F_2(l)=0. \tag{10}$$

The solution of Eqns. (7) with the boundary conditions (10) makes it possible to find the coefficients R and T [Eqns. (5)] [8,9]

$$R_d=\frac{[1-\exp(-2al)]\,R_\infty^d}{1-(R_\infty^d)^2\cdot\exp(-2al)},$$
$$T_d=\frac{[1-(R_\infty^d)^2]\exp(-al)}{1-(R_\infty^d)^2\exp(-2al)}, \tag{11}$$
$$R_\infty^d=1+\frac{\alpha}{\sigma\psi}-\left[\left(\frac{\alpha}{\sigma\psi}\right)^2+2\frac{\alpha}{\sigma\psi}\right]^{1/2}.$$

Here R_∞^d is the reflectance of an infinitely thick layer and a is the attenuation coefficient under bulk-phase conditions defined by

$$a=\frac{1}{\nu}[\alpha(\alpha+2\sigma\psi)]^{1/2}.$$

Similar expressions have been obtained by Gurevic [15].

Eqns. (11) are known in the literature as the Gurevic–Kubelka–Munk (G–K–M) relations [5,9]. The Kubelka–Munk (K–M) function can be readily obtained from them:

$$f(R_\infty^d)=(1-R_\infty^d)^2/(2R_\infty^d)=\alpha/(\sigma\psi). \tag{12}$$

The TFA formulae (11) and (12) are widely used in the interpretation of the experimental data. However, unfortunately many workers ignore the multiplier $1/\psi$ and use the G–K–M relations for directed illumination of the layer, although the relations can be obtained only for the layer illuminated with diffuse light.

Zege [9] examined in detail the possibility of applying the TFA formulae to the description of the light-scattering properties of a planar layer and arrived at the following conclusion as a result of comparison with data derived by the numerical solution of Eqn. (2) and also as a result of extrapolation to the bulk-phase light conditions in weakly absorbing media. When the parameters ν and ψ were chosen in the form

$$\nu=0.5,\quad \psi=\frac{3}{8}(1-\bar{\mu}), \tag{13}$$

where $\bar{\mu}$, defined by the expression

$$\bar{\mu}=\frac{1}{2}\int_{-1}^{1}\chi(\mu)\,\mu\,d\mu, \tag{14}$$

is the cosine of the scattering angle averaged with respect to the scattering indicatrix of the volume element, calculation by the TFA formulae (12) agrees with the results of the accurate calculation with an accuracy sufficient for practical purposes (the relative error is less than 10%). We may note that, for isotropic scattering (χ_1), $\psi\simeq 3/8$ was also obtained in other investigations [16,17]. Henceforth in calculations employing TFA formulae we shall likewise select the parameters ν and ψ defined by Eqns. (13).

Mention should also be made of the criterion imposed on the degree of extension of the scattering indicatrix of the volume element for which the TFA relations are valid [9]:

$$\frac{(8\psi_d q-1)^2}{8\psi_d q}\ll 1, \tag{15}$$

where

$$\psi_d=\frac{1}{2}\int_{0}^{1}\int_{-1}^{0}\chi(\mu,\mu')\,d\mu\,d\mu',\quad q=\frac{1}{3(1-\bar{\mu})}. \tag{16}$$

Evaluation of the left-hand side of inequality (15) for the scattering indicatrices of the volume elements χ_1, χ_2, and χ_3 yields 0.08, 0.17, and 0.64 respectively. Thus, for layers with the indicatrix χ_3, one may expect a less satisfactory agreement of the results of approximate calculations with accurate data compared with the calculations for the layers with χ_1 and χ_2 for which the criterion defined by formula (15) may be regarded as valid.

We shall now consider a scattering layer the refractive index of which is different from that of the surrounding medium. To simplify the treatment, we shall assume that the layer has optically smooth interfaces. The deviation of the refractive index of the layer from unity must be taken into account in the boundary conditions, since in this case the light flux supplied to the boundary no longer emerges from the layer in its entirety. This is due to the reflection of the light from the boundaries of the layer, the main contribution arising from the effect of the total internal reflection. In addition, we shall introduce yet another simplification, namely we shall assume that the light approaching the boundary from within the layer is diffuse.

We introduce the following notations for a layer with optically smooth boundaries: the coefficient ρ of reflection from the boundary of the diffuse light incident on the layer from outside and the reflectance r of the light incident on the boundary and directed outward from the layer. Explicit expressions for the coefficient ρ and the relation between ρ and r have been given, for example, by Gershun [14].

When account is taken of the refractive index, the boundary conditions become [14]

$$F_1(0)=1-\rho+rF_2(0),\ F_2(l)=r\cdot F_1(l).$$

The reflectance and transmittance are defined as follows:

$$R_d(N)=\rho+(1-r)F_2(0),\quad T_d(N)=(1-r)F_1(l). \tag{17}$$

Eqns. (17) have been published in an explicit form [14,18,19] and we shall merely formulate the coefficient of reflection for a semi-infinite layer:

$$R_\infty^d(N)=1-(1-\rho)(1-R_\infty^d)/(1-rR_\infty^d),$$

where R_∞^d is described by Eqn. (11).

For weakly absorbing layers, the asymptotic relation between $1/T_d(N)$ and the thickness of the layer may be found from the TFA formulae. The intercept which this straight line makes on the ordinate axis is $(1+r)/(1-\rho)$. This is qualitatively consistent with Gurevic's data [14] for the transmission of light through weakly absorbing milky glasses (Fig. 2).

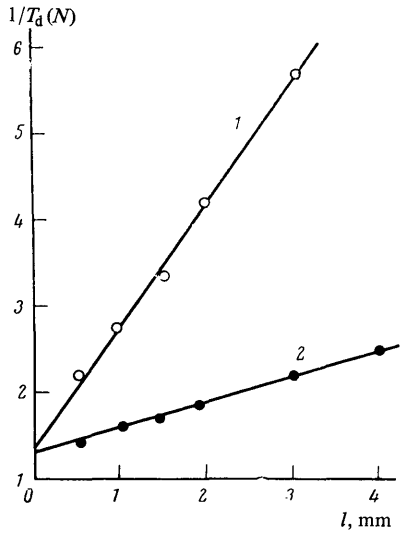


Figure 2. Dependence of $1/T_d(N)$ on the thickness of the layer (diffuse illumination): 1) highly opalescent (dense) milky glass [14]; 2) weakly opalescent milky glass [14].

2. Layers Illuminated with a Light Flux at Right Angles

The problem of the transmission of a directed light beam through a scattering layer is of practical importance. In this case Eqns. (7) are supplemented by terms taking into account the internal sources of photons [Eqn. (3)]. The solution of such equations for a layer with $N = 1$ and the boundary conditions

$$F_1(0)=0,\ F_2(l)=0$$

leads to the following expressions for the coefficients defined by Eqns. (5): [9]

$$\begin{aligned} T &= c_1 T_d + (1-c_1+c_2R_d)\exp(-(\alpha+\sigma)l), \\ R &= c_1R_d + c_2T_d\exp(-(\alpha+\sigma)l) - c_2, \\ R_\infty &= c_1R_\infty^d - c_2, \end{aligned} \qquad (18)$$

where the coefficients R_d, T_d, and R_∞^d are defined by Eqns. (11) and the parameters C_1 and C_2 satisfy the following equations when account is taken of Eqn. (13):

$$c_1=\frac{(1-\omega)(3\beta+1)+2\psi}{1+2\beta(1-4\psi)-3\beta^2},\quad c_2=\frac{\omega(\beta-1)+2\psi}{1+2\beta(1-4\psi)-3\beta^2}; \qquad (19)$$

the quantity ω is defined by the expression

$$\omega=\frac{1}{2}\int_{-1}^{0}\chi(\mu)\,d\mu.$$

Zege [9] suggests that, as for diffuse illumination, the quantities ν and ψ should be defined by Eqns. (13). Calculations carried out on this assumption within the framework of TFA are presented in Tables 1–5, which show that the proposed TFA version gives rise to a satisfactory accuracy of the calculation of the coefficients R and T for different scattering indicatrices over a wide range of variation of β.

Table 1. The coefficients R and T for a planar layer ($\chi_1 = 1$, $\mu_0 = 1$, $N = 1$).

τ_s	Exact calculation		TFA [Eqn.(18)]		P_1 [Eqn.(30)]	
	R	T	R	T	R	T
			$\Lambda=0.95$			
0.5	0.185	0.781	0.186	0.784	0.186	0.784
2	0.429	0.409	0.433	0.418	0.433	0.419
5	0.525	0.128	0.533	0.130	0.533	0.131
			$\Lambda=0.9$			
0.5	0.169	0.765	0.172	0.770	0.172	0.770
2	0.362	0.357	0.371	0.366	0.371	0.368
5	0.413	0.077	0.423	0.077	0.424	0.078
			$\Lambda=0.7$			
0.5	0.115	0.714	0.121	0.721	0.121	0.721
2	0.197	0.241	0.211	0.247	0.212	0.250
5	0.209	0.023	0.219	0.021	0.220	0.023

Table 2. The coefficients R_∞ for a planar layer ($\chi_1 = 1$, $\mu_0 = 1$, $N = 1$).

Λ	Exact calculation (Ref.31)	TFA [Eqn.(18)]	P_1 [Eqn.(31)]	Λ	Exact calculation (Ref.31)	TFA [Eqn.(18)]	P_1 [Eqn.(31)]
0.9999	0.972	0.972	0.972	0.8	0.285	0.296	0.297
0.999	0.913	0.913	0.914	0.7	0.209	0.219	0.220
0.9975	0.866	0.866	0.868	0.6	0.055	0.164	0.165
0.995	0.817	0.817	0.819	0.5	0.115	0.123	0.124
0.99	0.753	0.756	0.756	0.4	0.083	0.089	0.090
0.975	0.641	0.647	0.647	0.3	0.057	0.061	0.062
0.95	0.536	0.544	0.544	0.2	0.035	0.038	0.039
0.9	0.415	0.425	0.425	0.1	0.016	0.018	0.018

Table 3. The coefficients R_∞ for a planar layer with $\chi_2 = 1 + \mu$, $\mu_0 = 1$, and $N = 1$.

Λ	Exact calculation (Ref.31)	TFA [Eqn.(21)]	P_1 [Eqn.(36)]	TA with $m = 1.8$ [Eqn.(38)]	
				TFA [Eqn.(21)]	P_1 [Eqn.(32)]
0.999	0.894	0.895	0.895	0.886	0.886
0.995	0.779	0.781	0.781	0.767	0.767
0.99	0.703	0.706	0.706	0.691	0.691
0.975	0.573	0.579	0.579	0.564	0.564
0.95	0.455	0.464	0.463	0.451	0.452
0.9	0.327	0.338	0.336	0.331	0.332
0.8	0.200	0.213	0.210	0.212	0.214
0.7	0.133	0.146	0.142	0.148	0.149
0.6	0.091	0.103	0.099	0.170	0.108
0.5	0.062	0.073	0.069	0.077	0.078
0.4	0.041	0.051	0.047	0.054	0.055
0.2	0.015	0.020	0.018	0.022	0.023

We shall now turn to the consideration of a scattering layer with optically smooth interfaces and $N \neq 1$. We introduce the following notation: the coefficient of the specular reflection of the beam illuminating the layer

$\rho_{sp} = (N-1)^2/(N+1)^2$ and the coefficient of reflection of the light directed from the layer to the outside r. As before, r may be calculated from Gershun's formulae[14] on the assumption that the light incident on the boundary from inside is diffuse.

Table 4. The coefficients R and T for a planar layer ($\chi_2 = 1 + \mu$, $\mu_0 = 1$, $N = 1$).

τ_0	Exact calcn. (Ref.9)		TFA [Eqn.(18)]		TA with m = 1.8 [Eqn.(38)]			
					TFA [Eqn.(18)]		P_1 [Eqn.(30)]	
	R	T	R	T	R	T	R	T
				$\Lambda=0.95$				
0.5	0.092	0.835	0.111	0.859	0.113	0.859	0.113	0.860
2	0.309	0.505	0.323	0.527	0.304	0.565	0.304	0.565
				$\Lambda=0.9$				
0.5	0.084	0.817	0.102	0.840	0.103	0.842	0.103	0.842
2	0.252	0.444	0.269	0.462	0.257	0.506	0.257	0.506
				$\Lambda=0.7$				
0.5	0.055	0.759	0.069	0.773	0.072	0.778	0.072	0.778
2	0.121	0.298	0.137	0.301	0.138	0.346	0.139	0.349

Table 5. The coefficients R and T for a planar layer [$\chi_3 = 0.21/(1.1-\mu)^2$, $\mu_0 = 1$, $N = 1$].

τ	Exact calcn.		TFA [Eqn.(18)]		TA with m = 6.86 [Eqn.(38)]			
					TFA [Eqn.(18)]		P_1 [Eqn.(30)]	
	R	T	R	T	R	T	R	T
				$\Lambda=0.95$				
2	0.101	0.766	0.133	0.709	0.106	0.788	0.106	0.788
5	0.197	0.453	0.248	0.383	0.185	0.546	0.185	0.547
10	0.240	0.177	0.282	0.136	0.230	0.284	0.230	0.287
	0.244		0.291		0.242		0.243	
				$\Lambda=0.9$				
2	0.077	0.683	0.108	0.642	0.088	0.714	0.088	0.714
5	0.127	0.325	0.169	0.247	0.134	0.418	0.134	0.418
10	—	—	0.179	0.051	0.148	0.158	0.149	0.161
∞	—	—	0.182		0.150		0.151	
				$\Lambda=0.7$				
2	0.038	0.452	0.044	0.381	0.044	0.484	0.044	0.485
5	0.036	0.103	0.049	0.058	0.050	0.154	0.051	0.151
10	0.036	0.009	0.052	—	0.050	0.021	0.051	0.022
∞	0.036		0.053		0.050		0.051	

The boundary conditions for the equations describing the fluxes for directional illumination are as follows:

$$F_1(0) = rF_2(0), \quad F_2(l) = rF_1(l). \tag{20}$$

Reflectance and transmittance can be formulated by analogy with Eqns.(17), but in the expression for the coefficient $T(N)$ account must be taken of the direct light quanta which have passed through the layer. In particular, the coefficient $R_\infty(N)$ assumes the following form in this case:

$$R_\infty(N) = \rho_{sp} + (1-\rho_{sp})(1-r)\left[\frac{(c_1 - rc_2)R_\infty^d}{1-rR_\infty^d} - c_2\right]. \tag{21}$$

All the quantities in this formula were defined above [see Eqns.(11) and (19)]. Some of the values of $R_\infty(N)$ calculated from Eqn.(21) are listed in Tables 6 and 7 and their comparison with the results of the numerical solution of Eqn.(2) demonstrates a satisfactory agreement.

Table 6. The coefficients $R_\infty(N)$ for a planar layer with an optically smooth surface ($\chi_1 = 1$, $\mu_0 = 1$, $N = 1.5$).

Λ	Exact calculation (Ref.31)	TFA [Eqn.(21)]	P_1 [Eqn.(32)]	Λ	Exact calculation (Ref.31)	TFA [Eqn.(21)]	P_1 [Eqn.(32)]
0.999	0.841	0.846	0.846	0.7	0.129	0.148	0.147
0.995	0.691	0.702	0.702	0.6	0.102	0.118	0.117
0.99	0.602	0.617	0.617	0.5	0.084	0.097	0.096
0.975	0.469	0.489	0.488	0.4	0.071	0.080	0.080
0.95	0.361	0.386	0.385	0.3	0.061	0.067	0.067
0.9	0.260	0.286	0.285	0.2	0.052	0.057	0.056
0.8	0.172	0.195	0.194	0.1	0.046	0.048	0.047

Table 7. The coefficients $R_\infty(N)$ for planar layer with an optically smooth surface ($\chi_2 = 1 + \mu$, $\mu_0 = 1$, $N = 1.5$).

Λ	Exact calculation (Ref.31)	TFA [Eqn.(21)]	P_1 [Eqn.(36)]	TA with m = 1.8 [Eqn.(38)]	
				TFA [Eqn.(21)]	P_1 [Eqn.(32)]
0.999	0.811	0.816	0.816	0.802	0.802
0.995	0.639	0.651	0.651	0.631	0.631
0.99	0.542	0.558	0.558	0.537	0.537
0.975	0.400	0.423	0.422	0.404	0.404
0.95	0.294	0.320	0.318	0.306	0.305
0.9	0.197	0.226	0.223	0.218	0.217
0.8	0.121	0.147	0.144	0.145	0.144
0.7	0.087	0.110	0.106	0.110	0.109
0.5	0.057	0.073	0.070	0.074	0.074

In concluding this Section, we shall formulate the expression defining the coefficients $R(N)$ and $T(N)$ for a non-absorbing layer ($\alpha = 0$):

$$R(N) = 1 - T(N) = \rho_{sp} + (1-\rho_{sp})\left(1 - \frac{2p + (8\psi - 4\omega - p + 2)(1 - \exp(-\sigma l))}{8\sigma\psi l + 2p}\right), \tag{22}$$

where

$$p = 2(1+r)/(1-r). \tag{23}$$

IV. THE DIFFUSION APPROXIMATION

The diffusion approximation method is also widely used in practical calculations[12,20-27]. It is a special case of the P_n approximation, the essential feature of which is as follows. The functions I, χ, and Q at each point in the scattering medium are expanded in series in Legendre polynomials, the expansions being limited to the nth term. They are then substituted in the radiative transfer equation and, having multiplied the latter in succession by the Legendre polynomials ranging from P_0 to P_n, we carry out the integration with respect to the angular variable μ from -1 to 1. We obtain as a result a system of $n+1$ first-order differential equations, which may be solved with the appropriate boundary conditions.

The diffusion approximation is the lowest-order approximation (P_1). It has been used successfully in the description of the diffusion of neutrons[20-24] and of light scattering[25-28]. We shall now consider certain specific instances.

1. Isotropic Scattering; $\mu_0 = 1$, $N = 1$

The light intensity is represented by an expansion in terms of the first two Legendre polynomials ($P_0 = 1$, $P_1 = \mu$):

$$I(z, \mu) = \frac{1}{2}[n(z)c + 3\mu F(z)]. \quad (24)$$

The coefficients of the expansion have a simple physical significance[25]: $n(z)$ is the concentration of the diffusing quanta, $F(z)$ is their overall flux, and c is the velocity of light.

The applicability of the P_1 approximation depends on how well the intensity can be represented by a linear function of μ; this condition is equivalent to the inequality $n(z)c \gg F(z)$. In particular, this should hold for a virtually isotropic light intensity distribution (a non-absorbing medium with isotropic scattering)[3].

In conformity with the above procedure, we obtain the following system of equations:

$$\frac{dF}{dz} + \alpha cn - \sigma \exp(-(\alpha+\sigma)z) = 0$$
$$F = -\frac{c}{3(\alpha+\sigma)}\frac{dn}{dz}. \quad (25)$$

The second equation (25) resembles the form of Fick's law for diffusion in a gas and relates the light flux to the density gradient (this is the reason for the term diffusion approximation). The diffusion coefficient D in isotropic scattering is

$$D = c/3(\alpha+\sigma),$$

in agreement with the ideas of the gas-kinetic theory[29] on the assumption that the mean free path in the transport process is $1/(\alpha+\sigma)$. Clearly, the consideration of the diffusion of photons is significant only for weakly absorbing media ($\beta \ll 1$).

After eliminating the function $F(z)$ from Eqn.(25) we pass to the steady-state diffusion equation for diffusing quanta:

$$D\frac{d^2n}{dz^2} - \alpha cn + \sigma \exp(-(\alpha+\sigma)z) = 0. \quad (26)$$

We may note that Eqn.(26) may be obtained directly from general considerations when light scattering processes are treated as the diffusion of photons within the framework of the gas diffusion theory. In this case, the second term of Eqn.(26) describes the disappearance of quanta with a rate constant αc, and the third term describes the generation of the diffusing quanta from the direct beam as a result of scattering.

According to Eqns.(6) and (24), the expressions for the fluxes are

$$F_1 = \frac{nc}{4} - \frac{D}{2}\frac{dn}{dz}, \quad F_2 = \frac{nc}{4} + \frac{D}{2}\frac{dn}{dz}, \quad (27)$$

and the boundary conditions (17) become

$$\frac{nc}{2}\Big|_{z=\begin{cases}0\\l\end{cases}} = \pm D\frac{dn}{dz}\Big|_{z=\begin{cases}0\\l\end{cases}}. \quad (28)$$

The solution of Eqn.(26) can be formulated thus:

$$n = A\exp(-az) + B\exp(az) + E\exp(-(\alpha+\sigma)z), \quad (29)$$

where

$$A = \frac{E}{3\Delta}[-5(1+b)\exp(al) + (1-b)\exp(-(\alpha+\sigma)l)],$$
$$B = \frac{E}{3\Delta}[5(1-b)\exp(-al) - (1+b)\exp(-(\alpha+\sigma)l)],$$
$$a = [3\alpha(\alpha+\sigma)]^{1/2}, \quad b = 2[\alpha/3(\alpha+\sigma)]^{1/2},$$
$$E = -3\sigma/c(\sigma-2\alpha),$$
$$\Delta = (1+b)^2\exp(al) - (1-b)^2\exp(-al).$$

The coefficients R and T are defined on the basis of Eqns.(5) and (27):

$$R = \frac{c}{2}[A+B+E],$$
$$T = \frac{c}{2}\left[A\exp(-al) + B\exp(al) + \left(E + \frac{2}{c}\right)\exp(-(\alpha+\sigma)l)\right], \quad (30)$$

and the expression for the coefficient R_∞ is fairly simple:

$$R_\infty = \left[1 + 3\beta + \frac{5}{3}(3\beta(1+\beta))^{1/2}\right]^{-1}. \quad (31)$$

It is of interest to compare results of the calculation using the P_1 approximation with the results of the exact calculation. This is done in Tables 1 and 2, which show that the coefficients R and T, calculated in terms of the P_1 approximation with the boundary conditions (28), agree satisfactorily with the results of the exact solution of the radiative transfer equation and virtually agree with the TFA version.

2. Allowance for the Refractive Index. Isotropic Scattering ($\mu_0 = 1$)

We shall consider a scattering layer with optically smooth interfaces and $N \neq 1$. As before, the influence of the refractive index will be taken into account in the boundary conditions (20). Retaining the notation introduced in the previous section, the boundary conditions (20) will be reformulated as follows by simple transformations taking into account Eqn.(27):

$$\frac{nc}{p}\Big|_{z=\begin{cases}0\\l\end{cases}} = \pm D\frac{dn}{dz}\Big|_{z=\begin{cases}0\\l\end{cases}},$$

where p is defined by Eqn.(23). The expression for $R_\infty(N)$ then assumes the following form:

$$R_\infty(N) = \rho_{sp} + (1-\rho_{sp})/[1 + (1+p)\beta + (1+p/3)(3\beta(1+\beta))^{1/2}]. \quad (32)$$

The main contribution to the coefficient r comes from the effect of the total internal reflection. Taking only this into account and assuming that the light incident on the layer boundary from the inside is diffuse, it is easy to find[30]

$$r = 1 - 1/N^2. \quad (33)$$

The exact expression for the reflectance of diffuse light with allowance for Frenel's formulae is[14,31,32]

$$r = 1 - \frac{1}{N^2}\left[1 - \frac{3N^8 - 10N^7 - 6N^6 - 4N^5 + 16N^4 - 10N^3 + 2N^2 + 1}{3(N^4-1)^2} - \right.$$
$$\left. - \frac{N^2(N^2-1)^2}{(N^2+1)^3}\ln\frac{N+1}{N-1} + \frac{8N^4(N^4+1)}{(N^2-1)^2(N^2+1)}\ln N\right]. \quad (34)$$

However, the numerical difference between Eqns.(34) and (33) is small; for example, $r = 0.6$ and 0.56 respectively when $N = 1.5$. In approximate calculations, it is therefore fully justifiable to use the simpler formula (33).

When account is taken of Eqns.(33) and (23), the parameter p can be expressed thus:

$$p = 2(2N^2 - 1). \quad (35)$$

The coefficients $R_\infty(N)$ for a layer with an optically smooth boundary have been calculated[31] by the numerical

solution of the radiative transfer equation. These data are compiled in Table 6 for $N = 1.5$ and compared with the values calculated by Eqn. (32) taking into account Eqn. (35). The discrepancy does not exceed 3% (absolute deviation), which demonstrates the possibility of the practical application of the formulae based on the P_1 approximation. Similar results were obtained in calculations by the TFA Eqn. (21) taking into account Eqn. (35) [see Eqn. (6)].

3. Non-Isotropic Scattering ($\mu_0 = 1$)

For a layer with an optically smooth interface, the coefficient $R_\infty(N)$ is described by the formula

$$R_\infty(N) = \rho_3 + \frac{(1-\rho_3)\,[y - \bar{\mu}\,(3\beta y)^{1/2}]}{y[1+\beta\,(1+p)] + \left[y + \frac{p}{3}\,(1+\beta)(3\beta y)^{1/2}\right]}, \qquad (36)$$

where $\bar{\mu}$ is the cosine of the scattering angle [Eqn. (14)] averaged with respect to the scattering indicatrix of the volume element and $y = 1 + \beta - \bar{\mu}$.

Tables 3 and 7 present the results of the study by Giovanelli [31] and the calculations based on Eqns. (36), (18), and (21) for layers with a scattering indicatrix χ_2 [see Eqn. (4)]. The agreement between these results is quite satisfactory.

Analysis of Eqn. (36) makes it possible to determine readily the limitations imposed on the degree of anisotropy of the scattering indicatrix of the volume element in the P_1 approximation. Thus, when $\mu > 1/\sqrt{3}$, the coefficient $R_\infty(N)$ becomes negative starting from a certain value of β, which has no physical significance for the given problem. The application of the P_1 approximation is therefore limited to the range $0 \leq \bar{\mu} \leq 1/\sqrt{3}$. This postulate is satisfactorily consistent with the fact that the light intensity in the medium should differ only slightly from the isotropic intensity.

Finally, we have the formula for the coefficients of the non-absorbing layer:

$$R(N) = 1 - T(N) = \rho_{sp} + (1-\rho_{sp})\left[1 - \frac{(3+p) - (3-p)\exp(-\sigma l)}{2p + 3\sigma l\,(1-\bar{\mu})}\right]. \qquad (37)$$

For the scattering indicatrices χ_1 and χ_2 [Eqn. (4)], Eqn. (37) agrees with the TFA formula (22).

V. THE TRANSPORT APPROXIMATION

It is seen from the above considerations that the P_1 approximation can be used only for the scattering indicatrices of the volume element, which are not unduly extended in the forward direction ($\bar{\mu} < 1/\sqrt{3}$). On the other hand, in real systems $\bar{\mu}$ can probably be greater [33,34]. In order to apply the formulae of the P_1 approximation to systems with the scattering indicatrices of the volume element extended forward, use is made of the so called transport approximation (TA). In this case, the true scattering coefficient is replaced in the approximate solution of the problem for isotropic scattering by the effective coefficient σ_{eff}, which takes into account both σ and the form of the indicatrix [12,30,35] (the coefficient α then remains unchanged):

$$\sigma_{eff} = \sigma/m, \qquad (38)$$

where m is the parameter taking into account the anisotropy of the scattering.

The physical significance of the transport approximation consists in the replacement of, for example, a scattering indicatrix extended forward by a spherical indicatrix with a larger number of direct light quanta for compensation of the preferential forward scattering. In practice the choice of m makes it possible to bring into fairly good agreement with the exact calculation either the coefficient R or T. The transport approximation can be applied also to other approximate methods for the solution of the radiative transfer equation, for example to the TFA version. We may note that the transport approximation is empirical, since the exact TFA Eqn. (21) and the P_1 equation (36) contain both σ and $\sigma_{eff} = \sigma(1 - \bar{\mu})$.

The exact $R_\infty(\beta)$ relations for layers with the scattering indicatrices χ_1, χ_2, and χ_3 [Eqn. (4)] have the form of monotonically decreasing functions. By selecting the parameter m, it is possible to bring these curves into satisfactory agreement with the relation for isotropic scattering. The possibility of achieving the compatibility of the R_∞ curves for the $\chi = 1 + P_i(\mu)$ indicatrices, where $i = 0$, 1, 2, or 3 and P_i is the ith Legendre polynomial, has been demonstrated [36] by means of a similar operation. This factor also supports the validity of the transport approximation. As an example, Table 3 presents the values of R_∞ for a layer with the scattering indicatrix χ_2 [Eqn. (4)] calculated in the terms of the transport P_1 approximation and TFA for $m = 1.8$. They evidently agree satisfactorily with the results of the exact calculation over a wide range of variation of β. The principal feature of the transport approximation is that in this case the theory involves only two parameters: α and σ_{eff}. It is therefore very convenient to use it in the analysis of experimental data.

For a layer with an optically smooth interface ($N = 1.5$) and the indicatrix χ_2, the values of $R_\infty(N)$ were calculated in terms of the P_1 approximation and TFA as well as the transport approximation with $m = 1.8$ and compared with Giovanelli's results [31] (Table 7). The extent of the agreement of all the results is quite satisfactory and the TA data differ little from those obtained from the exact P_1 and TFA formulae.

Table 4 presents the results of the calculation of the coefficients R and T (P_1 and TFA) for all layers of final thickness with the indicatrix χ_2. As before, the extent of the agreement with the transport approximation is quite acceptable, although the difference between the T coefficients is greater. This is because the choice of the parameter m [Eqn. (38)] is determined by the best agreement between the coefficients R_∞. Similar calculations for layers with the scattering indicatrix χ_3 [Eqn. (4)] are presented in Table 5. The parameter m, found from the condition for best agreement between the coefficients R_∞ ($m = 6.86$), differs from $1/(1 - \bar{\mu}) = 4.55$. Table 5 shows that the agreement between the coefficients R is fairly good, but that between the coefficients T is only qualitative, which is also consistent with the method of selection of m.

The above data suggest that the transport approximation can yield satisfactory results when it is applied to real systems with anisotropic scattering.

Finally, we may note an important fact. The calculations of the coefficients R and T within the framework of the transport, TFA, and P_1 approximations reveals a discrepancy between the results, which does not exceed three units in the third decimal place. The range of the values covered was very wide:

$$0.01 \leqslant \beta \leqslant 3;\ 0.2 \leqslant (\alpha+\sigma)\,l \leqslant 15;\ 1 \leqslant m \leqslant 10.$$

This permits the conclusion that the transport, TFA, and P_1 approximations yield quantitatively concordant integral values of R and T, i.e. they are virtually equivalent.

VI. OTHER METHODS FOR THE DESCRIPTION OF LIGHT SCATTERING PROCESSES

These include in the first place the layer model where the scattering layer is regarded as an assembly of plane-parallel layers with a thickness equal to the average size of the scattering centre [37-40]. In this approach, the expressions for the coefficients R and T are analogous to the TFA formulae [Eqn.(11)].[37]

A novel approach to the solution of the radiative transfer equation was proposed by Rozenberg, who expanded the solution in series in terms of a small parameter γ equal to the ratio of the decay coefficient under bulk-phase conditions (a) to the attenuation coefficient of the medium [4,6,41,42]. For the diffuse illumination of weakly absorbing media, Rozenberg obtained the following expression ($N = 1$) with an accuracy to within a quantity of the order of magnitude of γ^3:

$$T_d = \frac{\sinh y}{\sinh(x+y)}, \quad R_d = \frac{\sinh x}{\sinh(x+y)}, \quad R_\infty^d = e^{-y}, \tag{39}$$

where $x = al$ and $y = 4q\gamma$. When the illumination is directional, the coefficients are expressed as follows:

$$T = gT_d, \quad R = R_\infty - T_d \exp(-x-y), \quad R_\infty = \exp(-Sy).$$

Here T_d and R_d are described by Eqns.(39) and g, q, and S are so called Rozenberg parameters, whose detailed investigation has already been carried out [8]. It is noteworthy that the unambiguous relation between the reflectance and transmittance, on the one hand, and the parameters x and y, on the other, makes it possible to obtain a simple expression for the absorption coefficient [6]:

$$\alpha = xy/4l.$$

We may also point out that Eqns.(39) are equivalent to the TFA formulae (11).[43] Rozenberg used a similar approach also for strongly absorbing media [44,45].

Yet another approach to the consideration of light scattering processes in powders was proposed by Melamed [46], assuming that a semi-infinite layer consists of spherical particles and, using a soundly based treatment of the light passing through the upper monolayer (similarly to the layer model), he obtained [46] the following expression:

$$R_\infty = 2x\rho + \frac{(1-2x\rho)(1-\rho R_\infty)xt}{(1-\rho R_\infty) - (1-x)(1-\rho)tR_\infty},$$

where x is the fraction of light emerging from the particle in the upward direction, t the transmission coefficient of the particle, and ρ a quantity having the same significance as in subsection 1 of Section III. Melamed has published these expressions in an explicit form [46].

The problem of the reflectances of a semi-infinite layer with $N \neq 1$ was dealt with by Giovanelli [31], who considered two types of interfaces of the layer: optically smooth and diffuse. We shall assume that the diffuse interface has a hypothetical property such that the radiation which has passed through it or which has been reflected from it is diffuse regardless of the type of incident radiation [31]. In order to find the reflectance of the layer, the author [31] separated the processes involving the passage of light through the surface of the layer from the reflection processes. Then, considering the radiation fluxes immediately at the boundary, directed inwards and outwards, Giovanelli obtained the following expression:

$$R_\infty(N) = \rho + \frac{(1-\rho)^2 R_\infty^d}{N^2(1-rR_\infty^d)}.$$

Either the exact function [1,2,11] or approximate expressions, for example Eqn.(11), may be used as the coefficient R_∞^d.

A similar approach was also used for a layer with an optically smooth interface. Assuming that the light intensity is independent of the angle, an approximate expression is obtained [31]:

$$R_\infty(N) = \rho_{sp} + (1-\rho_{sp})\frac{(1-\rho)R_\infty}{N^2(1-2J)},$$

where

$$J = \int_0^1 r(\mu) R_\infty(\mu)\mu\, d\mu;$$

$r(\mu)$ is the Fresnel reflectance for the light incident on the interface from within and the coefficients r, ρ, and ρ_{sp} have the previous significance. Giovanelli evaluated by numerical integration the coefficients $R_\infty(N)$ also taking into account the angular structure of the light [31]. Some of these data are presented in Tables 6 and 7.

An attempt at a description of photochemical reactions in powdered substances made by Simmons and Wendlandt [47,48] is noteworthy. Assuming that the powder consists of spherical particles which are capable of ideal scattering of radiation, the authors [48] obtained the following relation for the reaction $A \xrightarrow{h\nu} B$ within the framework of the one-dimensional layer model:

$$g(R_\infty) - g(R_\infty(A)) = \varphi\varepsilon N^2 I_0 t, \tag{40}$$

where R_∞ is the reflectance at time t from the start of the photochemical reaction, $R_\infty(A)$ refers to the pure substance A, φ is the quantum yield, ϵ the molar extinction coefficient of the substance A, I_0 the intensity of the incident light, and $g(R_\infty)$ a function whose explicit form has been published [48], Thus the plot of $g(R_\infty)$ against t should be linear and the quantum yield of the photochemical reaction can be estimated from the slope. In conclusion, we may indicate approximate methods for the solution of the radiative transfer equation analogous to the P_n approximation. In contrast to the usual method of spherical harmonics, an expansion in different series is carried for the upper ($\mu < 0$) and lower ($\mu > 0$) half-planes [the so called double P_n method $(DP)_n$] [12,49] or for four regions (with additional subdivision of the half-planes) [50]. In this approach, the light intensity can have a discontinuity at $\mu = 0$. However, as a result of the double expansion, the accuracy of the DP_1 method is higher than that of the P_3 approximation for the same complexity of the mathematical expressions [12]. In particular, one can formulate an expression for the coefficient R_∞ for an isotropically scattering layer obtained in the DP_0 approximation with the usual boundary conditions ($\mu_0 = 1$, $N = 1$):

$$R_\infty = [1 + 3\beta + 3(\beta(1+\beta))^{1/2}]^{-1}.$$

This formula resembles Eqn.(31), but agrees better with the results of the exact calculation, which probably also indicates a higher accuracy of the DP_0 method compared with the P_1 approximation.

VII. THE APPLICATION OF THE SPECTROSCOPY OF LIGHT SCATTERING MEDIA TO THE INTERPRETATION OF EXPERIMENTAL DATA

This section is devoted to the practical applications of the SLM. Naturally since not all the studies in this field can be described, we shall confine ourselves to the most typical investigations. These include in the first place the determinations of the absorption band maxima in the diffuse reflection spectra [51-58]. Studies designed to elucidate the coordination and valence states of transition metal ions on the surfaces of different carriers are related to these. By comparing the energies of the electronic transitions of the ions on the surface with the analogous transitions in solutions, it is possible to reach a conclusion, within the framework of the crystal field theory, about the coordination of valence states of the ion investigated. The study of the state of molybdenum [59] and cobalt [60] ions on the surfaces of magnesium and aluminium oxides, of cobalt and chromium ions on silica gel [61-63], and of copper [64], nickel [65], and neodymium [66] ions, as well as the study of the properties of nickel catalysts [67-69], the acid properties of catalysts [70,71], and the interaction of certain organic compounds with the surface of the catalyst [72,73] are typical investigations of this kind.

In practice, one encounters fairly frequently the problem of the determination of the optical characteristics of substances from diffuse reflection or transmission spectra and hence the problems of the determination of the structures of compounds and their concentrations. Most of the approximate models for the description of light scattering systems were described in previous sections. Among these, the TFA model, yielding relatively simple G–K–M relations [Eqns.(11)], is most widely used. We may recall that Eqns.(11) were obtained for homogeneous layers illuminated with diffuse light. Outwardly similar formulae are obtained when a one-dimensional scattering medium [2] or a layer model [37] are considered.

Numerous studies on the application of the spectroscopy of light scattering media in chemistry have been carried out by Kortüm and his coworkers [74-85]. Using the K–M functions [Eqn.(12)], the authors determined the form of the absorption spectra of molecular compounds of trinitrobenzene as a function of concentration, adsorbent, temperature, and degree of adsorption, and also estimated the dissociation constants of these compounds [76,77]. Kortüm and Vogel [78] described the dependence of the absorption spectra of powdered $K_3Fe(CN)_6$ and $KMnO_4$ on particle size taking into account certain refinements of the G–K–M theory [78,79]. Using polarised light, an attempt was made to separate the diffuse and specular components of the reflected radiation, and the influence of the particle size on the reflection spectra of the powders was demonstrated [80]. The luminescence characteristics of powdered substances were calculated [81] within the framework of the G–K–M model. Using the K–M function [Eqn.(12)], the photochemical reactions of adsorbed substances (anthracene, anthraquinone, substituted pyridines, and spiropyrans) were studied qualitatively [82-84]. However, all the studies enumerated above are only qualitative, owing to the use of a simplified model for the description of the properties of real systems (we may note that the K–M formula does not take into account the refractive index of the medium and, in addition, diffuse light was sometimes replaced by directed light in the experiments).

Ivanov et al. [86] determined the concentrations of dyes adsorbed on fibres. Several types of dyes and fibres were investigated, the results were interpreted with the aid of the K–M function, and the layer was illuminated at normal incidence. Satisfactorily linear relations between $f(R_\infty)$ and the dye concentration are quoted for the individual dyes and it was shown experimentally that the absorption coefficients for a mixture of dyes are additive quantities [86]. A method for the determination of microamounts of mercury from the coefficient of reflection from paper dyed with a mercury complex of diphenylcarbazone was described in a similar study [87]. As in the usual photometry, mercury was determined by comparing the experimental data with a calibration curve obtained by plotting $f(R_\infty)$ against [Hg].

Oelkrug [88] investigated the structure of copper complexes on the basis of reflection spectra with the aid of the K–M function and Gavrilova et al. [89] described the correlation between $f(R_\infty)$ for cellulose and the degree of its acetylation. Toporets [90] studied the light scattering processes in pigments and obtained a linear relation between $f(R_\infty)$ and the concentrations of various pigments in magnesium, zinc, and titanium oxides.

The light scattering processes in weakly absorbing milky glasses have been investigated within the framework of the TFA version [18,19,91]. Voishvillo [91] interpreted the results in terms of the G–K–M formulae, although light at normal incidence had been used in the experiments. The attenuation coefficient under bulk-phase conditions [the parameter a in Eqns.(11)] was estimated from the dependence of the coefficients R and T on the thickness of the layer, the error in the determination of this parameter was analysed, and the absorption coefficient of the glass was determined. The average cosines of the angles of inclination of the light beams [ν_1 and ν_2 in Eqn.(8)] were estimated by measuring the indicatrix of the radiation emerging from the layer [91]. They were found to be [virtually] equal, but their average (0.63) differs from the value (0.5) proposed by Zege [9]. This may be due both to the elongation of the scattering indicatrix and to the use of radiation emerging from the layer rather than the radiation within the layer. Voishvillo [18,19] interpreted experimental data in terms of the TFA formulae, taking into account the refractive index of the glass.

The limits of applicability of the G–K–M relations have been determined by Rozenberg et al. [92], who claim that the absorption coefficients of weakly absorbing media can be determined correctly with the aid of the K–M function by introducing an effective scattering coefficient. This postulate was confirmed experimentally for magnesium oxide and zinc oxide layers [92-95]. The region where the two-flux approximation is applicable has also been considered by Sakhnovskii and Kotik [96].

The experimental data have been interpreted within the framework of the layer model in a number of investigations [37-40], where the reflection spectra of powdered phosphors [39] and ground coloured glasses [37,38,40,97] were studied.

The absorption coefficients of powdered didymium glasses and GaP have been obtained [46] with the aid of Melamed's theory from reflection spectra. The results agree well with the true absorption coefficients of transparent specimens. Pool and Itzel [98] used the reflection spectra of chromium and aluminium oxides to determine the structures of the electronic transitions and the state of ions. The results were interpreted and, in particular, the extinction coefficients were determined on the basis of Melamed's theory [46].

The photochemical decomposition of powdered $K_3[Mn.(C_2O_4)_3].3H_2O$ was investigated by Simmons and Wendlandt [48]. The plot of $g(R_\infty)$ against t [Eqn.(40)] was indeed

linear for different wavelengths and light intensities and the observed quantum yields were 0.41 (λ = 400 nm) and 0.13 (λ = 350 nm).[48]

The P_1 approximation for the description of light scattering processes has been examined in a study[28] whose authors investigated the scattering properties of layers consisting of spherical methyl methacrylate particles. The extinction coefficient of methyl methacrylate was found within the framework of the diffusion model and the optical characteristics of such layers were predicted. In a subsequent study[99], the authors estimated theoretically the parameters of the scattering layers in dispersed radiation detectors and confirmed experimentally the calculated results.

The diffusion model for the description of radiative transfer processes from point sources in weakly absorbing media was used by Brinkworth[100]. The solution of the diffusion equation in the spherical coordinate system, taking into account the influence of the reflecting walls surrounding the given space, agreed satisfactorily with experimental data for the passage of light through aqueous solutions of poly(methyl methacrylate) and poly(vinyl chloride) [100]. The diffusion approximation method has been used successfully by Gribakin and Istomin to determine the optical behaviour in photographic emulsions and to find certain parameters of such emulsions[10,101]. The scattering properties of photographic emulsions have also been described in other studies[102,103].

The diffusion theory of neutron scattering has been used to describe the light scattering processes[104]. The specimens (blue and green glasses) were used to determine the absorption spectra from the reflection spectra of ground glasses with the aid of the P_1 approximation. A satisfactory agreement was achieved between the absorption spectra observed for the transparent glasses and the absorption spectra calculated from the reflection spectra. The P_1 approximation has been examined for diffuse illumination without taking into account the refractive index of the glass[104]. A similar approach has been used in another study[105] to determine the scattering cross-sections in dense suspensions of spherical particles (polystyrene latex).

The transport P_1 approximation has been used[30] to describe the scattering properties of pure and coloured filter paper. It follows from Eqn.(37) of the P_1 approximation that the following relation holds for weakly absorbing media with a fairly considerable optical thickness of the layer

$$\frac{1}{T(N)} = \frac{1}{(1-\rho_{sp})}\left[\frac{2p}{(3+p)} + \frac{3\sigma_{eff}}{(3+p)}l\right]. \qquad (41)$$

σeff can be found from the dependence of the coefficient $T(N)$ on the thickness of the paper (the number of filter papers) by Eqn.(41), since the paper absorbs only slightly in the visible part of the spectrum. Fig. 3 illustrates the variation of $1/T(N)$ with l for the filter paper (λ = 600 nm) from whose slope and the intercept on the ordinate axis it is possible to estimate α and σeff.[30] Using the characteristics of the medium found from the experiments on light transmission, it is possible to calculate $R_\infty(N)$ in terms of the P_1 approximation (Table 8). Table 8 shows that these data agree satisfactorily with experiment.

The reflectivity of coloured filter paper was also investigated. Nitratohexamminecobaltate(III), potassium hexacyanoferrate(III), and anthraquinone-2-sulphonate were used as dyes. This choice was dictated by the fact that the above substances show no tendency towards specific adsorption on the paper and it is therefore easy to determine their concentration on the paper. By measuring the reflection coefficient of the coloured paper and knowing the characteristics of the layer (α and σeff), it is possible to find from the Eqn.(32) of the P_1 approximation, taking into account the relation $\alpha = 2.3\epsilon c$, the concentration of the dye or its optical characteristics when the concentration is known.

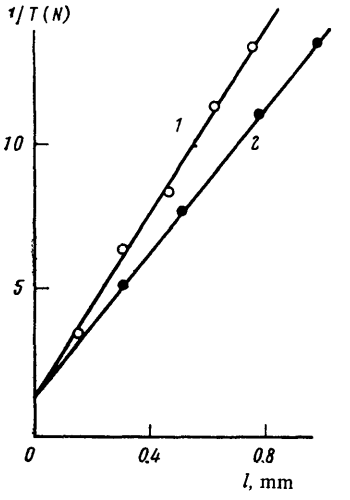


Figure 3. Dependence of $1/T(N)$ on the thickness of the layer (μ_0 = 1): 1) filter paper; 2) MS-14 milky glass[33].

As an example, Figs. 4 and 5 present the variation of the coefficients of specific absorption of the paper with the concentrations of the dyes and also the absorption spectra calculated from the diffuse reflection spectra[30], obtained on the assumption that the introduction of the dye does not alter σeff and that the dye is uniformly distributed throughout the paper.

Table 8. The coefficients $R_\infty(N)$ of filter paper [Eqn.(32)] (β determined from data for the transmission of light through the paper[30]).

λ, nm	400	420	450	480	500	600
$R_\infty(N)$, (calc.)	0.837	0.856	0.882	0.897	0.905	0.940
$R_\infty(N) \pm 0.02$, (expt.)	0.834	0.851	0.875	0.906	0.922	0.950

We shall now consider certain literature data which we interpreted in terms of the P_1 approximation. Fischer and Vratny[106] published the coefficients $R_\infty(N)$ for magnesium carbonate as a function of the amount of the light absorbing additive. We shall assume that the absorption coefficients are proportional to the weight fraction of the substance whereupon

$$\frac{1}{\beta} = \frac{m\sigma_d + \sigma_{MgCO_3}}{m\alpha'_d + \alpha'_{MgCO_3}}, \qquad (42)$$

where m is the weight fraction of the additive (subscript d) and α' are quantities proportional to the true parameters α. Since $R_\infty(N) \simeq 0.97$ in the visible part of the $MgCO_3$ spectrum[107], we neglect the term α'_{MgCO_3}. In this case, the plot of $1/\beta$ against $1/m$ should be linear. Indeed, measurements of the reflection of light from a mixture of $MgCO_3$ and Congo Red[106], interpreted in terms of Eqn. (42) ($N = 1.515$),[107] fit satisfactorily on a straight line (Fig. 6).

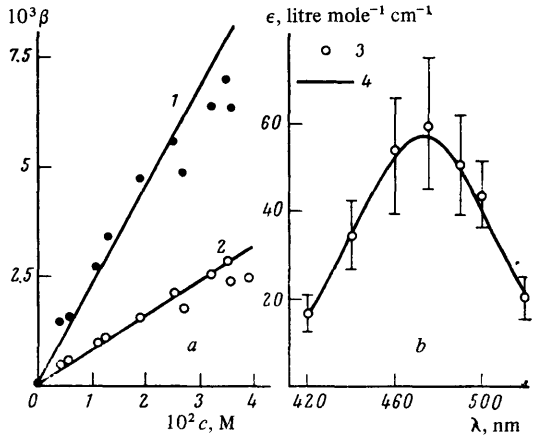


Figure 4. Nitratohexamminecobaltate(III) in filter paper[30]: *a*) dependence of β on concentration [1) λ = 475 nm; 2) λ = 520 nm]; *b*) [3) extinction coefficient calculated from reflection spectra; 4) ditto for an aqueous solution].

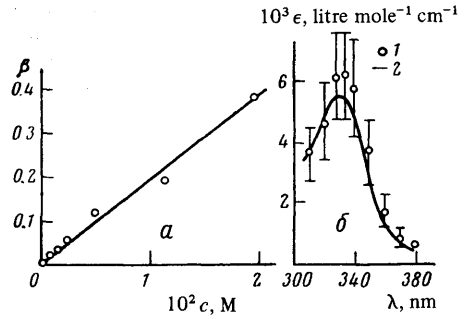


Figure 5. Anthraquinone-2-sulphonate in filter paper[30]: *a*) dependence of β on concentration (λ = 330 nm); *b*) [1) extinction coefficient calculated from reflection spectra; 2) ditto for aqueous solution].

A linear relation between the specific absorption coefficient and the concentration of the light absorbing additive (carbon black), analogous to the Beer–Lambert law, has been observed for aqueous suspensions of $BaSO_4$, ZnO, and TiO_2 ($N = 1.33$). The values of $R_\infty(N)$ for such systems, quoted by Blevin and Brown[108], have been interpreted in terms of Eqn. (32) (Fig. 7). We obtained a similar straight line from data[109] for eosin adsorbed on alumina.

We shall now consider the reflection spectra of coloured glass powders[97,110] ($N = 1.5$). General considerations suggest that $1/\sigma$ should be proportional to the average particle size in the layer. Indeed, knowing the absorption coefficients of ZhZS-1, NS-3, and ZS-6 coloured glasses and having calculated $1/\sigma$ in terms of the P_1 approximation, we obtain satisfactorily linear relations between $1/\sigma$ and the average particle size in the powder ($\bar{a}$), which are almost unaffected by the absorption coefficient (see, for example, Fig. 8).

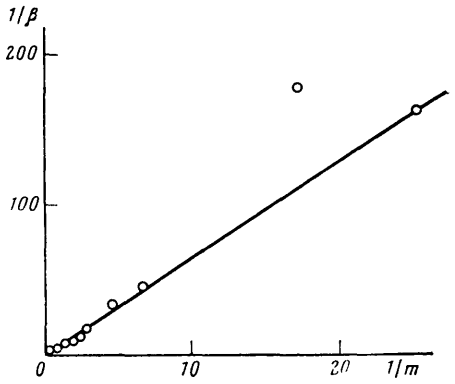


Figure 6. Dependence of $1/\beta$ on $1/m$ for a mixture of $MgCO_3$ and Congo Red powders. Data[106] interpreted in terms of the P_1 approximation.

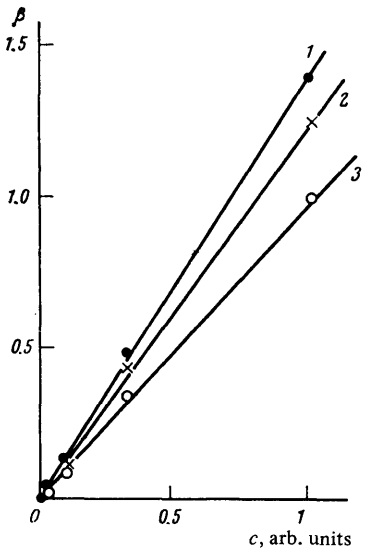


Figure 7. Dependence of β for an aqueous suspension of ZnO on the concentration of carbon black c. Data[108] interpreted in terms of the P_1 approximation; λ (nm): 1) 400; 2) 500; 3) 700.

The reflection and transmission coefficients of the MS-14 glass have been published[33] as a function of the layer thickness ($\mu = 1$, $N = 1.5$). Fig. 3 illustrates the variation of $1/T(N)$ with l (λ = 550 nm) based on these

data, which is linear, in agreement with Eqn.(41). The intercept on the ordinate axis is approximately 1.3, which is close to the values predicted by Eqn.(41). We may recall that a similar straight line for milky glasses has been found[14] to make an intercept greater than unity (Fig. 2). These findings apparently indicate the necessity for taking into account the refractive index of the scattering medium. The effective scattering coefficient of the MS-14 glass can be estimated from the slope of its straight line (Fig. 3) and α can then be found from the value of $R_\infty(N)$. Using the values of α and σ_{eff} obtained in this way, we calculated in terms of the P_1 approximation $R(N)$ and $T(N)$ for the MS-14 glass as a function of the layer thickness, the results agreeing with experimental data within the limits of the accuracy of the latter[33].

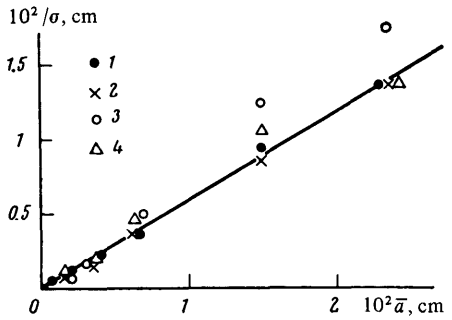


Figure 8. Dependence of $1/\sigma$ on $\bar{a}$ for ZS-6 glass powder ($\bar{a}$ is the average particle size). Data[97] interpreted in terms of the P_1 approximation; α (cm^{-1}): 1) 11; 2) 55; 3) 21.2; 4) 47.

Bearing in mind that the sum $[A] + [AH_2]$ is constant, it is possible to obtain the following expression for the initial section of the kinetic curve for the photolytic reaction[111]:

$$\varphi = -\frac{(d\beta/dt)_e \cdot \sigma_e/\sigma_p}{2.3(\varepsilon_A - \varepsilon_{AH_2})_e \cdot (\beta - \beta_0)_p c n_p}, \quad (43)$$

where the subscript e refers to the quantities corresponding to the experimental wavelength, p refers to photolysis, β_0 corresponds to pure paper, and n_p is the density of the quanta in the layer taking into account its illumination from both sides. A similar expression for φ is obtained also when it is assumed that the light which has entered the layer is fully absorbed by compound A.

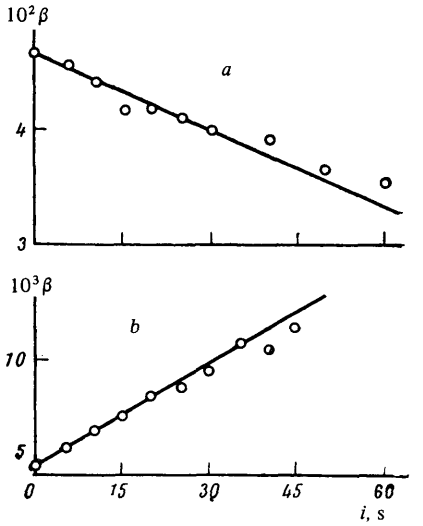


Figure 9. Initial sections of the kinetic curves for the photolysis of compound A in paper[111]; λ_p = 335 nm, λ_e = 335 nm (*a*); λ_e = 385 nm (*b*).

We estimated with the aid of SLS the quantum yield φ in the photochemical hydrogenation of anthraquinone-2-sulphonate (A) in filter paper[111]. A is reduced under the action of light to anthrahydroquinone-2-sulphonate (AH_2). The absorption band maxima for compounds A (335 nm) and AH_2 (385 nm) are well separated so that it is convenient to follow the photochemical reaction from the change in R_∞ (and hence also β) at the absorption band maxima. The methods described above, in particular the P_1 approximation, presuppose the homogeneity of the absorption coefficients throughout the layer, while the light profile has the form of a sharply decreasing function [Eqn.(29)]. As a result, the concentrations of A and AH_2 are significantly different throughout the layer. To a rough approximation, the light profile can be regarded as constant if thin sheets of paper are illuminated from both sides and then stacked to form a thick pile in order to measure R_∞.

Thus, assuming that the intensity of the photochemically active light is constant along the layer, we have at a certain instant t

$$\beta_e = \frac{2.3}{\sigma_e}(\varepsilon_A [A] + \varepsilon_{AH_2} [AH_2])_e + (\beta_0)_e.$$

The quantum yield of the photochemical hydrogenation of A, estimated by Eqn.(43), proved to be 0.12 ± 0.07, which agrees satisfactorily with the value obtained by an indirect chemical method. As an example, Fig. 9 presents the initial sections of the photolysis curves calculated by Eqn.(32) from the measured coefficients $R_\infty(N)$ for $[A] = 1.7 \times 10^{-3}$ M and $I_0 = 6 \times 10^{-14}$ quanta cm^{-2} s^{-1}, where I_0 is the intensity of the light incident on the layer.

The propagation of light in a medium having the shape of an infinitely long cylinder has been described with the aid of the diffusion theory[112], the description agreeing well with data for light scattering in polystyrene latices[113,114].

VIII. CONCLUSION

Approximate methods. The transport, two-flux, and diffusion approximations are most suitable for the analysis of experimental data and, when the specimen is illuminated with diffuse light, it is best to use the two-flux approximation. For directional illumination, both

approaches can be employed. However, we give preference to the transport diffusion approximation, since it can be used without resorting directly to the radiative transfer equation with which it is possible to take into account readily a wide variety of conditions within the specimen and on its surface. On the other hand, the diffusion equation is very frequently used to solve various chemical problems and for this reason physical chemists are much more accustomed to it than to the radiative transfer equation.

The Kubelka – Munk formula. The Kubelka – Munk formula [Eqn.(12)] is widely used in the analysis of experimental data even for directed illumination of the specimen. If the experimenter is satisfied with deducing a relation of the type $\alpha \propto c$, the application of the K–M formula does not lead to qualitatively incorrect results. However, in quantitative analysis it is best to employ the formulae of the transport, diffusion, or two-flux approximations, since the application of the K–M function for directed irradiation of the specimen is theoretically unjustified.

The radiative transfer equation. In the analysis of experimental data obtained for physicochemical systems such as powders, papers, fabrics, etc., the direct use of the radiative transfer equation can hardly be regarded as useful not only owing to mathematical difficulties, but because of certain fundamental considerations. The point is that it is not altogether clear how to formulate the radiative transfer equation for polydisperse systems such as powders or paper[115]. Furthermore, in complex polydisperse systems the coefficients α, σ, and χ depend not only on the coordinates but also on the direction of the incident beam. Consequently quantities averaged in some way must be substituted in the radiative transfer equation. However, the usefulness of employing average quantities within the framework of the exact radiative transfer equation is far from evident. The approach within the framework of the various approximations, some of which have been discussed above, appears more justified. Nevertheless, the rigorous solution of the problem of radiative transfer for different conditions should be the starting point for testing approximate methods.

There is apparently no great risk in extrapolating the solutions obtained to the region of strong absorption, provided that the treatment is restricted to the analysis of the coefficient R_∞ only, since the formal application of approximate theories to the region of strong absorption yields the following qualitative relation: $R_\infty \propto \beta^{-1} \propto c^{-1}$. We may note that the analogous relation $R_\infty \propto c^{-1}$ follows from Rozenberg's theory[4,6]. The proportionality coefficient between R_∞ and c^{-1} may be found experimentally.

The possibility of the quantitative measurement of the absorption coefficient. The spectroscopy of light scattering media is nowadays used inadequately in chemical research. With a few exceptions, no attempts have been made to determine the absorption coefficients. We may note that, in order to determine the absorption maximum of a substance in a scattering medium, no theories are required, since it is sufficient for this purpose to have, for example, the $R_\infty - \lambda$ or $(1 - R_\infty) - \lambda$ curves.

One of the ways of determining absorption coefficients quantitatively may be as follows. One may hope that in certain cases light scattering will be determined mainly by the light scattering matrix and not the admixtures introduced into it. This can be demonstrated by introducing into the matrix different substances which do not interact with it assuming at the same time that the absorption coefficient of the added substance does not change and is equal to that for the same substance in solution. The problem now is to what extent this assumption can be justified. One may note that the introduction of a substance into a light scattering matrix does not differ in principle in any way from dissolution. For this reason, the change in the extinction coefficient should be close to the change in the extinction coefficient when the compound is dissolved in various solvents. According to Stern and Dammons[116], in most cases it does not exceed 5–10%. The data quoted in their book[116] for the extinction coefficients of the $n - \pi^*$ transition of the acetone molecule in various solvents, show that it does not change by more than 25% on either side of the average value. We may note that the $n - \pi^*$ transitions are most sensitive to the environment. On the other hand, when molecules with internal transitions of the type $\pi - \pi^*$ or $a - d$, for example $Co(NH_3)_6^{3+}$, are used, one may hope that their extinction coefficients do not vary markedly when they are introduced into a light scattering matrix. By using several specially selected compounds, it is possible to determine the dependence of the scattering coefficient on the wavelength. This would make it possible to determine subsequently the absorption coefficient of any other compound introduced into the matrix. Naturally the objection arises that this procedure is not very accurate; however, the accuracy of the above approach is not lower than that of the ESR method, widely used in physicochemical research, for which the accuracy of the quantitative determination of free radicals is usually assumed to be approximately 40%.

Thus the present state of SLM permits the quantitative determination of the absorption coefficient. The absence of the relevant reports from the literature is incomprehensible.

The problem of the separation of ϵ and c. The knowledge of the absorption coefficient α does not of course permit the separate determination of ϵ and c. It is therefore necessary to employ other methods whereby the concentration can be measured directly, for example, the ESR method. Such combinations of ESR and SLM methods appears to be fairly promising, particularly in catalytic research.

Procedures involving the transition of the given substance from one form to another under the influence of some agent, for example chemical or radiation-chemical, are very important for the problem of the resolution of the two parameters. This factor also appears to have been overlooked by experimenters.

The size of light beams. In the approximate methods considered, light beams of infinite extent are postulated. On the other hand, in practice light beams of finite dimensions are used. However, they satisfy the problem formulated if their size is significantly greater than the characteristic parameter of the specimen: $1/(\alpha + \sigma\text{eff})$. The existence of halos, for example in the case of milk, indicates the unsuitability for research of beams approximately 1 cm long, since the characteristic size of the halos is of the same order of magnitude. Beams whose size is significantly greater than the geometrical dimensions of the powder particles are probably suitable for powders.

The specular component in the diffuse reflection spectra. For layers with an optically smooth surface, the specular component may be readily taken into account [31]. For powdered specimens, whose boundary cannot be clearly determined, the allowance for the specular component in the measurement of the reflection spectra is much more difficult. It apparently depends on the packing density of the powder particles [75]. On the other hand, in view of the uneveness of the boundary of the powdered medium, the specular component may be actually smaller than for an optically smooth surface. The problem has not been finally solved and is by no means always taken into account in experimental research.

Allowance for the effect of total internal reflection. The existence of total internal reflection must be taken into account for specimens with an optically smooth surface, for example solutions. The necessity for this in the case of powdered specimens is less clear. The elucidation of the above problem requires further experiments, although one can adduce arguments in support of allowance for total internal reflection in these media too.

Illumination of specimens at an angle. It is sometimes suggested that specimens be illuminated at an angle, for example 45°, since in this case the values of R_∞ obtained from the exact solution of the radiative transfer equation for a spherical scattering indicatrix and calculated from the Kubelka–Munk equation are approximately the same [2,31]. However, this approach has no appreciable advantages compared with the usual illumination of specimens at right angles ($\mu_0 = 1$) and may actually suffer from disadvantages. The point is that it is not clear how to proceed when the scattering indicatrix deviates from the spherical shape and in practice this situation does in fact occur. On the other hand, in the study of systems with an optically smooth surface one must take into account the refraction of the light beam and the angle must be varied in order that the light should enter the medium at an angle of 45°. Furthermore, for illumination at an angle the coefficient R_∞ increases and the method becomes less sensitive to small amounts of impurities.

The reference specimen. By analogy with the spectroscopy of transparent media, diffuse reflection spectra are sometimes measured relative to the light-scattering matrix assuming thereby that the absorption in the initial matrix, for example owing to impurities, is taken into account. However, as a result of the absence of a linear relation between $R_\infty(\lambda)$ and $\alpha(\lambda)$, this method of taking absorption into account is incorrect. $R_\infty(\alpha)$ can of course be measured relative to the initial light-scattering material, but in quantitative calculations the data obtained (R_∞^{exp}) must be converted into the true reflectance (R_∞^{true}) by means of the formula

$$R_\infty^{true} = R_\infty^{org} R_\infty^{ref},$$

where R_∞^{ref} is the reflection coefficient relative to a specimen giving 100% reflection. Either milky glasses [117–119] or white powders, for example MgO, ZnO, and $BaSO_4$ with known reflectances [120,121], are normally used as reference specimens with 100% reflection.

The apparatus. All types of apparatus for measurement of the integral coefficients R and T can be divided into two classes: devices with an integrating sphere [122] (SF-10 and SF-14 apparatus) and devices with elliptical or parabolic mirrors [4,8] (the PDO-1 and PDO-2 attachments). In both systems, light is directed in succession to the experimental and reference specimens. We may note that the PDO-1 attachment does not measure the entire reflected radiation but only its component reflected within conical angles of 10–80° relative to the normal. In the measurement of the true coefficient R_∞, it is therefore necessary that the angular characteristics of the radiation reflected from the test and reference specimens should be similar. Simpler devices can also be used to measure α max for reflection spectra [123].

Prospects. The present state of SLM is such that it permits quantitative measurements with an accuracy close to that of the ESR method (approximately 40%). One may hope that SLM will find much wider applications in studies on photochemical, radiation-chemical, and, particularly, catalytic processes.

REFERENCES

1. S. Chandrasekhar, "Radiative Transfer" (Translated into Russian), Inostr. Lit., Moscow, 1953.
2. V. V. Sobolev, "Perenos Luchistoi Energii v Atmosferakh Svezd i Planet" (Transfer of Radiant Energy in the Atmospheres of the Stars and Planets), GITTL, Moscow, 1956.
3. G. V. Rozenberg, Uspekhi Fiz. Nauk, 69, 57 (1959).
4. B. I. Stepanov (Editor), "Spektroskopiya Svetorasseivayushchikh Sred" (The Spectroscopy of Light scattering Media), Izd. Akad. Nauk Beloruss. SSR, Minsk, 1963.
5. W. W. Wendlandt and H. G. Heckt, "Reflectance Spectroscopy", Intersci. Publ., New York, 1966.
6. G. V. Rosenberg, Uspekhi Fiz. Nauk, 91, 569 (1967).
7. W. W. Wendlandt (Editor), "Modern Aspects of Reflectance Spectroscopy", Plenum Press, New York, 1968.
8. A. P. Ivanov, "Optika Rasseivayushchikh Sred" (The Optics of Scattering Media), Izd. Nauka i Tekhnika, Minsk, 1969.
9. E. P. Zege, "O Dvukhpotokovom Priblizhenii v Teorii Perenosa Izlucheniya" (The Two-flux Approximation in the Radiative Transfer Theory), Preprint from the Institute of Physics of the Academy of Sciences of Belorussian SSR, Minsk, 1971.
10. B. I. Stepanov and A. P. Ivanov (Editors), "Teoreticheskie i Prikladnye Problemy Rasseyaniya Sveta" (Theoretical and Applied Problems of Light Scattering), Izd. Nauka i Tekhnika, Minsk, 1971.
11. V. V. Sobolev, "Rasseyanie Sveta v Atmosferakh Planet" (Light Scattering in Planetary Atmospheres), Izd. Nauka, Moscow, 1972.
12. K. M. Case and P. F. Zweifel, "Linear Transport Theory" (Translated into Russian), Izd. Mir, Moscow, 1972.
13. K. S. Adzerikho, "Lektsii po Teorii Perenosa Luchistoi Energii" (Lectures on the Theory of the Transfer of Radiant Energy), Izd. Beloruss. Gos. Univ., Minsk, 1975.
14. A. A. Gershun, "Izbrannye Trudy po Svetometrii i Svetotekhnike" (Selected Works on Photometry and Illumination Engineering), GIFML, Moscow, 1958, p. 68.

15. M. M. Gurevich, "Vvedenie v Fotometriyu" (Introduction to Photometry), Izd. Energiya, Leningrad, 1968.
16. B. J. Brinkworth, J. Phys. D: Appl. Phys., 4, 1105 (1971).
17. K. Klier, J. Opt. Soc. Amer., 62, 882 (1972).
18. N. A. Voishvillo, Optika i Spektrosk., 37, 136 (1974).
19. N. A. Voishvillo, Optika i Spektrosk., 36, 1162 (1974).
20. Hsue-Seng Chiang, "Physical Mechanics" (Translated into Russian), Izd. Mir, Moscow, 1965.
21. G. I. Marchuk, "Metody Rascheta Yadernykh Reaktorov" (Computational Methods for the Design of Nuclear Reactors), Atomizdat, Moscow, 1961.
22. B. Davison, "Neutron Transport Theory" (Translated into Russian), Atomizdat, Moscow, 1960.
23. C. Goodman (Editor), "The Science and Engineering of Nuclear Power Engineering" (Translated into Russian), Inostr. Lit., Moscow, 1948.
24. S. Glasstone and M. C. Edlund, "The Elements of Nuclear Reactor Theory" (Translated into Russian), Inostr. Lit., Moscow, 1954.
25. D. A. Frank-Kamenetskii, "Fizicheskie Protsessy vnutri Zvezd" (Physical Processes Within the Stars), Fizmatgiz, Moscow, 1959.
26. P. M. Morse and H. Feshbach, "Methods of Theoretical Physics" (Translated into Russian), Inostr. Lit., Moscow, 1958, Vol. 1.
27. V. I. Kuznetsov, Optika i Spektrosk., 5, 606 (1958).
28. Yu. A. Tsirlin, L. E. Pargamanik, and A. R. Daich, Optika i Spektrosk., 12, 304 (1962).
29. I. V. Savel'ev, "Kurs Obshchei Fiziki" (A General Physics Course), Izd. Nauka, Moscow, Vol. 1, p. 391.
30. N. M. Bazhin and S. M. Baranov, Optika i Spektrosk., 34, 963 (1973).
31. R. G. Giovanelli, Opt. Acta, 2, 153 (1955).
32. S. E. Orchard, J. Opt. Soc. Amer., 59, 1584 (1969).
33. N. A. Voishvillo, Optika i Spektrosk., 31, 275 (1971).
34. A. P. Ivanov and V. A. Lojko, J. Signal AM, 3, 23 (1975).
35. K. D. Lathrop, Nuclear Sci. Eng., 21, 498 (1965).
36. W. R. Blevin and W. J. Brown, J. Opt. Soc. Amer., 51, 975 (1961).
37. B. I. Stepanov, Yu. I. Chekalinskaya, and O. P. Girin, "Trudy Instituta Fiziki i Matematiki" (Transactions of the Institute of Physics and Mathematics), Izd. Akad. Nauk Beloruss. SSR, Minsk, 1956, No. 1, p. 152.
38. Z. Bodo, Acta Phys. Hung., 1, 135 (1951).
39. V. V. Antonov-Romanovskii, Zhur. Eksper. Teor. Fiz., 26, 459 (1954).
40. O. P. Girin and B. I. Stepanov, Zhur. Eksper. Teor. Fiz., 27, 467 (1954).
41. G. V. Rozenberg, Optika i Spektrosk., 5, 440 (1958).
42. G. V. Rozenberg, Dokl. Akad. Nauk SSSR, 145, 775 (1962).
43. N. A. Voishvillo, Optika i Spektrosk., 31, 458 (1971).
44. N. A. Voishvillo, Dokl. Akad. Nauk SSSR, 98, 201 (1954).
45. A. A. Il'ina and G. V. Rosenberg, Dokl. Akad. Nauk SSSR, 98, 365 (1954).
46. N. T. Melamed, J. Appl. Phys., 34, 560 (1963).
47. E. L. Simmons, Opt. Acta, 18, 59 (1971).
48. E. L. Simmons and W. W. Wendlandt, J. Phys. Chem., 79, 1158 (1975).
49. S. Ziering and D. Schiff, Nuclear Sci. Eng., 3, 635 (1958).
50. D. Schiff and S. Ziering, Nuclear Sci. Eng., 7, 172 (1960).
51. A. E. Bradfield and A. E. Flood, J. Chem. Soc., 4770 (1952).
52. H. Zeitlin and A. Niimoto, Nature, 181, 1616 (1958).
53. T. P. Griffits, K. A. Lott, and M. C. R. Symons, Analyt. Chem., 31, 1338 (1958).
54. P. L. Hartman and R. C. Merill, J. Opt. Soc. Amer., 51, 168 (1961).
55. J. M. Turlet and M. R. Philpott, J. Chem. Phys., 62, 2777 (1975).
56. G. P. Vishnevskaya, R. Sh. Safin, I. N. Lipunov, E. I. Kazantsev, and V. A. Gorozhanin, Teor. Eksper. Khim., 10, 514 (1974).
57. T. A. Sidorov, Zhur. Prikl. Spektrosk., 5, 111 (1966).
58. S. V. Volkov and V. A. Sushko, Ukrain. Khim. Zhur., 39, 830 (1973).
59. G. N. Asmolov and O. V. Krylov, Kinetika i Kataliz, 11, 1028 (1970).
60. G. N. Asmolov and O. V. Krylov, Kinetika i Kataliz, 12, 463 (1971).
61. V. B. Kazanskii, Kinetika i Kataliz, 11, 455 (1970).
62. L. K. Przheval'skaya, V. A. Shvets, and V. B. Kazanskii, Kinetika i Kataliz, 11, 1310 (1970).
63. O. I. Brotikovskii, V. A. Shvets, and V. B. Kazanskii, Kinetika i Kataliz, 13, 1342 (1972).
64. V. G. Shinkarenko, V. F. Anufrienko, G. K. Boreskov, K. G. Ione, and T. M. Yur'eva, Dokl. Akad. Nauk SSSR, 223, 410 (1975).
65. Yu. I. Tarasevich and E. G. Sivalov, Ukrain. Khim. Zhur., 41, 354 (1975).
66. S. P. Tandon, P. P. Vaishnava, and R. C. Mathur, Solid State Comm., 15, 787 (1974).
67. Yu. I. Ermakov, B. N. Kuznetsov, L. G. Karakchiev, and S. S. Derebeneva, Kinetika i Kataliz, 14, 709 (1973).
68. L. G. Simonova, V. A. Dzis'ko, M. S. Borisova, L. G. Karakchiev, and O. I. Olen'kova, Kinetika i Kataliz, 14, 1566 (1973).
69. V. A. Dzis'ko, S. P. Noskova, M. S. Borisova, V. G. Bolgova, and L. G. Karakchiev, Kinetika i Kataliz, 15, 751 (1974).
70. L. G. Karakchiev, Symposium, "Osnovy Predvideniya Kataliticheskogo Deistviya" (Principles of the Prediction of Catalytic Activity), Izd. Nauka, Moscow, 1970, Vol. 2, p. 372.
71. L. G. Karakchiev, N. S. Kotsarenko, E. A. Paukshis, and V. G. Shinkarenko, Kinetika i Kataliz, 16, 1305 (1975).
72. N. S. Kotsarenko, L. G. Karakchiev, and V. A. Dzis'ko, Kinetika i Kataliz, 9, 158 (1968).
73. E. A. Paukshtis, N. S. Kotsarenko, and L. G. Karakchiev, Kinetika i Kataliz, 14, 1561 (1973).
74. G. Kortüm, W. Braun, and H. Herzog, Uspekhi Fiz. Nauk, 85, 365 (1965).
75. G. Kortum, "Reflexion Spektroskopie", Springer-Verlag, Berlin, 1969.
76. G. Kortum and W. Braun, Z. phys. Chem., 18, 242 (1958).
77. G. Kortum and W. Braun, Z. phys. Chem., 28, 362 (1961).
78. G. Kortum and J. Vogel, Z. phys. Chem., 18, 110 (1958).
79. G. Schreyer, Z. phys. Chem., 18, 123 (1958).
80. G. Kortum and J. Vogel, Z. phys. Chem., 18, 230 (1958).

81. D. Oelkrug and G. Kortum, Z. phys. Chem., 58, 181 (1968).
82. G. Kortum and W. Braun, Annalen, 632, 104 (1960).
83. G. Kortum, M. Kortum-Seiler, and S. D. Bailey, J. Phys. Chem., 66, 2439 (1962).
84. G. Kortum and G. Bayer, Z. phys. Chem., 33, 254 (1962).
85. G. Kortum, in "Advances in Molecular Spectroscopy", Pergamon Press, New York, 1962, p. 96.
86. A. P. Ivanov, V. G. Leitsyna, and I. N. Puplikova, Zhur. Anal. Khim., 17, 511 (1962).
87. R. Reisfeld, E. Greenberg, and W. J. Levene, Analyt. Chim. Acta, 74, 253 (1975).
88. D. Oelkrug, Z. phys. Chem., 56, 325 (1967).
89. M. Z. Gavrilova, I. N. Ermolenko, and G. L. Elina, Optika i Spektrosk., 18, 515 (1965).
90. A. S. Toporets, Optika i Spektrosk., 4, 494 (1958).
91. N. A. Voishvillo, Optika i Spektrosk., 31, 275 (1971).
92. G. V. Rozenberg, M. Yu. Sakhnovskii, and S. G. Guminetskii, Optika i Spektrosk., 23, 797 (1967).
93. M. Yu. Sakhnovskii, Optika i Spektrosk., 18, 179 (1965).
94. V. P. Rvachev and M. Yu. Sakhnovskii, Zhur. Prikl. Spektrosk., 4, 568 (1966).
95. L. V. Koval'skii and M. Yu. Sakhnovskii, Zhur. Prikl. Spektrosk., 8, 629 (1968).
96. M. Yu. Sakhnovskii and A. F. Kotik, Optika i Spektrosk., 34, 1187 (1973).
97. A. P. Ivanov and A. S. Toporets, Optika i Spektrosk., 1, 802 (1956).
98. C. P. Poole and J. F. Itzel, J. Chem. Phys., 39, 3445 (1963).
99. L. E. Pargamanik, M. A. Strzhemechnyi, and Yu. A. Tsirlin, Zhur. Prikl. Spektrosk., 2, 440 (1965).
100. B. J. Brinkworth, Brit. J. Appl. Phys., 15, 733 (1964).
101. G. G. Gribakin and G. A. Istomin, Zhur. Nauch. i Prikl. Fotogr. i Kinematogr., 12, 364 (1967).
102. G. Haase and H. Muller, Optik, 17, 3 (1960).
103. H. F. Gilmore, J. Opt. Soc. Amer., 57, 75 (1967).
104. L. F. Gate, J. Phys. D: Appl. Phys., 4, 1049 (1971).
105. L. F. Gate, J. Opt. Soc. Amer., 63, 312 (1973).
106. R. B. Fischer and F. Vratny, Analyt. Chim. Acta, 13, 588 (1955).
107. "Handbook of Chemistry and Physics", 49th Edition, Chemical Rubber Publishing Company, Cleveland, 1968–1969.
108. W. R. Blevin and W. J. Brown, J. Opt. Soc. Amer., 52, 1250 (1962).
109. M. M. Frodyama, R. W. Frei, and D. J. Williams, J. Chromotogr., 13, 61 (1964).
110. Z. V. Zhidkova, Zhur. Eksper. Teor. Fiz., 27, 458 (1954).
111. S. M. Baranov, N. P. Vdovina, and N. M. Bazhin, Khim. Vys. Energii, 9, 506 (1975).
112. D. K. Beridze, Optika i Spektrosk., 39, 920 (1975).
113. D. K. Beridze and G. V. Dzhobava, Optika i Spektrosk., 28, 504 (1970).
114. D. K. Beridze and G. V. Dzhobava, Optika i Spektrosk., 31, 788 (1971).
115. A. P. Ivanov and V. G. Danilyuk, Zhur. Prikl. Spektrosk., 22, 302 (1975).
116. E. S. Stern and C. J. Timmons, "Electronic Absorption Spectroscopy in Organic Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1974.
117. V. P. Rvachev and M. Yu. Sakhnovskii, Optika i Spektrosk., 18, 486 (1965).
118. A. S. Toporets, Optika i Spektrosk., 18, 704 (1965).
119. O. M. Mikhailov, Optika i Spektrosk., 28, 801 (1970).
120. N. A. Voishvillo, Opt.-Mekh. Prom., No. 5, 63 (1972).
121. A. S. Toporets, Optika i Spektrosk., 10, 528 (1961).
122. V. N. Pak, Zhur. Prikl. Spectrosk., 22, 350 (1975).
123. V. A. Shvets and V. B. Kazanskii, Pribory i Tekh. Eksper., 4, 213 (1966).

Institute of Chemical Kinetics
and Combustion, Siberian Division
of the USSR Academy of Sciences,
Novosibirsk