

*PHYSICAL BASIS OF THE SPECTROSCOPY OF LIGHT-SCATTERING SUBSTANCES**

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THE need for spectral investigations of substances in which, owing to optical inhomogeneity, the phenomena of propagation, absorption, or emission of light are inseparable from its scattering, arises more and more frequently and more and more insistently in the practice of spectroscopic laboratories. The number of such light-scattering objects is exceedingly large. It includes, for example, all biological matter (live tissues, compounds of all types, microorganism cultures), the principal astrophysical and geophysical objects (stellar and planetary atmospheres, soils, waters, and their covers), food products, dyes, and structural materials, powders, emulsions, and colloids, snow-like and paper-like substances (for example, chromatograms), cloths, most luminors and light sources, and even distilled water in the ultraviolet region of the spectrum. Many phenomena, such as coagulation and phase transformations, resonance fluorescence and the associated reversal of spectra, or Shpol'skiĭ's luminescence and absorption spectra, can be traced only in substances that exhibit strong light scattering.

It is no wonder that the use of spectroscopy for the investigation of various objects of this class ceases to be a rarity. Nevertheless, the number of times one resorts to it is incomparably small compared with the number of still unsolved problems for which it can be used. Frequently this is due to lack of faith in the very possibility of using spectroscopy for objects of this kind. It is more frequently the consequence of the inability to overcome the corresponding methodological difficulties.

The most frequent approach, however, is the other extreme, wherein being unable to take into account the specific features of the light-scattering media, the research workers merely attempt to ignore it completely and remain within the framework of the noncritical utilization of traditional procedures. If the latter turn out to be patently inconsistent, then they are replaced either by general arguments of crudely qualitative character, far removed from the contemporary level of knowledge, or by recommendations that are attractive for their simplicity, but known to be unreliable and generated by the primitive concepts of past times.

Among the many hundreds of papers devoted annually to the spectroscopy of light-scattering substances, one can hardly find one or two dozen in which the methodological aspect of the research is at the level of contemporary requirements and provides irreproachable results.

The cause of this situation can be seen in the fact that the few present-day theoretical and experimental researches especially aimed at developing the fundamentals of spectroscopy of light-scattering substances remain little known to the practicing spectroscopists (mostly at the fault of the authors themselves, who cast these researches in difficult-to-understand mathematical form). In particular, two fundamental facts, clearly established by these researches, remain little known.

First, the traditional methods of spectral analysis of optically homogeneous substances are utterly inconsistent as soon as scattering of light becomes barely perceptible. The optical singularities of light-scattering substances call for principally new approaches to the very formulation of the problem of spectral analysis. One must speak here not of running away from the light-scattering phenomena, but their intelligent utilization for analytic purposes. Artificial increase of light scattering can sometimes become a means of producing additional spectroscopic capabilities. To the contrary, ignoring the specific features of light-scattering substances frequently leads to gross and difficultly detected errors.

Second, in spite of the extreme variety of light-scattering substances, there exist certain general rules governing their optical properties and admitting of the unified treatment of the entire manifold of optical phenomena which take place in these substances. The existence of such laws indeed ensures, in final analysis, the possibility of developing concrete analytic procedures as applied to problems and objects of various kinds on the basis of a general theory, and not by empirical trials.

The general laws of the optics of light-scattering bodies, and by the same token the principles of their spectral analysis, were revealed essentially in the papers of A. A. Gershun, M. M. Gurevich and co-workers, P. Kubelka, É. V. Shpol'skiĭ and co-workers, V. A. Ambartsumyan, B. I. Stepanov and his students, V. A. Timofeeva, and also the author and his co-

*Expanded version of a lecture delivered at the Moscow State University on 1 February 1965 to the participants of the All-union Conference on Spectroscopy.

workers; see, for example ^[1-13] and also the reviews ^[14-19].

Serving as the basis for this group of researches are, on the one side, modern theory of radiation transport in light-scattering substances, which has provided a well developed mathematical formalism. On the other side, they are based on a sufficiently varied experimental laboratory material (primarily the investigations of A. S. Toropets, G. Kortum, and especially A. P. Ivanov and co-workers^[14-19]). Each of the disciplines has for a long time developed practically independently and has since become part of an extensive field of knowledge, worthy of an independent study going greatly beyond the framework of this article. The theoretical base of the spectroscopy of light-scattering substances was itself built up of new physical ideas that resulted from a combination of theoretical and experimental research and were formulated in more or less explicit form in the papers of the already-mentioned cycle, especially in recent years. These revealed not only ways and means of solving spectral-analysis problems, but also the capabilities and limitations of spectral-analysis methods as applied to light-scattering objects.

However, while the general theory is already at a satisfactory level, although far from complete, the particular procedures based on it and the apparatus needed for its realization have been developed very little. In this sense, the situation in the spectroscopy of light-scattering substances recalls the conditions that developed some quarter of a century ago in emission spectroscopy, when the practical application of the general principles came head on against the need for developing particular procedures, and by the same token of carrying out numerous researches of methodological character. The difference lies only in the fact that the general principles of the spectroscopy of light-scattering substances remains so far the preserve of a narrow circle of specialists and has escaped the attention of most experimental spectroscopists. Only this can explain the utterly unjustified but widespread nihilism in the evaluation of the capabilities of the spectroscopy of light-scattering substances. For this reason, scientific development of spectroscopic procedures is frequently replaced by a noncritical utilization of all possible palliatives of the type, for example, used in the tendentious and frequently simply erroneous review of G. Kortum and co-authors.^[19]

The review presented here does not pretend to be comprehensive and is addressed primarily to experimental spectroscopists who are not skilled in the fine points of mathematical theory. Therefore attention will be paid principally to the explanation of the physical picture of the phenomena and of the physical fundamentals of constructing a spectral analysis of light-scattering substances, and also to a clarification of its capabilities. Questions involved in the experimental realization of these fundamentals, as well as methods

for their verification, will be touched upon only to the extent needed to illustrate the general ideas. Part of the considerations advanced here are published by the author for the first time.

I. GENERAL PRINCIPLES OF ABSORPTION SPECTROSCOPY OF OPTICALLY HOMOGENEOUS SAMPLES. SPECTRAL TRANSMISSION FUNCTION

To clarify the essence of the problems that are faced by spectroscopy of light-scattering substances, we turn first to a general formulation of absorption spectral analysis for optically homogeneous samples, but considered from an aspect to which little attention is usually paid.

The purpose of absorption spectral analysis, in any of its variants, is to measure various parameters that characterize the state or structure of the substance. Essentially we are speaking of replacing difficultly realizable (and sometimes unrealizable) direct measurements of these parameters by more accessible measurements of the spectral dependence of the absorption coefficient κ (i.e., the imaginary part of the refractive index) of the investigated substance. The basis of such a replacement must inevitably be the theory of the act of light absorption by the substance. Usually this theory is indeed considered as the basis of spectroscopy, all the more because in the case of optically homogeneous objects all the theoretical difficulties are concentrated in it.

However, no less important a role is played in the realization of spectroscopic research by another theory, which usually remains in the shadow only because in the case of an optically homogeneous medium its deductions are elementary. Indeed, the quantities directly measured under conditions, say, of absorption spectroscopy are the geometrical dimensions of the sample and light fluxes at various wavelengths λ , incident on the sample (F_0) and emerging from it (F). As a result of these or equivalent measurements, one obtains the spectral dependence of the transparency of the sample

$$T(\lambda) = \frac{F(\lambda)}{F_0(\lambda)} \quad (1)$$

under specified conditions of its illumination. This, properly speaking, completes the experimental stage of the spectral analysis.

The next stage should be the conversion of the experimentally measured function $T(\lambda)$, which characterizes the sample as a whole, into the dependence on λ of various parameters characterizing the optical properties of the material of this sample, for example $\kappa(\lambda)$. Only then is it possible, by using the theory of the act of light absorption, to determine the structural parameters of the substance or its state. Thus, we are dealing with the need for establishing a connection between the quantity T and the volume (or mass) coef-

ficient α of light absorption by the material of the sample and, further, the connection between α and κ . For an optically inhomogeneous medium, both connections are established by the theory of propagation of light in matter.

In the case of a homogeneous unbounded isotropic medium and strictly monochromatic light, the results of this theory are so simple when considered in the framework of ray optics that they seem to be self evident. If we go over from light flux F to the brightness I of the light beam, then they reduce to Bouguer's law:

$$dI = -\alpha I dl, \quad (2)$$

where

$$\alpha = \frac{4\pi\kappa}{\lambda} \quad (3)$$

and dI is the element of length of the light beam, or, in integral form,

$$T(\lambda, l) = e^{-\alpha(\lambda)l}, \quad (4)$$

where l is the path traversed by the light in the matter.

Frequently, however, it is forgotten that such simple expressions are obtained only as a result of far reaching idealizations. If, for example, the sample boundaries are plane-parallel, then allowance for the light reflected by the end surfaces makes it necessary to replace (4) by the relation

$$T(\lambda, L) = \frac{2 \operatorname{sh}^2 \chi}{\operatorname{sh}(2\chi + \alpha L)}, \quad (5)$$

where L is the length of the sample, $\chi = -\frac{1}{2} \ln R$, and R is the energy coefficient of light reflection from the end surface, which also depends on α . Allowance for interference^[20] or for nonlinear effects complicates further the relations between T , α , and κ , and the form of these relations greatly influences both the character of the spectroscopic experiment and the number of independent measurements necessary for its unique interpretation. This becomes especially clearly manifest, for example, when determining the $\kappa(\lambda)$ dependence from measurements of light reflected by a mirror surface of the sample, when it is advantageous to supplement or even replace the photometric measurements by polarization and phase measurements (see, for example, [20, 21]).

Thus, the real scheme of a spectrum-analytic experiment, even in the case of an optically homogeneous sample, turns out to be much more complicated and acquires the form shown in Fig. 1.

The general scope of the experiment is determined on the basis of the theory of the structure of matter, which relates its optical parameters with the sought information concerning it. Further, the theory of propagation of light in matter, which relates its optical parameters with the optical parameters of the

sample as a whole, determines the formulation of the spectroscopic experiment, i.e., the character and number of the spectroscopic experiment, i.e., the character and number of measurement operations. Finally, the theory of the light field, which relates the measured parameters of the latter with the optical parameters of a sample situated in the field, determines the arrangement of the measuring apparatus.

The foregoing pertains directly to absorption spectroscopy. However, the scheme outlined above remains practically unchanged also for luminescence and emission spectroscopy. But in each concrete case the relations between the different elements of this scheme are different. Thus, if we are dealing with a standard quantitative spectrochemical analysis, then, within the validity of Beer's law, the stage connected with the use of the theory of structure of matter drops out completely and the procedure is based entirely on the theory of propagation of light in matter.

In order to make this even more evident, and incidentally to explain certain circumstances that will prove useful later, we return to the case of an unbounded medium, but assume that the absorption coefficient α of the substance depends essentially on λ inside the spectral interval $(\lambda, \lambda + \Delta\lambda)$ of the measuring instrument (or of the radiation source). This is the case, for example, when the spectral instrument does not resolve the rotational structure of the gas-absorption band, as frequently happens in the infrared region of the spectrum.

We then must consider in lieu of (1) the quantity

$$p(\lambda, \Delta\lambda, l) = \frac{F(\lambda, \Delta\lambda, l)}{F_0(\lambda, \Delta\lambda, l)}, \quad (6)$$

which is customarily called the "spectral transmission function" or, as the astrophysicists prefer, the "growth curve." We retain here the concept of "transparency" and the symbol $T(\lambda, l)$ for monochromatic

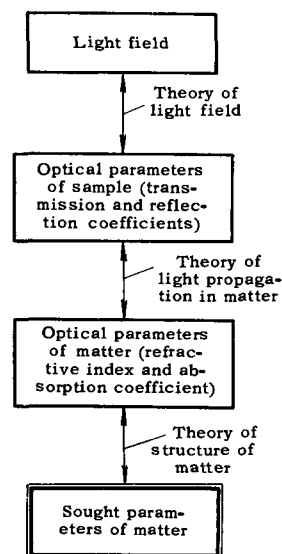


FIG. 1. Diagram of spectrum-analysis experiment with optically homogeneous sample.

light, or, more generally, for T independent of λ in the interval from λ to $\lambda + \Delta\lambda$. Since we are now dealing not with monochromatic light but with a finite spectral interval, it is essential that the measurements of the light fluxes entering and leaving the sample be carried out with an identical apparatus function $A(\lambda, \lambda' - \lambda)$ characterizing the spectral sensitivity of the system as a whole, including the spectral characteristics of the source and light receiver and the light-filtering devices.

Then, as can be readily seen

$$p(\lambda, \Delta\lambda, l) = \frac{1}{Z} \int_{\lambda}^{\lambda + \Delta\lambda} A(\lambda, \lambda' - \lambda) T(\lambda', l) d\lambda', \quad (7)$$

where $Z = \int_{\lambda}^{\lambda + \Delta\lambda} A(\lambda, \lambda' - \lambda) d\lambda$ and $T(\lambda, l)$ is defined

by relation (4) for a homogeneous medium and by relation (5), say, for a sample of length L . Frequently, if Beer's law is valid, it is convenient to change over from the volume to the mass coefficient of absorption of the matter. But this does not change relations (7), except that l is formally replaced by the amount m of matter which is pierced by the light beam.

On the other hand, taking into account the monotonic character of $T(\alpha)$, we can transform (7) into

$$p(\lambda, \Delta\lambda, l) = - \int_0^{\infty} w(\alpha) \frac{dT}{d\alpha} d\alpha,$$

where $w(\alpha')$ is the probability, weighted by the apparatus function, that in the interval $(\lambda, \lambda + \Delta\lambda)$ we have $\alpha \leq \alpha'$, i.e., $T(\alpha) \geq T(\alpha')$. In particular, if Bouguer's law (4) is valid, then

$$p(\lambda, \Delta\lambda, l) = l \int_0^{\infty} w(\alpha) e^{-\alpha l} d\alpha. \quad (8)$$

This notation has certain advantages.

It is easy to see that the spectral transmission function $p(\lambda, \Delta\lambda, l)$ depends uniquely and monotonically on l or m . However, the form of this dependence is determined entirely both by the choice of the apparatus function and of the spectral interval $\Delta\lambda$, and by the structure of the absorption spectrum in this interval. Therefore it becomes necessary to specify concretely each time the character of $p(l)$ or $p(m)$. However, no matter what the form acquired by the spectral transmission function, the changeover from $T(\lambda)$ to $p(\lambda, \Delta\lambda)$ is connected with radical changes in the approach to the spectral-analysis problems. The latter are then subdivided into two distinct groups—problems of quantitative spectrochemical control (i.e., determination of m) and problems of spectral structure, which require the determination of the spectral dependence of $\kappa(\lambda)$.

If the problem reduces to a determination of the amount or concentration of absorbing matter, then it is sufficient to confine oneself to isolated measurements

of $p(m)$ for suitably chosen values of λ and $\Delta\lambda$, under the condition that the form of the $p(m)$ dependence be known for these values beforehand, i.e., that a "calibration curve" be available. For multiple measurements of $p(m)$ under standard conditions, the calibration curve remains unchanged and it is best constructed by means of control measurements of p at known values of m . But it is not realistic to construct calibration curves covering the entire range of possible variations if the external conditions are variable, owing to the sensitivity of the function $p(m)$ to these conditions and its inherent dependence on many parameters.

The calculation of $p(m)$ is in this case equally unrealistic. First, it calls for a priori detailed information on the structure of the absorption spectrum of the given substance, including the structure of the remote sections of the wings of the spectral lines, and also their sensitivity to external conditions. Second, this path would again lead to the need for creating practically unmanageable and unjustified tables of $p(m)$ with many entries. Third, the use of such tables would presuppose the need for additional supplemental measurements to fix the state of the medium under the concrete conditions of the analysis.

There is, however, an alternate formulation of the problem, free of the foregoing difficulties. Let us assume that under certain experimental conditions the function $p(m)$ can be approximated with sufficient accuracy, for a sufficiently extensive class of particular cases, by an analytic form which is sufficiently simple and contains only a small number of parameters that characterize individual peculiarities of the structure and state of the investigated substance. Then, by choosing the corresponding experimental conditions and carrying out a certain aggregate of measurement operations, we can simultaneously obtain also the values of all the empirical parameters that determine the form of the function $p(m)$ for the given concrete sample (i.e., obtain for it an approximate individual calibration curve) and the sought value of m . This does not require knowledge of the structure of the absorption spectrum of the investigated substance, since all the necessary information are contained in the experimentally determined parameters. On the other hand, it is necessary to obtain a minimum amount of information which is essential for the determination of these parameters.

The analytic approximation of $p(m)$ can in general be either guessed or obtained from some leading considerations. In such a case, however, the degree of its reliability and the applicability limits remain unclear, and the reliability of the data obtained with its aid is doubtful. On the other hand, it is possible to search directly for approximate solutions of the integral in the form (7) or (8), but not for particular ones, in a general analytic form containing a minimum number of parameters that can be readily determined by experiment, without presupposing an a priori knowledge

of the properties of the investigated medium. The latter is particularly important, for only then does it become possible to analyze substances with properties that are not known beforehand. Therefore solutions based on concrete assumptions concerning the form of the absorption spectrum have no analytic value whatever.

Of course, the desired solutions are obtainable only in a limited number of experimentally realizable situations. Therefore searches for such situations and for the approximations of $p(m)$ corresponding to them, such as to ensure success of the spectroscopic experiment, have for a long time been the center of attention of spectroscopists working in the infrared region of the spectrum (see, for example [22-27]), although they have apparently not yet been considered from this point of view.

It is obvious from the most general considerations that, for any structure of the absorption spectrum and for any apparatus function, the transmission function $p(m)$ should decrease monotonically with increasing m , tending to unity in the absence of absorbing matter and to zero when the amount of matter increases without limit (Fig. 2). If m is so small that T differs little from unity in the entire interval $(\lambda, \Delta\lambda)$, then, confining ourselves to the first two terms in the expansion of T in powers of m , we get from (7)

$$p(m) \cong 1 - Bm \cong e^{-Bm}, \quad (9)$$

where B is an experimentally determined constant that depends on the structure of the absorption spectrum and on the form of the apparatus function.

With increasing m , the structure of the absorption spectrum begins to affect more strongly the form of $p(m)$. However, in the region of applicability of the Bouguer-Beer law, when the sample becomes practically opaque to the central sections of the principal absorption lines and the value of $p(m)$ depends essentially on the absorption in the wings of the lines and on the conditions of their superposition, the function $p(m)$ again assumes a practically universal form

$$p(m) \cong C(1 - D\sqrt{m}) \cong Ce^{-D\sqrt{m}}, \quad (10)$$

where the constants C and D , as well as the interval in which such an approximation is valid, depend on

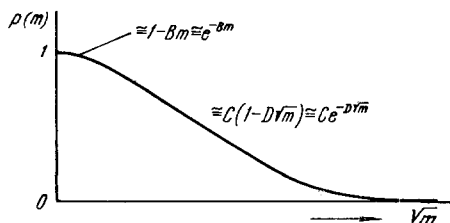


FIG. 2. Typical form of spectral transmission function.

the structure of the absorption spectrum, and also on the form of the apparatus function. Finally, at very large values of m , the concrete structure of the absorption spectrum again begins to affect strongly the form of $p(m)$. In some cases an expression of the type (10) remains valid for it, in other cases $p(m)$ approaches Bouguer's law with a certain effective absorption coefficient, in still others $p(m) \cong 1 - \text{erf}(c\sqrt{m})$, etc.

It is essential that in any of the foregoing cases, it is possible to describe the behavior of $p(m)$ over a wide range of m without a deep insight into the structure of the spectrum or the state of the sample, and it is possible to use directly one of the few and relatively simple formulas, the choice between which can be decided by a small number of auxiliary measurements which determine at the same time also the parameters entering in these formulas. Then the theory of propagation of light in matter predetermines beforehand also the possible form of these formulas and the conditions under which their agreement with reality can be expected.

An entirely different picture is encountered in spectral-structure problems. If we know the form of the function $T(\lambda)$ from the propagation theory, then the experimental problem reduces to determining the values of its parameters (for example, χ and L in case (5)) and the values of the function itself at certain values of L (or l). In other words, owing to the uniqueness of the dependence of T on κ , a certain set of suitably chosen combined measurements of T for a given λ makes it possible to determine $\kappa(\lambda)$.

If, on the other hand, the light-propagation theory leads to a spectral transmission function $p(\lambda, \Delta\lambda, l)$, then the problem of determining $\alpha(\lambda)$, and consequently also $\chi(\lambda)$, is aggravated by the need for first transforming from the function $p(\lambda, \Delta\lambda, l)$ to the function $T(\lambda, l)$. However, this additional step calls for the solution of an integral equation of the type (7) and (8), which entails, as is well known, serious difficulties of fundamental nature, and the discussion of which is not relevant here (see for example [28-30]). The only exception is the case when the form of the apparatus function $A(\lambda, \lambda' - \lambda)$ admits of a rigorous analytic inversion of an integral equation of the type (7) for the given form of $T(l)$, as occurs, for example, in the case of Fourier spectroscopy and low noise level. Only in this case, strictly speaking, is the reliable definition of $T(\lambda)$ possible, and with it the further transition to $\kappa(\lambda)$. It is important to emphasize once more that both the scope of the capabilities of the structural analysis and the ways of its realization are primarily determined precisely by the theory of propagation of light in matter, and not by the theory of the structure of matter as is customarily assumed, since the first essential step in this direction is unavoidably the solution of the inverse problem of the theory of light propagation.

2. SPATIAL AND STRUCTURAL TRANSMISSION FUNCTION FOR AN INHOMOGENEOUS MEDIUM WITHOUT SCATTERING. IMMERSION AND PRESSING METHODS

It was assumed in the preceding section that the sample is optically homogeneous and, if bounded, its boundaries (or those of the cell containing the substance) are plane-parallel. We now turn to the case when the sample has a spatial structure, but diffraction and scattering of light by this structure can be neglected.

The simplest example is an unbounded body in which the state of the matter (say, the pressure, temperature, dye concentration) vary smoothly in the direction of one of the coordinate axes, say along the Z axis, as is the case in the ocean or in the atmospheres of planets, i.e., $\alpha = \alpha(\lambda, Z)$. For a ray inclined at an angle ϑ to this axis, we then have in view of (4) (without allowance for refraction)

$$T(\lambda, Z_1, Z_2, \vartheta) = e^{-\tau}, \tag{11}$$

where

$$\tau = \int_{Z_1}^{Z_2} \alpha(\lambda, Z) \sec \vartheta dZ \tag{12}$$

is the optical thickness measured along the ray.

Thus, the value of T is determined not only by the amount m of matter along the path of the ray, but also by the character of its altitude distribution. Accordingly, the form of the spectral transmission function $p(\lambda, \Delta\lambda, Z_1, Z_2, \vartheta)$ varies with Z_1, Z_2 , and ϑ , as a result of which the possibilities of its analytic approximation are greatly restricted. This is one of the main difficulties of the spectral analysis of atmospheric gases (for example, hygrometry or ozonometry) by the most frequently realizable Bouguer method, namely, by measuring the spectral brightness of the sun at different zenith distances and at different levels above the earth's surface.

Under laboratory conditions, a realistic scheme of an absorption experiment usually takes the form shown in Fig. 3. Parallel light beams produced by a collimator 1 pass through different regions of the cross section of the sample 2 and are gathered in the focal plane of the exit lens 3. The light propagating in other directions is then filtered out by a spatial filter, the role of which is assumed by diaphragm 4, behind which is placed a light receiver 5. This averages the trans-

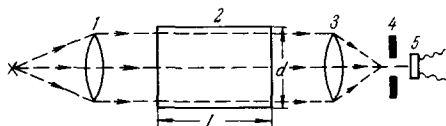


FIG. 3. Diagram of an experiment in which the attenuation coefficient is measured.

parency of the sample over its area, since the light flux incident on the receiver is

$$\Phi = I_0 \int_S T(x, y) dS, \tag{13}$$

where I_0 is the brightness of the light incident on the sample, S is the cross section area of the light beam in the sample, and x and y are the coordinates of an element dS of this section. If the sample is homogeneous, then $\Phi = I_0 TS$ or

$$T = \frac{\Phi}{I_0 S}. \tag{14}$$

Assume now that the sample is made up of a set of N parallel bars or cells of different lengths L_i and cross sections S_i , all of the same material (Fig. 4a). We can then no longer speak of the transparency of the sample as a whole. This concept is replaced by the spatial transmission function

$$p(\alpha) = \sum_{i=1}^N w(L_i) T(\alpha, L_i), \tag{15}$$

where $T(\alpha, L_i)$ is defined by (5), and $w(L_i) = S_i/S$ corresponds to the probability that a photon incident on the sample will enter into the channel of length L_i .

If the sample has an irregular, say prismatic, form (Fig. 4b) then, disregarding the refraction on its boundaries,

$$p(\alpha) = \int_0^{L_{\max}} w(L) T(\alpha, L) dL. \tag{16}$$

but if the sample has a regular form (i.e., $L = \text{const}$), then the attenuation function α varies over its cross section, i.e., $\alpha = \alpha(x, y)$; assume that this is a set of cells with solutions of different concentrations (Fig. 4c), and then we have in lieu of (16)

$$p(L) = \int_0^\infty w(\alpha) T(\alpha, L) d\alpha, \tag{17}$$

where $w(\alpha)d\alpha$ is the probability that the photon incident on the sample will pass through it in a place

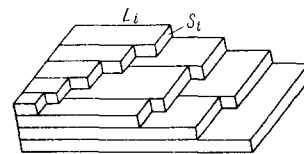


FIG. 4a

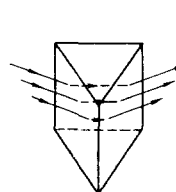


FIG. 4b

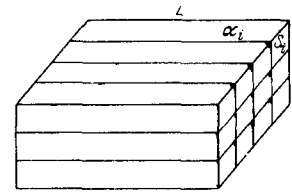


FIG. 4c

where α lies in the interval between α and $\alpha + d\alpha$.

Attention must be called to the fundamental difference between expressions (16) and (17). The former, which corresponds to the spatial transmission function, depends uniquely on the absorption coefficient of the substance, whereas the second depends uniquely on the dimensions of the sample and the character of this dependence is determined entirely by its internal structure. This is why (17) can be called the structural transmission function of an inhomogeneous sample.

Whereas the changeover from transparency to the spatial transmission function does not essentially change the approach to the spectral-structure research, the transition to the structural transmission function changes greatly the formulation of the problem, just as in the case of the spectral transmission function. This is clearly seen from a direct comparison of (17) and (8).

Finally, if we investigate a sample which is inhomogeneous along its length and we must employ an unresolved spectrum, then (16) is replaced by the more complicated spatial-spectral transmission function

$$\begin{aligned} \overline{p(\lambda, \Delta\lambda)} &= \int_0^{L_{\max}} w(L) \int_0^{\infty} w(\alpha) T(\alpha, L) d\alpha dL \\ &= \int_0^{L_{\max}} w(L) p(\lambda, \Delta\lambda, L) dL, \end{aligned} \quad (18)$$

where $p(\lambda, \Delta\lambda, L)$ is the spectral transmission function for a beam segment of length L .

Of course, the foregoing examples are of no practical interest. Any spectroscopist will attempt to make the investigated sample homogeneous and of convenient shape for only then will the theory of propagation of light in matter lead to sufficiently simple and clear experimental procedure and assure the success of the experiment. But this is precisely the principal lesson. The theory of propagation leads, generally speaking, to complicated transmission functions. Their determination calls for a priori knowledge of the geometrical, structural, spectral, and other characteristics of the sample (something almost never feasible), and their knowledge does not guarantee at all the possibility of uniquely solving the problem.

Therefore, in the case of optically inhomogeneous samples, even those that do not scatter light, the experimenter is faced by the same problem as in the case when unresolved spectra are used. Namely, he must seek experimental conditions such that the transmission function is approximated in general form by a simple analytic formula with a small number of empirical parameters. When dealing with the spatial transmission function this solves the problem completely. But if the transmission function is structural, then the situation becomes equivalent to the case of the spectral transmission function considered above,

and the possibilities of the spectral analysis are greatly limited.

To clarify this conclusion further, let us consider one more case which is already of direct applied interest. Let us assume that the sample is a two-phase system, and that a homogeneously absorbing medium is randomly distributed in the form of isolated inclusions (for example, emulsions or powders)(Fig. 5). The assumption that there is no scattering is equivalent to the requirement that there be no refraction on the boundaries of the inclusions. Therefore the two-phase nature of the system will be manifest only in the fact that the rays penetrating the sample in different places will pass through different thicknesses of absorbing matter (including cases when they bypass the absorbing particles completely).

If $w(l)$ is the probability that the photon will traverse a path l in the absorbing substance, and if we disregard the influence of the cell boundaries, then in accord with (16) and (4) we have

$$p(\alpha, L) = \int_0^L w(l) e^{-\alpha l} dl. \quad (19)$$

It is easy to verify that we always have $p(\alpha, L) > \exp(-\alpha l_{\text{eq}})$, where l_{eq} is the equivalent thickness of the absorbing phase, since a fraction of the light passes through a relatively small thickness of absorbing matter.^[18, 31] For the same reason, we obtain an appreciable "smoothing" of the absorption spectrum. In fact, it follows from (19) that $d \ln p(\alpha, L)/d\alpha = -\bar{l}$, where \bar{l} is the average integral path of the photon in the absorbing medium, with $\bar{l} < l_{\text{eq}}$.

If the object is a liquid dye emulsion, i.e., if the colored particles are spherical, then, knowing their distributions by size and concentration, we can theoretically calculate $w(l)$. Some authors consider this procedure promising. However, even if we disregard the fact that in more complicated cases such calculations are not feasible, and the microstructure of the sample usually remains unknown, the very concept of absorbing but non-scattering particles is a far-fetched idealization.

In fact, scattering and diffraction vanish only when not only the real but also the imaginary parts of the refractive indices of the medium and of the particle are identical, i.e., when the medium is perfectly homogeneous. In the case of suspensions of lampblack

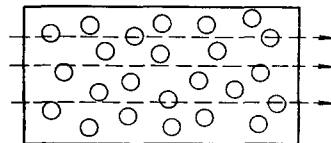


FIG. 5. Illustrating the determination of the spatial transmission function of a two-phase system.

particles or india ink, the scattering is far from small, and in the case of metallic spheres it greatly exceeds the absorption. Therefore for any substance in which the absorbing substance is inhomogeneously distributed it is necessary to take light-scattering phenomena into consideration, i.e., it is necessary to resort to the specific methods of the spectroscopy of light-scattering media.

The frequent tendency of "facilitating" the experiment by completely or partially ignoring this circumstance is fraught with serious not easily detected errors, as is now well known and as was first pointed out by É. V. Shpol'skiĭ.^[6]

This has given rise to the tendency of suppressing light scattering by artificial means. At first glance it is most natural to introduce for this purpose immersion, i.e., equalization of the refractive indices of the medium and the inclusions. This method is widely used in biological research,^[33] for example by R. Barer.^[32] It is easy to verify, however, that this method is not as reliable as it might seem. First, as we have already seen, no immersion makes it possible to get rid completely of scattering, and special experiments are necessary to be assured of the efficacy of the method as applied to each concrete case. Second, even if the scattering becomes insignificant, this only leads to the already considered case of inhomogeneous media, i.e., to transmission functions and not at all to transparencies, so that reliable calculation of $w(l)$ is made impossible as a rule by the lack of information concerning the microstructure of the sample (say a biological one).

As an alternative, the so-called "pressing method" has found extensive use in the study of inorganic substances. This method consists of preparing quasi-homogeneous samples from inhomogeneous matter by pressing in vacuum at high pressure.^[34] But even here there are many reservations which are very frequently not allowed for by many experimenters.

If the pressing is effected without a solvent and if a sufficiently high degree of microoptical homogeneity results, then this method raises no objections, except that not all substances will withstand such an operation. In most cases, however, pressing is carried out with a solid solvent or by immersion (for example, in potassium chloride), both to ensure mechanical integrity of the substance and to dilute the investigated substance so as to increase its transparency. It is particularly necessary to resort to the latter in the case of substances having strong absorption and those which are generally opaque in bulk form. We then return in essence to the immersion method with all its shortcomings, since a substance pressed together with the immersion will not become optically microhomogeneous, even if the scattering in the substance can be suppressed, and consequently the use of Bouguer's law is no longer justified. Moreover, owing to the differences between the dispersion curves of the substance and the

immersion, the light scattering frequently acquires an appreciable spectral dependence (the Christiansen filter). Therefore many results obtained by this method call for a critical review.

The third way consists of attempting to find empirically experimental procedures in which the scattering phenomena are somehow compensated and can be ignored. This includes, for example, various recipes using photometric spheres, mirror or capillary cells, etc. All these recipes, however, are based on primitive photometric considerations of qualitative character, and are not backed by a rigorous theory that takes into account all the peculiarities of light propagation in the scattering medium. Therefore, as a rule, such recipes lead to a clearly pronounced qualitative effect, but closer examination shows them not to be well founded and their use frequently leads to gross errors.

Finally, we have a fourth way, which in our opinion is the only one scientifically justified. This is to forego circuitous manoeuvres and attempts to eliminate scattering effects, i.e., a conscious utilization of these phenomena to create specific methods of spectroscopy with allowance for all the optical singularities of the light-scattering substances. The basis for this should obviously be a disclosure of the laws governing the propagation of light in a scattering medium.

III. PROPAGATION OF LIGHT IN A SCATTERING MEDIUM. TRANSPORT MATRIX AND ITS CONNECTION WITH THE PARAMETERS OF THE MEDIUM

The propagation of light in a scattering medium is essentially a statistical process, the evolution of which depends entirely on the character of the inhomogeneity of the medium. Strictly speaking, we should be speaking of an interaction between the electromagnetic field and matter in a unified matter + field system. However, the weakness of the action of the light and the optical properties of the material allow us to regard this action as a small perturbation and confine ourselves in first approximation to the effect of the matter on the field only. By the same token, the field and the matter become separated into independent systems and the general problem of their interaction breaks up into two independent parts—the problem of scattering of light by a single inhomogeneity as a function of the parameters of the latter, and the problem of propagation of light in a medium with a specified scattering ability.^[12, 35, 36] With this, it becomes necessary to describe the light field in the scattering medium by means of a coherence matrix or by equivalent statistical parameters.^[12, 35-41]

A program of this kind for the construction of the theory of light propagation in a scattering medium, based directly on the equations of electrodynamics, is so far unrealizable, with the exception of a small number of strongly idealized models (see, for example,

[42]). In the general case it is therefore necessary to modify the problem further by using the approximation of ray optics under the assumption that the light beams having different prior histories are incoherent. It is necessary with this to take into account the fact that the state of the polarization of the light beam greatly influences the result of its scattering.

Accordingly, the light field in the medium can be represented^[12, 35, 37] as an aggregate of incoherent light beams of different directions l , each of which is characterized by a quantum-mechanical density matrix or an equivalent four-component Stokes vector-parameter $S(l)$. All the components of the latter are

$$S_1 = I; \quad S_2 = I_p \cos 2\psi; \quad S_3 = I_p \sin 2\psi; \quad S_4 = I_q, \quad (20)$$

(p is the degree of polarization, q the degree of ellipticity of the polarization, ψ the angle of rotation of the plane of maximum polarization relative to the reference plane^[35, 43]) have the dimensions of brightness and are additive for incoherent light beams.

Propagating in the scattering medium, each of the light beams experiences two kinds of action on the part of the latter. First, it becomes attenuated because the absorbed and scattered photons are removed from it, and second, it becomes intensified because photons removed by scattering from other light beams are added to it. The ability of the medium of extracting, absorbing, and scattering photons is characterized respectively by the coefficients of extinction ($k = \alpha + \sigma$), absorption (α), and scattering (σ), which have the meanings of the probabilities of the corresponding processes per unit volume. The probability that a photon propagating in the direction l_1 and having a polarization state $S_k^{(1)}/S_1^{(1)}$ will be scattered in a unit volume of the medium in the direction l_2 with a changed polarization state, is characterized by a scattering matrix $D_{jk}(l_1, l_2) = (\sigma/4\pi)f_{jk}(l_1, l_2)$; for more details see^[35, 43]. Thus, in the case of an isotropic medium, the change in the Stokes vector-parameter in a length element of the light beam can be written in the form^[12, 35-37, 43, 44]

$$(l, \text{grad } S_i(l)) = -kS_i(l) + \frac{\sigma}{4\pi} \sum_{h=1}^3 \oint f_{ih}(\bar{l}, l') S_h(l') dl', \quad (21)$$

where the first term on the right side takes into account the photon removal process, and the second, the enrichment of the beam with photons removed from light beams in all other directions l' . In the case of scattering by anisotropic particles or in a force field, the extinction coefficient k is transformed into an extinction matrix, which takes also account of the dichroism of the medium.^[35]

The derivation of Eq. (21), which is the basis of modern radiation-transport theory, is based on intuitive photometric representation and is not well founded from the point of view of the equations of electrodynamics. Moreover, although the mathematical analysis of this matrix integro-differential equation and the de-

velopment of methods for its solution has been the subject of one of the most extensive branches of mathematical physics (see^[44-46] etc.), it is still impossible to point to experiments that directly confirm or refute the correctness of this equation or of its corollaries. An experimental verification of the transport theory encounters two main difficulties. One is connected with the limited nature of the models of the scattering medium that are amenable to a full mathematical analysis. As a result, an experimental reconstruction of these models (for example, the assumption that scattering is isotropic or that radiation polarization effects are insignificant) is not realizable. Another difficulty is due to the imperfection of the existing methods of measuring the material parameters contained in Eq. (21).

Real experiments are therefore limited as a rule to a check of the character of various relationships that follow from the theory, against an empirical choice of effective values of the material parameters (essentially, of values that lead to a fit). Within the framework of such, incidentally, rather numerous and varied comparisons with nature, transport theory is valid for a rather extensive group of objects and in a wide range of variation of their properties. This affords a certain justification for trusting Eq. (21), even though its rigorous derivation and direct experimental verification continue to remain among the foremost problems of modern optics.

Equation (21) relates the characteristics of the light field $S_i(l)$ inside or on the boundaries of a light-scattering medium with its optical parameters α , σ , and f_{jk} . But even in the simplest cases the methods of solving Eq. (21) turn out to be quite complicated and, with rare exceptions, end up with numerical calculations with an electronic computer. The situation is always reduced here to finding (for given boundary conditions) the characteristics of a monochromatic light field in a medium whose optical parameters are assumed known. Solutions of this kind are not suitable for use in spectrum analysis, where the unknown quantities are the very parameters of the medium. On the other hand, there are still no effective methods for directly solving the inverse problems of transport theory. Therefore, when turning to the needs of spectral analysis, it is no longer possible to use the ordinary apparatus of radiation-transport theory, and a radical review of the entire formulation of the problem is necessary.^[11-13, 47]

Let us consider a beam of photons in a state $S_k^{(1)}$, passing through a point 1 inside a scattering medium in a direction l_1 . Some of these photons arrive at the point 2 and produce there a light beam in the direction l_2 . Owing to the homogeneity and linearity of the equations of electrodynamics, the state of this beam can be written in the form^[35, 47]

$$S_i^{(2)}(l_2) = \sum_k P_{ik}^1 S_k^{(1)}(l_1), \quad (22)$$

where p_{ik}^{12} is the matrix of radiation transport from point 1 to point 2, characterizing the optical coupling of these two points, and is determined by the optical properties of the light-scattering sample as a whole. Obviously, the aggregate of transport matrices for different pairs of points and different sections of the spectrum contains all the optical information on the light-scattering body. Therefore it is precisely these matrices that should be the measured quantities in spectroscopic investigations. The component P_{11}^{12} of this matrix can be called the transport function of the radiation from the point 1 to point 2, and has the meaning of the probability of the transition of the photon from point 1 to 2, averaged over all possible states of its initial and final polarizations.

However, the photon can arrive at point 2 from point 1 via a great variety of paths (Fig. 6), experiencing different numbers of scattering acts and being subjected in each of them to different changes of the state of polarization. The probability of the choice of any particular path depends exclusively on the form of the scattering matrix f_{ik} characterizing the probabilities of the different changes in the direction of motion and the states of polarization of the photon during the scattering act, and also on the geometrical parameters of the volume filled with the scattering medium, parameters which determine the probability that the photon will emerge to the outside of the medium. With this, a relation of type (22) holds for each of the possible photon paths, and the total transport matrix P_{ik}^{12} is the sum of the corresponding matrices for all the possible paths.

Let us assume that, in the absence of absorption, the matrix for the transport from 1 to 2 is equal to $w_{ik,n}^{12}$ for any path on which the photon experiences n scattering acts and is equal to $w_{ik}^{12}(l)$ for any path of length l . Then, obviously,

$$P_{ik}^{12} = \sum_{n=1}^{\infty} w_{ik,n}^{12} = \int_0^{\infty} w_{ik}^{12}(l) dl. \quad (23)$$

In the presence of absorption, but for the same scattering matrix and for the same geometrical parameters of the light-scattering body, the probabilities that the photon will choose any particular path [i.e., the matrices $w_{ik,n}^{12}$ and $w_{ik}^{12}(l)$] remain unchanged. But, in each of the possible paths, an additional probability appears of the photon becoming lost by absorption. The probability that the photon will survive in the

medium during the scattering act or in the mean path from one scattering act to another is

$$\Lambda = \frac{\sigma}{\alpha + \sigma} = \frac{1}{1 + \beta}, \quad (24)$$

where $\beta = \alpha/\sigma$ is the per unit absorptivity of the medium.

Accordingly, the photon survival probability on a path with n scattering acts is Λ^n , and the total transport matrix from 1 to 2 takes the form

$$P_{ik}^{12} = \sum_{n=1}^{\infty} w_{ik,n}^{12} \Lambda^n. \quad (25)$$

A relation of the type (25) is the inevitable result, for each particular case, of any solution of the radiation transport equation, obtained by the method of successive calculation of the scattering acts of increasing multiplicity n .^[7, 48] In general form, however, formula (25) was obtained for the first time and interpreted for spectroscopy applications in^[11, 49, 50]. Its most important feature turned out to be the clear cut separation, on the one side, of the indicatrix and geometrical-optical effects, which determine entirely the probabilities $w_{ik,n}^{12}$, and on the other, of the absorption effects, which are also taken into account fully in terms of the photon survival probability Λ (this quantity is frequently called, without sufficient justification, the "albedo of a scattering particle or of a volume element of the medium"). It is also important to note that relation (25) is derived from very general considerations, which are independent of the transport equation (21), and therefore is not connected with the aforementioned difficulties of justifying this equation. In particular, allowance for cooperative effects (including coherent scattering at small angles), which should greatly influence the form of Eq. (21), cannot influence the form of (25). Therefore the limits of validity of (25) are incomparably wider than the limits of validity of (21).

If the absorption takes place only on the path of the photon between two scattering acts, but not during the scattering act itself, i.e., if it depends not on the number of scattering acts but on the length l of the path traversed by the photon, then the photon survival probability is replaced by the transparency $T(\alpha, l)$ and expression (25) becomes

$$P_{ik}^{12}(\alpha) = \int_0^{\infty} w_{ik}^{12}(l) T(\alpha, l) dl. \quad (26)$$

This relation admits (as first pointed out by H. D. Van de Hulst and W. Irvine^[51]) as applied to the transport function P_{11} of a substantial generalization, which overcomes the limitation, inherent in the transport equation (21), that the light must be strictly monochromatic. To extend the transport theory to include the case of an unresolved structure of the absorption spectrum it suffices to replace $T(\alpha, l)$ in (26) by the spectral transmission function $p(\lambda, \Delta\lambda, l)$:

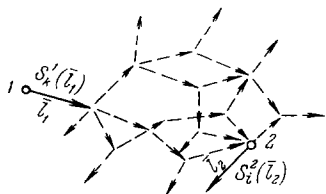


FIG. 6. Illustrating the concept of the transport function.

$$P_{ik}^{12}(\lambda, \Delta\lambda) = \int_0^{\infty} w_{ik}^{12}(l) p(\lambda, \Delta\lambda, l) dl. \quad (27)$$

On the other hand, if absorption takes place both during scattering and on the path from one scattering act to the other, then, obviously,

$$P_{ik}^{12}(\lambda, \Delta\lambda) = \sum_{n=1}^{\infty} \Lambda_0^n \int_0^{\infty} w_{ik,n}^{12}(l) p(\lambda, \Delta\lambda, l) dl, \quad (28)$$

where $w_{ik,n}^{12}(l)$ is the transport matrix from 1 to 2 in the absence of absorption along any path of length l under the condition that the photon experiences on this path n scattering events, and Λ_0 pertains only to the scattering event itself.

It was already noted above that the concept of the transport matrix makes it possible logically to subdivide further the problem of radiation transport in a scattering medium into two independent parts,^[11-13, 47, 49-51] namely the determination of the values of Λ and $T(\alpha, l)$ or $p(\lambda, \Delta\lambda, l)$, which depend only on the absorption and scattering coefficients, and the determination of the matrices $w_{ik,n}^{12}(l)$, which depend only on the form of the scattering matrix f_{ik} and on geometrical-optics parameters of the light-scattering body (i.e., those measured in a scale of optical thicknesses τ ; (see (12)).

This leaves as the subject of the transport theory proper only the problem of determining the quantities $w_{ik,n}(l)$, $w_{ik,n} = \int_0^{\infty} w_{ik,n}(l) dl$, or $w_{ik,n}(l) = \sum_{n=1}^{\infty} w_{ik,n}(l)$. We can use to this purpose Eq. (21)

with $k = \sigma$ (i.e., $\alpha = 0$ and $\Lambda = 1$), which in itself greatly decreases the size of the problem. A small modification of the reasoning that has led to (21) makes it also possible to replace this equation directly by an equivalent equation for the components of the matrix $w_{ik}(l)$; see^[52, 53]. The behavior of the corresponding transport function $w_{11}(l)$ was investigated, for example, by L. M. Romanova.^[53, 54]

A direct comparison of (26) with (16) and of (25) with (15) reveals a complete analogy, thus immediately pointing out possibilities and means of developing a spectral analysis of light-scattering substances. In particular, a complete analogy is revealed between the transport function P_{11} , which is arrived at by an optical investigation of any light-scattering body in monochromatic light, and the spatial transmission function $p(\alpha)$, the only difference being that in the case of (25), for example, the argument α is replaced by the photon survival (or loss) probability.

However, the transport matrix P_{ik} remains a single-valued and monotonic function of the absorption coefficient α only if the scattering medium is statistically continuous and macroscopically homogeneous. The former requirement ensures the possibility of introducing the coefficients α and σ (or k and Λ), and also of the scattering matrix f_{ik} , referred to a unit

volume and characterizing the medium as such. To this end it is necessary that the scale of the inhomogeneities (particles, pores, fibers) be incomparably smaller than the photon mean free path in the medium (which is equal to k^{-1} , where k is the extinction coefficient). This requirement ensures continuity of the average brightness and of its first moment along the light beam when averaging over cross sections whose dimensions are much smaller than k^{-1} , and by the same token the possibility of introducing the concept of elementary volume.

The second requirement reduces to invariance of the parameters α , σ , and f_{ik} over the entire body. Violation of this requirement leads immediately to the change in the form of the transport matrix, equivalent to the transformation of the spatial transmission function into a structural function, and we have seen that this changes radically the very formulation of the spectrum-analysis problem.

The essence of the changes, just as in the case of the structural transmission function, is that T depends not only on the path length, but also on the path location, so that the separation of the energy and geometric effects is feasible only along one ray, and not for the entire aggregation of the possible photon paths. Formulas such as (25) or (26) are therefore incorrect in this case.

On the other hand, the local values of α , σ , and f_{ik} can be obviously determined only by variation of the integral transport function P_{ik}^{12} as the points 1 or 2 are shifted, which leads to the need of solving the corresponding integral equation. We encounter such a situation, for example, in astrophysical investigations of stellar and planetary atmospheres, which are light-scattering media whose parameters can be regarded in first approximation as relatively regular functions of one coordinate—the height.

However, the solution of such integral equations belongs to the class of so-called mathematically incorrect problems and entails serious difficulties.^[29, 30] Insufficient caution in the avoidance of such equations leads as a rule to erroneous results. An analysis carried out from this point of view has shown that many of the methods employed in astrophysics (especially planetary astrophysics) to interpret the observational data do not satisfy the main requirements and cannot provide either reliability or uniqueness of the obtained information (this question is considered, for example, in^[55] in reference to Venus). In particular, one must reject as unfounded all methods of analysis of polarimetric, photometric, and spectral-analytic data based only on a direct analogy with laboratory-measurement data without proof of uniqueness of the analogy or without satisfying the requirement of optical similarity, for such an approach ignores by the same token to one degree or another the singularities of the scattering medium itself (for example, the influence of scattering on the form of the absorption bands^[12, 13, 56-58]).

However, even when the analytic methods are based on detailed solutions of the transport equation, the latter is usually referred to particularly strongly idealized models with a priori properties, without experimental verification of the correspondence of these premises to reality, and without proof of the uniqueness of the results of the analytic procedure, which consists essentially of inversion of these results. Therefore, data provided by such methods are not trustworthy unless a special investigation is made of the degree of their reliability and sensitivity to noise.

Highly promising from this point of view are new ideas developed in connection with methods for directly solving the inverse problems of the theory of radiation transport in planetary atmospheres, applied to the problem of using meteorological satellites.^[29, 30, 59] Another way is spectrophotometric analysis of a planetary atmosphere by observing it in daylight or in twilight from the surface of a planet or from outside the planet (from spaceships or from other planets), and was used in^[43, 60]. The main idea of this method is to search for general approximate analytic solutions (unrelated to a priori concepts regarding the properties of the medium) of the direct transport-theory problem in a form that would admit of unique inversion and experimental determination of the parameters characterizing the structure and state of the medium under the concrete experimental conditions. As shown above, in the absence of methods for directly solving the inverse problem of transport theory, such a way is the only promising one.

Finally, if the scattering or emitting medium is not macroscopically homogeneous, but has a statistical structure, the very formulation of the problem in transport theory should change. The object of study should be the connection between the statistical characteristics (moments, structure functions and spatial spectra) of the radiation field, on the one hand, and the parameters of the scattering or radiating medium on the other.^[61] Such a formulation of the problem has turned out to be fruitful in cases involving thermal radiation of an inhomogeneous medium, when the effect of its scattering can be neglected.^[30, 59] For the general case, when the scattering of light becomes important, this problem has not yet been mathematically formulated and one can speak so far only of preliminary searches for ways of analytically using the spatial spectra of the scattering-radiation field (see, for example,^[62]).

IV. GENERAL FORMULATION OF THE PROBLEM OF SPECTRAL ANALYSIS OF MACROSCOPICALLY HOMOGENEOUS LIGHT-SCATTERING BODIES

We have seen that the only source of spectrum-analytic information on a light-scattering body are its transport matrices. If the body is macroscopically

homogeneous, the monochromatic transport matrices depend monotonically and mutually uniquely on the absorption coefficient of the light-scattering medium, or more accurately on the photon survival probability as the light propagates in the medium. Indeed, for monochromatic radiation the transparency $T(\alpha, l)$ has the direct meaning of the photon survival probability on a path of length l , and the most general form (28) of the expression for P_{ik}^1 acquires the form (25) with Λ_0 replaced by $\Lambda \cong \Lambda_0 T(k^{-1})$, where k^{-1} is the photon mean free path between two scattering acts, as follows indeed from the direct solution of the transport equation in each concrete case.

Thus, relation (25) is the starting point for any spectrum-analysis problem.^[11-13] Since $w_{ik,n}$ depends only on the geometric parameters of the body and on the quantities σ and f_{ik} , which characterize (just as Λ does) the scattering medium as such, the result of the solution of the inverse problem of the radiation propagation (transport) theory in a scattering medium can be at best a determination of the optical parameters of this medium. In the absence of scattering, such a step has led directly to the optical constants of the medium (including $\kappa(\lambda)$), thus uncovering a direct possibility of carrying through the spectrum-analysis problem to conclusion. On the other hand, in the case of light-scattering media, the result of the analysis are the quantities α , σ , and f_{ik} , and the need for proceeding further to determine the optical constants of the medium calls for going through a number of intermediate steps connected with the use of additional theoretical concepts (Fig. 7).

When dealing with molecular scattering, we can, by resorting to statistical theory in the style, say, of Cabannes^[63-65], relate directly the parameters of the medium with the polarizability tensor of the molecules, and further, making use of the theory of molecular structure, determine the unknown structural parameters. In exactly the same manner, a phenomenological theory of molecular scattering of light in the style of the ideas of Einstein-Smoluchowski or Debye^[63-67] establishes a direct connection between the parameters α , σ , and f_{ik} on the one hand and the optical constants of the medium on the other, and further, through the theory of the structure of matter, also with the unknown parameters of the latter. In other words, in the case of molecular scattering the solution of the spectrum-analysis problems can be carried through to conclusion, at least in principle.

The situation is much more complicated in the case of two- or many-phase systems, such as suspensions, polymer substances, or biological objects.

It becomes necessary first, to relate the optical parameters (α , σ , f_{ik}) of the medium with the optical parameters (α^0 , σ^0 , f_{ik}^0) of an individual particle or inhomogeneity, which can be done in principle on the basis of the statistical theory of scattering by a system of particles or, as is frequently said, the theory

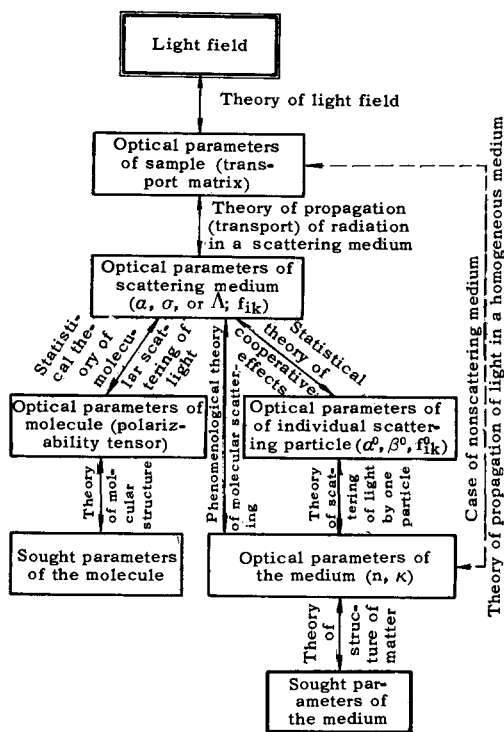


FIG. 7. Scheme of spectrum-analysis experiment with light-scattering substances.

of cooperative effects. However, this theory is so far only in the initial stages.^[12, 35, 36, 42, 68] If the mean distance between particles is much larger than the wavelength of light, the following simple relations hold:

(29)

where N is the particle concentration (α^0 and σ^0 have the dimension of cm^2 , whereas α and σ have the dimension of cm^{-1}). In the general case, however, the character of this dependence has not been investigated either theoretically or experimentally. There are only some clear indications of appreciable deviations from (29).

Further, the connection between the quantities α^0 , σ^0 and f_{ik}^0 and the optical constants of the medium is established by the theory of scattering of light by small particles. The direct problem of scattering theory has been studied in sufficient detail, albeit only for particles of simplest form—spherical, ellipsoidal, cylindrical.^[69, 70] On the other hand, the solutions of the inverse problems entail serious difficulties here, too, and ways of overcoming these difficulties are in many respects not yet clear.

Of decisive significance is the fact that the optical properties of the particle depend strongly on its shape, especially on its dimensions. For example, when the particle is much smaller than the wavelength, the refractive index of the medium $\beta = (1 - \Lambda)/\Lambda$ is proportional to r^{-3} , where r is the

particle radius, i.e., it decreases rapidly with increasing r .^[69] With increasing r , β goes through a minimum in the vicinity of $r \cong \lambda$, and when $r \gg \lambda$ (if the particles are made up of weakly absorbing material) we have

$$\beta \cong K \frac{2\pi x}{\lambda} r, \quad (30)$$

where K is the shape factor.^[71] On the other hand, if the absorption takes place not in the dispersed medium, but in the dispersant or in the adsorbent covering of the surface of the particle, the dependence of β on r assumes a different form. Furthermore, β , together with the extinction coefficient and the scattering pattern, depends strongly on the refractive index of the medium surrounding the particle. This sometimes causes strong changes in the spectral variation of these quantities (see, for example^[12, 34]), a fact used for example in the construction of optical filters of the Christiansen type. One can likewise not neglect the influence of surface phenomena on the optical properties in a finely-dispersed phase.

A consequence of the dependence of β on r is first of all a strong influence of the particle size distribution on the optical properties of the medium^[8, 9, 18, 19, 71-77] (it also influences w_{ik}, n). This is particularly clearly pronounced in a fact well known to artists, that a tone becomes saturated and whiteness is subsequently produced when the paint material is more finely ground (for a quantitative analysis see^[71]). Moreover, it is obvious from general considerations and has been shown by direct measurements^[19, 73] that the sequence of states having increasing dispersion comprises a continuous transition from the solid to the gas or (if immersion is used) to the solution, and the same holds for the transformation of the optical properties of the medium. Therefore knowledge of the particle-dimension distribution spectrum is a necessary condition for solving the inverse problem of the theory of scattering of light. An equally strong influence is exerted on the optical properties of the medium, on the spectral variation of the refractive index, both of the particles and of the immersion.^[12, 34, 73, 78]

This not only leads to the need for auxiliary measurements, but also greatly complicates the formulation of the problem. In fact, if the medium is polydispersed, relations (29) are replaced by a system of equivalent integral equations of the first kind (see, for example^[43]), for which correct solution methods are far from fully developed, if one bears in mind the difficulties that are common to such problems.^[29, 30] Serious steps in this direction were initiated only in the most recent time.^[79]

Thus, when dealing with disperse systems, a complete solution has been obtained only for the first part of the spectrum-analysis problem, namely the determination of the optical parameters of the light-

scattering medium as such. The contemporary theory of light propagation provides the experimenter with sufficiently reliable means for this purpose. Their analysis will be the subject of the next part of the article.

As to the possibilities of determining the optical parameters of the medium itself, we can separate here a rather large group of problems that are amenable to solution, and, most important, point to ways of increasing this group. Of particular significance in this case are two circumstances—the possibility of determining the limits of reliability and refuting unfounded hopes and inconsistent prescriptions, and the possibility of a reliable determination of the nature of the experimental information, such as to ensure uniqueness of the solution of the analytic problem. It is known that the most widespread cause of spectrum-analysis errors in the case of light-scattering substances is precisely the ambiguity of interpretation of the experimental data, owing to the fact that the nature of the information does not correspond to the gist of the solved problem. Neglect of this aspect of the problem is, for example, the main shortcoming of the review,^[19] which incidentally is provided with a bibliography which can only mislead the reader.

No less important is a third conclusion. Inasmuch as the propagation theory operates with the parameters α , σ , and f_{ik} , no development of this theory can serve as a source of additional information for the realization of the succeeding steps in the spectral analysis indicated in Fig. 7. To obtain such information it is essential to vary the physical state of the investigated medium itself, for example by dilution, immersion, dispersion, chemical or mechanical action, etc. The possibilities that are uncovered in this manner are far from thoroughly investigated and are quite promising. Frequent attempts of circumventing this situation (see, for example, the reviews^[8, 12, 14-19]) turn out, upon closer examination, to be constructed on certain arbitrary assumptions and do not ensure a reliable interpretation of the data.

We now turn to the choice of means of determining the optical parameters of a light-scattering medium. Knowing these parameters and making use of transport theory we can (usually by numerical calculations) obtain the transport matrix P_{ik}^{12} . The overwhelming majority of papers on transport theory is devoted to the solution of this problem for different more or less idealized models of a scattering medium (see, for example, ^[44-46, 48, 52-54, 76, 77]). It is easy to see that from the point of view of spectrum-analysis applications, calculations of this kind are perfectly analogous to calculations of the spectral transmission function $p(m)$ when the structure of the absorption spectrum of the matter is known in detail. Just as in the case when unresolved spectra are used, these calculations turn out to be little suitable for the solution of inverse problems.^[12, 13]

The alternate way, which consists of finding such experimentally realizable situations for which the transport matrix (similar to the transmission function in ^[22-27]) is approximated by convenient analytic expressions which admit of inversion and play, in final analysis, the role of a calibration curve whose parameters are determined experimentally, turns out to be identical (see Sec. 1). As applied to the spectroscopy of light-scattering substances, this version of the problem was first clearly formulated by the author in ^[11, 12, 36, 49, 50, 82, 83] and systematically treated by him in ^[13, 47, 55, 56, 71, 84-88]. Without requiring a priori knowledge of the properties of the medium, and firmly based on the general theory of light propagation, it ensures the possibility of reliably solving an extensive group of hitherto insoluble spectrum-analysis problems. By now these possibilities and their theoretical foundation have been developed along a number of paths, and were also thoroughly verified experimentally and theoretically for a large group of different objects and theoretical models. This has clearly defined the limits of applicability of the corresponding concepts. A very important role in the establishment of these concepts was played on the one hand, by the experimental^[10] and theoretical^[83] investigations of the singularities of the optical conditions inside a light-scattering medium, and on the other hand by the ideas of V. A. Ambartsumyan concerning the dependence of the average scattering multiplicity on the photon survival probability,^[7] and also the invariance principles formulated by him.^[89]

The third path has found specially extensive use in applied spectroscopy of light-scattering substances, and has frequently led to serious confusion. We refer again to the finding of an approximate analytic relation $P_{11}(\alpha)$, but in this case not on the basis of the general theory of light propagation, which is ignored, but by resorting to intuitive concepts which do not always reflect reality. In this case the source of errors is usually the lack of correspondence between the experimental conditions and the real physical premises on which the theory is based.

The most widely used (and the most solidly founded theoretically) is the Gurevich-Kubelka-Munk formula,^[2, 4] which is a direct consequence of the so-called two-flux approximation, which stems from the work of Schuster and Schwarzschild (see ^[12]) and which was used in explicit or implicit form in the work of A. A. Gershun,^[1] M. M. Gurevich,^[2] P. Kubelka and F. Munk,^[4] B. I. Stepanov and his students,^[8, 9] and by many others. It must be emphasized that the cited studies and many other experimental and theoretical researches based on them (see the reviews ^[14, 15, 17-19]) have played an exceedingly important heuristic role in the process of development of the modern concepts.

E. S. Kuznetsov has shown, however,^[90] that the two-flux approximation is valid only if the angular

structure of the radiation field in the medium is spatially invariant, thus imposing special limitations (the quasidiffuseness requirement) on the conditions of illumination of the scattering medium.^[12, 13]

One actually obtains under these conditions a simple relation between the transport function P_{11} and the absorption coefficient α . However, as shown by analysis,^[12, 56] the parameters of this relation depend in turn on α , making it, strictly speaking, unsuitable for spectrum-analysis purposes, in spite of the statements, say, by the author of the review.^[19] To be sure, if we confine ourselves to very small specific absorption and trace only the relative variations of α , then the Gurevich-Kubelka-Munk formula is valid,^[12, 56] as evidenced also by extensive experimental material (see the reviews^[14-19]), but only when applied to the albedo of an infinitely thick layer of large dimensions and under conditions when this layer is diffusely (more accurately, quasidiffusely^[13]) illuminated. One can point to a large number of experiments which illustrate that the two-flux approximation patently contradicts reality when these requirements are not satisfied. Nonetheless, many authors (for example,^[19]) continue to recommend and use this approximation persistently, without taking into account the limits of its consistency.

V. CONCRETE METHODS OF SPECTROSCOPY OF LIGHT-SCATTERING SUBSTANCES

The program described above can be realized only in a few definite but sufficiently varied experimental situations, the choice between which is governed by the concrete properties of the object (which incidentally are usually also subject to variation) and by the nature of the analytic problem. We outline below schematically the possibilities and conditions for applying some of the already developed methods.

A. Method of Narrow Directional Beam

This is the most traditional method, but its use calls for a number of precautions.

The optical phenomena accompanying the propagation of a narrow directional beam in a scattering medium have been considered in detail in^[91] and in the cycle of papers.^[92] If the aperture angle of the beam is sufficiently small and its cross section is considerably smaller than k^{-1} , then the overwhelming number of photons scattered by the substance leave the beam permanently. Therefore, up to optical distances τ on the order of several units, we can disregard multiple scattering of light.^[91] This means that on the right side of (21) there remains only the first term, and if the receiving unit spans the entire beam, Bouguer's law (4) holds true with α replaced by k . However, as shown by D. K. Beridze and M. I. Shakhparonov,^[93] at sufficiently large τ , even in a very narrow beam

(for example, inside a capillary), only multiply scattered light is retained, and a state is established analogous to that under depth conditions, but with a modified damping coefficient, as a result of the photon loss,^[92, 93] which again leads to a law similar to (4), except that the extinction coefficient is replaced by some other quantity.

Thus, a setup similar to that shown in Fig. 4 makes it possible to determine directly the extinction coefficient $k = \alpha + \sigma$, provided only that $d \ll k^{-1}$ and kL does not exceed several units, the optimal sensitivity being reached when $kL \cong 1$.^[3]

Further, attention was already called by A. A. Gershun^[94] to the fact that owing to the finite aperture of the receiving unit (the diaphragm 4 in Fig. 4) and to strong elongation of the scattering indicatrix, part of the light that is scattered only once by the medium will nevertheless reach the receiver, as a result of which the measured value k_{meas} turns out to be less than the true value, i.e., $k_{\text{meas}} = k - \Delta k$. Numerous experimental and theoretical estimates have shown that Δk depends not only on the parameters of the setup but also on the variable properties of the medium, and consequently also on the wavelength. Therefore, say in the presence of a large-droplet fraction of an aqueous aerosol, measurements of the transparency of the atmosphere by means of the brightness of the sun lead to erroneous result owing to the large angular dimensions of the latter, whereas measurement with the aid of stars or measurement with the sun but in the absence of large drops are practically free of errors. It turns out^[95] that if the angular aperture of the light beam does not exceed several minutes of angle and if the measurements of k are carried out while gradually decreasing the diameter of the diaphragm 4 (Fig. 4), extrapolation of k_{meas} into the region of small diaphragm apertures ensures elimination of the error in measurements of the extinction coefficient.

So long as the influence of the multiple scattering of the light is negligibly small, measurements of the brightness and of the polarization of the scattered light emerging from the beam in different directions make it also possible to determine the components f_{ik} of the scattering matrix and their angular dependences (including the scattering indicatrix f_{11}),^[91] and after integration with respect to the angles also the scattering coefficient σ . However, the experimental setups usually do not make it possible for the measurements to be extended to very small scattering angles (smaller than $7-10^\circ$). This leads to an appreciable error in σ and its spectral variation, since approximately half of the entire power of the scattered light is concentrated within this angle interval as a rule.^[95-97] Introduction of a correction for the scattering of light at small angles is effected in the same manner as the introduction of the correction in the measurements of k .^[95] Thus, measurements with a directional beam

make it possible to determine simultaneously k and σ , from which α can also be obtained (if $\beta \geq 1$).

B. Methods Based on the Use of Small-multiplicity Scattering

Substitution of (24) in (25) transforms the expression for the transport matrix into

$$P_{ik} = \sum_{n=1}^{\infty} w_{ik,n} \left(\frac{1}{1+\beta} \right)^n. \tag{31}$$

With increasing specific absorption β , the contribution of the multiply scattered light to the transport matrix decreases the more rapidly, the larger the scattering multiplicity n . The influence of β on the brightness, on the angular characteristics, and on the polarization of the light reflected or transmitted by the scattering medium reduces essentially to this effect. [12, 13, 49, 50]

This can be made immediately obvious by comparing (31) with (15) and turning to Fig. 4a. It follows hence, in particular, that the spectral composition of light that is diffusely reflected or transmitted by the scattering substance is determined, on the one hand, by the spectral variation of β (but not α), and on the other hand by the character of the dependence of $w_{ik,n}$ on n . As shown by V. A. Ambartsumyan, [7] the average scattering multiplicity upon reflection from a semi-infinite medium, in the case of a spherical scattering indicatrix and diffuse illumination, is equal to

$$\bar{n} = \sqrt{1+\beta^{-1}}, \tag{32}$$

i.e., it depends uniquely on β . (For other scattering indicatrices or for directional illumination of the surface, β must be multiplied by a coefficient.)

On the other hand, the quantities $w_{ik,n}$ are deter-

mined, as already shown, by the dimensions of the body and by the conditions of its irradiation and observation. A decrease in the optical dimensions of the body leads, in particular, to a decrease in the probability of the long photon ranges, i.e., to vanishing of the coefficients $w_{ik,n}$ with large scattering multiplicity, and by the same token to a decrease in \bar{n} . And since it is precisely the ratio of the contributions of the scatterings of different multiplicity to P_{ik} (i.e., the quantity \bar{n}) which determines the spectral, angular, and polarization characteristics of the light reflected diffusely by the medium, changes in the dimensions of the body lead qualitatively to the same consequences as changes in β . [11-13]

Thus, if β is large or if the optical dimensions of the body are small (at least in one dimension), we can confine ourselves in (31) to only the first few terms of the expansion, and this directly leads to simple expressions which are convenient for analytical purposes. [49-50]

a) Reflection from a thick layer of strongly absorbing matter. If $\beta \gg 1$ then, according to (32), $\bar{n} < 2$ and we can confine ourselves to the first two terms of the expansion (31), obtaining an expression for the brightness coefficient r of the surface of the scattering substance with large specific absorption: [49-50]

$$r(\beta) = r_0 \frac{1+\beta/Q}{(1+\beta)^2}, \tag{33}$$

where r_0 and Q are constants that depend on the form of the scattering matrix f_{ik} and on the directions of illumination and observation of the substance. When $\beta \gg 1$ this expression turns into

$$r(\beta) = \frac{1}{4\pi} \frac{\mu}{\mu+\mu_0} f_{11} \beta^{-1}, \tag{34}$$

where $\mu_0 = \cos \vartheta_0$, $\mu = \cos \vartheta$, and ϑ_0 and ϑ are the angles between the illumination and observation directions normal to the surface. The foregoing relations are well confirmed by experiments, as is the follow-

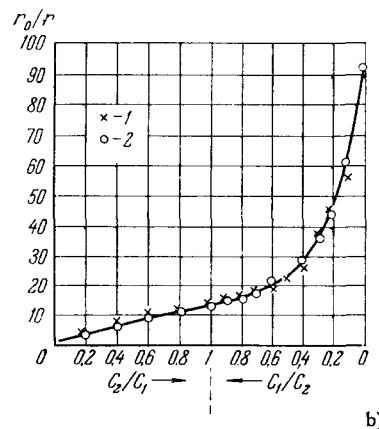
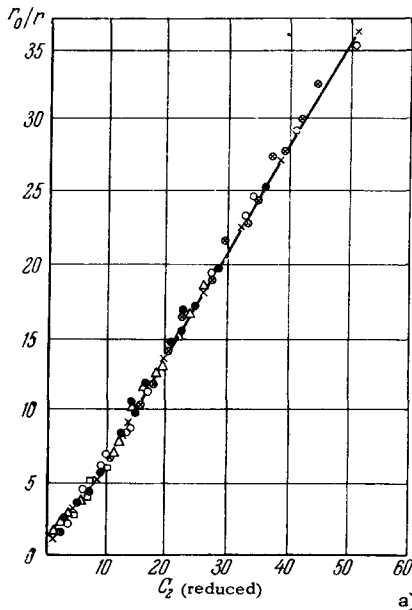


FIG. 8. Dependence of $r^0(\beta = 0)/r(\beta)$ on the impurity concentration: a) Milk in different sections of the spectrum with different dyes as impurities. Abscissas—reduced concentration of the dye, which is proportional to β ; b) mixture of magnesium oxide (C_1) and lamp black (C_2): 1—measured values, 2—values calculated from (33) and (35).

ing relation, which is obvious for a mixture of several components (or for a polydispersed medium),

$$\beta = \frac{\alpha}{\sigma} = \frac{\sum \alpha_i C_i}{\sum \sigma_i C_i}, \quad (35)$$

where C_i is the relative concentration of the i -th component. Examples^[82] are shown in Fig. 8. The combination of (33) and (35) makes it possible to carry out a quantitative analysis by varying the concentration of the mixture (for example, by diluting the medium with a nonabsorbing or a nonscattering component).^[11-17, 82]

From (31) and (34) we find also^[49, 50] that when $\beta \gtrsim 1$ the degree of polarization of the reflected light, when the surface is irradiated by unpolarized light is

$$p(\beta) \cong p_\infty \frac{A + \beta}{B + \beta}, \quad (36)$$

where usually $A \ll B$ and $p_\infty = f_{21}/f_{11}$ is the polarization of the light for single scattering in the same direction. The resultant $p(\beta)$ dependence (the "Umov effect") can also be used for analytic purposes,^[11] but calls for a more detailed study.

Relation (31) and all its consequences are valid if the surface of the scattering medium does not coincide with the phase-separation boundary (i.e., if the refractive indices of the dispersing phase and of the medium over the surface are the same; for example, a system made up of powder and air, or of an emulsion and an identical liquid). In this case the reflected light is only produced by scattering of different multiplicity (see (31)), since there are no reflections from the separation boundary ("external component" in the terminology of A. S. Toporetz^[98]).^[11] To the contrary, if a specular or rough phase boundary exists (for example, the surface of milk or glass), then its role must be taken into account separately. Without touching upon the numerous investigations devoted to this question, we note that there are still no verified methods or criteria for separating volume effects from surface effects, and it is necessary where possible to eliminate the influence of the surface in analytic investigations (for example by immersion^[99]). One must also bear in mind the possibility of quasispecular reflection from the scattering medium^[12] or from its rough surface.^[100]

b) Thin layer of light-scattering substance. If an extended layer of light-scattering substance is uniformly illuminated and if its geometrical thickness satisfies the condition $\sigma L \lesssim 0.1$, then we can again confine ourselves to single scattering of light, thus obtaining the relations (see, for example,^[43])

$$I \cong \frac{E}{4\pi} \frac{f_{11}}{1 + \beta} \frac{1 - e^{-\frac{kL}{\mu + \mu_0}}}{\mu + \mu_0} \quad (37)$$

for the brightness of diffusely reflected light and

$$I \cong \frac{E}{4\pi} \frac{f_{11}}{1 + \beta} \frac{e^{-\tau/\mu} - e^{-i/\mu_0}}{\mu - \mu_0} \quad (38)$$

for the brightness of light diffusely transmitted by the layer, where E is the illumination of the layer. If in addition $\alpha L \ll 1$, then both expressions can be reduced to the same form

$$I \cong \frac{E}{4\pi} \frac{f_{11}}{\mu \mu_0} \sigma L \left[1 - \frac{kL}{2} \frac{\mu + \mu_0}{\mu \mu_0} \right], \quad (39)$$

which depends only weakly on α , making it possible to measure σ with sufficient reliability. We add that since both experimental schemes (a and b) are limited to single scattering, they make it possible also to determine the scattering matrix.

C. Spectrum-analytic Utilization of Measurements of the Light Field Inside a Scattering Medium

In some cases the physical properties of a medium (for example, gas or liquid) make it possible to introduce measuring apparatus in it. This uncovers additional possibilities of carrying out spectrum-analysis experiments. Their realization, however, calls for the satisfaction of certain conditions connected with the experimental technique, namely it is necessary for this purpose to have $\beta \ll 1$ and $kl \ll 1$, where l is the characteristic dimension of the measuring instrument. Violation of these conditions leads immediately to a serious error in the result.

a) Determination of the absorption coefficient from the divergence of the light vector. A. A. Gershun^[101] has already called attention to the fact that the absorption coefficient α of a scattering medium is connected with the divergence of the light vector \mathbf{E} introduced by him (proportional to the Poynting vector) by the simple relation $\alpha \Phi = \text{div } \mathbf{E}$, where Φ is the so-called "spherical illumination" at a given point of the medium, which can be readily measured with the aid of the spherical photometer developed by A. A. Gershun in 1936.^[94] If the medium is a flat layer of large dimensions and if this layer is uniformly illuminated from above, then the relation assumes the following form, which is convenient for experiment and follows directly from the analysis of the radiation transport equation:^[12, 83]

$$\alpha = k' \frac{E_\downarrow - E_\uparrow}{\Phi}, \quad (40)$$

where E_\downarrow and E_\uparrow are the illuminations of the horizontal area from above and below respectively, and

$$k' = - \frac{d \ln E_\downarrow}{dz} \quad (41)$$

is the attenuation coefficient at a given depth.*

The validity of (40) was checked experimentally numerous times, particularly for optical conditions at great depths,^[103] when k' does not depend on the

*According to^[202], a similar conclusion was arrived at, but not published, by R. Preisendorfer.

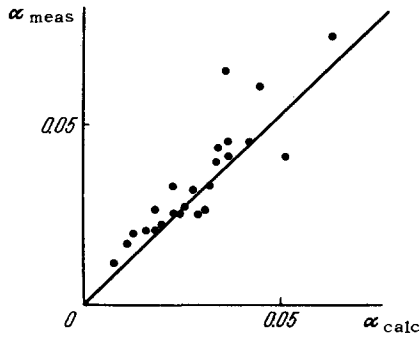


FIG. 9. Comparison of the direction of the directly measured values of α with those obtained from formula (40).

depth (Fig. 9). It is significant that all the quantities in the right side of (40) can be directly measured, making this method the only one so far to ensure reliable results in measurements of absorption spectra of sea water.^[102, 104, 105] If the conditions of the illumination are not uniform (say, the medium is illuminated by a bounded light beam), then the measurement procedure becomes somewhat more complicated but remains essentially the same.^[106]

b) Measurements at great depths. In 1933, V. V. Shuleïkin^[107] noted (see also^[1, 44-46, 108]) that an asymptotic optical regime is established deep inside a scattering medium; the characteristics of this regime are determined by the properties of the light-scattering medium itself and do not depend on the conditions of its illumination. It turned out further^[10, 12, 13, 83, 84] that the depth regime is precisely one of those situations when the transport equation admits of an approximate solution in a form which is convenient for spectrum analysis.

The exponential attenuation of the illumination with depth, which is characteristic of the depth regime, has a depth-independent attenuation coefficient k' , which differs significantly from the extinction coefficient, namely

$$k' = \gamma k, \tag{42}$$

where for $\beta \ll 1$ we have

$$\gamma \cong \sqrt{\frac{\alpha}{qk}} \cong \sqrt{\frac{\beta}{q}} \tag{43}$$

and q is a constant that depends only on the form of the scattering matrix f_{ijk} and is closely connected with the form of the brightness distribution of the light scattered inside the medium. The latter does not change in form with depth and for small values of β is given by^[83, 12]

$$I(\mu) \cong \text{const} [1 + a(\mu) \gamma], \tag{44}$$

where $a(\mu)$ is an odd function of the cosine μ of the angle between the sighting direction and the z axis (which depends only on f_{ijk}), with $q = \frac{1}{2} \int_{-1}^{+1} \mu a(\mu) d\mu$.

For symmetrical scattering indicatrices $q = \frac{1}{3}$; for asymmetrical indicatrices q increases with increasing elongation of the indicatrix, reaching, say, values of approximately 1.5 for fogs and finely dispersed powders, and several units for more coarsely dispersed media.

It follows from (42) and (43) that $k' \cong \sqrt{\alpha k/q}$ or

$$\frac{\alpha}{q} = \frac{k'^2}{k}. \tag{45}$$

This relation, which has been confirmed, like all others, by numerous experiments (Fig. 10) can serve, as shown by V. A. Timofeeva,^[109] as a convenient means of measuring α (for example, by introducing an additional non-scattering dye into the medium).

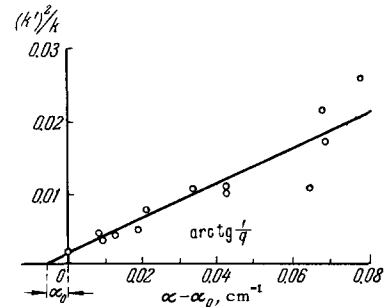


FIG. 10. Dependence of the ratio k'^2/k on $(\alpha - \alpha_0)$ for dyed milk. α_0 - absorption coefficient of undyed milk.

This method can be especially effective for very small α , when in conjunction with artificial addition of turbidity to the medium by a nonabsorbing strongly scattering admixture (or, we add, under conditions of critical opalescence), the sensitivity threshold with respect to α is decreased by 1.5 or 2 orders of magnitude compared with the threshold attained in the absence of scattering, as can be readily seen from (42) and (43).

Further, it follows from (41)-(43) that

$$\beta = \frac{1}{4q} \left(\frac{E_{\downarrow} - E_{\uparrow}}{\Phi} \right)^2, \tag{46}$$

which is also convenient for the determination of β . In addition, according to (44) an increase in β leads to an elongation of the brightness distribution and by the same token also to a monotonic dependence of the degree of polarization of the light on β in the depth regime.^[83, 12, 110]

Finally, the illumination from above at a sufficiently large depth z , in the depth-regime zone, is equal to^[13]

$$E_{\downarrow}(z) = E_0 g(\mu_0) e^{-x}, \tag{47}$$

where E_0 is the surface illumination,

$$x = \gamma \tau = \gamma k z \tag{48}$$

and $g(\mu)$ is a function characterizing the distribution of the light emerging from a thick layer of a turbid medium, and depends only on the form of the scattering matrix but not on α .^[13, 99, 111] Relations (47) and (48) determine the spectral course of the illumination at a given depth z .

However, (47), like (42), is valid only in a "bottomless" medium. In the presence of a black bottom situated at a depth L we have for a height $z' < L$ above the level of the bottom^[13]

$$E_{\downarrow} = E_0 g(\mu_0) \frac{\text{sh}(x' + y)}{\text{sh}(x_0 + y)}, \quad \frac{d \ln E_{\downarrow}}{dz} = -k' \text{cth}(x' + y), \quad (49)$$

where $x' = \gamma k z'$, $x_0 = \gamma k L$, k' is determined by relations (42) and (43), and

$$y = l\gamma \quad (l = 4q). \quad (50)$$

D. Spectroscopy of Thick Layers of Scattering Substances with Small Specific Absorption

The simple relations given in the foregoing sections were obtained^[83] by expanding the solutions of the transport equation (21) in powers of γ and retaining the first terms of the expansion. Comparing (43) and (32), we can easily see that γ is inversely proportional to the average multiplicity of scattering \bar{n} when $\beta \ll 1$.^[12, 13] In other words, the physical meaning of the operation that has led to these relations reduces to a re-expansion of the transport matrix (31) in powers of the quantity $(\bar{n})^{-1}$, which is small when $\beta \ll 1$. Obviously this procedure can be extended also to any transport matrix provided $\bar{n} \gg 1$, i.e., when the specific absorption is small and the geometrical dimensions of the body are large. It must be recognized here that the average multiplicity of scattering will be different, according to (31), for different components of the transport matrix, and the relation indicated by V. A. Ambartsumyan^[7] holds in this case (for P_{11}), namely

$$n_{ik} = -(1 + \beta) \frac{d \ln P_{ik}}{d\beta}. \quad (51)$$

Realization of this program with account of V. A. Ambartsumyan's invariance theory and the reciprocity theorem has made it possible^[12, 13, 47, 56, 82] to obtain, in sufficiently simple analytic form, approximate solutions of the transport equation for the matrices of reflection and transmission of light by a thick layer of a scattering medium with small specific absorption. The corresponding solutions were extensively verified experimentally in a great variety of objects^[12, 13, 56, 58, 71, 99, 112, 113, etc.] and also verified by computer solution of the transport equation for several models^[77, 111, etc.]. It was established^[56, 58, 99, 111, 112] that, at any rate for samples whose albedo exceeds 0.6–0.7 (this corresponds to $\bar{n} \gtrsim 7-10$), the relations are valid with a high degree of accuracy. The generality of the obtained relations makes their field of applica-

tion almost unlimited, so that they can be recommended for use in spectroscopy practice.

In addition to the requirement that β be small, the feasibility of using the methods described below entails the observation of the conditions $\sigma L \gtrsim 5$, $d \gg k^{-1}$, and $d \gg L$, where d is the cross section of the sample. It is important here to illuminate the entire surface of the sample uniformly and limit the observed part of its surface to a region whose boundaries are at least $(50-100)k^{-1}$ away from the boundaries of the sample. The latter requirement and the requirement $d \gg L$ can be relaxed if the lateral surfaces of the sample are covered with a specular or diffuse reflector with an albedo that comes as close as possible to unity and which at any rate is much larger than the albedo of the sample.

As the photometric characteristics of the sample it is convenient to choose the following^[13, 43] linear combinations of the possible transport functions P_{11} .

1. Brightness coefficients for diffusely reflected ($r(\mu, \mu_0)$) and diffusely transmitted ($t(\mu, \mu_0)$) light, defined as the ratio of the brightness I of the light scattered by the sample in a given direction to the illumination of the surface of the sample.

2. Coefficients of diffuse reflection $R(\mu_0)$ and transmission $T(\mu_0)$ in the direction of the flux of the directional illumination

$$T(\mu_0) = 2\pi \int_0^1 \mu t(\mu, \mu_0) d\mu, \quad R(\mu_0) = 2\pi \int_0^1 \mu r(\mu, \mu_0) d\mu.$$

3. Diffuse transmission \mathcal{F} and albedo \mathcal{R} under quasidiffuse illumination (i.e., illumination in which the angular structure of the light field is identical with the angular structure of the light field in the depth regime for the given sample), defined as the ratio of the light fluxes reflected or transmitted by a unit surface of the sample to the illumination of its surface.

Under the conditions stipulated above, we have the following relations, which are accurate to quantities of order γ^3 .^[13]

$$\mathcal{F} = \frac{\text{sh } y}{\text{sh}(x + y)}, \quad \mathcal{R} = \frac{\text{sh } x}{\text{sh}(x + y)}, \quad (52)$$

$$T(\mu_0) = g(\mu_0) \mathcal{F}, \quad R(\mu_0) = e^{-y} - T(\mu_0) e^{-x-y}, \quad (53)$$

$$t(\mu, \mu_0) = \frac{1}{\pi} g(\mu) T(\mu_0), \quad r(\mu, \mu_0) = \frac{h}{\pi} e^{-y} - t(\mu, \mu_0) e^{-x-y}, \quad (54)$$

where g , h , and s are functions of the directions of illumination and observation, which depend only on the form of the scattering matrix (see^[13, 99, 111, 112]). An idea of the behavior of these functions is gained from Figs. 11a, b, and c, borrowed from^[99]. It is important to bear in mind that the parameters q , g , h , and s are much easier to determine experimentally than the angular dependence of the components of the scattering matrix f_{ijk} which enters in (21), and are relatively insensitive to its variations. In particular, for

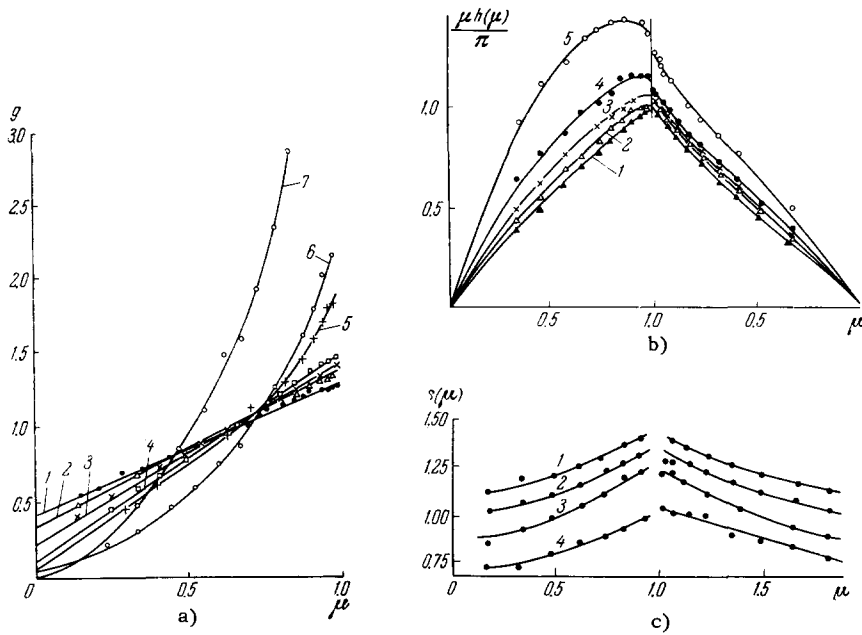


FIG. 11. Behavior of the parameters g , h , and s : a) Plot of $g(\mu)$ for $\mu_0 = 1$ for powders of different glasses in immersions. The relative refractive indices are: 1-1.624, 2-1.518, 3-1.4586, 4-1.14, 5-1.09, 6-1.03, 7-1.01 (in the latter cases the satisfaction of the condition $\sigma L \geq 5$ is doubtful); b) Plots of $\mu h(\mu)/\pi$ water at different μ_0 : 1-1.0, 2-0.98, 3-0.92, 4-0.82, 5-0.67; against μ (in the incidence plane) for powdered BS-10 glass in c) Dependence of s on μ (in the plane of incidence) for milk at different μ_0 : 1-1.0, 2-0.92, 3-0.82, 4-0.67.

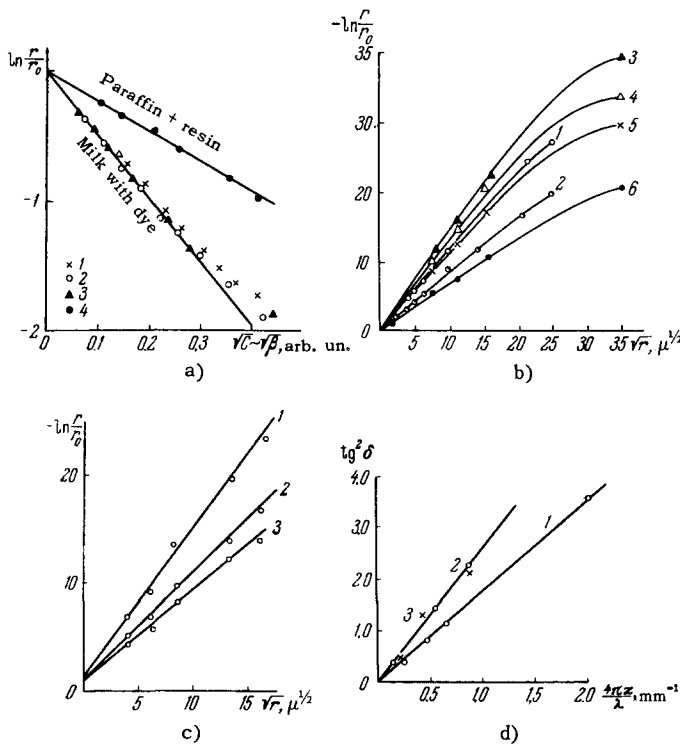


FIG. 12. Influence of dye concentration C (a), particle dimensions (b and c), and refractive index κ on the degree of brightness of a thick layer: a) According to recalculated data of [82]; milk with crystal-violet (1) and india ink (2 and 3)—various filters; b) Glass powders in different parts of the spectrum according to data of [72] (1 and 2—different light filters) and [73] (3-0.7 μ , 4-0.8 μ , 5-0.6 μ , 6-0.55 μ). c) Mixture of glass powders according to data of [74] (1-650 μ , 2-450 μ , 3-525 μ). d) Dependence of $\tan^2 \delta$ (δ —angle of inclination of curves in Figs. 12 b and c) on $4\pi\kappa/\lambda$ according to the data of [71].

a large class of objects we have approximately^[13] $g(\mu) \cong 1/3 + \mu$.

We note that (52) (unlike (53) and (54)) is valid for samples of arbitrary thickness. However, if quasidiffuse illumination is replaced by diffuse illumination, then for sufficiently small β (i.e., large \mathcal{R}) relations (52) become valid (and approximately, at that) only for samples that are not too thin. If the sample is on a diffusely reflecting surface with a non-zero albedo, the formulas become more complicated.^[13, 55, 87]

Special notice must be taken of two limiting cases:

1. $x \ll 1, y \ll 1$;

$$\mathcal{F} = \frac{l}{\tau+l} \frac{1 + \frac{2}{3} l\beta}{1 + \frac{2}{3} \frac{(\tau+l)^2}{l} \beta}; \quad \mathcal{R} = \frac{\tau}{\tau+l} \frac{1 + \frac{2}{3} \frac{\tau^2}{l} \beta}{1 + \frac{2}{3} \frac{(\tau+l)^2}{l} \beta}, \quad (55)$$

2. $x \gg 1, y \ll 1$;

$$\mathcal{F} = 2ye^{-x}, \quad \mathcal{R} = e^{-y} (1 - 2ye^{-2x}). \quad (56)$$

In the case of directional illumination and observation we have in lieu of the latter relation, in accord with (54), (50), and (43)

$$\ln \frac{r(\beta)}{r(\beta=0)} = -4sq^{1/2} \sqrt{\beta} \quad (57)$$

and in the case of relatively large particles made of weakly absorbing material we get approximately, in accordance with (30),^[13, 71]

$$\ln \frac{r(\beta)}{r(\beta=0)} = -4sq^{1/2} \sqrt{K \frac{2\pi}{\lambda} \kappa r} \quad (58)$$

The degree and limits of applicability of the foregoing relations can be seen from the examples illustrated in Fig. 12.

The quantities α and σ enter in formulas (52)–(56) only in the form of the quantities x and y . Consequently, variation of the experimental conditions can influence only the form of the parameters that relate these quantities with the measured ones. But in any case the measurements can yield only two quantities, namely:^[56]

$$\alpha = \frac{xy}{4L} \text{ and } \Sigma \equiv \frac{\sigma}{l} = \frac{x}{Ly}. \quad (59)$$

An experiment of a different type is necessary to determine l .

The scattering medium plays in this case the role of a multiple-path cuvette, in which the effective number of passes depends on β . The sensitivity threshold with respect to α is smallest for \mathcal{R} as $x \rightarrow \infty$ (it is equal to $\alpha \cong 10^{-4} \Sigma$), whereas the relative sensitivity $\delta\alpha/\alpha$ is the largest in measurements of \mathcal{T} and for $x \gg 1$ ($\delta\alpha_{\text{thr}} \cong 10^{-2} \sqrt{\alpha/L\sqrt{\Sigma}}$). When compared with Bouguer's law in the absence of scattering, this corresponds to an increase in the effective path of the light beam in the medium by a factor $\sqrt{\Sigma/\alpha}$,^[56, 58, 88] which results, in particular, in a change in the line shapes and the absorption-band shapes.^[12, 13, 58, 114] The sensitivity is discussed also in^[123].

Inasmuch as we are dealing with samples that have relatively low absorption, it is convenient to use for the measurements a photometric sphere,^[115] the absorptivity of the sample being $\mathcal{A} = 1 - (\mathcal{T} + \mathcal{R})$ in the case of diffuse illumination and $\mathcal{A} = 1 - (T + R)$ in the

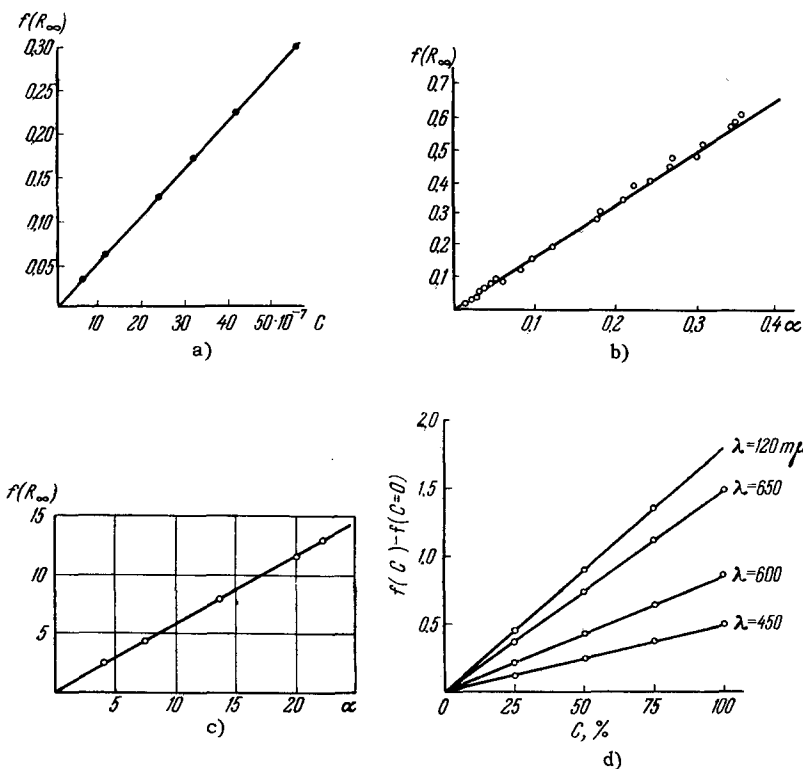
case of directional illumination, in accordance with (52) and (53).

Formulas (52) are outwardly similar to those obtained with the aid of the two-flux approximation.^[1, 2, 4] Actually, however, they differ in principle from the latter, since they take into account in explicit form the dependence of the shape of the brightness distribution on β .^[56] This necessitates a marked alteration in the character of the obtained spectral relations. However, when β is small, the formal expression for the Gurevich-Kubelka-Munk formula^[2, 4] remains approximately valid, except that the right side is modified, namely:^[56]

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{2\alpha}{\Sigma}, \quad (60)$$

where $R_\infty = R_{(x \rightarrow \infty)} = e^{-Y}$. With this correction, the use of this formula is perfectly justified in the range $R_\infty \gtrsim 0.6$, as well as all the deductions obtained with its aid, this being a subject of an extensive literature (see, for example, ^[14-19]). Figure 13a, which is borrowed from ^[116], shows the dependence of $f(R_\infty)$ on the concentration of the substance coloring the scattering medium at large R_∞ , i.e., small β . With increasing β , at $R_\infty \gtrsim 0.6$, formula (60) begins to deviate from the true situation, as can be seen from Fig. 13b, which is taken from ^[117]. At R_∞ close to 0.15–0.3, formula (60) already leads to patently erroneous values of α .^[12, 56, 119] However, when $\beta \gg 1$, i.e., $R_\infty \lesssim 0.1-0.15$, corresponding to a range when (34) is already valid,

FIG. 13. a) Linear dependence of $f(R_\infty)$ on C for $\beta \ll 1$; b) violation of linear dependence of $f(R_\infty)$ on α with increasing β ; c) linear dependence of $f(R_\infty)$ on α for $\beta \gg 1$; d) linear dependence of the difference $f(C) - f(C=0)$ on C for a mixture of colored and uncolored glass powders.



formula (60) again begins to be valid, except that the coefficient of α in the right side is markedly different.^[12] This is illustrated in Fig. 13c, which is taken from^[118]. Figure 13d shows the dependence of the difference of the Gurevich-Kubelka-Munk function, $f(C) - f(C = 0)$ on the concentration C of colored glass powder mixed with colorless powder (for identical values of Σ and small β , this difference should be proportional to C).^[119]

It follows from (52)-(54)^[54] that when $\beta \ll 1$

$$\frac{R_\infty}{R_\infty - R_L} \cong 1 + \Sigma L, \tag{61}$$

and

$$-\ln \left(\frac{R_\infty - R_L}{T_L} \right) \cong 2 \sqrt{\alpha/\Sigma} + 2 \sqrt{\alpha\Sigma} L, \tag{62}$$

where the subscript L denotes that the measurements pertain to a layer of thickness L . Thus, variation of the layer thickness makes it possible to determine α and Σ , as illustrated^[56] in Fig. 14. We note that relation (62) is valid also when (54) is used, but provided the measurements are carried out in the reflected and in the transmitted light for equal values of μ . It follows in a somewhat less explicit form (subject to all the stipulations) also from the two-flux approximation.^[120]

E. Luminescence Analysis

Questions of luminescence of light-scattering media, including their spectroscopic aspects, were considered by many authors (see, for example^[121]), but either from the point of view of the two-flux approximation, or starting from an a priori specified model of the structure of the medium.

The method employed above makes it possible to consider luminescence phenomena from more rigorous and consistent points of view. In fact, if $P^{(1)}(\mathbf{r})$ is the function describing the transport of exciting light of wavelength λ_1 to a volume element dV at a point with coordinates \mathbf{r} , and $\tilde{P}^{(2)}(\mathbf{r})$ is the transport function of luminescence of wavelength λ_2 from the element dV to the observer, then the total transport function (luminescence) is $P = \int P^{(1)}(\bar{\mathbf{r}}) \alpha_1 \Gamma(\bar{\mathbf{r}}) \tilde{P}^{(2)}(\bar{\mathbf{r}}) dV$, where $\Gamma(\mathbf{r})$ is the luminescence yield and $\alpha_1(\mathbf{r})$ is the absorption coefficient for λ_1 . Execution of this program^[47] for a homogeneous thick flat layer illuminated in quasisidiffuse fashion leads to an expression (under conditions of weak specific absorption at λ_1 and λ_2) for the luminescence flux from the layer

$$F_{lum} \cong E_0 \cdot 4\alpha_1 \Gamma e^{-2q\gamma_1} \frac{1 - 4q_2\gamma_2}{\gamma_1 k_1 - \gamma_2 k_2}, \tag{63}$$

where the subscripts 1 and 2 pertain to λ_1 and λ_2 re-

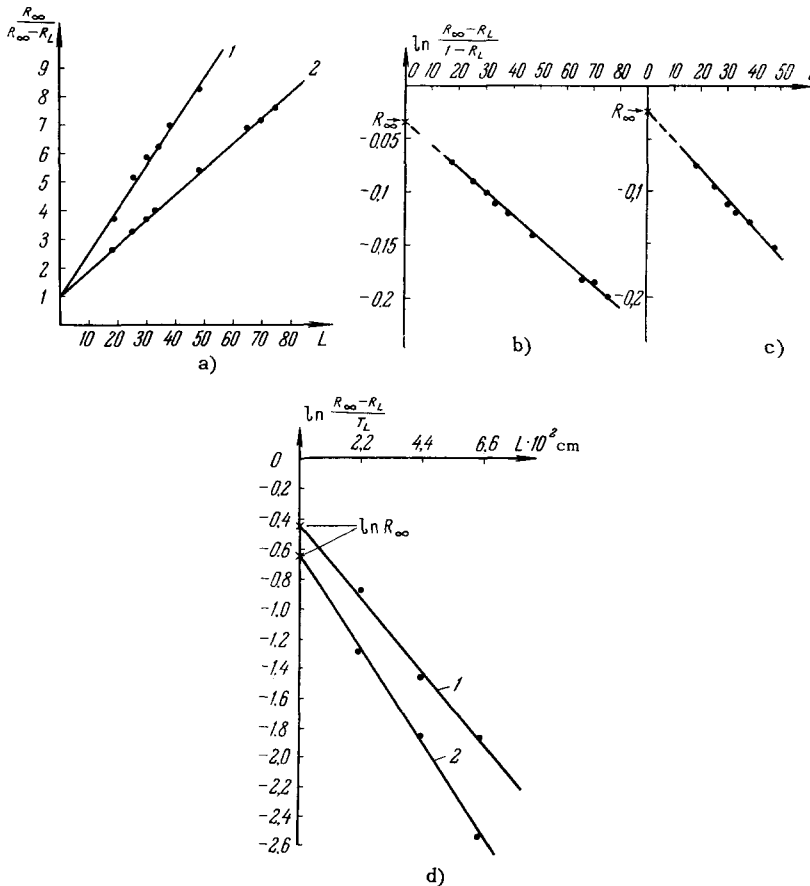


FIG. 14. Examples illustrating the use of relations (61) and (62) for two parts of the spectrum: a) Magnesium oxide layers, relation (61); b) and c), the same, relation (62) with T_L replaced by $1 - R_L$, since $A_L \ll 1$; d) live leaf, relation (63).

spectively, thus again improving somewhat on their results obtained with the aid of different variants of the two-flux approximation and, most important, delineating the limits of their applicability. The more general case of directional illumination of a luminescent body has not yet been analyzed.

F. Other Methods

The methods described above far from complete the list of capabilities of the spectroscopy of light-scattering objects. In particular, we have not touched upon the important and interesting problem of investigating Shpol'skiĭ's absorption and luminescence spectra. Nor did we mention problems of emission analysis, including the phenomenon of reversal of spectral lines—the most typical effect of light propagation in a scattering medium. Unfortunately this group of problems has not been treated with the degree of generality and clarity which is required for the solution of the inverse problems of light-propagation theory, i.e., for a quantitative solution of spectroscopic problems.

However, even absorption and luminescence analysis contains unexplored prospects. In particular, recently L. M. Romanova^[122] proposed to determine $T(\alpha, l)$ or $P(\lambda, \Delta\lambda, l)$ on the basis of relations (26) and (27) by time selection of a light pulse of duration $t \ll 1/kc$ scattered by the medium (c —velocity of light); this can be used, for example, in optical radar sounding of atmospheres of other planets.

A standardization method, consisting of obtaining a calibration curve for spectral analysis with the aid of a series of standards with graduated properties, is extensively used in laboratory practice. If one is assured that the standard and investigated dyes have the same nature and color the medium in an identical manner, then this method is beyond reproach. But if differences are possible in the distribution of the dyes in the medium or in the structures of the standard and investigated media, then this method must be deemed unsuitable. We have likewise not mentioned many investigations, of both methodological and applied character, which have played an important role in their time. These investigations, as well as an examination of the technical aspect of spectrum-analytic procedures, are worthy of special treatment.

Finally, we have disregarded completely many recommendations which can be found in reviews^[8, 9, 14-19] and in the original papers related to them. Some of them are promising but, from the author's point of view, have not been justified with sufficient reliability. Others, sometimes even widely used, must be downgraded as incorrect and producing unreliable results. Their criticism, however, would necessitate an increase in the size of this article, something that can hardly be justified. Accordingly, the cited bibliography is far from full and reflects only that aspect of the problem which serves as the main subject of the review.

In conclusion we note that no matter how limited the scope of the methods of spectroscopic research of light scattering substances considered above, it is sufficient for a complete solution of a number of most varied and hitherto insoluble problems. The limitations are the result of the very nature of the problem and it is these limitations which should become the starting point for the next stage of development of particular procedures for solving problems of different types. However, in spite of this, the present status of the problem already permits extensive practical utilization of the methods described above in spectrum-analysis laboratories of different natures and a most rapid introduction of these methods is a paramount task of spectroscopy.

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