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APPROXIMATE SOLUTIONS TO THE KUBELKA AND MUNK EQUATIONS

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SUMMARY

The present paper discusses the simulation of the optical characteristics of plane parallel isotropic media under special conditions where the general solutions either degenerate or else may be considerably simplified. The first case is mainly that of a scattering medium with vanishing absorbance. The second one assumes high scattering and medium absorbance. In this latter case both transmittance and reflectance may be approximated by an $e^{-\mathrm{const}\sqrt{K}}$ function. Other sections consider the determination of the basic constants of the solutions by optical measurements on the blank medium and the character of the optical noise in transmittance and reflectance measurements. Reflectance is shown to be less susceptible to optical noise than transmittance.

INTRODUCTION

In a recent paper[1] the authors discussed the electrical modelling of the optical behavior of plane parallel scattering media. The results derived were completely general and covered the whole range of media to which the KUBELKA AND MUNK theory[2] may be applied. There are, however, certain particular situations where the solutions obtained may be much simplified and which might, therefore, merit a more detailed consideration; several of these are considered in this paper.

It has been shown[1] that the transmittance A_T and reflectance A_R of a medium can be expressed in terms of the characteristic impedance ζ_0, the attenuation constant γ and the reflection coefficient ϱ of a 3-terminal electrical model circuit. The meaning of these terms was briefly described in ref. 1. They will not be repeated here. The relations found were:

$$A_T = \frac{e^{-\gamma}(1-\varrho^2)}{1-\varrho^2\cdot e^{-2\gamma}} = \frac{2v(1)}{v(0)+i(0)} \tag{1}$$

$$A_R = -\varrho\frac{1-e^{-2\gamma}}{1-\varrho^2\cdot e^{-2\gamma}} = \frac{v(0)-i(0)}{v(0)+i(0)} \tag{2}$$

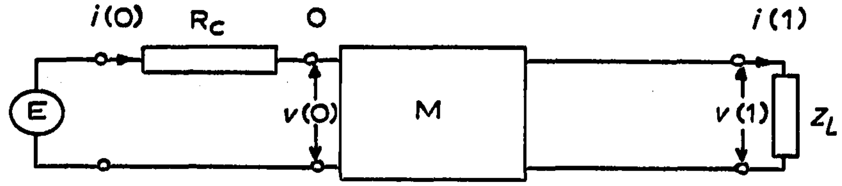

Fig. 1. General model diagram. M = Model; R_c = 1 = current measuring resistor; Z_L = 1 = load resistor; E = input generator with voltage E.

The symbols v and i on the right-hand side of eqns. 1 and 2 designate voltage and current, respectively, of the electrical model; the numbers in brackets refer to the terminal at which these values are observed, 0 marking the input and 1 the output (see Fig. 1).

The parameters ζ_0, γ, and ϱ are related to each other and to the coefficient of scattering S and of absorbance K of the medium by the following relationships:

$$\zeta_0 = \sqrt{\frac{2S + K}{K}}$$

$$\varrho = \frac{1 - \zeta_0}{1 + \zeta_0}$$

$$\gamma = \sqrt{\{K(2S + K)\}} = K \cdot \zeta_0 = K \frac{1 - \varrho}{1 + \varrho} \tag{3}$$

For ζ_0 and ϱ apply the limitations:

$$1 \leqslant \zeta_0 \leqslant \infty \qquad -1 \leqslant \varrho \leqslant 0 \tag{4}$$

THE DEGENERATE CASE WITH EITHER S OR $K \to 0$

A special situation arises if one of the variables S or K vanishes. In this case our model equations degenerate and cannot be applied immediately. The case of either S or K tending towards infinity is of no practical importance and need not be considered here.

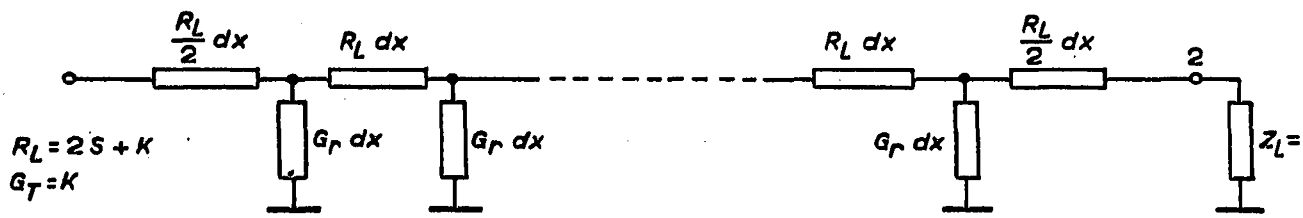

Fig. 2. Basic diagram of transmission line model.

If K tends to zero, the basic expressions (1) and (2) become meaningless. It is easy, however, to obtain the desired result by using the basic transmission line model illustrated in Fig. 2 (the derivation of this was discussed in ref. 1) and setting $K = 0$. What is obtained is a simple voltage divider network (see Fig. 3b).

Fig. 3. (a) Equivalent circuit for transmission and reflection with $K = 0$. (b) Model of a degenerate case with $K = 0$.

Using eqns. 1 and 2 we find the transmittance and reflectance for this case from the model circuit in Fig. 3b which represents a degenerate line. Since scattering alone only changes the direction of flow of the radiant energy without producing any losses, the sum of transmittance and reflectance euals 1 (ref. 3).

$$A_T(0) = \frac{1}{1 + S}$$

$$A_R(0) = 1 - A_T(0) = \frac{S}{1 + S} \tag{5}$$

These particular relationships are modelled by the circuit shown in Fig. 3a.

The second limiting case with $S = 0$ can easily be determined from the basic equations, since in this case ζ_0 becomes 1 and $\varrho = 0$. We obtain an attenuating pad with attenuation $\gamma = K$ and characteristic impedance $\zeta_0 = 1$. This case corresponds of course to the ideal relations prescribed by Beer's Law. It can probably best be modeled by a bridged T-network (see Fig. 4). Reflection is zero, since the impedance

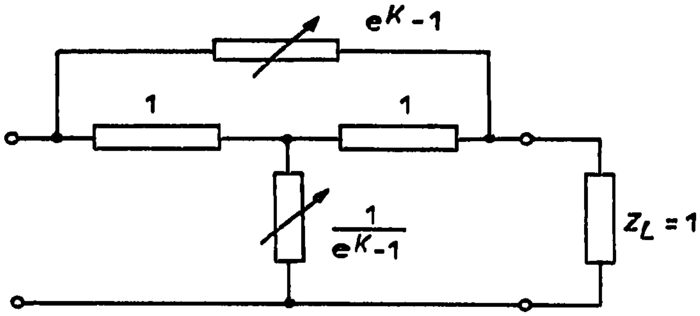

Fig. 4. Bridged T-model for case $S = 0$; $\zeta = 1$; $\gamma = \log e^K = K$.

of the model is constant (unity) and matched to the load at all values of K. Expressed in optical terms it is zero, because no backscatter occurs. The transmission A_T is obviously e^{-K}.

THE NEARLY DEGENERATE CASE WITH $0 < K \ll 1$

When a finite but very small amount of absorbance $K \ll 1$ is present on the medium, the equivalent transmission line ceases to be degenerate. The resulting decrement in transmittance ΔA_T or reflectance ΔA_K can of course then be found from the basic eqns. 1 and 2. The results may be read from the graphs of $A_T' = \partial A_T/\partial K$

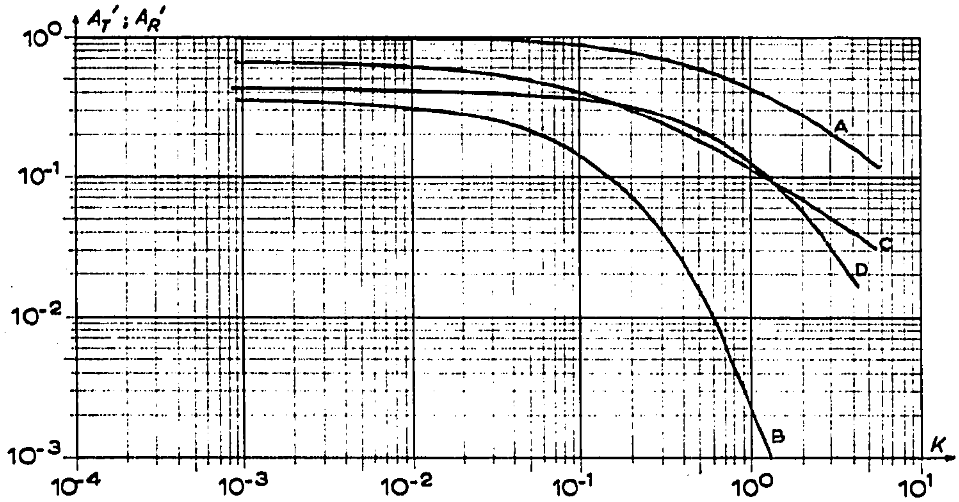

Fig. 5. Sensitivity curves for transmittance and reflectance at extreme values of S. (A) A_T' (S = 0); (B) A_T' (S = 20); (C) A_R' (S = 1); (D) A_R' (S = 20).

and $A_R' = \partial A_R/\partial K$, which are shown for two extreme values of S in Fig. 5. These curves were calculated from eqns. 1 and 2.

For small increments in absorbance, ΔK, both transmittance and reflectance can be approximated by a linear dependence,

$$\begin{aligned} \Delta A_T &\simeq A_T' \cdot \Delta K \\ \Delta A_R &\simeq A_R' \cdot \Delta K \end{aligned} \tag{6}$$

The useful signal obtained during actual measurement is proportional to ΔA_T or ΔA_R. A_T' and A_R' therefore characterise the absolute sensitivity of the method. From the graphs shown in Fig. 5 it may be seen that the largest value of the derivative of both transmittance and reflectance occurs at small values of K. With respect to S the highest sensitivity is obtained in transmittance measurements, if $S = 0$, that is if Beer's Law is valid. The smallest absolute change and thus the smallest value of useful signal for a given value of K is encountered when the medium is strongly scattering (*i.e.*, $S = 20$). Curves of $A_T' = f(K)$ for intermediate values of S will fill the space between these two extreme curves.

The sensitivity of reflectance measurements lies between the extreme values for transmittance. Quite surprisingly, however, the curves for different values of the coefficient of scattering intersect, so that the value of S giving the best sensitivity depends upon the absorbance K of the medium.

Instead of the absolute sensitivity it may sometimes be more convenient to consider the relative sensitivity $A'(K)/A(K)$ with $\Delta K = 0$. For small values of K the relative sensitivity increases with increasing scattering, whilst at larger values of K the opposite condition prevails.

THE REFLECTANCE OF MEDIA WITH MEDIUM TO LOW TRANSMITTANCE

A particular case, frequently encountered in technical application, is a medium with relatively strong scattering and a certain minimum of absorbance. This minimum value of K is dependent upon the coefficient of scattering S and may be expressed as the requirement:

$$1 < \gamma = \sqrt{\{K\,(2S + K)\}} \simeq \sqrt{2SK} \tag{7}$$

Expression (2) may now be simplified to:

$$e^{-2\gamma} \ll 1$$
$$A_R \simeq \varrho \tag{8}$$

Most practical measurements using reflectance spectroscopy are based upon this approximation. Its accuracy increases with increasing values of γ and decreasing values of ϱ^2. Inspection of eqns. 3 reveals that the reflection factor ϱ is solely a function of the ratio K/S. The inverse expression $K/S = f(\varrho)$ is usually called the remission function*. It can be obtained by solving the equations defining ϱ for the variable $u = K/S$.

$$\frac{K}{S} = u$$

$$\zeta_0^2 = \left(\frac{1 - \varrho}{1 + \varrho}\right)^2 = \frac{2 + u}{u}$$

$$u = -\tfrac{1}{2}\left(\frac{1}{\sqrt{\varrho}} + \sqrt{\varrho}\right)^2 \tag{9}$$

A closer examination of eqn. 9 reveals that on a logarithmic scale for u the right-hand side is symmetrical to the axis $|\varrho| = 1$. A graph of $u = f(\varrho)$ is shown in Fig. 6. From this figure it is evident that in order to obtain good accuracy, the range of ϱ over which reflectance measurements are to be made, should be restricted to approximately $-1 \leqslant \varrho \lesssim -0.3$, or $K/S < 1$. At very small values of K/S it is necessary to be care-

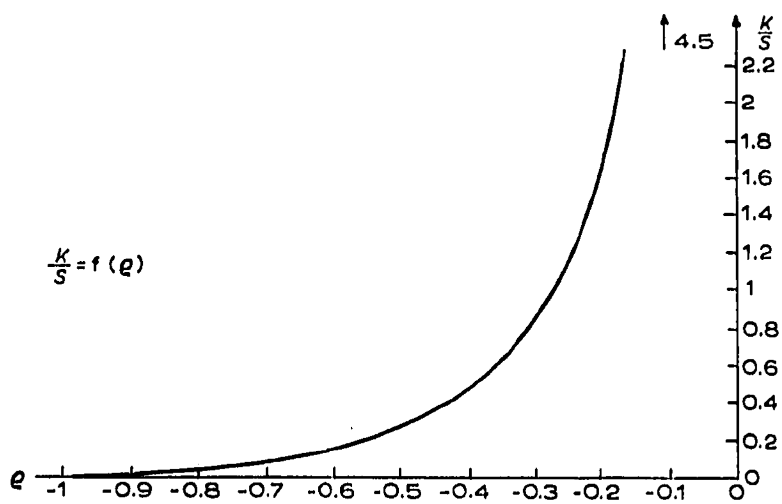

Fig. 6. The remission function $K/S = f(\varrho)$.

* Most frequently the remission function is defined in terms of $R = -\varrho$. See also ref. 4.

ful since γ may become too small for the approximation to be valid, in which case considerable errors will ensue.

In practice the approximate value for A_R may be used for all media with an optical density above about one unit. To illustrate this, the following argument may be used.

Optical density is defined as the decimal logarithm of A_T^{-1} or 2.3 times its natural logarithm. Inspection of eqn. 1, however, shows that the factor $(1-\varrho^2)/(1-\varrho^2 \cdot e^{-2\gamma})$ can only appreciably contribute to the optical density when $1-\varrho^2$ is very small. *E.g.*, for $\varrho = -0.9$ the smallest value of this factor is evidently 0.19, which is approximately 0.7 optical density units. For $\varrho = -0.9$ the value of K/S (read from Fig. 6) is, however, so small that it will only infrequently be encountered in actual practice. This means that a medium with an optical density D larger than 1 will nearly always have a γ value of at least $(D-0.7) \times 2.3$. For optical density values $D > 1$ we therefore nearly always find $e^{-2\gamma} \ll 1$.

AN APPROXIMATE EXPRESSION FOR THE REFLECTION FACTOR

It was pointed out above that for reasonable accuracy the value of ϱ should be below -0.35, or $u \lesssim 1$. It will now be shown that for this range, which is of considerable practical importance, the remission function $u = f(\varrho)$ can be closely approximated by an exponential function. In order to do this we write:

$$u = 2q^2$$

$$\varrho = \frac{1-\zeta_0}{1+\zeta_0} = \frac{q-\sqrt{(1+q^2)}}{q+\sqrt{(1+q^2)}}$$

$$\log \varrho = \log [q-\sqrt{(1+q^2)}] - \log [q+\sqrt{(1+q^2)}] \qquad (10)$$

However

$$[q-\sqrt{(1+q^2)}]\,[q+\sqrt{(1+q^2)}] = -1$$

therefore

$$\log [q+\sqrt{(1+q^2)}] = -\log |\,[q-\sqrt{(1+q^2)}]\,|$$

$$\log |\varrho| = -2 \log [q+\sqrt{(1+q^2)}] \qquad (11)$$

The right-hand side of this relation can be expanded into a power series[5]:

$$\log [q+\sqrt{(q^2+1)}] = q - \frac{1}{2\cdot 3} q^3 + \frac{1\cdot 3}{2\cdot 4\cdot 5} q^5 - \frac{1\cdot 3\cdot 5}{2\cdot 4\cdot 6\cdot 7} q^7 + - \qquad (12)$$

The series expansion in eqn. 12 is valid for $q^2 < 1$. At the other end of the scale, that is for $q > 1$, another expansion may be applied.

$$\log [q+\sqrt{(q^2+1)}] = \log 2q + \frac{1}{2\cdot 2}\cdot\frac{1}{q^2} - \frac{1\cdot 3}{2\cdot 4\cdot 4}\cdot\frac{1}{q^4} + \frac{1\cdot 3\cdot 5}{2\cdot 4\cdot 6\cdot 6}\cdot\frac{1}{q^6} - \cdots \qquad (13)$$

There is a well known theorem about the error committed in terminating a uniformly convergent power series with terms of alternating sign. This theorem states that the error committed in this way is less in magnitude than the first omitted term. Applying this to series (12), we find that the first term in eqn. 12 is thus an adequate representation of the remission function provided the next term is reasonably smaller (*e.g.*, less than 10%). This leads to the approximation

$$\log \varrho \simeq 2q = \sqrt{\frac{2K}{S}}$$

If $$\frac{q^3}{6q} = \frac{u}{12} \lesssim 10\%$$

$$u \lesssim 1.2, \text{ that is } \varrho \lesssim -0.23)$$

$$\varrho \simeq -e^{-\sqrt{\frac{2K}{S}}} \tag{14}$$

As already mentioned, the range for which this approximation is valid coincides closely with the range most suitable for reflectance spectroscopy.

For very large values of u, series (13) can be used as a basis for a simplified approximate expression. Allowing an error of similar magnitude, we obtain:

$$\log \varrho \simeq -2 \log 2q = -\log 2u$$

$$u = \frac{K}{S} = \frac{1}{2\varrho}$$

If $$\frac{1}{4q^2 \cdot \log 2q} = \frac{1}{u \log 2u} \lesssim 10\%$$

$$\text{that is for } u \gtrsim 4.5 \tag{15}$$

In other words, for very large values of the ratio K/S, that is for media with little scattering and high absorbance, the remission function becomes inversely proportional to K.

THE TRANSMITTANCE OF MEDIA WITH STRONG SCATTERING AND INTERMEDIATE ABSORBANCE

The considerations in this section apply to the case where $\varrho^2 \ll 1$; a value of $|\varrho| \leq 0.4$ will in general be adequate. From Fig. 6 it may be seen that this corresponds to $K/S \geq 0.4$, and that beyond this value ϱ^2 changes only relatively slowly with K. Eqn. 1 thus reduces to:

$$A_T \simeq e^{-\gamma} \left(\frac{K}{S} \gtrsim 0.4\right) \tag{16}$$

In the range

$$1 \gtrsim \frac{K}{S} \gtrsim 0.4$$

we may make the further approximation

$$\gamma = \sqrt{\{(2S + K)\cdot K\}} \simeq \sqrt{2SK}$$

resulting in

$$A_T = e^{-\sqrt{2SK}} \tag{17}$$

Approximation (17) is appropriate principally for strong scattering and intermediate values of absorbance (*e.g.* paper). A comparison with expression (14) shows that in both cases the logarithm of the transfer function is proportional to $\sqrt{K}$. The range in which eqn. 14 may be applied includes that for expression (17), which is, however, somewhat more restricted towards smaller values of K/S.

DETERMINATION OF THE OPTICAL CONSTANTS OF THE MEDIUM

Before the transfer eqns. 1 and 2 can be solved for a particular application or before they can be simulated on a model arrangement, the optical constants of the blank (unstained) medium must first be determined by optical measurements. In general two independent measurements will be required to determine S and K. In order to eliminate statistical variations in the values of these parameters, however, it may frequently be desirable to perform two series of such measurements.

As described earlier, the reflectance of a layer (or multiple layers) of a medium with a sufficiently high optical density is equal to ϱ. Care has to be taken to exclude the surface component of the reflected light by using for example polarised light filters[4]. Using eqn. 9 or Fig. 6 the ratio K/S can be determined from the measured value of ϱ. The second measurement may be the transmittance of the same medium. Introducing the measured value of ϱ into expression (1), the corresponding value of $e^{-\gamma}$ (and from that of course γ) can easily be determined. Provided $e^{-2\gamma}$ is small enough, the simplified results are:

$$\gamma = \log \frac{A_T}{1 - \varrho^2} \tag{18}$$

$$K = \frac{\gamma}{\zeta_0} = \frac{1 + \varrho}{1 - \varrho} \cdot \log \frac{A_T}{1 - \varrho^2}$$

$$S = \frac{K}{2}(\zeta^2_0 - 1) = K \cdot \frac{2\varrho}{1 - \varrho^2} = \frac{2\varrho}{(1 - \varrho)^2} \cdot \log \frac{A_T}{1 - \varrho^2} \tag{19}$$

If the approximations (14) and (17) both hold, the relations above can be further simplified to yield:

$$\begin{aligned} \log \varrho \cdot \log A_T &= 2K \\ \log A_T / \log \varrho &= S \end{aligned} \tag{20}$$

On occasions it may be preferable to measure just reflectance or else transmittance. In these cases a chromogen with known increments in absorbance is applied to the medium and from the values of the transfer for K and $K + \Delta K$ the values S and K may be calculated. The calculation is, of course, easier to perform if one of the approximations described in eqns. 8, 14 or 16 can be applied. If a general purpose model such as the one described in ref. 1 is available, the calculation may be replaced by successive adjustment of the model parameters on a trial and error basis, until the values of A_R and A_T measured on the model agree with the optical values obtained from the medium. This procedure is very much facilitated if the approximate values of S and K are known beforehand.

Fluctuations in the basic parameters of the medium (variations in thickness, density, etc.) produce fluctuations in the transfer function, which for the purpose of measuring changes in absorbance are equivalent to the noise in a communication system[6].

As long as these fluctuations affect S and K equally, we can consider them as a change ΔX in the effective thickness of the medium. ζ_0 as a ratio value will in this case remain unchanged and so by the same token will ϱ. Only γ will be affected and that in proportion to ΔX:

$$\Delta\gamma = \gamma \cdot \Delta X \tag{21}$$

Turning back to eqns. 1 and 2 we find that A_R is principally a function of ϱ. Reflectance, therefore, does not change very much with variations in the optical thickness of the background medium. It is, however, sensitive to inhomogeneities in the medium, affecting K and S to a different degree and therefore producing fluctuations in ζ_0 and ϱ as well as in γ. In general, however, fluctuations of the first type seem to prevail, and as a consequence of this, reflectance measurements are relatively insensitive to optical noise, provided surface effects can be disregarded.

A_T, on the other hand, is influenced by fluctuations in the effective thickness of the medium.

$$\Delta A_T \simeq A_T(0) \cdot e^{-\Delta\gamma} = A_T(0) \cdot e^{-\gamma \cdot \Delta X} \tag{22}$$

From eqn. 22 we see that for a given variation ΔX the change in transmittance produced is proportional to the mean value of transmittance $A_T(0)$. In consequence of this, noise is produced which is basically multiplicative in nature. This is a fundamental difference from the predominantly additive noise in electrical systems. One important feature of multiplicative noise is that it can be largely suppressed by forming the ratio of two equally affected signals. Difference procedures, which would be the method of choice in additive systems, are less efficient in these cases.

CONCLUSION

Summarising the results obtained we arrive at the following conclusions:

As previously shown[1], a resistive transmission line is a convenient model for studying, in general, the optical properties of thin media that can be adequately described by the KUBELKA AND MUNK theory. For certain special cases, that is for some limited ranges of optical parameters, it can be shown that the general solutions may be very much simplified. Circuit arrangements to model these expressions will be described in a future publication.

Reflectance measurements are to be recommended mainly when the medium in question has high scattering power and low to medium absorption at high optical density. In this case such measurements are less susceptible to optical noise than is the case for transmission measurements.

Transmission measurements can be used in all cases provided the optical density is not too high and that the output signal is larger in amplitude than the optical equivalent of the electrical noise of the detector assembly. The optical noise in transmission measurements is essentially multiplicative and to reduce it, a double-beam arrangement with ratio forming at the output seems to be the best solution. The strictly exponential dependence of transmittance upon absorbance postulated by Beer's Law represents a limiting case, which is attained only if the coefficient of scattering S tends towards zero. In the practically important case of a medium with high scattering power, intermediate absorbance values and high optical density the law of dependence of both transmittance and reflectance can be approximated by an $e^{-\text{const} \sqrt{K}}$ function.

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