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AN ELECTRICAL MODEL FOR THE OPTICAL BEHAVIOUR OF THIN-MEDIA CHROMATOGRAMS

VICTOR POLLAK
Division of Bio-medical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan (Canada)
AND
ALAN A. BOULTON
Psychiatric Research Unit, University Hospital, Saskatoon, Saskatchewan (Canada)

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SUMMARY

Described is an electrical transmission line with resistive parameters as a model simulating the optical behaviour of chromatographic media as described by the KUBELKA AND MUNK equation. The model is characterised by its attenuation constant γ, its characteristic impedance ζ_0 and the reflection coefficient ϱ. The significance of the latter is derived from Ohm's Law, in order to make the treatment understandable to persons not possessing a background in electrical engineering. A concentrated parameter multi-section representation of the transmission line model is described covering the whole range over which the KUBELKA AND MUNK equations are valid. In order to reduce the complexity of the model, the number of sections may be reduced making the simulation valid only for a restricted range of optical parameters of the medium.

(1) INTRODUCTION

In two earlier papers[1,2] we discussed the quantitative evaluation of paper and thin-layer chromatograms by spectrophotometric methods mainly with regard to the limitations imposed by the optical "noise" upon the obtainable accuracy and sensitivity. The optical noise is caused by irregularities in the transmittance or reflectance of the background material of the chromatogram from one part to another. The discussion was partly based on the simplifying assumption that there is a linear dependence of the transmission decrement upon the concentration of the investigated substance. This assumption is justified, however, only for very low concentrations. In this paper we intend to investigate the relationship between the decrement in transmission or reflection and the concentration of analysed substance for the more general case, where neither linearity nor even logarithmically linear dependence can be assumed without considerable error.

Paper and other thin-media supports used in chromatographic separations have mostly a rather complex physical structure. As a consequence of this, their optical behaviour is too complicated to be described by simple mathematical relationships. For most practical purposes, however, simplified expressions may be used and these give an adequate picture of the optical performance of the medium. One of these relations, which is extensively used in technical applications, is based upon a simplified theory proposed by KUBELKA AND MUNK[3] and is generally known as the KUBELKA AND MUNK set of equations. It relates to plane parallel isotropic heterogeneous media. The assumption of isotropy is frequently valid only to a limited extent, so that measured results need not always completely agree with the values predicted by the theory. In most practical cases, however, these deviations are relatively insignificant, in which case the KUBELKA AND MUNK theory is perfectly adequate and represents a powerful tool for the solution of many technical problems. The KUBELKA AND MUNK equation can be solved in an easy and straightforward manner. The solutions, however, are rather difficult to interpret for practical purposes. Because of this, graphical representations[4] and simplified solutions valid only for a limited range of parameters of the medium[5] have been developed.

In another paper recently published[6] one of us showed that under these conditions the optical behaviour of the medium may be simulated by an electrical transmission line composed of purely resistive elements. As shown in Fig. 1, a transmission line of this type is characterised by a longitudinal resistivity R and a transversal conductivity G. Both are related to the optical parameters of the medium by the relations:

$$\begin{aligned} R &= 2S + K \\ G &= K \end{aligned} \tag{1}$$

In the equations K is the absorbance of the medium and S its coefficient of scattering. The electrical length of the model is assumed to be unity and the same applies to the thickness of the medium.

Wheh the medium is illuminated by a light intensity I, part of the incident light I_S is reflected at the surface[7]. This component does not enter the medium at all and does not therefore convey any useful information about its interior. For the purposes envisaged here, this surface or specular reflectance may be disregarded. The amount of light reflected in this way has to be substracted from the total illuminating light flux. The remaining light enters the medium, which is assumed to be made up of homogeneous particles embedded in a heterogeneous environment. At every particle boundary scattering takes place, whilst inside the particles themselves part of the light is absorbed and converted to heat. No energy loss is produced by scattering. According to KUBELKA AND MUNK the result of this multiple scattering and absorption may with good approximation be represented by splitting the entering light flux into two components, *viz.* one travelling in the forward direction and the other travelling in the reverse direction (Fig. 2). For technical purposes we are only interested in these components at the surfaces, where they are entering or leaving the medium.

It has been shown by POLLAK[6] that the forward light component $j(x)$ and the backwards component $r(x)$ at a distance x from the near surface may be expressed by the voltage $v(x)$ and current $i(x)$ at the corresponding point in the transmission line model according to the following relations:

$$j(x) = \tfrac{1}{2}[v(x) + i(x)]$$

$$r(x) = \tfrac{1}{2}[v(x) - i(x)] \tag{2}$$

In order to obtain the corresponding values at the near (illuminated) surface, we have to put $x = 0$, and for the far surface $x = 1$. $v(0)$ and $i(0)$ are then the input values of voltage and current of the model, respectively, while $v(1)$ and $i(1)$ are the respective output values. No optical back scattering of course takes place at the far end, so that $r(1) = 0$. From this we obtain:

$$v(1) = i(1) \tag{3}$$

It therefore follows that the load impedance ζ_L of the model has to be equal to 1.

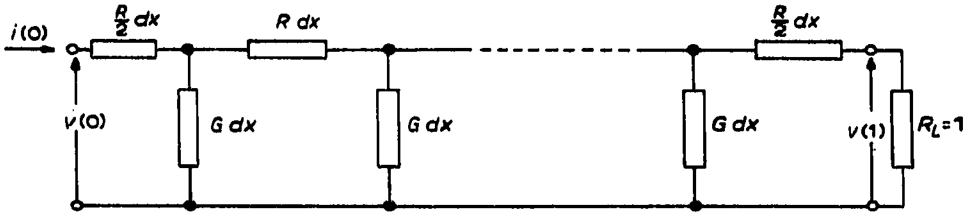

Fig. 1. Basic diagram of a resistive homogeneous transmission line.

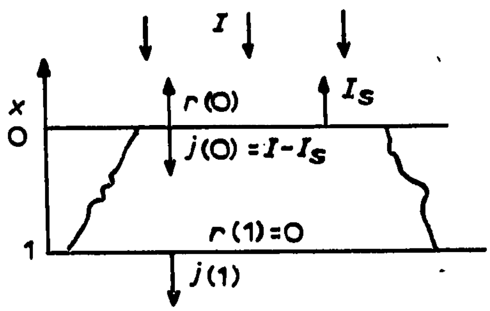

Fig. 2. Schematic diagram of light distribution at the surfaces of a plane parallel scattering medium. I = Illuminating flux; I_S = surface reflected flux; r = diffusely reflected component; j = forward travelling flux.

The transmittance of the medium (A_T) is defined as the ratio of the light intensity $j(1)$ leaving the far end of the medium and the incident light $I(0)$. Applying eqns. 2 and 3 we obtain:

$$A_T = \frac{j(1)}{j(0)} = \frac{v(1) + i(1)}{v(0) + i(0)} = \frac{2v(1)}{v(0) + i(0)} \tag{4}$$

In an analogous way we obtain for reflectance (A_R):

$$A_R = \frac{r(0)}{j(0)} = \frac{v(0) - i(0)}{v(0) + i(0)} \tag{5}$$

(2) THE INPUT–OUTPUT REPRESENTATION

A transmission line can be considered as a special case of a three-terminal electrical network. The response of such a network to an applied electrical signal is completely specified by a set of input–output parameters without knowing its internal set-up. The network itself may then be considered as a black box with unknown content.

For a transmission line the most convenient set of parameters specifying the input–output behaviour of the network is: the characteristic impedance ζ_0, the propagation constant γ and the reflection coefficient ϱ. ζ_0 and γ can be expressed in terms of the electrical parameters of the line; in our case, where the line is homogeneous and purely resistive, these reduce to the total longitudinal resistance R and transversal conductance G. It may easily be shown that

$$\zeta_0 = \sqrt{\frac{R}{G}} = \sqrt{\left(\frac{2S + K}{K}\right)} \tag{6}$$

$$\gamma = \sqrt{RG} = \sqrt{\{K(2S + K)\}} = K\zeta_0 \tag{7}$$

ζ_0 is defined as the impedance of a line of infinite length. Another, but equivalent, definition states that ζ_0 is the impedance seen at the one end of a line of finite length if this is terminated at the other end by an impedance equal to ζ_0. The line is then said to be matched. γ is the logarithm of the ratio of output to input voltage under matched conditions. On a resistive line γ determines only the amplitude relations, that is the attenuation of the line. In the general case it would also specify its phase properties.

The coefficient of reflection ϱ is determined by the characteristic impedance ζ_0 and the load impedance ζ_L. Under matched conditions $\varrho = 0$ and no reflection occurs. As is evident from eqn. 3 the load impedance in our case is equal to 1.

$$\varrho = \frac{\zeta_L - \zeta_0}{\zeta_L + \zeta_0} = \frac{1 - \zeta_0}{1 + \zeta_0} \qquad (\zeta_L = 1) \tag{8}$$

The meaning of the reflection coefficient ϱ is best understood and eqn. 8 verified from the simple diagram in Fig. 3.

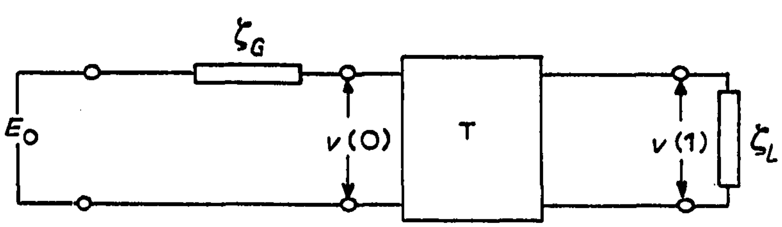

Fig. 3. Explanation of the reflection coefficient. T = network equivalent to the line with attenuation; ζ_G = generator impedance; ζ_L = load impedance.

The characteristic impedance ζ_0 is by definition the impedance seen at the input, if the network is terminated by ζ_0. Since the network considered here is bidirectional, the impedance seen at any terminal equals ζ_0, if the other one is terminated by an impedance equal to ζ_0. Let us now assume that $\zeta_G = \zeta_L = \zeta_0$. Under these conditions we have evidently $v(0)_M = E_0/2$ and $v(1)_M = v(0)\cdot e^{-\gamma}$, the index M indicating the matched condition.

Let us now consider a mismatch at the load terminal with $\zeta_L \neq \zeta_0$. Looking to the left into the network from the load terminals we see all the time the impedance ζ_0, since the generator terminal is still matched. Putting for the moment $\gamma = 0$, the whole diagram reduces to a simple voltage divider, the output voltage becoming

$$v(1) = E_0 \frac{\zeta_L}{\zeta_L + \zeta_0} \tag{9}$$

This voltage can be considered as the sum of a forward component equal to $v(1)_M$ and a reflected component $v(1)_R$ travelling in the backward direction.

$$v(1) = v(1)_M + v(1)_R = E_0 \frac{\zeta_L}{\zeta_L + \zeta_0} = \frac{E_0}{2}\left(1 + \frac{\zeta_L - \zeta_0}{\zeta_L + \zeta_0}\right) = \frac{E_0}{2}(1+\varrho) \tag{10}$$

Now let us consider the effect of attenuation. For $v(1)$ we obtain evidently:

$$v(1) = \frac{E_0}{2} \cdot e^{-\gamma}(1+\varrho) \tag{11}$$

The situation is more involved at the input. For $\gamma = 0$ we evidently have $v(0) = v(1)$. With $\gamma \neq 0$, $v(0)$ is again the sum of the forward component $v(0)_M$ and the component reflected at the load terminal. Travelling back to the input, the latter is attenuated by a factor $e^{-\gamma}$. This results in

$$v(0)_R = v(1)_R \cdot e^{-\gamma} = \frac{E_0}{2} \cdot \varrho \cdot e^{-2\gamma}$$

$$v(0) = v(0)_M + v(0)_R = \frac{E_0}{2}(1 + \varrho \cdot e^{-2\gamma}) \tag{12}$$

Similar reasoning applies to the current values. They too may be considered as the sum of a forward and a reflected component. For the matched case we have:

$$i(0)_M = E_0 \frac{1}{2\zeta_0}$$

$$i(1)_M = E_0 \cdot \frac{1}{2\zeta_0} \cdot e^{-\gamma} \tag{13}$$

In the general case we obtain:

$$i(1) = i(1)_M + i(1)_R = \frac{v(1)}{\zeta_L} = E_0 \cdot e^{-\gamma} \cdot \frac{1}{\zeta_L + \zeta_0} = \frac{E_0}{2\zeta_0} \cdot e^{-\gamma}(1-\varrho) \tag{14}$$

$$i(0) = i(0)_M + i(0)_R = \frac{E_0}{2\zeta_0}(1 - \varrho \cdot e^{-2\gamma}) \tag{15}$$

It should be noted that in the model all reflection takes place at the load terminals, whilst in the optical medium reflection occurs throughout the medium.

It may also be worth mentioning that the relations above are usually derived in a straightforward way from the differential equations of the general transmission line problem. It is felt, however, that the approach chosen here is more illustrative for the reader, who is not familiar with electrical transmission line theory. It should be kept in mind that the forward component and the reflected wave are not mere mathematical fictions, but real entities. In most cases they are accessible to direct measurements, though this does not apply to the purely resistive line, which represents a degenerate condition.

(3) REFLECTANCE AND TRANSMITTANCE IN TERMS OF LINE PARAMETERS

Following the brief comments above it now remains to express eqns. 4 and 5 in terms of the parameters which were just introduced. First we wish to define the limiting values which ζ_0 may assume. From eqn. 6 it follows that

$$1 \leqslant \zeta_0 \leqslant \infty \tag{16}$$

Remembering that in our case $\zeta_L = 1$, we obtain for ϱ:

$$-1 \leqslant \varrho \leqslant 0 \tag{17}$$

Further we can write

$$v(0) + i(0) = \frac{E_0}{2}\left\{1 + \frac{1}{\zeta_0} + \varrho \cdot e^{-2\gamma}\left(1 - \frac{1}{\zeta_0}\right)\right\}$$

$$= \frac{E_0}{2\zeta_0}(1 + \zeta_0)(1 - \varrho^2 \cdot e^{-2\gamma}) \tag{18}$$

$$v(0) - i(0) = \frac{E_0}{2}\left\{1 - \frac{1}{\zeta_0} + \varrho \cdot e^{-2\gamma}\left(1 + \frac{1}{\zeta_0}\right)\right\}$$

$$= \frac{E_0}{2\zeta_0}(1 + \zeta_0) \cdot \varrho\,(e^{-2\gamma} - 1) \tag{19}$$

$$A_T = \frac{v(1) + i(1)}{v(0) + i(0)} = \frac{e^{-\gamma}(1 + \varrho)}{1 - \varrho^2 \cdot e^{-2\gamma}} \cdot \frac{2\zeta_0}{1 + \zeta_0} = \frac{e^{-\gamma}(1 - \varrho^2)}{1 - \varrho^2 \cdot e^{-2\gamma}} \tag{20}$$

$$A_R = \frac{v(0) - i(0)}{v(0) + i(0)} = -\varrho\,\frac{1 - e^{-2\gamma}}{1 - \varrho^2 \cdot e^{-2\gamma}} \tag{21}$$

Eqns. 20 and 21 are very general. For many cases of practical interest, however, they can be considerably simplified, as will be shown in a future publication[8].

(4) IMPLEMENTATION OF THE MODEL

The implementation of a model of a general transmission line, the electrical parameters of which should be variable and distributed over the whole physical length of the line, is rather difficult. In order to build a model with purely resistive parameters, sheets of resistive material, semiconductive plastics or thin- or thick-film technics may be used; the problem therefore becomes somewhat easier. Even for this case, however, it appears that a model with lumped parameters is preferable; this means a model in which the electrical parameters, normally distributed over the length of the line, are concentrated in the form of resistors etc. A model of this type, however, can only approximate the real case with distributed values.

The most common representation of a transmission line by a lumped parameter network is a so-called T or Π ladder configuration. A T-equivalent is shown in Fig. 4. The branch impedances are here of course again pure resistances. In first order approximation they may be chosen equal to the series and shunt impedance of the line. The error committed in this way in the characteristic impedance and the propagation constant of the model as compared to the line is approximately[9]:

$$\zeta_0 = \sqrt{(\zeta_1 - \zeta_2)} = \zeta_{0T}\left(1 - \frac{\gamma_0^2}{8}\right)$$

$$\gamma_0 = \sqrt{\frac{\zeta_1}{\zeta_2}} = \gamma_{0T}\left(1 + \frac{\gamma_0^2}{24}\right) \tag{22}$$

The index T refers to the corresponding characteristic value of the T-approximation. A Π-network using the same values results in errors of approximately the same size but of opposite sign.

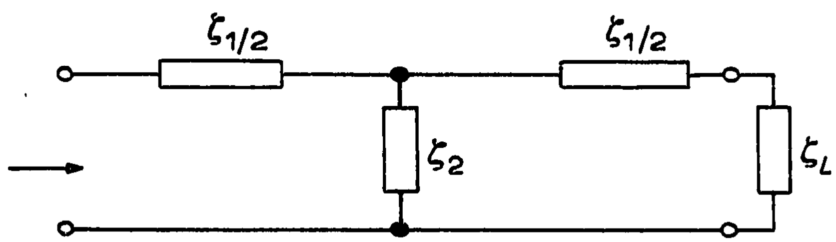

Fig. 4. Lumped T-approximation to a transmission line. $\zeta = R = 2S + K$; $\zeta_2 = 1/G = 1/K$; $\zeta_L = 1$.

For larger values of γ_0 the error becomes rather significant. To reduce it, corrections may be applied to the values of ζ_1 and ζ_2, which are illustrated in eqn. 23.

$$\zeta_1 = \zeta_0 \frac{e^{\gamma_0} - 1}{e^{\gamma_0} + 1}$$

$$\zeta_2 = \frac{\zeta_0^2 - \frac{\zeta_1^2}{4}}{\zeta_1} \tag{23}$$

For the purposes envisaged in this application these corrections do not result in a convenient procedure of implementing the model; a better way of reducing the deviations of the model from the continuous line is to build the model from individual sections each representing a relatively short length of the line. The number of sections n should be chosen so that, depending upon the permissible overall error in γ, the propagation constant of the individual sections γ_s is $\leqslant 0.5$. For the parameters of the individual section we then obtain the relations:

$$\zeta_{1s} = \frac{\zeta_1}{n} \qquad \gamma_s \simeq \frac{\gamma_0}{n}$$

$$\zeta_{2s} = \zeta_2 \cdot n \qquad \zeta_{0s} \simeq \zeta_0 \tag{24}$$

The error in characteristic impedance of the model is then determined by the value of γ_s according to eqn. 22. The error in propagation constant is determined, however, by the sum of the errors of the individual sections. For this reason n has to be chosen larger than at first might appear from eqn. 22. The schematic diagram of such a multisection model is shown in Fig. 5.

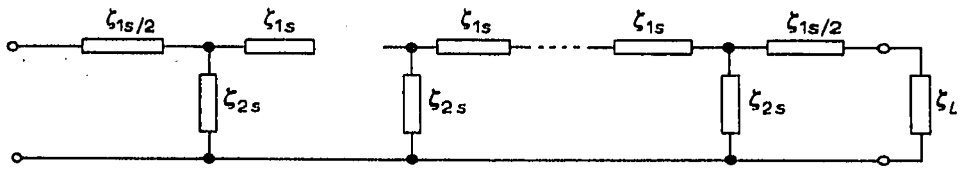

Fig. 5. A multisection transmission line model.

For our purposes the variable ΔK in the model should be represented both in the series and the shunt arms of the model according to Figs. 4 and 5 by independent variable resistances (see Fig. 6).

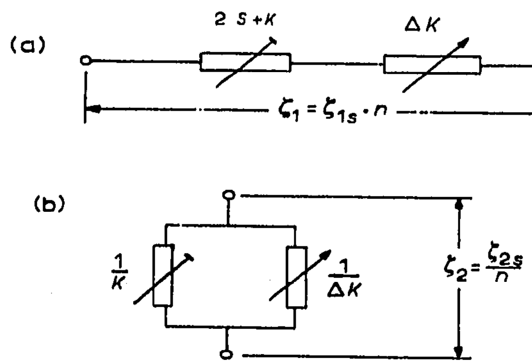

Fig. 6. The representation of the increment in absorption in the model.

ΔK is of course the increment in absorption due to the chromogen on the chromatogram. The elements marked with a ——| are to be set at the beginning of the measurement according to the optical parameters of the medium itself. The procedures for determining them will be described in a following paper[8].

Elements of the same type in all the sections should be mechanically coupled together so that a common control element may be used for adjustment.

Elements marked with an arrow ——→ (representing ΔK) are to be adjusted during the measurement so that the values read on the model agree with the optical results obtained (see Section 6). The value of ΔK, corresponding to a given change in transmittance or reflectance, is read on a common dial. If required, automatic setting by a servo-follower system is feasible.

(5) MODELS WITH A SMALL NUMBER OF SECTIONS

The number of sections required in a model of this type to simulate the optical transmission of media with high optical density becomes very large. For example, when simulating a medium with optical density 3.4 (Whatman No. 3 paper), γ becomes of the order of 6 to 8. To keep the error small, the value of γ_s per section has to be small also. Assuming a value of $\gamma = 0.25$ per section, then 25 to 30 sections are required. Though models of this size are technologically perfectly feasible, the large number of variable elements ganged together makes them cumbersome and costly. The difficulties increase if automatic and high-speed adjustment of the model is required. This would be the case, for example, if the model were to be incorporated into a scanning photodensitometer, in order to provide for a linear dependence of the output signal upon ΔK. In such a case digital modelling of eqns. 13 and 14 would seem to be the method of choice. On- or off-line digital modelling may be performed on almost any type of digital computer. On-line modelling, however, would require much computer time and in most cases this would be considered excessive. Digital modelling requires that the output data of the photodensitometer or reflectometer be available in digital form. Very few of the currently available instruments are so equipped and only a few laboratories possess the necessary accessories for digital conversion and storage of the analogue signal. This is one of the reasons why the experimental photodensitometer now being developed in our laboratories will be equipped with both a digital and an analogue output.

For media of medium and low optical density, perhaps up to a γ value of 3.2 (that is approx. 1.4 in decimal units) a multisection transmission line model of the type described seems to be quite adequate. Assuming eight sections with a transfer constant $\gamma_s \simeq 0.4$ per section, the overall error in γ is below 5%. The error in ζ_0 is about 2%; this means, that the error in ϱ may be neglected.

It should be noted that the optical density of the medium is not exclusively determined by $e^{-\gamma}$, but contains also a term dependent upon the reflection coefficient ϱ. In a medium with high scattering power such as paper, $1 - \varrho^2$ becomes small and this term may then contribute up to about one optical density unit to the density of the medium. This means that for media of this type the model described may be adequate up to an optical density value of approximately 2.5 decimal units. For reflectance measurements the value of ϱ alone is all important if γ exceeds the value of approximately 2.5 (see eqn. 21). Because of this we may conclude that a model with about eight sections is adequate for simulating the reflectance of a medium with any optical density, since ϱ is represented with satisfactory accuracy.

For high-speed on-line analog simulation of the effect of changes in absorbance of the medium, electronic techniques for adjusting ΔK and $1/\Delta K$ have to be employed. For a limited number of sections this approach need not be too costly, since relatively inexpensive switching modules in integrated design are now available. To adjust the transversal impedance $1/\Delta K$, one end of which is grounded, a simple counting circuit can be used. More difficulties are encountered with the longitudinal impedance ΔK, which is floating. A transistor operated reed relay arrangement probably represents the simplest solution. This should allow for speeds of adjustment of the order of milliseconds, and for most practical purposes this ought to be sufficient.

There are several special cases, however, quite frequently encountered in practice, where relatively simple special purpose circuits may be employed. An important application, which has already been mentioned, is the linearisation of the output of reflectometers and densitometers. If we are content with a limited range of applicability, these circuits are simpler and less expensive than digital instrumentation. These aspects will be described in detail in another paper to be published soon.

(6) THE MEASUREMENT OF TRANSMITTANCE OR REFLECTANCE ON THE ELECTRICAL MODEL

To measure the transmittance or reflectance of a certain medium using the model, we have first to set the basic model parameters to the corresponding optical values S and K of the blank medium. How these are to be determined will be described in a later publication. The elements to be set in this way at the beginning of the measurement are marked in the figures by —|. The variable elements representing an increment in absorbance ΔK are marked by ——›, and these are to be set in the zero position.

The actual measurement is done in accordance with the definitions set out in the right-hand part of eqns. 4 and 5. To simplify the procedure, $v(0) + i(0)$ is kept constant at a value E.

$$v(0) + i(0) \cdot 1 = E$$

$$A_T = \frac{j(1)}{j(0)} = \frac{v(1) + i(1)}{v(0) + i(0)} = \frac{2v(1)}{E}$$

$$A_R = \frac{r(0)}{j(0)} = \frac{v(0) - i(0)}{v(0) + i(0)} = \frac{v(0) - i(0)}{E} \tag{25}$$

To measure these values, the arrangement shown in Fig. 7 may be used. The transmission line model is here shown just as a black box M.

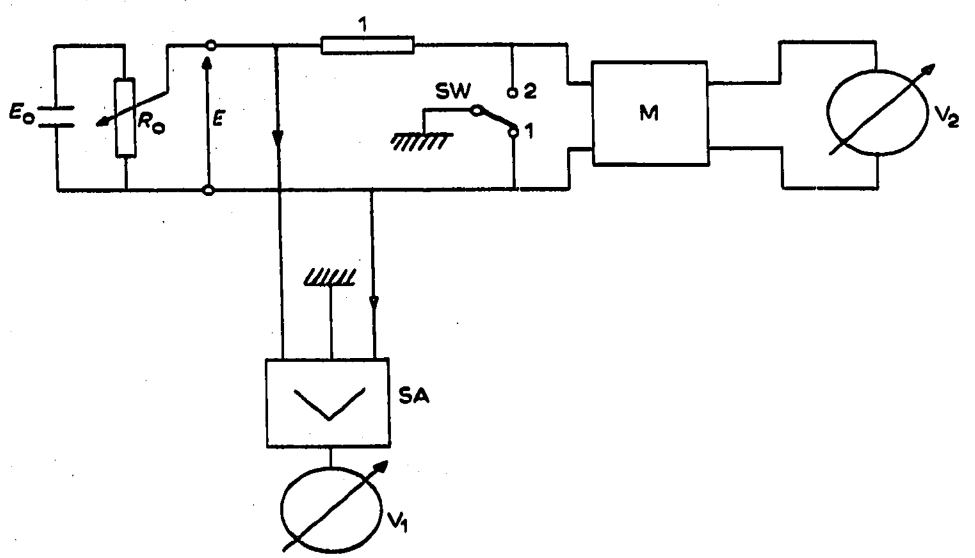

Fig. 7. Block diagram of the procedure for measuring A_T and A_R. SA = summing amplifier; M = transmission line model; SW = transmission–reflection measurement switch.

The circuit operates in the following way: first the variable parameters of the model have to be adjusted to the required values. Then with switch SW in position 1 the potentiometer R_0 is adjusted to give the reading 1 unit at meter V_1. This sets in eqn. 25 $E = 1$; meter V_2 immediately reads the value of $A_T/2$. For measuring A_R switch SW is now brought into position 2. Meter V_1 then indicates the value of A_R under investigation. The gain of the summing amplifier SA also of course has to be considered in the calibration of the instruments; it is here assumed to be unity.

An actual fact of much more importance is the inverse procedure. Here the elements of the model marked with —| (see Fig. 6) are set to represent the basic optical parameters of the medium. The elements modelling ΔK (marked —→) (see Fig. 6) are then varied, until the change in transmittance or reflectance measured on the medium is reproduced on the model. The corresponding value of ΔK is then read on the calibrated dial for these elements.

(7) CONCLUSIONS AND EXTENSIONS

It is hoped that the modelling approach described in this paper will represent a helpful and convenient procedure for solving, in terms of incremental absorbance, the transfer equations of a class of optical media for which the KUBELKA AND MUNK theory is valid. By replacing the resistances of the model by complex valued impedances, wavelength dependences of the optical parameters may to a certain extent be considered. A further possible extension of the method could be two- and three-dimensional models using semiconductive surface and volume conductors. In this way it might be possible to consider a certain degree of anisotropy of the medium. In general the application of the highly developed theory of homogeneous and non-homogeneous electrical transmission lines may become a helpful tool for the treatment of more complex and involved optical situations.

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