

Applied Spectroscopy 0(0) 1–13 © The Author(s) 2017 Reprints and permissions: sagepub.co.uk/journalsPermissions.nav DOI: 10.1177/0003702817694182 journals.sagepub.com/home/asp



Diffuse Reflectance Spectroscopy of Hidden Objects, Part I: Interpretation of the Reflection–Absorption-Scattering Fractions in Near-Infrared (NIR) Spectra of Polyethylene Films

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Abstract

Investigation of a sample covered by an interfering layer is required in many fields, e.g., for process control, biochemical analysis, and many other applications. This study is based on the analysis of spectra collected by near-infrared (NIR) diffuse reflectance spectroscopy. Each spectrum is a composition of a useful, target spectrum and a spectrum of an interfering layer. To recover the target spectrum, we suggest using a new phenomenological approach, which employs the multivariate curve resolution (MCR) method. In general terms, the problem is very complex. We start with a specific problem of analyzing a system, which consists of several layers of polyethylene (PE) film and underlayer samples with known spectral properties. To separate information originating from PE layers and the target, we modify the system versus both the number of the PE layers as well as the reflectance properties of the target sample. We consider that the interfering spectrum of the layer can be modeled using three components, which can be tentatively called transmission, absorption, and scattering contributions. The novelty of our approach is that we do not remove the reflectance and scattering effects from the spectra, but study them in detail aiming to use this information to recover the target spectrum.

Keywords

Near-infrared diffuse reflectance spectroscopy, NIR, multilayer systems, reflectance, scattering, polyethylene films, spectrum recovery, multivariate curve resolution, MCR

Date received: 7 October 2016; accepted: 24 January 2017

Introduction

Investigation of properties of samples through layers of materials of various thickness is increasingly in demand for process control in pharmaceutical and chemical industries, ^{1,2} for confirmation of quality of the end products,³ for non-invasive biochemical analysis⁴, for the development of new methods of investigation of biological objects^{5,6} and for many other applications. Near-infrared (NIR) spectroscopy is well suited for these purposes as a beam of light penetrates the sample material several millimeters, scatters inside, and reflects back, carrying information regarding chemical and physical properties of the material. Moreover, NIR measurements are rapid and need no special sampling preparation. The collected spectra carry mixed information about the layers of the covering material and the target sample; hence, the challenge of separating

information originating from the cover and from the target is of great importance.

When routine measurements are conducted using rather thin polymeric bags or films with more or less constant thickness, i.e., for investigation of small quantities of powders specially packed in polyethylene (PE) bags, spectral analysis does not encounter any problems caused by the packaging.^{7–9} It is a different story when one needs to

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analyze samples through several layers of PE, i.e., conduct input control of packed raw materials in a warehouse.¹⁰

In general terms, the problem is very complex. To solve it, we start with the particular problem of analyzing the system, which consists of several layers of PE film and an underlayer sample with known spectral properties. Polyethylene films are widely used for packaging and protection of different objects, and the solution of this particular problem has a significant practical meaning. To separate the information originated from the PE layers of an unknown thickness and the determined target, it is necessary to understand how a spectrum of the sample varies by the number of PE layers/thickness, and the reflectance properties of the target sample covered by the PE layers.

The penetration of NIR light through PE layers,^{1,11} or, in general, into a turbid medium has already been studied by various authors.^{12,13} For the interpretation of the acquired spectra, it is necessary to understand the phenomena that take place in the sample during irradiation such as transmission, absorbance, and scattering/remission. There is a large body of literature devoted to this issue. In various studies, different theories and levels of abstraction are applied. For example, Mie scattering¹⁴ relates primarily to the scattering of radiation by isolated spherical particles. Classical radiative transfer equation (RTE)^{15,16} describes absorbance and scattering in terms of particles and ensembles of particles. Many other approaches, e.g., the Kubelka-Munk approach,^{17,18} are approximations of RTE. The representative layer theory¹¹ shows that a sample composed of a series of distinct layers can be modeled straightforwardly and accurately using a discontinuous theory. Detailed descriptions of various theories are discussed in special papers and handbooks and may be found elsewhere. $^{19-23}$ In almost all studies, the authors tried to separate scattering and absorption effects mathematically, or through a combination of theoretical approaches with various experimental set-ups.²³⁻²⁵ The information depth approach²⁶ is a more formal one. It was shown that the information curve clearly describes properties of the PE spectrum. However, these information curves were constructed mainly for several specific wavelengths.

The goal of this paper is to describe the dependence of PE spectra variations on the number of layers and on the reflectance factor of an underlayer covered by the PE films. The second part of the study is devoted to applications of the proposed approach to reconstruction of the target sample spectrum measured through the PE films. The distinguishing features of our research are: (1) the empirical approach; (2) the analysis of the whole spectrum behavior rather than changes at specific wavelengths; and (3) the variation of the number of PE layers and the underlayer reflectance factor for data collection.

Constrained multivariate curve resolution-alternative least squares (MCR-ALS) is used as a mathematical tool for the sequential spectra deconvolution.

Methods

General Considerations

In spectroscopic measurements, a detector collects only a fraction of incident photons. Some of them are lost due to absorption and scattering in the medium, or leave the medium in unfavorable directions. The collected fraction can be determined if either the exact or an approximate RTE is solved. However, in order to predict experimental results, we still need to account for the device-specific coefficients like source and detector apertures, stray scattering etc., which are hard to obtain. These data also contain uncertainties, so the total analytical problem can easily become excessively complex. Thus, in our approach, we completely abandon any attempts to solve the equations. Instead, we are going to approximate the measurable spectral properties directly, while considering the physics of light propagation in medium.

If we consider a stationary non-radiating medium, the corresponding RTE is an integral-differential equation, the solution of which depends on two sets of medium properties: microscopic properties and macroscopic properties. The former characteristics comprise specific probabilities $\kappa(\lambda)$ and $\sigma(\lambda)$ of absorption and scattering, per unit volume, or per unit length. They enter into the RTE as coefficients, which depend on the wavelength λ (photon energy). In terms of RTE, the medium can be characterized by two terms. The negative extinction term, $-(\kappa(\lambda)+\sigma(\lambda))$, determines the overall loss of intensity of any photon flux. Some of the photons may scatter again and return back to the flux, yielding the positive scattering term, which is proportional to $\sigma(\lambda)$. Macroscopic properties are physical dimensions of the medium layer, the light source/detector apertures, and the relative position of the source and the detector. In terms of RTE, they determine the boundary conditions and integration limits. In this study, it is of primary importance that: (1) microscopic properties depend on the wavelength, while macroscopic do not; (2) two microscopic properties $\kappa(\lambda)$ and $\sigma(\lambda)$ have different dependence on wavelength and produce different effects on the solution; and (3) macroscopic properties do not depend on microscopic properties; in case of a homogeneous medium, the reverse is also true.

Regarding the light source, the detector can be located on the opposite side of the sample (transmittance mode, TM), or it can be located on the same side (diffuse reflectance mode, DR). In the first case, the captured signal comprises the transmitted fraction (truly transmitted or ballistic photons, and forward-scattered photons), while the reflected fraction (back-scattered photons) is lost. In the second case, conversely, the transmitted photons are lost and only the reflected fraction is registered. The absorbed and side-scattered photons are not captured by the detector, thus these effects can be modeled only theoretically or empirically. In this paper, we focus on the DR mode. Here, the signal captured by the detector is called reflectance, R. It varies from 0, which means "no reflection," until 1 (or 100%), which means "full reflection." We refer to spectral readings presented in these units as R-domain. These values are very often converted using logarithmic transformation, $X = -\ln(R)^a$), into "absorbance units," or optical density, which are referred to as A-domain. In the A-domain, signal X varies from 0, which corresponds to full reflectance, R = 1, to infinity, when R = 0. In this paper, we model measurements in the A-domain, for a number of reasons which will be explained later. Since the microscopic and macroscopic properties of the layer are independent, it is convenient to approximate the acquired DR spectra by a generalized limited series expansion:

$$X(r,h;\lambda) = \sum_{k=1}^{K} c_k(r,h) \cdot s_k(\lambda) + \dots$$
(1)

In Eq. 1, r is the reflectance factor of the surface of a substance, which lies under the medium (underlayer). This coefficient varies from r = 0 (no reflection, e.g., black body or void space) to r = 1 (full reflection, e.g., mirror). The thickness of the layer is h; c_k are coefficients that depend only on macroscopic properties; s_k are coefficients that depend only on λ via probabilities $\kappa(\lambda)$ and $\sigma(\lambda)$; and K is the number of terms.

By increasing K, we can bring Eq. I very close to the exact solution of RTE. However, in practice, the number of terms is dictated by uncertainties of the measurement. The expansion given by Eq. I is abstract and highly ambiguous. We are going to make it more specific by pursuing two goals: finding the approximation with the least number of terms, and selecting c and s which have physical meaning in the limiting cases.

Let us consider a situation, when both $\kappa(\lambda)$ and $\sigma(\lambda)$ are small, and develop the first approximations in Eq. I. In the zero-order approximation of the RTE solution, when $\kappa(\lambda) = \sigma(\lambda) = 0$, and the layer is completely transparent, the measured DR spectra comprise:

$$X^{(0)}(r,h;\lambda) = c_0(r,h) + \dots$$
(2)

This measure is typically set to c_0 (r=1, h=0)=0 through calibrating the measurements of an ideal diffuse reflector. In general, this term depends on h, because the source/detector apertures change with h; however, in well-designed instrumentation this dependence is weak.²⁸ The zero-order term does not depend on the wavelength λ .

At the next step of the approximation, we account for the extinction in the layer, but ignore the positive scattering input. In this case, all the fluxes in the medium decay exponentially. In the A-domain, the exponentials of h are close to linear functions. Just that very fact explains the convenience of the A-domain:

$$X^{(1)}(r,h;\lambda) = c_0(r,h) + c_1(r,h)(\kappa(\lambda) + \sigma(\lambda)) + \dots$$
(3)

For a homogeneous non-scattering layer, $c_1(h)$ is proportional to h; for collimated light and mirror reflectance it further reduces to the Bouguer-Lambert law, so that $c_1(h) = 2h$.

For the next approximation, we should account for the light, which is scattered towards the detector. Here we ignore the secondary scattering and absorption of the scattered radiation; therefore, the new term depends on $\sigma(\lambda)$ only. This term is negative in the A-domain, as it corresponds to the increase in the reflected light:

$$X^{(2)}(r,h;\lambda) = c_0(r,h) + c_1(r,h)(\kappa(\lambda) + \sigma(\lambda)) - c_2(r,h)f(\sigma(\lambda)) + \dots$$
(4)

After regrouping the absorption and scattering terms in Eq. 4, we obtain a bi-linear three-component model:

$$X(r,h;\lambda) = c_t(r,h)s_t + c_a(r,h)s_a(\kappa(\lambda)) + c_s(r,h)s_s(\sigma(\lambda)) + \dots$$
(5)

In Eq. 5, $c_t = c_0$, $s_t \equiv 1$. Spectra s_a and s_s represent contributions from absorption and scattering. Coefficients c_a and c_s can be viewed as virtual optical depths for these two phenomena. It should be noted that in the presented definition, $c_{a,s}$ and $s_{a,s}$ are non-negative. For very small values of $\kappa(\lambda)$ and $\sigma(\lambda)$, Eq. 5 should be close to the Taylor series expansion of the true solution. For an optically thin layer (small h, or small $\kappa(\lambda)$ and $\sigma(\lambda)$, or both), only the first order terms survive. Therefore, we obtain the following limiting relation:

$$X(r,h; \lambda) \approx -\ln(r) + D_1 \kappa(\lambda)h + D_2 \sigma(\lambda)h$$
(6)

where D_1 and D_2 are constants. Eq. 6 means that $s_a \approx \kappa$, and $s_s \approx \sigma$, and $c_a \approx c_s \approx h$. Additionally, we ignore the dependence of c_t on h, because we assume that the source and detector apertures are well matched. In conventional transmittance spectroscopy, the weighting factors c are linear functions of the concentrations and the optical depth is proportional to physical thickness (Beer's law). However, as soon as we agreed to drop the idea to calculate c and s in Eq. 1, we have to abandon the linearity between the optical depth and thickness of the layer, and treat $c_k(h, r)$ and $s_k(\lambda)$ as empirical functions, which have the limits given by Eq. 6. We consider that flexibility of $c_k(h, r)$ and $s_k(\lambda)$ can potentially account for a very broad range of effects. Moreover, we can add more terms to Eq. 5 to increase the accuracy of the model. However, as demonstrated

below, three components are sufficient to model the DR spectra.

The significance of the three-component model can be explained in relation to the three elementary processes of photon transport at microscopic level-propagation (transmission, ballistic transport), absorption, and scattering. Each of these processes depends on λ differently, therefore at least three terms in Eq. I should be kept to describe these spectral effects. We denote the components in Eq. 5 as transmission (t), absorption (a), and scattering (s) terms, correspondingly. Using the terminology of the conventional MCR approach, we can view a DR spectrum of scattering layer as a mixture of three spectrally different components, which independently transmit, absorb, and scatter the incident light, while their "concentrations" depend nonlinearly on h and r to compensate for the actual dependences of these three processes. More components in Eq. 5 may be required when approximate factorization of scattering and absorption is not possible. The prerequisites for such cases will be addressed in the future work.

It is very unusual to keep the transmission component $X^{(0)} = c_t s_t$ in Eq. 5 in multivariate spectral analysis, so we discuss this in more detail. It is worth mentioning that conventional transmittance is understood as intensity of the incident light captured by the detector in the transmittance mode. Here, transmittance depends on scattering and absorption, and thus it depends on wavelength. In our study, the transmission component corresponds to the ballistic photons that did not undergo interactions inside the layer, so the respective term does not depend on wavelength. However, because of the empirical extension of Eq. 5 to optically thick multilayer samples, $X^{(0)}$ will also account for the constant parts of the processes that do not depend on λ in the selected wavelength region (e.g., wavelengthindependent part of reflectance at the air-polymer interfaces). In practice, $X^{(0)}$ manifests itself as a baseline shift that is routinely removed by a well-known¹⁹ pre-processing operation:

$$\tilde{x}(\lambda, h) = x(\lambda, h) - \min x(\lambda, h).$$
(7)

The benefits of keeping this component in Eq. 5 are clarified in the following sections. Here we can only claim that $X^{(0)}$ has the most profound relation to the sample reflectance factor, which is very important for the interpretation of the PE layer spectra. We have already explained that the reflectance factor, r, belongs to the R-domain and it varies from r = 0 (no reflection) to r = 1 (full reflection). Therefore, $X^{(0)}$ varies from zero (no transmission, complete reflection) to infinity (full transmission, no reflection). At the end of this paper, we demonstrate that

$$r = \exp\left(-X^{(0)}\right) \tag{8}$$

Equation 5 can be readily recognized as a multivariate curve resolution problem.²⁷ It should be emphasized that this approach can be effectively applied only when a number of the diffuse reflectance spectra of samples with variable thickness *h* is available. In this case, we can use the first order advantage²⁹ and decompose the acquired spectra into different components using MCR-ALS as a tool for deconvolution.

Multivariate Curve Resolution–Alternative Least Squares

Multivariate curve resolution–alternate least squares is an iterative method of data $\operatorname{processing}^{27,30}$ that is based on model bi-linearity

$$\mathbf{X} = \mathbf{C}\mathbf{S}^{\mathrm{t}} + \mathbf{E} \tag{9}$$

Here, **X** is the $(I \times J)$ matrix that contains spectra of I samples recorded for J wavelengths. **C** is the $(I \times N)$ matrix of the component concentrations and **S** is the $(J \times N)$ matrix of "pure" spectra. N is the number of pure components in the system. **E** is the $(I \times J)$ matrix, which contains variations not explained by the model.

The ALS procedure consists of two types of steps, the C-type step and the S-type step, which are repeated until convergence. At the C-type step, the value of $\mathbf{S} \equiv \mathbf{S}_{hat}$ is fixed, and the **C** matrix is calculated using the unconstrained least squares (LS) estimator

$$\mathbf{C}_{\rm in} = \mathbf{X}(\mathbf{S}_{\rm hat})^+ \tag{10}$$

Here ⁺ means that the matrix is pseudo-inverse, i.e., $\mathbf{A}^+ = \mathbf{A}(\mathbf{A}^t \mathbf{A})^{-1}$. Afterwards, matrix \mathbf{C}_{in} is transformed into matrix \mathbf{C}_{hat} to incorporate the constraints for the concentration profile.

For the S-type step, the value of $\bm{C}\equiv\bm{C}_{hat}$ is fixed and matrix \bm{S} is found applying a similar LS estimator

$$\mathbf{S}_{\rm in} = \mathbf{X}^{\rm t} (\mathbf{C}_{\rm hat})^+ \tag{11}$$

Subsequently, matrix \mathbf{S}_{in} is transformed into matrix \mathbf{S}_{hat} to account for the spectral profile constraints.

All constraints are applied to give a physicochemical meaning to the LS estimates C_{in} and S_{in} and, where it is possible, to resolve rotation and/or scaling ambiguity. For example, there are natural non-negativity restrictions that force the concentrations and spectra to be equal to or greater than zero. Prior knowledge regarding some spectral components is a special type of constraint. Consider the case when matrix **S** consists of two parts: the known spectra **S**₁ and the unknown part **S**₂, i.e., **S** = {**S**₁, **S**₂}. In this case, Eq. 11 is replaced with the following equation:

$$\mathbf{S}_{\text{in}} = \left\{ \mathbf{S}_1, \quad (\mathbf{X} - \mathbf{C}_1 \mathbf{S}_1^{\text{t}})^{\text{t}} (\mathbf{C}_2)^+ \right\}$$
(12)

where C_1 and C_2 are the corresponding parts of the concentration matrix, i.e., $C = \{C_1, C_2\}$. A very special case is the one where all spectra are known. Then the MCR problem is solved in one C-step given by Eq. 10.

The application of MCR-ALS in the current study has several specific features. Usually, in order to start the iteration procedure, we have to know the number of components N and an initial approximation of matrix **S**. In our case, **S** comprises three "pure components," which are effective transmission, absorbance, and scattering coefficients, introduced earlier as spectra $s(\lambda)$ in Eq. 5. The NIR spectrum of PE has been reported in many papers,^{11,26} so the initial approximation is known from literature. Moreover, it is evident that matrix **C** is not really a concentration matrix, because we analyze samples made of the same material. The elements of **C** depend on the number of layers (thickness) of the PE sample. Therefore, we will refer to **C** as a weighting matrix.

To assess the quality of the MCR modeling of the spectral matrix \mathbf{X} , we calculate the relative lack of fit (LoF%) as follows:

$$LoF = \|\mathbf{X} - \mathbf{C}_{hat}\mathbf{S}_{hat}^{t}\| / \|\mathbf{X}\|$$
(13)

Experimental

Material

The material is a large sheet of low-density polyethylene of $87 \pm 4 \,\mu\text{m}$ thickness of household appliances grade. Small pieces of $5 \times 5 \,\text{cm}$ are cut off from the entire sheet and piled together to obtain samples with different number of PE layers. The number of layers is in the range of 1–48 and the overall corresponding thickness is in the range of 0.087–4.18 mm.

PE is a well-studied material with the main absorption bands around 8237 cm^{-1} (C–H, second overtone), 7184 cm^{-1} , 7062 cm⁻¹ (first overtone of C–H combinations), 5785 cm^{-1} , 5668 cm^{-1} (C–H, first overtone), and very intensive peaks around 4350 cm^{-1} , 4000 cm^{-1} (combinations of C–H stretch and bend modes found in CH or CH₂ groups). Even though our main goal is to analyze the entire spectrum, we also consider the behavior of specific peaks as well.

Measurements

The PE sheets are measured with a micrometer. A Fourier transform near-infrared (FT-NIR) spectrometer Nicolet 6700 (Thermo Fisher) with InGaAs detector was used for spectra acquisition in the range of $4000-12400 \text{ cm}^{-1}$, with resolution 8 cm^{-1} , and the number of scans is equal to 64. The region in the range of $12400-9000 \text{ cm}^{-1}$ is excluded as a low informative one. The region in the range of $4450-4000 \text{ cm}^{-1}$ is excluded due to early peak saturation.

As a result, the working range of $9000-4450 \text{ cm}^{-1}$ is used for the analysis of all spectral data.

The DR spectra were collected with the help of Thermo Scientific's SabIR reflectance probe. The probe is of a multifiber type with so-called salt and pepper configuration and the length of 1.5 m. The probe connected to the spectrometer using a Smart Near-IR FiberPort accessory. The powerful multi-lens optics of this accessory send a NIR beam into the optical fibers and efficiently focus the returned light onto the spectrometer detector. The probe tip geometry is of 45° normal to the sample, thus the majority of the specular light is not collected by the probe. The probe is fixed in the mounting. The PE samples are positioned on the mounting table pressed by a special heavy frame, which does not overlap with the probe bundle. The light source within the fiber probe accessory illuminates the samples from below (Figure SI, Supplemental Material). One set, called B 0.0, is collected with nothing on top of the PE layers. This collection corresponds to the zero reflection underlayer (black body). Four sets are acquired with various reference disks on the top. These disks represent a selection of diffuse gray standards, which are spectrally flat over a wide wavelength range (Labsphere, Inc.).³¹ Disk SRS-99, with a 0.99 reflectance factor, is used to collect data set B 1.0. Spectralon gray materials, SRS-80, SRS-40, and SRS-10 with reflectance factors of 0.80, 0.40, and 0.10, respectively, are used to acquire the spectra for data sets $B_{0.8}$, $B_{0.4}$, and $B_{0.1}$. Data set B 0.8 is used as a test set and all other data sets are used for training. The system is calibrated by taking reference scans. The 0.99 diffuse reflectance disk, SRS-99, is used as white light reflectance standard.

We also perform an additional experiment in the transmittance mode. The PE samples are placed in the compartment for the transmittance measurements and fixed with the help of a special holder. For reference spectrum, 64 scans of the empty compartment were used. The acquired spectra are collected in the *Trans* data set.

Spectra collected in experiment $B_{1.0}$ (see Figure 1a) show that the measured DR signal decreases along with the increase of the depth of the PE. The baseline shifts to a lower intensity as well. The highest spectrum corresponds to a one-layer sample and the lowest one corresponds to the 48-layer sample. The 30-layer sample can be considered as the first sample with an infinite optical thickness, as the signal does not change any more when the number of layers increases.

In experiment $B_0.0$ (see Figure 1b), we observe an opposite picture. For the one-layer sample, the beam goes through the sample with practically no absorption or remission, and, therefore, it is not registered by the detector. The spectrum of this sample is the lowest one in Figure 1b. As the PE depth grows, the signal increases along with it up until the 28-layer sample, afterwards the intensity does not change. Therefore,



Figure 1. DR measurements in the *R*-domain for the underlayers with (a) r = 1.0 and with (b) r = 0.0 reflectance factors. Arrows show the increase of the PE depth *h*.

the samples with more PE layers can be considered as optically thick.

For further analysis, all spectra are converted to the A-domain.

Results of the One-Component Multivariate Curve Resolution

Preprocessing

Let us consider data set $B_{1.0}$, obtained with a 100% reflectance underlayer. For illustrative purposes, four of such spectra are presented in Figure 2a. It is evident that we deal with a highly scattering material. Therefore, our first attempt is to eliminate this effect using conventional pre-treatment methods, such as multiplicative signal correction (MSC)³² or the standard normal variate (SNV).³² Multiplicative signal correction performed on the whole spectral region removes the evident baseline shift and transforms the spectra in such a way that the spectrum, which corresponds to a one layer sample, becomes very similar to the 30-layer one (see Figure 2b).

The SNV preprocessing leads to similar results. We can conclude that these preprocessing techniques do not match our goal. This result agrees with the conclusions of other analysts regarding a potential invalidity of application of MSC and SNV for scatter correction due to the assumption of constant scattering across the wavelength axis.^{21,25}

Our second attempt is to eliminate the baseline offset using the correction presented in Eq. 7. Each spectrum is individually shifted along the *y*-axes in such a way that its minimum becomes equal to zero (Figure 3).

Data Analysis

All data sets $B_{0.0}$, $B_{0.1}$,..., $B_{1.0}$ and *Trans* are preprocessed using the same offset correction as described above. After that, the MCR-ALS procedure with one component is applied to the spectra.

The quality of the MCR modeling is presented in Table 1, in the One-comp column. It can be seen that the approximation is not satisfactory for the DR data sets. The dependence of *c*-values on the PE thickness, *h*, is shown in Figure 4a. This dependence is clearly linear for Trans data set (line 3) at all h values. As to the DR measurements (curves 1 and 2), linearity holds for the small values of h, whereas for large h, the c-values tend to some limit. This is quite a straightforward result, as in TM measurements the optical pathway increases with h, so the losses in photon flux gradually increase. In DR measurements, the physical distance between the source and the detector is always the same, and once the layer becomes so optically thick that the photons do not effectively interact with its distant part, the signal does not change further. In particular, the samples with the PE depth greater than 2.5 mm should be considered as optically thick. At the same time, even this simple approach has helped us to presort samples of the packed pharmaceutical substances regarding to the number of the PE layers.^{33,35}

The low quality of MCR modeling can be explained by another essential problem that is observed for the PE spectra acquired in the DR mode. It can be noticed that the spectra of the various PE thicknesses not only differ in their intensities, but also change their shape. To present this fact, we consider the ratio of the heights of two selected



Figure 2. Four spectra (1, 10, 20, and 30 layers) in B_1.0 experiment. (a) Raw data and (b) data after the MSC.



Figure 3. Four spectra (1, 10, 20, and 30 layers) in $B_{1.0}$ data set after baseline correction.

spectral peaks. The first peak is observed at 5777.8 cm^{-1} and its height is labeled as *IP*. The second peak is near 5669.8 cm⁻¹ and its height is denoted as *sP* (see Figure 3). Figure 4b shows that in the DR mode the ratio *IP/sP* depends on the PE depth (curves I and 2 in Figure 4b). At the same time, in the transmittance mode (curve 3 in Figure 4b), we observe a stable ratio of these peaks.

Thus, we can assume that the structure of the acquired spectra is more complex than that we expected and more

Table I. Quality of data description. The LoF values obtained using various MCR procedures for different data sets. The last row $B_0.8$ is a test set

Data set	One-comp	MCR-3	MCR-2	MCR-I	MCR-0
Trans	2.5%				
B_0.0	5.2%	0.1%	0.2%	0.2%	0.4%
B_0.1	9.4%	0.1%	0.1%	0.2%	0.2%
B_0.4	9.7%	0.2%	0.2%	0.3%	0.3%
B_1.0	6.8%	0.3%	0.4%	0.4%	0.5%
B_0.8	8.5%				0.4%

pure components should be used in MCR-ALS for an accurate DR spectra approximation.

Results of the Three Component Multivariate Curve Resolution

Preprocessing

All DR spectra are transformed to the A-domain. No additional preprocessing is used.

Data Analysis

Each data set obtained in the DR mode ($B_0.0$, $B_0.1$, etc.) is processed separately. Afterwards the corresponding outcomes are compared. An acquired spectrum is considered as a linear combination of three pure spectra, s_1 , s_2 , and s_3 , which compose matrix **S**. The non-negativity constraints

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IP/sP (b) (a) С 3 2.0 2 1.6 1 PE depth, h PE depth, h 1.2 0 1 2 3 1 2 3 0

Figure 4. Comparison of data sets: (1) B_0.0, (2) B_1.0, (3) and Trans. (a) The c-profile versus the PE sample depth. (b) The ratio of the selected peak heights *IP/sP* versus PE depth.

are applied both to **S** and **C** matrices. To resolve the scaling ambiguity, the first component spectrum, \mathbf{s}_1 , is weighted to be close to 1. From Figure 4a, we see that the weighting factors \mathbf{c}_2 and \mathbf{c}_3 tend towards a constant level as the thickness of the PE sample *h* increases. Therefore, these vectors are scaled in such a way that they are equal to 1 for the last samples, where $h \gg 1$. In order to describe and separate the absorbance and scattering effects, each training data set, $B_0.0, \ldots, B_1.0$, is modeled according to a multi-stage procedure, given in Figure 5.

At the first stage, which is denoted as MCR-3, we consider that all three pure components are unknown. As a result, we achieve an essential improvement in the quality of the modeling (Table I, MCR-3) in comparison with a one-component MCR applied to the preprocessed data (Table I, One-comp). We also find out that spectrum s_1 is very close to constant in each data set. Therefore, at the second stage we fix vector $s_1 \equiv I$, and apply the MCR-ALS procedure again as it is given in Eq. 12. This step is called MCR-2 because only two components are unknown. The accuracy of data description is shown in Table I, column MCR-2.

The result of this stage is a set of vectors \mathbf{s}_2 . The most important finding is that all these spectra are very similar for all training data sets. Thus, independently of both the underlayer reflectance factor, and the PE thickness, we succeed in selecting two common pure spectra $\mathbf{s}_1 = \mathbf{I}$ and $\mathbf{s}_2 = \mathbf{s}_a(\lambda)$. The latter is the mean spectrum calculated over all training data sets. Therefore, at the next stage (MCR-1, Figure 5) these components are considered to be known.

Now, our goal is the assessment of the last component \mathbf{s}_3 . For this purpose, we keep constant two known spectra



Figure 5. Flow-chart of the multi-stage MCR-ALS procedure as applied to each data set.

in the **S** matrix, so that only one unknown component is sought. The scaling ambiguity is resolved in the same way as at the previous stage. The quality of modeling is presented in Table 1, column MCR-1. All spectra s_3 obtained from the training data sets are very similar, regardless of the reflectance factor of the underlayer as well as the thickness of PE. The averaged spectrum is denoted as $s_s(\lambda)$.

At the final stage, we apply MCR keeping all three spectra in the S-matrix fixed: $\mathbf{s}_1 = \mathbf{I}$, $\mathbf{s}_2 = s_a(\lambda)$, and $\mathbf{s}_3 = s_s(\lambda)$. At this step, only *c*-profiles are determined. The quality of the obtained modeling is presented in Table I, column MCR-0.

The concluding step in our modeling is validation. For this purpose, we use data set $B_0.8$ that does not participate in the multi-stage procedure. These spectra are analyzed using the MCR-0 method in which all spectral components **S** are fixed and only **C** components are estimated. The last row in Table I, column MCR-0, shows that LoF = 0.4%. It confirms that the test data set $B_0.8$ perfectly fits the developed three-component model. Certainly, this check cannot be considered as a full validation of the proposed approach. Proper testing involves spectra obtained with various real underlayers, which essentially differ from the standard disks employed in the model development. These investigations will be presented in the second part of this research.

In the multi-stage procedure shown in Figure 5, we successively fixed spectral components in the MCR calculations. These restrictions should impair the optimization results. Analyzing the outcome in Table I row by row, we conclude that the applied restrictions have, in fact, a rather small influence on the quality of the modeling. Therefore, we consider the obtained three spectra, \mathbf{s}_1 , \mathbf{s}_2 , and \mathbf{s}_3 , to be natural pure components, which are not burdened with artificial elements forcing them to fit the data.

Discussion

Pure Spectra

Analyzing the nature of the three pure spectra found in the multi-stage procedure (Figure 6), we can conclude that spectrum $\mathbf{s}_{l} \equiv \mathbf{I}$, which does not depend on wavelength, stands for the direct transmission through PE. It represents the "transmission" component introduced in Eq. 5.

Spectrum $\mathbf{s}_2 = s_a(\lambda)$ can be interpreted as the PE absorbance term in Eq. 5. It is similar to the spectra presented in literature.^{11,26} Spectrum $\mathbf{s}_3 = s_s(\lambda)$ reflects the PE scattering term in Eq. 5. In many spectral ranges, it is very similar to the absorbance spectrum. In particular, we see that most of the scattering effects take place near the bands where PE absorbs. This fact is in line with the increase in scattering and reflectance near the absorption bands in the elementary theory of dispersion (Lorenz model of matter).³⁴ There is also an overall increase of scattering at smaller wavenumbers. The most peculiar is the band round



Figure 6. Pure component spectra found during the multistage MCR procedure. (1) Transmittance, (2) absorbance, and (3) scattering coefficients.

5778 cm⁻¹ of the highest PE absorption. In the scattering spectrum, this area manifests a sharp decrease of intensity. Similar effects have already been reported.¹¹ From theoretical point of view this may be explained by the fact that the probabilities of photon absorption, scattering, and transmission per physically small unit of volume sum up to one, so that an increase in absorption would at some point result in a decrease of scattering. There are also empirical considerations. The MCR model based on Eq. 5 assumes that the absorbance and scattering terms can be determined independently. This is not true for strong absorption bands, where most of photons are absorbed. In this case, X(h) saturates at a very low h, and this effect is modeled by $c_a(h)$ only (local rank deficiency). Apparently it looks like the absence of scattering and the model assigns smaller values of $s_s(\lambda)$ to damp the contribution of the profile $c_s(h)$, which cannot be detected at this point.

C-Profiles

Values presented in the *c*-profiles reflect the input of each type of *s*-spectrum into the entire spectrum collected by the detector. We begin discussing these results with the *c*-profiles obtained for the first component, which is connected to transmission/reflection effects.

The plot in Figure 7a demonstrates values c_1 calculated at the last stage (MCR-0) for all datasets. These values belong to the A-domain. Figure 7b represents the corresponding reflectance factors *r* recalculated in the *R*-domain. The latter values are easier to interpret, so we consider them in what follows. First, we see that the initial value of each profile naturally equals to the reflectance factor,



Figure 7. The *c*-profiles of the first component. Data (marks) and models (curves): (1) $B_0.0$, (2) $B_0.1$, (3) $B_0.4$, (4) $B_0.8$, (5) $B_1.0$. (a) Term $X^{(0)}$; (b) reflectance factors $r = \exp(-c_1)$.

 r_{UL} , of the underlayer used in the corresponding data set, i.e., $r(0) = r_{\text{UL}}$ The second finding is that all profiles merge at large PE depth *h*, i.e., $r(h > 3) \approx \text{const.}$ We observe that profiles related to the data sets with weakly reflective underlayers (*B_0.0*, *B_0.1*) grow with the PE depth, whereas profiles that correspond to highly reflective underlayers (*B_0.4*, *B_0.8*, and *B_1.0*) drop with the PE thickness. This means that if we could change the reflectance factor continuously, we would get a straight line for the underlayer, which has the same reflectance factor as PE. In view of the fact that at greater PE depths the underlayer effect can be neglected, this common level is attributed to the PE reflectance factor, which is $r_{\text{PE}} = 0.27$. All reflection profiles can be perfectly fit to a simple relaxation model

$$r(h, r_{\rm UL}) = r_{\rm PE} + (r_{\rm UL} - r_{\rm PE})e^{-kh}$$
 (14)

where k is an empirical decay constant, h is the PE thickness, and r_{UL} is the underlayer reflectance factor. According to Eq. 14, the contribution of the underlayer spectrum to the observed spectrum decays exponentially with the PE thickness. This masking effect is described by constant k, which is about 1 mm⁻¹. This model is illustrated in Figure 7 by curves that are very close to the corresponding data marks. Another interesting result is that the c_1 -values (Figure 7a) for all data sets agree well with the spectral baseline shifts, i.e.,

$$\{\mathbf{c}_1\}_i \approx \min(\mathbf{x}_i) \tag{15}$$

where i = 1,.., l is the sample number. These last two facts will be extensively used in practical applications presented in the second part of this research.

Profiles related to the absorption (\mathbf{c}_2) and scattering (\mathbf{c}_3) phenomena are shown in Figure 8. These plots demonstrate that both profiles have a similar shape. In particular, it can be seen that they start at zero, and at a large PE depth all profiles converge to a common level. Such a behavior can also be explained by the fact that at greater PE depths a sample becomes optically thick and the underlayer ceases to influence the signal registered by the detector. The limit value of I, both for \mathbf{c}_2 and \mathbf{c}_3 , was selected arbitrarily in the procedure presented in Figure 5. This value can be interpreted as the absorbance and scattering weighting factors $(c_a \text{ and } c_s)$ for an optically thick PE layer.

It is interesting that some profiles pass through a maximum. In particular, we observe this behavior when the underlayer reflectance factor is greater than the PE reflectance factor. The absorbance profiles have a maximum at PE thickness $h = 0.87 \,\mathrm{mm}$ (ten PE layers) and the scattering profiles maximum happens at h = 1.740 mm (20 PE layers). It can be seen that the maximal absorbance is 1.4 times greater than the ultimate absorbance achieved for an optically infinite PE layer. The scattering maximum is 1.25 times of the corresponding limit. At present, we are unable to give a sound theoretical interpretation of these phenomena, but can only exclude several factors that have no influence on it. In particular, our experiments show that a maximum is not connected to the fiber probe application, because spectra obtained using the integrating sphere demonstrate the same phenomenon. Another experiment proves that the growing gap between the probe tip and the sample²⁸ is also beyond suspicion.

Nevertheless, the models that describe the absorption (\mathbf{c}_2) and scattering (\mathbf{c}_3) profiles as computable functions of the PE thickness, *h*, and the underlayer reflectance factor,



Figure 8. The c_2 and c_3 profiles. Data (marks) and models (curves): (1) $B_0.0$, (2) $B_0.1$, (3) $B_0.4$, (4) $B_0.8$, (5) $B_1.0$. (a) Absorbance c_2 ; (b) scattering c_3 effects.

 r_{UL} , will be very useful in the second part of this research. In contrast to the first profile, c_1 (see Eq. 14), the models for the c_2 and c_3 profiles are not so elegant, and therefore they are not presented here. The reader can find them in the supplementary materials. In Figure 8, these models are presented by curves that fit the data (marks) obtained in the experiments.

Thin Layer Theory

The case of a thin PE cover (less than 0.6 mm) deserves special attention. In this interval, it can be observed (see Figure 8) that both the absorbance and scattering profiles have a linear dependence on *h*. Moreover, if the \mathbf{c}_s data are plotted versus the \mathbf{c}_a data (see Figure S2, Supplemental Material), it becomes clear that there is a linear trend, $\mathbf{c}_s = \gamma \ \mathbf{c}_a$, which is common for different underlayers.

This finding is completely in line with Eq. 6 developed for a case of a thin PE layer. Consider a DR spectrum, which is pre-preprocessed using Eq. 7. Then,

$$\tilde{x}(\lambda, h) = hc_u(r)s_u(\lambda) + e \tag{16}$$

In this equation, spectrum

$$s_u(\lambda) = s_a(\lambda) + \gamma s_s(\lambda) \tag{17}$$

represents a joint attenuation coefficient that is calculated for the slope coefficient, $\gamma = 0.34$, found from the trend line (6) shown in Figure S2. The weighting coefficient $c_u(r)$ depends on the underlayer reflectance factor r, but not on the PE depth, h. The value of $\gamma = 0.34$ has no special meaning, as it is a consequence of scaling of the absorbance and scattering profiles (see Figure 5), which are arbitrarily set to be equal to I at infinite thickness. If we select another scaling, the value of γ will change respectively, e.g., if $c_a(\infty) = 1$, and $c_s(\infty) = 1/0.34 = 2.9$, then γ will be equal to 1.

Equation 16 demonstrates that thin-layer DR spectroscopy is very similar to the conventional TM spectroscopy, which is based on Beer's law. To illustrate this similarity, we have conducted very simple modeling using data set *Trans*, obtained in the transmittance mode.

First, we found the *c*-profiles for the pre-processed *Trans* data using a two-component MCR model

$$\tilde{x}(\lambda, h) = c_a(h)s_a(\lambda) + c_s(h)s_s(\lambda) + e \tag{18}$$

where spectra $s_a(\lambda)$ and $s_s(\lambda)$ are set to be equal to the pure spectra found at the end of the DR data modeling (see Figure 6). The estimation of *c*-profiles can be done in one *C*-step presented in Eq. 10. To resolve the scaling ambiguity, c_a profile is normalized as $c_a \approx h$. The results shown in Figure 9a demonstrate that both profiles are clearly linear

Moreover, it can be observed that the slope of the c_s profile equals to the same value $\gamma = 0.34$ that has been found from Figure S2 (supplementary material). This result gives another justification for the proposed attenuation coefficient.

Obviously, *Trans* profiles are described by a single linear component, so the two-component model given in Eq. 18 is inapplicable, as it becomes degenerate in the case that the spectra are not fixed. Therefore, we return to a one-component MCR model that has been used as described in Results of the One-Component Multivariate Curve



Figure 9. Modeling of *Trans* data. (a) *c*-profiles obtained in a two-component model at the fixed pure spectra: (1) absorbance, (2) scattering. (b) (1) Spectrum obtained in one-component model, (2) attenuation coefficient.

Resolution above. Figure 9b demonstrates two spectra. The first one (1) is found when the one component MCR model is applied to the *Trans* data. The second spectrum (2) is the attenuation coefficient $s_u(\lambda)$ obtained when the three-component MCR model was applied to the DR data. It can be seen that the attenuation spectrum coincides with the transmittance spectrum of PE, which is widely presented in the literature.²⁶

In our opinion, the thin layer concept is a very important result that links the proposed three-component theory to the conventional one-component approach.

Conclusions

We succeeded in the decomposition of the collected spectra of PE layers into three components. The first one does not depend on wavelength and manifests itself as a vertical shift in spectral intensity. This component depends on the reflection properties of both the PE layer surface and the underlayer. In this particular study, we could simply apply individual spectra shifts as preprocessing before the whole procedure. At the same time, the possibility to find this shift for each specific spectrum numerically makes the whole procedure more flexible and helps to avoid subjective decisions. We do not try to get rid of it as is routinely done in most experiments. We consider that this will be especially important in cases of more complex systems.

The second and the third components characterize the attenuation of light in the material independent of the reflectance properties of the underlayer. These components characterize the optical properties of a material and carry chemical information. Having different dependence on wavelength, they can be nominally viewed as absorption and scattering contributions.

It was demonstrated that in case of a thin PE layer, the proposed three-component approach turns into a conventional spectroscopic Eq. 16, which in fact is the Beer–Lambert–Bouguer law, typically used in transmittance spectroscopy.

In the second part of this research,³⁵ we apply the developed theory to reconstruct a spectrum of an unknown target object covered with a PE layer of an undefined depth.

Conflict of Interest

The authors report there are no conflicts of interest.

Funding

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

Supplemental Material

Supplemental material for this paper can be found at the journal website online.

Note

 a. In practice, a decimal logarithm is routinely used, but we prefer a Napierian logarithm as it is more suitable for a theoretical discussion.

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