

A Theoretical Model for Measuring and Sensor Characterization in Optical Spectroscopy

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Abstract

The optical and digital resolution, as well as the signal-to-noise ratio are important characteristics of optical spectrometers and available in data sheets. But how can an optical spectrometer system be selected for a specific application? The article shall serve as an aid to characterize optical spectrometers and hyperspectral cameras by introducing a benchmark calculation which indicates the measurement uncertainty of absorption bands.

1 Introduction

In optical spectroscopy, the wavelength depended intensity of light is measured. Due to the interaction between light and matter, the direction of the light propagation can change by elastic scattering processes. Furthermore, light can be absorbed by interaction with molecules, which changes the intensity of the light. The wavelength dependent probability of light scattering and absorption depends on the material properties of the sample. Therefore, it is possible

to determine material properties of the sample by recording its reflected or transmitted optical spectrum. Applications can be found in various fields like smart agriculture, food industry as well as in petro chemistry [9].

Due to the continuously advancing development of microsystems technology (MEMS), miniaturized spectrometers and hyperspectral camera systems can be manufactured cost-effectively and in large quantities. In order to achieve a comparability of sensors of different types, a benchmark parameter is presented below, which links the sensor noise with the optical and digital resolution.

In the following chapter the state of the art in chemometrics is briefly explained. Afterwards, signal generation and detection are discussed in more detail. Finally, the findings are used to define spectral features and sensor characterization.

2 State of the art in chemometrics

For the statistical analysis of spectroscopic data, the research discipline of chemometrics has developed within the field of chemistry. In the following, the state of research on theoretical simulation and in addition, the established pre-processing methods of chemometrics are referred.

Mainly core statements are given. For detailed information meaningful sources are given in each section.

2.1 Theoretical spectroscopy and simulation of spectroscopic results

Molecular vibrations can be excited by interaction with light, which causes an absorption of the light due to the law of energy conservation. For better understanding it is useful to consider light as particles, which are called photons. The energy of a photon is given by its frequency, which can also be expressed by a wavelength using the speed of light. And as result from quantum mechanics, only discrete energy levels of molecular vibrations can be excited. Both, the fundamental law of energy conservation and the discrete energy levels

of molecular vibrations lead to the simple result, that only photons with a wavelength, that matches these energy levels can be absorbed.

However, the anharmonic potential of atomic forces lead to a non-linearity in the energy levels of molecular vibrations. Therefore, the energy levels change strong in a solid-state or liquid sample caused by the presence of additional atoms, temperature or pressure. For this reason, theoretical spectroscopy is still a field of research. Simulation of spectroscopic results is only possible in case of simple molecules in solutions with a sparse concentration [1].

Furthermore, the transfer of chemometric calibration models to other products is quite impossible. This means, the calibration of sugar content of apples only can be applied to apples and not to other types of fruit.

2.2 Chemometric methods for spectral preprocessing

In the previous sections, the focus was on absorption and its relationship to material properties. However, the absorption can only be detected indirectly, whereas the reflected or transmitted light can be detected directly. Therefore, several methods have been developed to correct non-linearity of absorption, scattering effects and transfer of chemometric calibration models.

2.2.1 Absorbance units

In chemometrics, light which is not detected by the sensor ($1 - r$) is referred as absorption, often this signal is also expressed in

$$a := \log(1 - r) \tag{2.1}$$

absorbance units (AU). Where r describes the reflected signal detected and discretized by the sensor and logarithms are used due to the exponential relationship between absorption and substance concentration by the Beer-Lambert-Law.

2.2.2 Scatter correction

In chemometrics, no distinction is made between the physical processes of elastic and inelastic light scattering. Only the terms absorption or reflection/transmission are used. Nevertheless, it is known that elastic scattering effects from Mie or Rayleigh theory have an impact on the spectrum and a scatter correction is necessary. Therefore, a Multiplicative-Scatter-Correction (MSC) or a Standard-Normal-Variate (SNV) is often applied as a pre-processing method [10]. Another approach is to derive the spectrum, which is often combined with smoothing operations [8, 4, 7].

2.2.3 Instrument transfer

An optical spectrometer records the spectrum of the light and converts it into a digital measurement signal. Depending on the instrument used, the spectrometers differ in their spectral range as well in their optical and digital sampling resolution. However, devices of the same type and manufacturer often differ in mechanical tolerances. For this reason, various methods for the transfer of calibration models have been developed [6, 3].

3 The spectral signature of a sample

The following section will describe the signal components of the optical spectrum in the near and short wave infrared (780 nm – 2500 nm). In the optical spectrum the physical effects of scattering and absorption are superimposed. Nevertheless, the spectrum can be evaluated by chemometric calibration models or machine learning methods. The amount of training data required for this can be reduced by making specific pre-assumptions. With the following model some physically motivated assumptions about properties (baseline, absorption bands) of the spectral signature (see fig.3.1) can be formulated.

This information model is used in chapter 5.1 to define characteristics. Finally, in chapter 5.2 a characterization of spectral sensor systems based on the detection of these features is proposed.

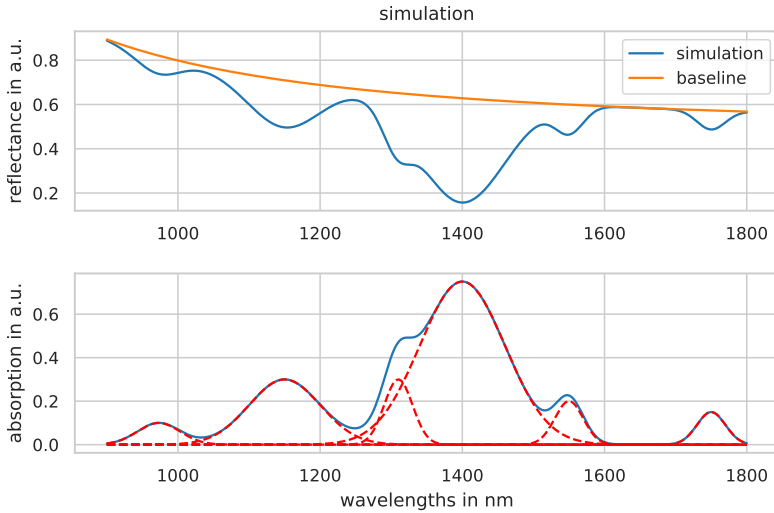


Figure 3.1: The spectral signature of an object is generated from the superposition of elastic and inelastic scattering (absorption). The absorbing molecule groups create Gaussian-shaped absorption bands. Their size allows quantitative analysis of the ingredients. Due to the wavelength-dependent elastic scattering processes (Mie- and Rayleigh scattering), a smooth baseline is created.

3.1 A stochastic model to describe the spectral signature of a sample

The interaction between light and the sample can be described by a model of stochastic processes [5]. Therefore, the spectral signature of the sample is given by the probability density functions of $r_{\theta,\phi}(\lambda) \in [0, 1]$ and transmission $t_{\theta,\phi}(\lambda) \in [0, 1]$, depending on the wavelength λ , the angle $\phi \in [-\pi/2, \pi/2]$ of the incident light from the light source and the angle $\theta \in [-\pi/2, \pi/2]$ of the reflected or transmitted light. Both angles are related to the surface normal. A graph is used to describe the light and matter interaction (see fig.3.2): The light source radiates photons with the probability of $N_{\phi}(\lambda) \in [0, 1]$ within the time period T onto the sample. Multiple elastic scattering processes $s_{i,j}(\lambda) \in [0, 1]$

can occur within and between different layers $i, j \in \mathbb{N}$ of the sample. For homogeneous materials without packaging, the number of layers can be reduced to one. From the surface, photons can be emitted in different angels θ as observable reflection and transmission. In addition, photons in each layer $n \in \mathbb{N}$ can be absorbed $a_n(\lambda) \in [0, 1]$. For better readability the wavelength dependence is not explicitly referred at every point. The angles are usually unknown and cannot be measured. The angle-dependent scattering effects mainly appear when using very different samples or when comparing different measuring instruments. Therefore these quantities are given as an index.

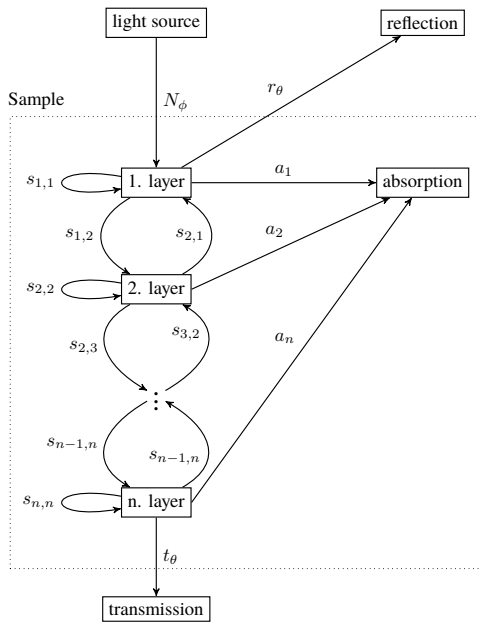


Figure 3.2: The spectral signature of the transmitted t_θ or reflected r_θ light from a sample is formed by multiple scattering $s_{i,j}$ and absorption a_n processes within the sample. The scattering or absorption can differ in the different layers such as packaging, peel, pulp. In addition, the spectral response of the light source is also described as a probability density function N_ϕ . The angles of incidence of the light source are named by ϕ . The angles of emission of transmission and reflection are named by θ .

The probability for emissions $a_i \in [0, 1]$ in the state of absorption is depending on the concentrations $c_j \in [0, 1]$ of absorbing molecules. So the chemical information is not directly observable. But energy conservation can be assumed, such that

$$\sum_n a_n + \int r_{\theta,\phi} d\theta + \int t_{\theta,\phi} d\theta = N_\phi \quad (3.1)$$

is valid. A general case for multiple light sources or directions from diffuse illumination can be created by adding a sum or integral over ϕ .

Using eq. 3.1, some fundamental cases can be named:

- **Specular reflection** $\int r_\theta d\theta = N_\phi$: In case of specular reflection, all light is reflected. There is no transmission or absorption of the light.
- **Total absorption** $\sum_n a_n = N_\phi$: There is no measurement signal in case of total absorption.
- **Diffuse reflection** $\int t_\theta d\theta = 0$: This assumption is valid for samples of an infinite thickness. The reflected light is given by

$$\int r_\theta d\theta = N_\phi - \sum_n a_n$$

- **Diffuse transmission** $\int r_\theta d\theta = 0$: This assumption is valid for liquid samples. The transmitted light is given by $\int t_\theta d\theta = N_\phi - \sum_n a_n$

To minimize the angular dependency of the reflected signal, a diffuse illumination is usually used.

3.2 Absorption

The origin of absorption bands in the near and short-wave infrared are molecule groups with an polar hydrogen bonds like (OH, CH, NH, SH, COOH, ...) absorb the light. An absorption process becomes possible when the wavelength (energy) of the light matches the energy levels of the polar hydrogen bond within these functional molecule groups.

The absorption

$$a_n(\lambda) = \sum_j^N \frac{c_j}{\sqrt{2\pi}\rho_j} \cdot e^{-\left(\frac{\lambda-\lambda_j}{\sqrt{2}\rho_j}\right)^2}, \quad (3.2)$$

is a sum over all absorbing molecule groups [2]. The energy levels λ_i of the molecule groups mentioned are overlapping and also shifting non-linear depending on the sample composition. The width of the absorption band is given by ρ_j and the concentration follows the Beer-Lambert law

$$c_j = 1 - e^{-\alpha_j} \quad (3.3)$$

with an absorption coefficient $\alpha_j \in \mathbb{R}$ depending on the dipole moment of the molecule. As described in the model (see fig.3.2), the absorption can also change in different layers, e.g. apple peel and fruit flesh. Therefore different absorption functions $a_i(\lambda)$ must be used.

However, the analysis of spectral data results in an ill-posed inverse problem: based on an detected absorption band, it is usually not possible to know which molecular group is the origin of the absorption.

3.3 Diffuse reflection and transmission

The scattering parameters $s_{i,j}(\lambda)$ of a sample vary depending on the microstructure (surface roughness and particle as well as molecule size). Using this scattering parameter, the reflected (transmitted) spectral signature

$$r_\theta(\lambda) = \left(1 - \sum_i a_i(\lambda)\right) s_{1,\theta}(\lambda) \quad (3.4)$$

results from light, which is not absorbed and scattered out of the top (bottom) layer of the sample. The scattering parameter can be explained by the Mie and Rayleigh theory. Because the required parameters such as illumination angle and measuring distance are not known in many cases, the scattering parameter s is assumed to be a continuous and smooth function. Furthermore, it is assumed that the scattering parameter in the region of an absorption band can be assumed to be locally constant.

4 Model for measurement systems in optical spectroscopy

The individual steps of signal generation are shown step by step in fig. 4.1. After the explanation of the spectral signature in the previous section, the spectroscopic measurement system is now in focus. An optical system is used to project the spectrum onto a detector. The detector converts the optical signal into a digital measurement signal.

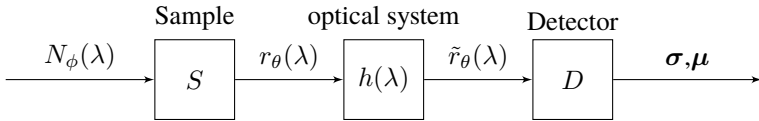


Figure 4.1: The $N_\phi(\lambda)$ photons emitted by a light source are reflected after interaction with the sample S . The angular and wavelength dependent reflectance of the sample forms the spectral signature $r_\theta(\lambda)$. An optical system (e.g. poly- or monochromator) is used to project the transformed reflectance spectrum $\tilde{r}_\theta(\lambda)$ onto a detector D .

4.1 Optical system

The optical resolution is diffraction-limited in the case of grating spectrometers and can be calculated with known grating, slit and distances. For this the Rayleigh criterion is used, the resolution limit $\Delta\lambda$ describes the radius of the Airy disk. However, this profile can also be well approximated by a Gaussian curve. Therefore, a spectral band $i \in \mathbb{N}$ of the optical system can be approximated with a *point spread function* (PSF) based on a Gaussian function

$$h_i(\lambda) = \frac{1}{\sqrt{2\pi}\rho_{\text{PSF}}} \cdot e^{-\left(\frac{\lambda-\lambda_i}{\sqrt{2}\rho_{\text{PSF}}}\right)^2} \quad (4.1)$$

which is mathematically easy to handle. In the case $\Delta\lambda = 0$ of an ideal optical system the transfer function $h_i(\lambda) = \delta(\lambda - \lambda_i)$ is generated. In data sheets the resolution of the optical system is usually specified by the *FWHM* (Full width (at) half maximum). Which is also related to $\rho_{\text{PSF}} = \frac{\text{FWHM}}{2\sqrt{2 \ln(2)}}$.

The reflection signal

$$\tilde{r}_\theta(\lambda) = h(\lambda) * r_\theta(\lambda) =: \mu_p(\lambda) \quad (4.2)$$

which is projected onto the detector defines also the photon current which used in the next chapter.

Another property of the point spread function is the smoothing of the reflection signal. This leads to an attenuation of the absorption bands (eq. 3.2). Using eq. 4.2 and assuming Gaussian functions in eq. 4.1 and eq. 3.2 a new attenuated parameter for the concentration

$$\tilde{c}_j = \frac{\rho_j}{\sqrt{\rho_{\text{PSF}}^2 + \rho_j^2}} c_j \quad (4.3)$$

can be specified.

4.2 Detector model based on EMVA1288

The EMVA1288 standard contains a comprehensive description of the various signal contributions in semiconductor detectors and the digitization that follows. However, the EMVA1288 standard is used to characterize camera sensors without optics and refers to illumination with monochromatic light.

The noise (variance) of the grey values of a spectral band

$$\sigma_i^2 = K^2 \sigma_d^2 + \sigma_q^2 + K (\mu_i - \mu_{i,\text{dark}}) \quad (4.4)$$

results from the amplified dark noise σ_d , the quantization noise $1/12$ DN. The fluctuations of the photon stream are subject to a Poisson distribution and are signal dependent.

The signal

$$\mu_i = \int_{-\infty}^{\infty} \text{rect}\left(\frac{\lambda - \lambda_i}{\Delta\lambda}\right) \tilde{r}_\theta(\lambda) \eta(\lambda) K d\lambda + K \mu_{\text{dark}} \quad (4.5)$$

of a spectral band results from the signal sampled over the range $\Delta\lambda$.

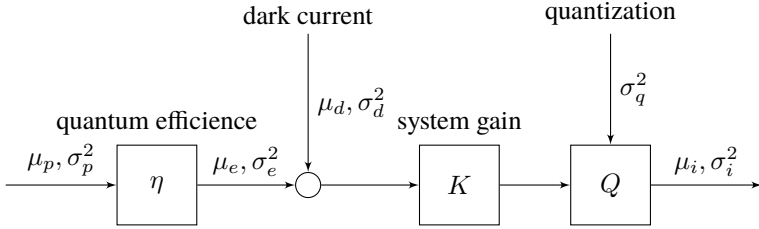


Figure 4.2: EMVA1288 Sensor system: The photon current μ_p is subject to a fluctuation σ_p . In the semiconductor, the photons generate electrical charge carriers μ_e with the quantum coefficient η . Thermal excitation produces an additional dark current μ_d . The charge carriers are amplified analogously by the factor K and then converted into a quantized measurement signal μ_i by an analog-digital-converter (ADC).

4.3 White and black balance

A white and black balance necessary is because of the spectral characteristics of the light source $N_\phi(\lambda)$, the quantum efficiency $\eta(\lambda)$, as well as the additional dark current of the detector $\mu_{y,\text{dark}}$. The signal

$$g_i = \frac{\mu_i - \mu_{i,\text{dark}}}{\mu_{i,\text{ref}} - \mu_{i,\text{dark}}} \quad (4.6)$$

can be calculated based on a reference spectrum of a sample with known reflectance and the dark signal. This wavelength dependent scaling leads to an amplification

$$\sigma_{g,i} = \frac{\sigma_i}{\mu_{i,\text{ref}} - \mu_{i,\text{dark}}} \quad (4.7)$$

of the noise of spectral bands. In many cases, a significant increase in noise can be observed at the borders of the spectrum.

5 Sensor characterization

In order to characterize a spectrometer system (see fig.4.1) the already introduced properties of light source $N_\phi(\lambda)$, optical system $h(\lambda)$ and detector D will be combined in the following. The aim is an estimation of the measurement uncertainty for the detection of absorption bands.

5.1 Features in optical spectroscopy

The intensity of an absorption band can be used to quantify sample properties, as introduced above by Beer-Lambert's Law. Therefore, the absorption bands will be defined as features

$$m_j := \int_{-\infty}^{\infty} \frac{c_j}{\sqrt{2\pi}\rho_j} \cdot e^{-\left(\frac{\lambda-\lambda_j}{\sqrt{2}\rho_j}\right)^2} s_{1,\theta}(\lambda_j) d\lambda = c_j \cdot s_{1,\theta}(\lambda_j), \quad (5.1)$$

where the scattering parameter $s_{1,\theta}(\lambda_j)$ is assumed to be locally constant. These features are attenuated by the optical system and are recorded with noise. Using the relation $m_j \propto c_j$ and eq. 4.3 and 4.7 lead to a standard deviation

$$\sigma_{m_j} \propto \frac{\sqrt{\rho_{\text{PSF}}^2 + \rho_j^2}}{\rho_j} \frac{\sigma_g}{\sqrt{n}} \quad (5.2)$$

in the detection of spectral absorption bands. The optical attenuation of the absorption bands in the first term has an amplifying effect. Depending on the digital resolution, the noise influence is reduced by acquisition with n channels.

5.2 Example for a new benchmark calculation in optical spectroscopy

From laboratory tests it is known that for recording moisture the feature m at $\lambda_m = 1350$ nm with a width of $\rho_m = 50$ nm must be used. Two spectrometer systems with different characteristics are available. One system with low noise (sensor A) and high resolution (sensor B).

Table 5.1: Sensor comparison: Sensor A has a lower optical resolution, the spectral range of 900 – 1650 nm is recorded with 128 bands. Sensor B has a high optical resolution, the spectral range of 900 – 1700 nm is recorded with 255 bands. Due to the lower light per spectral band the noise of sensor B is increased compared to sensor A.

	Sensor A	Sensor B
ρ_{PSF} in nm	20	5
Bands/nm	0.18	0.32
$\sigma_g @ \lambda_m$ in nm	0.01	0.02

By multiplying the digital resolution Bands/nm by the width of the absorption band ρ_m the number of n spectral bands involved in the sensor can be determined. This results in an estimated standard deviation of the feature m with $\sigma_{m,A} = 0.0039$ for sensor A and $\sigma_{m,B} = 0.005$ for sensor B. For a general comparison of the two sensors the trend from σ_m over ρ_m is shown in figure 5.1.

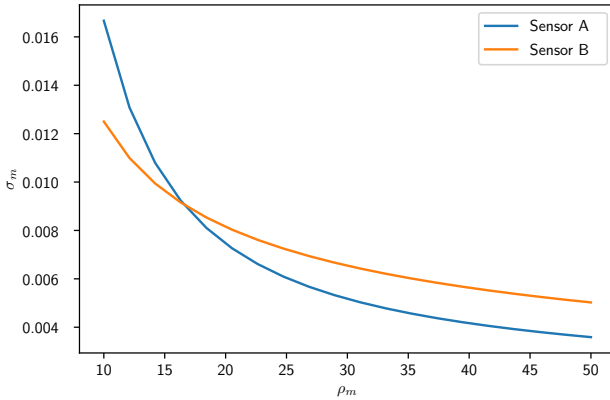


Figure 5.1: With increasing width of the absorption band which is to be detected, the number of spectral channels in the sensor increases, whereby the influence of the optical resolution also decreases in proportion. With a defined absorption band, the measurement uncertainty of the sensors can therefore be compared in the graph.

6 Summary

The signal generation in optical spectroscopy was described in terms of stochastic processes starting from the light source up to interpretable features. The focus was on signals in the near and short wave infrared spectrum. For quantitative statements on sample properties, the characteristics of absorption bands were justified and their signal portion was presented in reflection and transmission measurements.

Based on the absorption bands as quantitative features in optical spectra an estimation of the stochastic measurement uncertainty was formulated. For this purpose, the optical resolution was combined with the detector properties according to EMVA1288. As a result, spectroscopic measurement systems can be characterized by the expected stochastic measurement uncertainty. The definition of task-specific requirements for the resolution of certain absorption bands enables a benchmark for spectroscopic measurement systems as a whole. The approach can be generally used for hyperspectral cameras including illumination and optics or novel compact spectrometers from the consumer sector.

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