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Review

Insight into the Bouguer-Beer-Lambert Law: A Review

Moses Kayanda Kiteto[1], **Cleophas Achisa Mecha**[1,2*]

[1]Renewable Energy, Environment, Nanomaterials and Water Research Group, Department of Chemical and Process Engineering, P.O. Box 3900-30100, Eldoret, Kenya
[2]Department of Environmental Sciences, University of Arizona, Tucson, AZ 85721, USA
E-mail: achemeng08@gmail.com

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Abstract: The Bouguer-Beer-Lambert law, a fundamental principle in spectroscopy that establishes a linear relationship between absorbance and concentration, has been indispensable for chemical analysis and quantitative measurements. Its elegant simplicity and robust utility have enabled the determination of solute concentrations in various solutions, leading to applications across diverse scientific disciplines. However, the inherent assumptions and limitations of this law have resulted in deviations, mostly fundamental, chemical, and instrumental, which have inspired a fervent pursuit of modifications aimed at enhancing its accuracy and expanding its scope. This review aims to shed light on the ongoing quest for its modification, providing an in-depth analysis of the law and delving into its historical overview, from the work of Pierre Bouguer to the modern formulation. Moreover, the classical and electromagnetic formulations of the law have been thoroughly studied, and a comprehensive overview of the law's limitations is presented. Furthermore, some of the major modifications that have been made in attempts to expand its reach across different realms are evaluated. Advanced approaches toward generalized modification of the law have also been extensively discussed. Finally, the review addresses the challenges in formulating a generalized Bouguer-Beer-Lambert law and proposes possible solutions and future directions that should be taken to improve the accuracy and wide applicability of the law.

Keywords: Bouguer-Beer-Lambert law, spectroscopy, fundamental deviations, chemical deviations, instrumental deviations, modifications

1. Introduction

The Bouguer-Beer-Lambert law or simply the Beer-Lambert law postulates that the amount of light absorbed by a solution containing an absorbing substance is directly proportional to the concentration and path length of the light through the solution[1-4] illustrating a linear relationship between absorbance and concentration.

$$\log_{10}\left(\frac{I_o}{I}\right) = A = \varepsilon cl \tag{1}$$

Where I_o is the intensity of the incident radiation, I is the intensity of the attenuated radiation, A is the absorbance, ε is the molar extinction coefficient, c is the concentration of the absorbing species and l is the optical path length.

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The law has found applications across diverse scientific disciplines and industries and despite the complexities of the modern world, it remains an essential tool for acquiring quantitative data with remarkable accuracy and precision.[5] Its versatility extends to realms such as environmental science, pharmaceuticals, food and beverage industries, forensics, and astronomy. However, the constraining limitations of the law mostly attributed to its formulating assumptions, have resulted in deviations from the expected linear relationship. The deviations, encompassing fundamental, chemical, and instrumental limit the scope and applicability of the law[4,6] Fundamental or real deviations arise from the inherent limitations of the law, especially at high concentrations where interactions between particles alter the analyte's absorptivity. Chemical deviations are due to the specific chemical properties of the analyte; whereby depending on the surrounding environment, such as changes in pH and concentration, the analyte chemical equilibrium shifts resulting in new chemical species with different maximum absorption wavelengths. Instrumental deviations are caused by imperfections in how the absorption measures are made which are a result of using a polychromatic and defects of the wavelength selector resulting in stray radiation. These deviations have sparked a passionate drive for adjustments to the law focused on enhancing precision and extending its scope. This paper thus aims to provide insights into the developments in the ongoing quest to formulate a modified law.

2. Historical overview

The Bouguer-Beer-Lambert law dates back to 1729 when the French Mathematician Pierre Bouguer Published his extensive work, *'Essai d'optique sur la gradation de la lumière'*,[7] considered the foundation of Photometry. The second chapter of the *Essai d'optique* deals with transparency and opacity of matter where Bouguer explains in detail how the intensity of light decreases as it passes through a transparent body. In this model, the body is divided into several layers of equal thickness and incident light rays are perpendicular to the layers. He then argues that the intensity of the light rays will decrease in geometric progression. Therefore, the intensity of light can be represented by logarithmic curve ordinates which have the thickness of the medium as its x-axis. This is illustrated using a perfectly homogenous body ABCD, divided into layers of equal thickness (Figure 1).

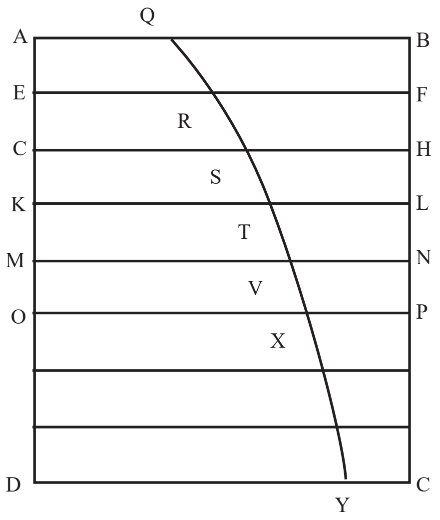

Figure 1. The transmission of light in a transparent body ABCD[7]

The light hits the face AB at a right angle, with the length QB indicating its initial intensity. Once it travels through the depth BF or AE, it moves into the second layer via the face EF, where its intensity becomes RF. This change in intensity over depth can be represented by the logarithmic curve QRXY, with BC serving as the x-axis. A less transparent material will exhibit a steeper decrease in intensity, as shown by the transmission curve shape, which depends on factors like the sub-tangent and the initial radiation intensity. As seen, Pierre Bouguer provided a correct model for light transversing a transparent media, though he did not offer a mathematical formulation of the phenomenon which would have to wait until Johann Heinrich Lambert in 1760.

The Swiss-French polymath Johann Heinrich Lambert recognized as one of the best mathematicians of his day published his groundbreaking work, *'Photometria sive de mensura et gradibus luminus, colorum et umbrae'*[8], where he mathematically formulates the Bouguer model by stating that the loss of intensity of light when it propagates through a media is directly proportional to intensity and path length. He considered a differential layer of thickness dx at a distance x into the absorbing medium and using the assumption that the fractional reduction of the intensity of the incident radiation, $-dI/I$ is proportional to layer thickness dx, he came up with the following differential equation:

$$-\frac{dI}{I} = \alpha dx \tag{2}$$

which is compatible with Bouguer's observations. Upon integrating equation (2) at distance d into the body we arrive at the Bouguer-Lambert law:

$$\int_{I_o}^{I} \frac{dI}{I} = -\alpha \int_0^d dx$$

$$\ln\left(\frac{I}{I_o}\right) = -\alpha d$$

$$I = I_o e^{-\alpha d} \tag{3}$$

Where the constant of proportionality α is the Napierian absorption coefficient.

German Physicist and chemist August Beer much later in 1852 in his seminal paper *'Bestimmung der Absorption des rothen Lichts in farbigen Flüssigkeiten'*[9] explored another attenuation relation. Through studying how red light is absorbed in various colored aqueous salt solutions, he reached the conclusion that it is possible to derive the transmittance of a concentrated solution from the measurement of the transmittance of a diluted one. His paper demonstrates his grasp of exponentiation when he states that if λ represents the decrease in light intensity through the solution, then this decrease will be λ^2 for a double thickness. Beer further argues that if we define the absorption coefficient as the factor that determines the decrease in amplitude of a light ray passing through a unit length of absorbing material, then:

$$\lambda = \mu^D \tag{4}$$

where is μ the absorption coefficient and D is the length of the absorbing material traversed in the experiment. Equation 4 is the Beer's law. As shown, Beer did not introduce concentration; neither did he introduce absorbance nor see the concentration and path length as symmetrical values in his equation in the manner of equation (1). In fact, Beer published a compressive book, *'Einleitung in die höhere Optik'*[10], on optics a year later after formulating his absorption law where he deliberately excluded absorption from the discussion from the beginning, noting that space, air, water, and glass are entirely transparent and colorless. It is speculated[4] that had he not met an early demise only at the age of 38, he might have been the originator of the Bouguer-Beer-Lambert law. Instead, it took a considerably longer time for the eventual development of what we now refer to as the Bouguer-Beer-Lambert law.

Five years after Beer's pioneering paper, in 1857 German chemists, Robert Wilhelm Bunsen and Sir Henry Anfield Roscoe published their paper, *'Photochemische Untersuchungen'*[11] considered the bedrock towards the modern formulation of the Bouguer-Beer-Lambert law. By studying the photochemical absorption of light through chlorine and knall (oxyhydrogen) gases, Bunsen and Roscoe reported that light passing through a layer of chlorine knall-gas was much more weakened in its chemical activity than when it had passed through a layer of pure chlorine of the same thickness. In both cases, the light is weakened by the absorption of chlorine, neglecting the absorption by hydrogen. In the second instance, the weakening is due to optical absorption; the loss of energy of the light reappears in the heat developed and in the first case, light energy is consumed in performing chemical work, which causes a stronger absorption. Despite the different pathways through which energy is absorbed, the fundamental law governing the absorption of light remained unchanged. Therefore, they concluded that absorptivity could best be described by the following equation:

$$A = \frac{1}{d}\log_{10}\left(\frac{I_o}{I}\right) \tag{5}$$

Subsequent years witnessed the evolution and enhancement of Equation (5) and in 1888, Ferdinand Hunter and Vero Charles Driffield published their paper on photochemical investigations and a new method of determination of sensitiveness of photographic plates[12] where they defined optical density, transparency and opacity. By studying the light absorption behavior of Indian ink on substances that do not reflect much light such as black opaque bodies or transparent colored bodies, Hunter and Driffield found out that the reduction in light intensity due to the ink is due to the black particles and depends upon their number interposed per unit area. They then reasoned that the intensity of light I passing through A molecules of a substance is a fraction of the original intensity I_o, such that:

$$\frac{I}{I_o} = e^{-kA} \tag{6}$$

Where k is the coefficient of absorption. From equation (6), they thus defined transparency T, opacity O and optical density D as:

$$T = \frac{I}{I_o} = e^{-kA}$$

$$O = \frac{I_o}{I} = e^{kA}$$

$$D = \log_{10} O = -\log_{10} T \tag{7}$$

From equations (7), optical density is thus the logarithm of the opacity and negative logarithm of the transparency.

Robert Luther in 1900 made an important step to further develop equation (5). In his paper, *Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre*,[13] Luther defines the German term Extinktion, a quantity equivalent to absorbance, as the decadic logarithm of opacity in reference to Hunter and Driffield work. Luther then continued to work on light absorption and in 1913 together with his colleague Andreas Nikolopulos in their phenomenal paper *Über die Beziehungen zwischen den Absorptionsspektren und der Konstitution der komplexen Kobaltamminsalze Kobaltamminsalze*[14] merged the Bouguer-Lambert law and Beer's law in a manner of equation (1) giving the first modern formulation of the Bouguer-Beer-Lambert law.

$$\log_{10}\left(\frac{I_o}{I}\right) = \varepsilon cl \tag{8}$$

3. Formulation of the Bouguer-Beer-Lambert law

3.1 *Classical formulation*

The classical formulation of the Bouguer-Beer-Lambert is a simple and straightforward approach based on the empirical observational relationship between light intensity, path length and concentration.[15] When a monochromatic light is passed through a solution containing an absorbing substance, the decrease in light intensity with path length is proportional to the concentration of the solution and intensity of light.

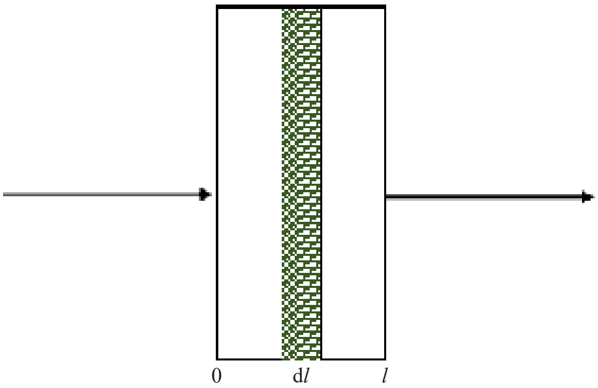

Figure 2. Light passing through a differential element

Considering the differential element, as illustrated in Figure 2.

$$-\frac{dI}{dl} \propto cI$$

$$-\frac{dI}{dl} = kcI$$

$$-\frac{dI}{I} = kcdl$$

$$-\int_{I_o}^{I} \frac{dI}{I} = kc\int_{0}^{l} dl$$

$$\ln\left(\frac{I_o}{I}\right) = kcl$$

$$\log_e\left(\frac{I_o}{I}\right) = kcl$$

$$\frac{\log_{10}\left(\frac{I_o}{I}\right)}{\log_{10} e} = kcl$$

$$2.303\log_{10}\left(\frac{I_o}{I}\right)=kcl$$

$$\log_{10}\left(\frac{I_o}{I}\right)=\frac{k}{2.303}cl \tag{9}$$

We define absorbance, A, as the quantity of light absorbed by a solution mathematically expressed as:

$$A=\log_{10}\left(\frac{I_o}{I}\right)$$

For a particular substance, molar extinction coefficient (ε) measures how strongly a chemical species or substance absorbs light at a particular wavelength. It is dependent upon their chemical composition and structure mathematically expressed as:

$$\varepsilon=\frac{k}{2.303}$$

Equation (9) thus becomes:

$$A=\varepsilon cl \tag{10}$$

3.2 *Electromagnetic formulation*

Electromagnetic formulation of the Bouguer-Beer-Lambert law[4,16] provides a more fundamental and detailed understanding of how light interacts with matter at the molecular level incorporating effects of polarizability, electric displacement, refractive index and molecular absorption cross-sectional area, bridging the gap between classical optics and quantum mechanics. On a microscopic scale, the matter is made up of molecules that constitute dipole moments and assuming the absence of interactions between the dipole moments, we define polarization, P as the product of molecular dipole moments, p and their number N:

$$P=N\cdot p$$

The molecular dipole moment depends on the polarizability, a' of the material and the electric field thus:

$$p=\alpha'\cdot E$$

Consequently:

$$P=N\alpha' E \tag{11}$$

Polarization is also a measure of the electric dipole moment per unit volume induced in a dielectric material when an electric field is applied to it.

$$P=\epsilon_o\chi_e E \tag{12}$$

Where x_e is the electrical susceptibility of the material and ϵ_o is the vacuum permittivity. We then define, the electric displacement field, D that accounts for the electromagnetic effects of polarization and that of the electric field:

$$D = \epsilon_o E + P$$

$$D = \epsilon_o E + \epsilon_o \chi_e E$$

$$D = \epsilon_o E \left(1 + \chi_e\right)$$

The electric displacement is also proportional to the electric field, $D = \epsilon E$. Where ϵ is the permittivity of the material.

$$\epsilon E = \epsilon_o E \left(1 + \chi_e\right)$$

$$\frac{\epsilon}{\epsilon_o} = \left(1 + \chi_e\right)$$

The quantity ϵ/ϵ_o is the relativity permittivity or dielectric constant ϵ_r and is a measure of how easily a material can be polarized by an external electric field.

$$\begin{aligned} \epsilon_r &= 1 + \chi_e \\ \chi_e &= 1 - \epsilon_r \end{aligned} \tag{13}$$

Combining equations (11), (12) and (13) we get:

$$P = \epsilon_o \left(1 - \epsilon_r\right) E$$

$$\frac{P}{\epsilon_o E} = 1 - \epsilon_r$$

$$\epsilon_r = 1 + \frac{P}{\epsilon_o E}$$

$$\epsilon_r = 1 + \frac{N\alpha'}{\epsilon_o} \tag{14}$$

The Number of dipole moments equals the number of molecules in the material assuming negligible interactions between the dipoles:

$$N = N_A c \tag{15}$$

Where N_A is the Avogadro's number and c is the molar concentration. Equation (14) thus becomes:

$$\epsilon_r = 1 + c\frac{N_A \alpha'}{\epsilon_o} \tag{16}$$

Using Maxwell equations, the relativity permittivity ϵ_r is related to the index of refraction, n as shown by taking the Faraday's and the Ampere-Maxwell laws in the absence of charges:

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad [\mathit{Faraday's\ law}]$$

$$\vec{\nabla} \times \vec{B} = \mu_o \int_o \frac{\partial \vec{E}}{\partial t} \quad [\ \mathit{Ampere\ -\ Maxwell\ law}\ ]$$

Taking curl on both sides of the Faraday's law:

$$\vec{\nabla}(\vec{\nabla} \times \vec{\mathrm{E}}) = -\frac{\partial \vec{\nabla} \times \vec{\mathrm{B}}}{\partial t}$$

$$\vec{\nabla}(\vec{\nabla} \times \vec{\mathrm{E}}) = -\overrightarrow{\nabla^2}\vec{\mathrm{E}} + \vec{\nabla}(\vec{\nabla} \cdot \vec{\mathrm{E}})$$

In a vacuum, $\vec{\nabla} \cdot \vec{\mathrm{E}} = 0$

$$\vec{\nabla}(\vec{\nabla} \times \vec{\mathrm{E}}) = -\vec{\nabla}^2\vec{\mathrm{E}} = -\frac{\partial \vec{\nabla} \times \vec{\mathrm{B}}}{\partial t}$$

$$\vec{\nabla}^2\vec{\mathrm{E}} = \frac{\partial \vec{\nabla} \times \vec{\mathrm{B}}}{\partial t}$$

Substituting the Ampere-Maxwell law in the above expression:

$$\vec{\nabla}^2\vec{\mathrm{E}} = \frac{\partial}{\partial t}\left(\mu_o \epsilon_o \frac{\partial \vec{\mathrm{E}}}{\partial t}\right)$$

$$\vec{\nabla}^2\vec{\mathrm{E}} = \mu_o \epsilon_o \frac{\partial^2 \vec{\mathrm{E}}}{\partial t^2}$$

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\vec{\mathrm{E}} = \mu_o \epsilon_o \frac{\partial^2 \vec{\mathrm{E}}}{\partial t^2}$$

Considering the one-dimensional form of the above equation in the x direction:

$$\frac{\partial^2 \vec{\mathrm{E}}}{\partial x^2} = \mu_o \epsilon_o \frac{\partial^2 \vec{\mathrm{E}}}{\partial t^2} \tag{17}$$

Which is a wave equation. A possible solution to the equation is a sinusoidal wave of wavelength λ and speed c:

$$\vec{\mathrm{E}} = E_o \sin\left(2\pi \frac{x - ct}{\lambda}\right)$$

Differentiating the solution twice with respect to *x* and *t*:

$$\frac{\partial^2 \vec{\mathrm{E}}}{\partial x^2} = -E_o \left(\frac{2\pi}{\lambda}\right)^2 \sin\left(2\pi \frac{x-ct}{\lambda}\right)$$

$$\frac{\partial^2 \vec{\mathrm{E}}}{\partial t^2} = -E_o \left(\frac{2\pi c}{\lambda}\right)^2 \sin\left(2\pi \frac{x-ct}{\lambda}\right)$$

Substituting the derivatives back to the wave equation (17):

$$-E_o \left(\frac{2\pi}{\lambda}\right)^2 \sin\left(2\pi \frac{x-ct}{\lambda}\right) = -\mu_o \epsilon_o E_o \left(\frac{2\pi c}{\lambda}\right)^2 \sin\left(2\pi \frac{x-ct}{\lambda}\right)$$

The wave equation satisfies the sinusoidal solution, thus the LHS should be equal to the RHS:

$$-E_o \left(\frac{2\pi}{\lambda}\right)^2 = -\mu_o \epsilon_o E_o \left(\frac{2\pi c}{\lambda}\right)^2$$

$$1 = \mu_o \epsilon_o c^2$$

$$c = \left(\frac{1}{\mu_o \epsilon_o}\right)^{\frac{1}{2}}$$

A similar equation is applicable to speed of light in any non-magnetic material:

$$c_m = \left(\frac{1}{\mu_o \epsilon}\right)^{\frac{1}{2}}$$

The index of refraction is defined as the ratio of the speed of light in a vacuum to the speed of light in that material:

$$n = \frac{c}{c_m}$$

$$n = \frac{\left(\frac{1}{\mu_o \epsilon_o}\right)^{\frac{1}{2}}}{\left(\frac{1}{\mu_o \epsilon}\right)^{\frac{1}{2}}}$$

$$n = \left(\frac{\epsilon}{\epsilon_o}\right)^{\frac{1}{2}}$$

$$n = \epsilon_r^{\frac{1}{2}}$$

$$\epsilon_r = n^2 \tag{18}$$

Substituting (18) into (16)

$$n^2 = 1 + c\frac{N_A\alpha'}{\epsilon_o}$$

$$n = \sqrt{1 + c\frac{N_A\alpha'}{\epsilon_o}}$$

Using binomial expansion for $\sqrt{1+x}$ and neglecting higher order terms:

$$\sqrt{1+x} = 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \frac{1}{16}x^3 - \ldots$$

Thus;

$$n \approx 1 + c\frac{N_A\alpha'}{2\epsilon_o} \tag{19}$$

We then introduce the complex refractive index, which takes into account scattering and absorption, respectively;

$$\hat{n} = n + ik$$

The real part, n is the ratio of the free-space speed of light to the phase speed of an electromagnetic wave in the medium. The imaginary part, k is related to the absorption coefficient by:

$$k = \frac{\alpha}{4\pi v} \tag{20}$$

Where a is the linear Napierian absorption coefficient and v is the wave number. From equation (19), we focus on the imaginary part, which takes into accounts absorption:

$$n \approx 1 + c\frac{N_A\alpha'}{2\epsilon_o} = n + ik$$

$$k \approx c\frac{N_A\alpha'}{2\epsilon_o} \tag{21}$$

Finally, we use the expression that relates absorbance to the Napierian absorption coefficient:

$$\ln\left(\frac{I}{I_o}\right) = -\alpha d$$

$$\log\left(\frac{I}{I_o}\right) = -\frac{\alpha d}{\ln 10}$$

$$A = \log\left(\frac{I_o}{I}\right) = \frac{\alpha d}{\ln 10}$$

$$A = \frac{\alpha d}{\ln 10} \tag{22}$$

Substituting Napierian absorption coefficient, *a* from equation (20) and the index of refraction, *k* from equation (21).

$$A = \frac{4\pi v k d}{\ln 10}$$

$$A = \frac{4\pi v}{\ln 10}\left(c\frac{N_A \alpha'}{2\epsilon_o}\right)d$$

$$A = \frac{2\pi N_A v \alpha'}{\epsilon_o \ln 10} \cdot c \cdot d \tag{23}$$

Equation (23) is the Bouguer-Beer-Lambert law.

4. Limitations of the Bouguer-Beer-Lambert law

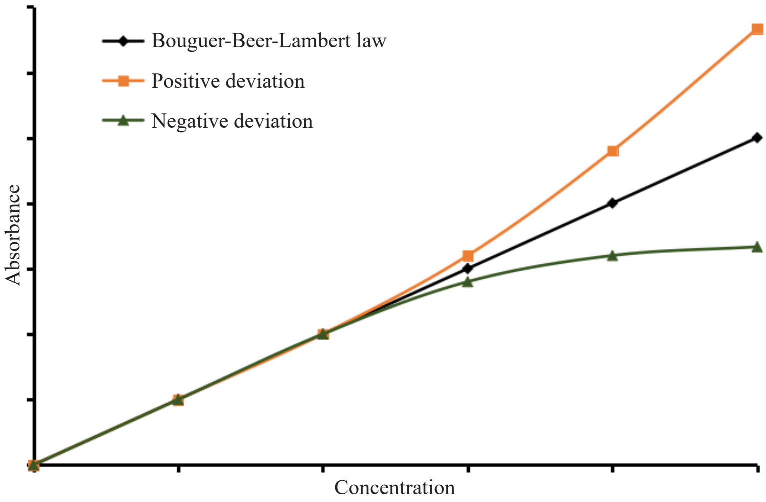

Figure 3. Deviations from the Bouguer-Beer-Lambert law

The Bouguer-Beer-Lambert law defines a linear relationship between absorbance, the concentration of the absorbing species and the path length the light travels through a sample. However, in most practical situations, deviations from this linearity are frequently observed which may be positive or negative.[17] Positive deviations occur when the absorbance is higher than expected from Bouguer-Beer-Lambert law suggesting that absorbing molecules are interacting with each other in a way that enhances the light absorption. Negative deviations occur when the absorbance is lower than predicted from the law indicating weaker interactions between absorbing molecules compared to what the law assumes. The deviations from the Bouguer-Beer-Lambert law are broadly classified into real or fundamental deviation, chemical deviation and instrumental deviation. Figure 3 summarizes the negative and positive deviations from the Bouguer-Beer-Lambert law.

4.1 *Fundamental deviations*

Fundamental deviations also known as real deviations arise from the inherent limitations of the law itself.[4,18] The Bouguer-Beer-Lambert law is valid only at low analyte concentrations usually < 0.01 M. As seen from the electromagnetic formulation, the law assumes the absence of interactions between the molecules, which is only true at low concentrations. At high concentrations, the intermolecular distances are diminished to the point where each particle affects the charge distribution of the neighboring particles resulting to solute-solute interactions such as hydrogen bonding and electrostatic interactions, which alters the ability of the analyte species to absorb radiation of a given wavelength. Another contribution to the fundamental deviation stemming from electromagnetic theory is the absorbance dependence on refractive index.[6] At low concentrations, the refractive index is essentially constant, and the law holds. At high concentrations, however, the higher order terms of the refractive index from equation (19) come into play resulting to deviation from the anticipated linear relationship, ultimately causing the breakdown of the law.

4.2 *Chemical deviations*

Chemical deviations are caused by specific properties of the analyte itself or its interactions with the surrounding environment including changes in pH, increase in concentration or the presence of other ions which results in a shift in the analyte chemical equilibrium.[19] This shift dissociates the analyte according to the Le Chatelier's principle to produce products with different maximum absorption wavelengths from the analyte, hence resulting in a deviation from the Bouguer-Beer-Lambert law. A common example of the phenomenon is found in acid-base indicators. Consider the general acid-base indicator color-change equation shown, where Hln is the acid form of the indicator, H^+ is the hydrogen ion (proton) released as Hln dissociates and ln^- is the conjugate based on the indicator after it has lost a proton.

$$\mathrm{Hln} \rightleftharpoons \mathrm{H^+} + \mathrm{ln^-}$$

The equilibrium of Hln dissociation to ln^- determines the indicator's color change. At low concentrations, equilibrium is maintained between the Hln and ln^- and thus the absorbance increases linearly with concentration following the Bouguer-Beer-Lambert law. Increasing the concentration causes the equilibrium to shift towards the formation of color ions ln^- disrupting the linear relationship between concentration and absorbance. The solution becomes more colored than predicted by the law, resulting in a positive deviation from linearity.

4.3 *Instrumental deviation*

Instrumental deviations arise from inconsistencies or imperfections in the spectrophotometer or flaws in how absorption measurements are performed. These deviations are a result of two contributions.[19] The first contribution is because the Bouguer-Beer-Lambert law strictly applies when absorbance measurements are carried out using a monochromatic source of radiation-the radiation reaching the sample is of a single wavelength. This is the ideal scenario, however, in practical situations, polychromatic light sources are used causing a deviation from the expected linearity of the Bouguer-Beer-Lambert law especially when the analyte absorbs strongly across a range of wavelengths. Another contribution is caused by stray radiation, extraneous light that reaches the detector beyond the monochromatic spectral region[20], originating from imperfections in the wavelength selector, permitting light to enter the instrument and reach the detector without traversing the sample, thereby introducing an extra component to the intensity of the radiation received by the detector.

$$A = \log_{10}\left(\frac{I_o + I_{\text{stray}}}{I + I_{\text{stray}}}\right) \tag{24}$$

For small analyte concentrations I_{stray} is significantly smaller compared to I_o and I and thus absorbance is unaffected by stray radiation. For higher concentrations, however, minimal light passes through the sample and hence I_{stray} becomes very large almost similar to I resulting in a negative deviation from the Bouguer-Beer-Lambert law.

5. Modifications of the Bouguer-Beer-Lambert law

In practical applications, the ideal conditions under which the Bouguer-Beer-Lambert law holds such as the use of monochromatic radiation, maintaining a low concentration of the analyte and utilizing a non-scattering medium are often not met, making the law only accurate within well-specified, constrained configurations. Consequently, this has sparked considerable interest in modifications aimed at expanding its scope and accuracy. The following are some of the major modifications done across different scientific disciplines. Figure 4 shows the results of their modification.

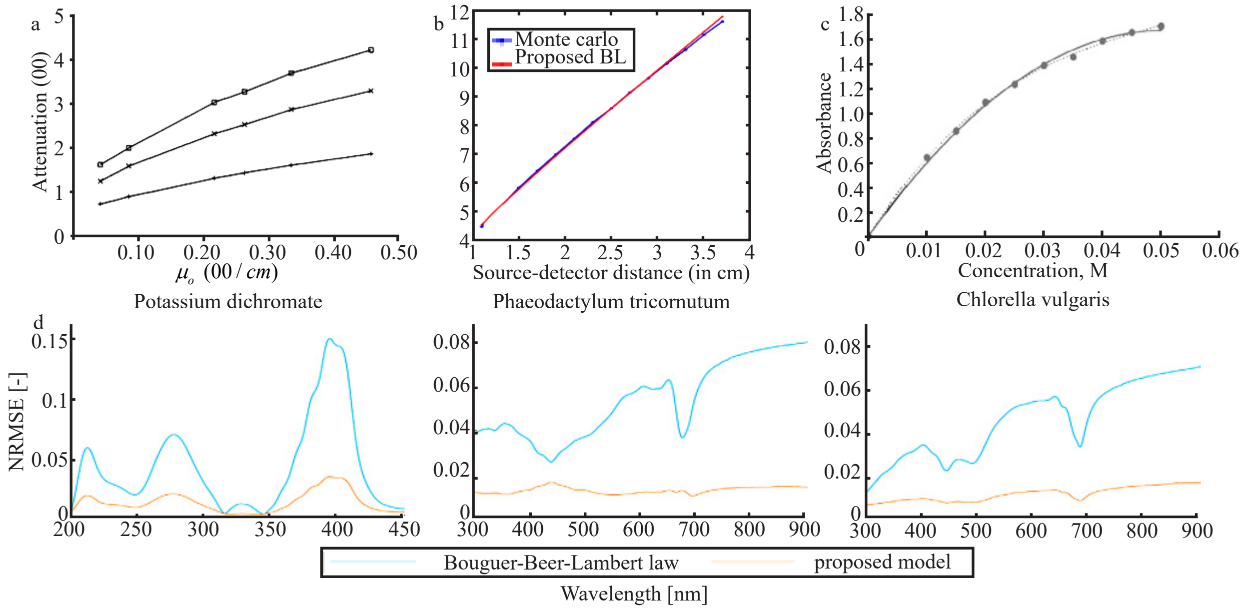

Figure 4. (a) Modified Bouguer-Beer-Lambert law for oxy-and deoxyhemoglobin tissue chromophores Monte Carlo simulation,[21] (b) comparison between the proposed modified Bouguer-Beer-Lambert law and Monte Carlo simulation,[23] (c) Bozdoğan polynomial modification taking into account fundamental deviation for ceric ion[24] and (d) comparison of NRMSE for modified Bouguer-Beer-Lambert law and Bouguer-Beer-Lambert law[27]

5.1 *Modified Bouguer-Beer-Lambert law for oxy-and de-oxyhemoglobin tissue chromophores*

Delpy and collaborators proposed a modification of the Bouguer-Lambert-Beer law to take into account the multiple scattering in natural chromophores, e.g., hemoglobin in the red blood cell and cytochromes *a*, *b*, and *c* in the mitochondrial cell membrane.[21] Optical techniques have long been employed to track changes in cerebral oxygenation and metabolism. These methods rely on oxygen-dependent absorption changes in tissue due to natural chromophores. Near-infrared light (NIR) within the 700-1,300 nm range is utilized to observe oxygen-dependent absorption of hemoglobin and cytochrome. By analyzing absorption changes across multiple wavelengths, continuous monitoring of cerebral oxygenation in various animals and, through reflection mode, in human adults and newborns is achievable. However, the measured attenuation of light through the head is influenced by factors such as detector and transmitter geometry, head shape, and tissue scattering and absorption properties, making it a complex process. Taking into account all these, Delpy and coauthors, propose a modification of the Bouguer-Beer-Lambert law by assuming the attenuation in optical density can be expressed as;

$$\text{Attenuation } (OD) = -\log\left(\frac{I}{I_o}\right) = B\mu_a d_p + G \tag{25}$$

Where I is the transmitted intensity, I_o the input light intensity, B is a pathlength factor dependent upon the absorption and scattering coefficients μ_a and μ_s (scattering coefficient) and the scattering phase function, G is an unknown geometry dependent factor, and d_p is the inter-optode distance between source and detector. The validity of equation (25) depends on how much B varies with the attenuation and scattering coefficients and phase function.

Angelo Sassaroli and Sergio Fantini, 16 years after Delpy and coworkers modification, in their paper, Comment on the modified Beer-Lambert law for scattering media[22] argue that the Bouguer-Lambert-Beer modification in equation (25) is incorrect in that the path length factor B (a pathlength factor is the width of the cuvette used for the absorbance measurement and is typically 1 cm.) must be substituted by its average over the range of absorption coefficients 0 ~ μ_a. They then go ahead to propose a correction of the model by asserting that the correct change in the attenuation must be calculated as:

$$\delta A(\mu_a) = \overline{\langle L\rangle}\delta\mu_a + \mu_a\delta\overline{\langle L\rangle} \tag{26}$$

Where $\overline{\langle L\rangle}$ represents the 'mean average path length' of detected photons over the range of absorption coefficient 0 ~ μ_a:

$$\overline{\langle L\rangle}(\mu_a) = \frac{1}{\mu_a}\int_0^{\mu_a}\langle L\rangle\mu_a'$$

5.2 *Modified Bouguer-Beer-Lambert law for near-infrared light propagation in thick biological tissues*

In their generalized Bouguer-Beer-Lambert model for near-infrared light propagation in thick biological tissues, Bhatt and coauthors demonstrate that the modified Bouguer-Beer-Lambert used to quantify the changes in tissue chromophore concentrations in NIR spectroscopy in equation (26) suffers from its applicability across tissue types and tissue dimensions.[23] To solve the problem and extend its applicability to thick tissues, Bhatt and collaborators introduce the Lambert-W function-based modelling for light propagation in biological tissues, which is generalized version of the Bouguer-Beer-Lambert model, providing parameterization of properties including two attenuation coefficients μ_o and η. Starting with the standard Beer-Lambert Law.

$$I = I_o e^{-\bar{\mu}d}$$

where, $\bar{\mu}$ is the total attenuation coefficient given by the equation.

$$\bar{\mu} = \mu_o + \eta\frac{I}{I_o}$$

Where μ_o and η are two unknown parameters that represent the optical properties in the proposed parameterization scheme. Substituting for the total attenuation coefficient in the Bouguer-Beer-Lambert we get:

$$I = I_o e^{-\left(\mu_o + \eta \frac{I}{T_o}\right)d}$$

$$\frac{I}{I_o} = e^{-\mu_o d - \eta d \frac{I}{T_o}}$$

$$\frac{I}{I_o} = \frac{e^{-\mu_o d}}{e^{\eta d \frac{I}{I_o}}}$$

$$\eta d \frac{I}{I_o} e^{\eta d \frac{I}{I_o}} = \eta d e^{-\mu_o d}$$

The above equation is of the Lambert-W function which takes the form:

$$W(x) e^{W(x)} = x$$

Consequently, by equating the two equations:

$$x = \eta d e^{-\mu_o d};\ W(x) = \eta d \frac{I}{I_o}$$

whose solution involves the Lambert-W function given as:

$$I = \frac{I_o}{\eta d} W\left(\eta d e^{-\mu_o d}\right) \tag{27}$$

Equation (27) represents a generalized form of the Bouguer-Beer-Lambert law. The optical density can then be written by taking the decadic logarithm on both sides of the equation:

$$OD = -\log\left(\frac{I}{I_o}\right) = \log(\eta) + \log(d) - \log\left[W\left(\eta d e^{-\mu_o d}\right)\right] \tag{28}$$

The generalized Bouguer-Beer-Lambert model fully described light propagation in thick biological tissue, offering a distinct advantage due to its universal applicability akin to the Monte Carlo model for tissue thicknesses beyond 1 cm. This showcases its potential to revolutionize near-infrared spectroscopy (NIRS) for brain and breast imaging.

5.3 *Modified Bouguer-Beer-Lambert law based on polynomial equations considering deviations from linearity and absorption flattening*

Abdürrezzak Bozdoğan proposes a modified Bouguer-Beer-Lambert law based on polynomial equations taking into account the negative and positive deviation from linearity in path length, concentration and absorption flattening as shown respectively[24]:

$$A=\log_{10}\left(\frac{I_o}{I}\right)=\frac{\alpha}{2.303}d\pm\frac{\alpha^2}{2(2.303)}d^2\pm\frac{\alpha^3}{3(2.303)}d^3\pm\frac{\alpha^4}{4(2.303)}d^4\pm\ldots\pm\frac{\alpha^n}{n(2.303)}d^n \tag{29}$$

$$A=\log_{10}\left(\frac{I_o}{I}\right)=\frac{kd}{2.303}c\pm\frac{(kd)^2}{2(2.303)}c^2\pm\frac{(kd)^3}{3(2.303)}c^3\pm\frac{(kd)^4}{4(2.303)}c^4\pm\ldots\pm\frac{(kd)^n}{n(2.303)}c^n \tag{30}$$

$$A=dc\varepsilon-\frac{2.303(cd)^2}{2}\varepsilon^2+\frac{2.303^2(cd)^3}{3}\varepsilon^3+\frac{2.303^3(cd)^4}{4}\varepsilon^4+\ldots+\frac{2.303^{n-1}(cd)^n}{n}\varepsilon^n \tag{31}$$

Where A is the absorbance, α is the Napierian absorption coefficient, ε is the molar extinction coefficient, d is the thickness of the absorbing medium, k is the proportionality constant, c is the concentration of the sample and ± represent the positive and negative deviations from the Bouguer-Beer-Lambert law. Equations (29) to (31) were then fitted to experimental data to describe the positive and negative chemical, fundamental and instrumental deviations and absorption flattening. Chemical deviations from linearity of the Bouguer-Beer-Lambert law were investigated using unbuffered solutions of acidic indicators. Instrumental deviations were considered by fitting the proposed model in deviations from linearity due to polychromatic radiation and in the presence of stray radiation. Real or fundamental deviations were also taken into consideration by analyzing the behavior of absorbance at high concentrations in ferrozine, acetylsalicylic acid, ferrocene, ceric ion, dichromate ion. Bozdoğan then goes ahead to analyze and model the non-linear absorbance as a function of thickness for polythene and finally absorption flattening was investigated and modeled using 8-µM cytochrome c entrapped in phospholipid vesicles. The result demonstrated a precise depiction of the deviations, both positive and negative and absorption flattening from the Bouguer-Beer-Lambert law.

5.4 *Modified Bouguer-Beer-Lambert law for space -time dependency of concentration and deviations due to spatial memory*

The space-time dependency of absorbance stemming from the degradation or alteration of light absorbing species and spatial memory due to random correlated obstacles has been a major problem in photochemistry, particularly in the application of the classical Bouguer-Beer-Lambert. Space-time dependency of absorbance refers to the variation of light absorbance in a sample in both spatial and temporal dimensions. Spatial dependence is caused by the presence of obstacles or uneven distribution of the absorbing molecules. Temporal dependence is evident where light itself causes the degradation or transformation of absorbing molecules leading to a decrease in absorbance over time. Spatial memory is a relatively novel concept that refers to the way light interacts with molecules in a non-uniform way within the system mainly caused by the presence of obstacles or the way molecules are arranged in space. The first to explore this challenge were Parnis and Oldham who derived a modified formulation of the Bouguer-Beer-Lambert law to incorporate the temporal evolution of concentration of a light absorbing solute.[25]

$$\frac{\partial}{\partial x}I(x,\ t)=-\varepsilon c(x,\ t)I(x,\ t) \tag{32}$$

Where ε is the molar absorptivity, $c(x,\ t)$ is the analyte spatial and temporal concentration variation. The time evolution of concentration dependence of $I(x,\ t)$ is described by the relationship;

$$\frac{\partial}{\partial x}c(x,\ t)=-\phi\varepsilon c(x,\ t)I(x,\ t) \tag{33}$$

Where ϕ is the quantum yield. In the absence of solution mixing, the modified formulation indicates a significant symmetry where the relationship between light intensity and distance aligns with the relationship between concentration and time. An extension of equations (32) and (33) to take into account spatial memory due to the presence of random obstacles has been formulated by Casasanta and collaborators neglecting the time-dependency and using the Mittag-Leffler function as shown[26]

$$p_o(x) = E_a\left(-\lambda\left[\int_0^x c(s)ds\right]^\alpha\right) \tag{34}$$

Where $p_o(x)$ is the transmission probability and E_a is the Mittag-Leffler function. Casasanta and coauthors' formulated modification thus takes into account the concentration space dependecy and exponential decay due to spatial memory.

5.5 *Modified Bouguer-Beer-Lambert law for potassium dichromate solutions and microalgae suspensions*

Yen-Cheng Yeh and collaborators propose a novel analytical modification of the law to solve the problem of chemical deviation in potassium dichromate solutions and the light scattering effect in microalgae suspensions.[27] Chemical deviation arises from the equilibria of chemical species within the analyte, where the concentrations of these species do not follow a linear relationship with the total analyte concentration. In potassium dichromate solutions under weakly acidic conditions, the equilibria equation involves the dimerization of the monomer $HCrO_4^-$ to form the dimer $Cr_2O_7^{2-}$.

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

This leads to deviations from the Bouguer-Beer-Lambert law, particularly at wavelengths where the molar absorption coefficients of $HCrO_4^-$ and $Cr_2O_7^{2-}$ differ significantly. It is important to note that these deviations are not inherent to the law itself but are a result of the non-linear equilibria involving the individual ions, $HCrO_4^-$ and $Cr_2O_7^{2-}$. Light scattering used in their work is Mie scattering by microalgae cells, which refers to the elastic scattering of light by homogenous spherical particles that have a diameter similar to or larger than the wavelength of the incident light. To solve the deviations, Yen-Cheng Yeh and collaborators, propose a non-linear absorbance model by introducing two exponents in the classical Bouguer-Beer-Lambert law.

$$A = \log\frac{I_o}{I} = \varepsilon' \cdot c^\alpha \cdot l^\beta \tag{35}$$

Where A is the apparent absorbance, I_o is the input light intensity, I the output light intensity transmitted through the sample, ε' the effective specific absorbance, α the correction coefficient of the concentration c, and β the correction coefficient of the path length l. Both α and β are real positive numbers and as seen from the equation, if both are equal to one, the proposed equation is identical to Bouguer-Beer-Lambert law. To test their model, solutions of potassium dichromate and two microalgae suspensions (*Phaeodactylum tricornutum* and *Chlorella vulgaris*) were prepared and analyzed using designed systematic experiments with simultaneously varying concentration and path length. They then compared the performance of the Bouguer-Beer-Lambert law and the proposed model using the correlation coefficient (R^2) and the normalized root mean square error (NRMSE) giving an R^2 exceeding 0.995 for all tested materials, greater than the Bouguer-Beer-Lambert law, which had an R^2 of 0.94. The proposed model thus described the chemical deviation in potassium dichromate solutions and the light scattering effect in microalgae suspensions.

6. Advanced approaches to the Bouguer-Beer-Lambert law modification

The Bouguer-Beer-Lambert law as previously stated is only applicable within narrowly defined, restricted parameters. This has thus inspired attempts to extend the applicability of the law beyond its ideal scenarios resulting in various modifications, which have taken into account real world complexities such as polychromatic light sources, concentration gradients, chemical deviations and scattering effects.[4,28] However, the current modifications are still case-specific, lacking the required generality for broad applicability across diverse fields. As a result, more sophisticated, advanced approaches are increasingly demanded for capturing the nuances of light-matter interactions. The following are some of the advanced techniques utilized in the pursuit for a more comprehensible and applicable generalized framework.

6.1 *Monte Carlo simulation*

The Monte Carlo simulation is a mathematical technique used to model the probability of different outcomes in a process that cannot be easily predicted due to the interaction of random variables.[29] The method involves identifying the sources of uncertainties in the parameters of the Bouguer-Beer-Lambert law usually caused by instrumental errors, sample inhomogeneity, intermolecular interactions and fluctuations in the light transmissions originating from light scattering, reflection, and fluorescence. The appropriate probability distribution is then assigned to these uncertain parameters and simulation is done to generate random samples for each variable obtaining a range of outcomes. The impact of the uncertainties is then analyzed and based on the findings, the Bouguer-Beer-Lambert is modified to better account for the observed variabilities and validated to ensure its accuracy and relevance.[30-32] This ultimately allows researchers to simulate the path of either an individual photon or a ray of light through a sample and analyze the various deviations from theoretical prediction, offering a better and fundamental understanding into the law and its limitations.

6.2 *Machine learning algorithms*

Machine learning algorithms are computational techniques that allow systems to learn and make predictions based on some data set. Unlike conventional programming, which involves the writing of an algorithm or code for each instruction, machine learning algorithm, uses statistical procedures to find a pattern in the data and make a prediction.[33] By collecting and reprocessing a large data set of absorbance measurements, parameters of the Bouguer-Beer-Lambert can be engineered, for example, the introduction of exponents of concentration and path length to capture potential non-linear relationships between concentration, path length and matrix components. Suitable machine learning algorithms including support vector, neural networks, or regression are then trained on the data. The trained model based on the learned relationship is then validated and tested experimentally ensuring it generalizes well with every other data set and makes better and more relevant predictions.[34] The leveraging of machine learning algorithms thus offers an instinctively accurate way of dealing with deviations from the Bouguer-Beer-Lambert Law, adjusting for factors such as scattering, reflection, or electrostatic interactions of solute molecules that the original law fails to account.

6.3 *Numerical methods and finite element analysis (FEA)*

Numerical methods and finite element analysis (FEA) are highly efficient techniques for modifying the classical Bouguer-Beer-Lambert Law to account for complex scenarios. Numerical methods are used to solve mathematical problems that are difficult to solve analytically by approximating the solution using numerical algorithms.[35] Of particular interest, the finite-difference-time domain (FDTD),[36] a 3D full wave electromagnetic solver, has proven to be useful in solving Maxwell equations numerically, providing a better understanding on how light interacts with matter at the micro-nano scales where fundamental or real deviations from the Bouguer-Beer-Lambert Law occur.[37] Conversely, FEA divides a complex mathematical structure into simpler elements, solving the equations and combining the results to obtain a generalized solution.[38] The method can thus be used to solve the complex differential equations that govern light interactions in a heterogonous media where the classical Bouguer-Beer-Lambert Law fails.[39]

6.4 *Molecular dynamics simulation*

Molecular dynamics simulation is a computational method used to simulate the behavior of molecules and their interactions in the presence of electromagnetic radiation, providing insights into how molecular properties influence absorption and scattering.[40] The technique involves the construction of a molecular model through the definition of various parameters such as atom types, their positions and intermolecular forces with experimental data for known structures with quantum and statistical calculations used to define the geometry. The model is then simulated by fitting in the appropriate boundary and initial conditions to study and calculate the evolution of the molecular model with time. An electromagnetic radiation is then introduced and the simulation is used to calculate the shift in the intermolecular forces and the energy absorbed and scattered by the molecules.[41] The insights from the simulation are then used to modify the Bouguer-Beer-Lambert Law to include factors influencing light absorption, such as molecular structure, inter-molecular interactions and concentration correlated with Avogadro's number of particles.

6.5 *Quantum mechanical density functional theory (DFT)*

Density functional theory (DFT) is a computational method in quantum mechanics used to investigate the electronic structure of atoms and molecules based on electron density rather than the systems wave function, striking a balance between accuracy and computational efficiency.[42] DFT can thus be utilized to calculate and study the electronic structure of molecules including energy levels, electronic transitions and dipole moments, enabling the refinement of the Bouguer-Beer-Lambert Law to consider for specific molecular interactions. The technique also allows for the study of how electronic states couple with molecular vibrational states leading to a more accurate prediction of absorption spectra, particularly in complex heterogonous media.[43] Through the examination of structure, transitions and vibronic coupling, the theory reveals the limitations of the classical Bouguer-Beer-Lambert Law, providing a blueprint for the development of more accurate models that account for non-linear effects, especially at high analyte concentrations and media heterogeneity.

7. Challenges and prospects

The Bouguer-Beer-Lambert law is an essential framework in absorption spectroscopy finding applications across diverse scientific disciplines and industries. However, its scope and applicability are limited to the various scenarios identified above. These limitations remain a major problem that has motivated a pursuit of the modification of the law across different scientific areas. Firstly, despite the efforts, realizing a universally accepted and simple to apply modified Bouguer-Beer-Lambert law remains elusive due to different factors. The review has demonstrated that the assumption of a simple linear relationship between absorbance and concentration for a specific wavelength of light does not reflect reality. Light-matter interactions are complex, often involving interacting phenomena such as multiple scattering, fluorescence, and non-linear effects. Secondly, the current law is valid for a monochromatic light source, therefore when dealing with broad-spectrum or polychromatic light sources, the absorption characteristics vary significantly across wavelengths. Moreover, real-world samples often exhibit heterogeneity in terms of composition, particle size, and optical properties which leads to deviations from the idealized assumptions of the law. There is a need for more studies to identify ways to adapt the law to broad-spectrum or polychromatic light sources. Thirdly, high concentrations or the non-linear regimes of the law require more advanced mathematical formulations and experimental validation to account for the fundamental deviations, which can be a complex task. However, with advancements in computational technologies this can be addressed. Finally, the law assumes the absorbing species is uniform in the spatial and temporal dimensions, which is not the case in some materials. These challenges make generalizing Bouguer-Beer-Lambert difficult because it requires incorporating additional factors that deviate from the simple assumptions of the original law. Developing a universally applicable modification needs to consider these complexities while maintaining a balance between accuracy and computational feasibility. We propose that more studies are needed to explore the deviations of the law and develop more robust models for analyzing light absorption, extending the applicability of the law beyond its current limits. This is possible through the leveraging of computational techniques such as the Monte Carlo simulations to model complex light interactions within a material and machine learning approaches to identify patterns that inform the development of the generalized modification. The focus should also extend to experimental validation where rigorous testing of any proposed modifications against experimental data should be carried out to ensure they accurately represent real-world light-matter interactions.

8. Conclusions

The Bouguer-Beer-Lambert law remains an indispensable tool in chemical analysis and quantitative measurements. However, limitations based on the inherent assumptions in the law limit its scope and accuracy outside its current limit. This study has thus provided a compressive overview of the law starting with a trace of its historical evolution from Pierre Bouguer's initial work to its contemporary structure, classical and electromagnetic formulation, and an in-depth analysis of the law's limitations. A detailed review of the major modifications of the law across different disciplines has also been presented and explained. Advanced approaches towards the formulation of a generalized modification of them have been studied in detail. Finally, challenges and prospects towards the formulation of a generalized modification of the law and proposed solutions and directions that should be taken have been presented.

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Conflict of interest

The authors declare no conflict of interest.

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