MAS.020UF

Basic Laboratory for Advanced Materials Science

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Optics

Spectrophotometer

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1 Introduction

1.1 Brief introduction to the experiments

In this work, a spectrophotometer will be used to conduct various experiments, to generate a basic understanding of this measurement method for the students of this course. A spectrophotometer was used to determine the absorption spectra of two different color filters (red and blue, respectively) separately and together. The spectra were then used to show the transmission and extinction values, as well as the additivity of the extinction for the two filters. In a further experiment, the transmission and extinction of an aqueous methylene blue solution was measured relative to that of the pure solvent, with the intention of determining the molar concentration of the methylene blue under consideration of the molar extinction coefficient. In the last experiment, the UV-Vis spectrum of a glass plate was determined, and the reflection losses were quantified for various wavelengths. Finally, the thickness of the glass plate could be calculated based on the maxima of the interferences between the transmitted and the twice reflected waves.

1.2 Experimental theoretical background

When electromagnetic waves encounter matter (such as liquid solutions or solid-state materials), they can either be transmitted, absorbed, or scattered. In the first instance, the light passes through the material without directly interfering with its atoms. While this is the predominant case for transparent or semi-transparent materials, the other two interactions also occur. For the case of absorption, the photon is, as the name suggests, absorbed by an atom which then subsequently enters an excited state, which for light in the visible spectrum usually results in an electron from a lower band to transfer to a higher, previously unoccupied band. Most commonly, this energy is subsequently transformed to heat. Scattering results in a change of the propagation direction of the photon, and if this happens at smooth surfaces it is referred to as reflection. When illuminating a sample with light of a certain intensity I_0, the photons *have to* either be transmitted through the sample, become absorbed or scattered or reflect at either one of the two interfaces between the material and the external medium (such as air). The total amount of light that is not transmitted (total light attenuation) can be represented as follows:

$$1 - T = \frac{I_A + I_S + I_R}{I_0}$$

Where I_0 is the initial light intensity, I_A is the intensity of the absorbed light, I_S that of the scattered light and I_R that of the reflected light, and T is the transmittance.

However, the term "extinction" is more often used in spectroscopy. It is defined as the logarithmic scale of the inverse of the transmittance, and can be expressed using the following formula:

$$E = -\log(T) = -\log\left(\frac{I_T}{I_0}\right) = \log\left(\frac{I_0}{I_T}\right)$$

Where E is the extinction and I_T the intensity of the transmitted light. If light passes through multiple mediums, the respective extinction coefficients can be added together to yield the total extinction coefficient for the whole system. How much light is attenuated depends on the thickness of the layer as well as a material-related property, which can be referred to as the extinction coefficient α. In case of a substance dissolved in a solvent, the extinction coefficient is dependent on the concentration of the dissolved species c, as well as the natural molar extinction coefficient ε_n, which when divided by *ln(10)* leads to the base 10 molar extinction coefficient. The molar extinction coefficient basically shows how much light is absorbed by the molecular species per centimeter of sample thickness and per concentration unit of dissolved species. Using this coefficient, the following expression can be used to describe the extinction of the system (Lambert-Beer-law):

$$E = log\left(\frac{I_0}{I_T}\right) = \varepsilon * c * d$$

Where ε [L/(mol*cm)] is the common molar extinction coefficient, c [mol /L] is the concentration of the dissolved species and d [cm] is the thickness of the sample.

When white light shines on a glass plate with a certain thickness, interference phenomena might occur between waves that are transmitted and those that are reflected twice, at the respective interfaces. For a constructive interference to appear, the additional distance that the twice reflected light goes through the glass compared to the purely transmitted one has to be a multiple of their wavelength (assuming that both rays have the same wavelength). This condition can be written as follows:

$$\Delta s = 2n_p * d = m * \lambda_m$$

Where Δs is the pathway difference between the interfering light waves, n_p is the reflective index of the glass plate, d the thickness of the glass plates, m is a positive integer and λ_m is the wavelengths of the two photons that interfere. When written relative to the frequency, the above equation transforms to this:

$$v_m = \frac{m}{2n_p * d}$$

Where v_m is the frequency of the incoming light.

This effect is not limited to glass plates but can also be seen in other instances: If a puddle of water is stained with a small amount of oil, the oil will form a thin film on the surface of the water, due to their immiscibility with one another. The different refractive indexes of the two substances leads to a similar system as the one with the glass plate: While some of the light is reflected directly from the oil phase, some amount is also transmitted through the oily phase and reflects at the oil-water interface, leading to two different possible distances the photons can travel. Depending on the thickness of the oil layer, photons of various wavelengths interfere, thus, if the layer has a thickness gradient, the typical rainbow colors appear.

2 Experimental setup

2.1 Description of the experimental setup

For the experiments, a spectrophotometer was used. It consists of a halogen light source, a sample holder capable of holding filters as well as cuvettes, a glass fiber, and CCS-200 spectrometer by Thorlabs, Inc. . A sketch of the measurement setup can be found in figure 1. It has to be noted that the light path from the halogen lamp up to the fiberoptic cable was not shielded from ambient light, and so the measurement error from the ambient light has to be taken into account before conducting the experiments.

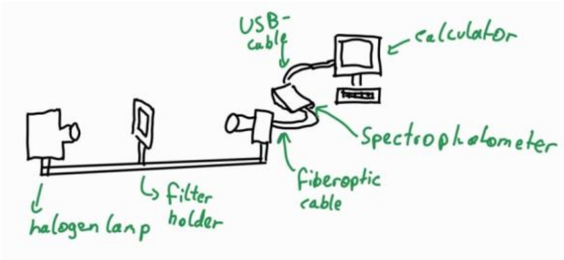

Figure 1: Schematic representation of the measurement setup.

The pathway of the light is as follows: the photons are emitted from the halogen lamp and make their way to the sample holder, where they interact with the sample (in our case, filters or the aqueous solution) in a combination of the three ways (transmission, scattering, absorption). The transmitted waves then enter the optical cable and are transmitted to the spectrophotometer, which consists of a Czerny-Turner monochromator and a diode array (in our case, it was a charge coupled device line camera), a sketch of the inside of the spectrometer being visible in figure 2.

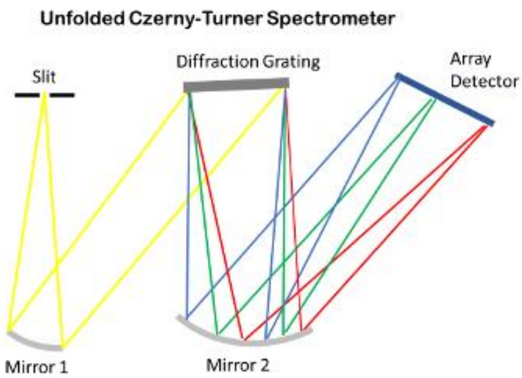

Figure 2: Schematic representation of an (unfolded) Czerny-Turner monochromator with a diode array detector

As seen in the figure above, the light enters the monochromator through a narrow slit and hits a concave mirror, which redirects the light waves (that are now parallel to each other) onto the diffraction grating. As the name might suggest, the grating diffracts the light, leading to a separation of the different wavelengths (for positive orders, the longer the wavelength, the smaller the outgoing angle). The photons (that are still parallel to each other) hit a second concave mirror, which focuses each light waves with a certain wavelength onto certain points of the diode array detector. Based on the position and the intensity of the light measured at the detector, the respective light intensities for each wavelength can be plotted. Considering that our Czerny-Turner monochromator also possesses an array detector at the end, this measurement setup can be considered a spectro(photo)meter.

2.2 List of devices

Here are again all the devices and components used within this experiment, in the form of a list for a better overview.

- Halogen lamp
- Filter and cuvette holder
- Two cuvettes, filled with distilled water and methylene blue solution, respectively
- One red and one blue light filter (for absorption measurements)
- A glass plate (for interference measurements)
- A fiberoptic cable for transferring the light to the spectrophotometer
- A CCS-200 spectrophotometer by Thorlabs, Inc., containing a Czerny-Turner monochromatograph and a charge coupled line camera as a detector
- A cable connecting the spectrophotometer with a computer
- A computer with a program that can be used to visualize the measured data ("Splicco")

3 Experimental process

3.1 Process of experiments 1 and 2

Before starting the experiments, the halogen lamp was turned on and left on for around ten minutes for it to heat up and achieve a constant illumination rate throughout the whole experiments. In the meantime, the measurement software from the computer was turned on and the integration time (the time over which the signal intensity is integrated) was set to 0,8 milliseconds, so that the signal intensity can be displayed without overshoot. The number of average scans was set to 50.

A background correction had to be made prior to any of the measurements. In our case, we covered the halogen lamp with a thick notebook to block any of its light and allow only ambient light to enter the spectrophotometer, and selected "Set Background Correction", which subtracted that spectrum from all subsequent measurements. Next, the reference spectrum was determined in the absence of a sample, as well as the light transmission intensities of the red and blue light filter separately and together, in alternating order. The measurements were repeated multiple times, enabling an accurate error assessment.

3.2 Results and discussion of experiment 1 and 2

The measured intensities of the reference spectrum, the red and blue filters separately and together are shown in figure 3. As there are multiple slots in which the filters can be placed, in this case, the filters were always placed as closely to the spectrophotometer as possible. When both filters were measured, the blue one was closer to the spectrometer.

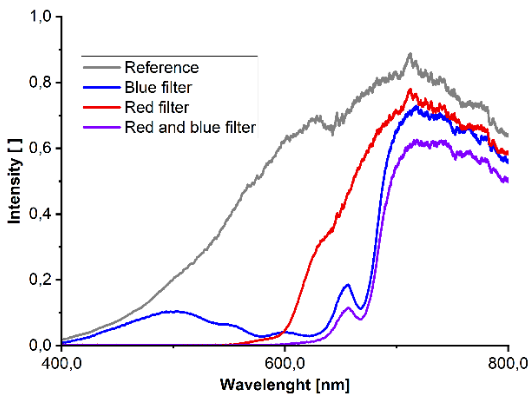

Figure 3: Light intensities of the respective wavelengths for the reference measurement, the red and blue filter separately and together. The plot was created using Origin 2022

As can be seen from figure 3, the filters lead to an overall reduction in the intensity of the light arriving to the optic cable when compared to the reference measurement. When comparing the filters to one another, the blue filter resulted in a higher light intensity at lower wavelengths compared to the red filter, especially in the region of 400 nm until around 600 nm, while the red filter allowed a higher intensity of light from 600 to 800 nm. However, not much other information can be obtained from this curves, as the halogen lamp does not emit light of all wavelengths with the same intensity, as can be seen from the reference measurements. Therefore, the reference curve has to be taken into account, and for a more accurate assessment, the transmission (I_T/I_0) and extinction $\log(I_0/I_T)$ values were calculated (I_0 are the values from the reference plot and I_T that of the filters) and presented in the following plots in figure 4:

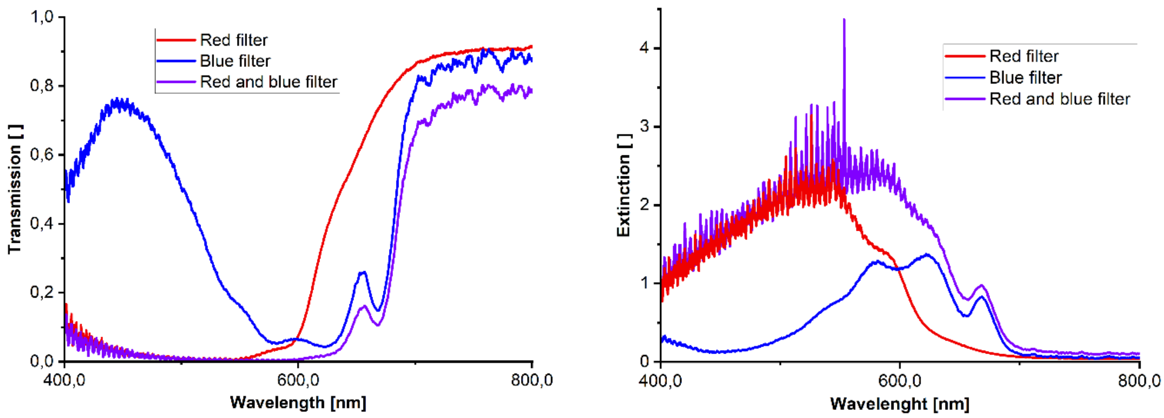

Figure 4: Plots for the calculated transmission and extinction values versus their wavelengths for the red, blue, and both filters.

As can be seen from the plots above, the blue filter shows a higher transmission at lower wavelengths (400-600 nm), while the red one has higher transmission at higher wavelengths (600-800 nm). Based on the spectra, it makes sense why the red color filter appears red: When (white) light is shining through it, the lower (blue) wavelengths are absorbed by the atoms/molecules/lattice within the filter, leaving only red light to pass and enter the human eye. The opposite is the case for the blue filter. The colors of the filters can easily be explained by their respective spectra. The transmissivity of both filters together is always smaller than that of the filters measured separately. When looking at the extinction, obviously, the opposite is true: The extinction of the red filter is higher at lower wavelengths and vice versa. The extinction for both filters together is always larger than that of the two filters when measured separately, because the light passes through both filters, which then absorb more light than just one filter. It could also be noticed that the data points for the extinction at lower wavelengths for the red and for both filters were fluctuating strongly. This is because the extinction is calculated from the transmission values, which in turn are close to zero for those filters at lower wavelengths, leading to the noise having a much stronger effect, which in turn leads to imprecise calculation values for the extinctions. For this reason, multiple measurements were taken using the red, blue and both filters. Ideally, three measurements should have been done for each of the filter configurations, however as during the measurements the extinction curves were not calculated yet, and during the repeat measurements for the blue filter, no large differences were noticed at the curve's profile, not too much attention was placed on repeating all measurements. This lead us to have three repeating measurements for the blue filter, but only two for the red and both filters. The average values of the extinction measurements are presented in figure 5.

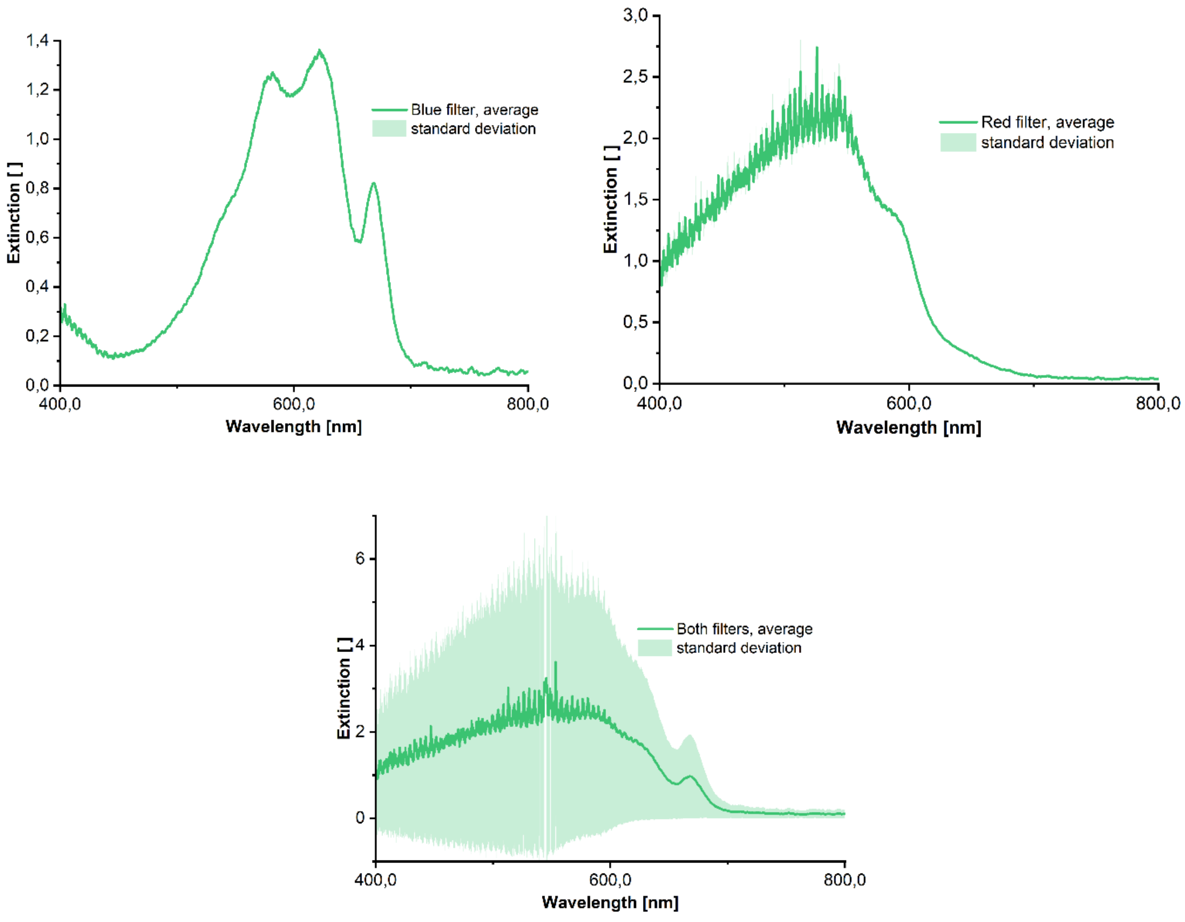

Figure 5: Average and standard deviation for the blue, red and both filters.

As can be seen, the red and the blue filters showed a high reproducibility of the results, and apparently even of the noise, as no standard deviation can be seen in the plots. When both filters were applied, however, a high standard deviation can be seen, and averaging the results has somewhat brought down the noise that could be seen before. It is believed that more nice results could have been achieved if the measurements would have been repeated for more than just two times.

3.3 Process of experiment 3

In this experiment, the molar concentration of a methylene blue solution was calculated by measuring the extinction and using the already known decadic extinction coefficient. To achieve this, the filter holder was replaced by a cuvette holder, the cuvette with the distilled water was placed inside and the reference spectrum was measured. , thereby determining I_0. Then, the methylene blue cuvette was placed in the cuvette holder and its spectrum was measured, which is then the I_T.

For a more precise assessment of the data, the measurements were repeated for a total of three times.

3.4 Results and discussion of experiment 3

The intensities of the measured light for the reference spectrum as well as the methylene blue spectrum and the subsequently calculated transmissions and extinctions can be seen in figure 6. From the three measured reference values, the average was calculated and then used to determine the respective transmissions and extinctions, using the average of the three measurements from the methylene blue solution.

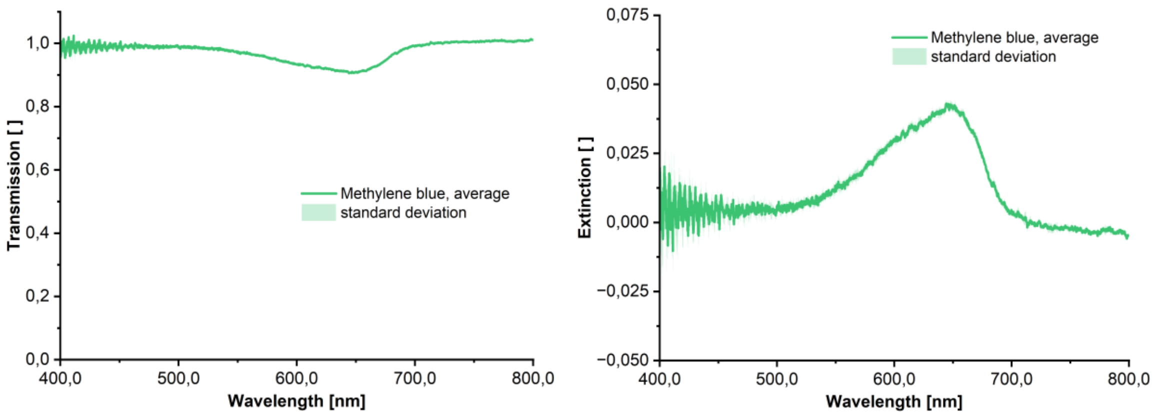

Figure 6: Average transmission and extinction curve of the methylene blue solution, including standard deviation.

The determined transmission and extinction curves are very similar to those found in literature,[1] showing a peak at the extinction measurements at 647 nm, with an extinction coefficient of 0,04299. The minima of the transmission spectrum coincides perfectly with the maximum of the extinction spectrum, as was to be expected. While the extinction spectra show only one peak and a small shoulder at around 612 nm, measurements from literature also show a second peak present at around the same point.[2] The barely noticeable presence of the peak in our measurements might be due to the lower concentration of methylene blue compared to that of the literature. In general, our measurements showed barley visible standard deviations, which we interpret as our results having a high precision.

As the molar extinction coefficient at 664 nm is known to be 77 790 L/(mol*cm), the concentration of the methylene blue from our sample could be determined using the Lambert-Beer Law: by determining the extinction coefficient from the extinction curve at 667 nm (in our case, 0,0341 ± 0,0013), and knowing the molar extinction coefficient as well as the thickness of our cuvette (1 cm), the concentration could be determined as (43,8 ± 1,7) $*10^8$ mol/L.

3.5 Process of experiment 5

In this experiment, a reference measurement was made, and then a glass plate was placed in the filter holder and its spectrum was measured as well. The aim of this experiment is to see whether we can accurately calculate the thickness of our glass plate using only interference phenomena. This was carried out the following way: After determining the peak distance graphically, the formula from chapter 1.2. was slightly changed so that it could be written relative to a new variable, k, where k = m_0 + m, where m_0 is the m-value for the peak in which the counting of the k-values started:

$$v(k) = \frac{k}{2n_P d} - \frac{m_0}{2n_p d} = \alpha k + \beta$$

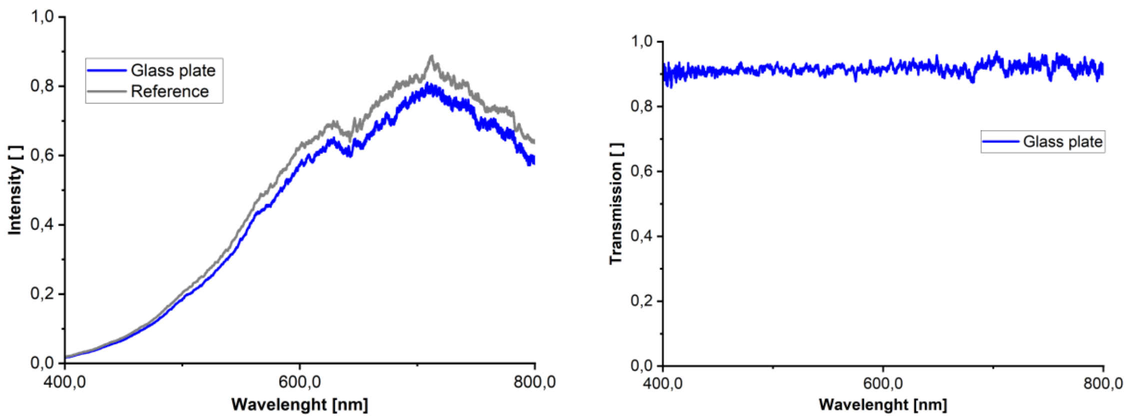

Figure 7: Intensity measurements of the glass plate and the reference (left), and the calculated transmission (right)

As can be seen from the results above, the transmissivity has a constant value of around 0,92, as would have been expected for a glass sample. The periodic peaks of the interference maxima are, however, barely visible, which might arise from us forgetting to adjust the software settings accordingly for this experiment. At around 750 nm, somewhat more pronounced peaks were visible which somewhat stuck out from the noise, which for our sake were interpreted as the interference maxima. The distance between multiple of those peaks were determined graphically and the mean value was calculated, which was around 18 nm. Starting from 799 nm, each 18 nm towards lower wavelengths, it is assumed that k increases by 1. By converting the wavelengths to frequencies, the following datapoints are determined:

k-values	Frequency (cm^{-1})
0	12 516
1	12 804
2	13 106
3	13 423

By plotting the frequencies against the k-values, a plot can be made from which the slope α can be determined. Using the equation $\alpha = \frac{1}{2n_p d}$, the thickness d can be calculated. The plot is visible in figure 8.

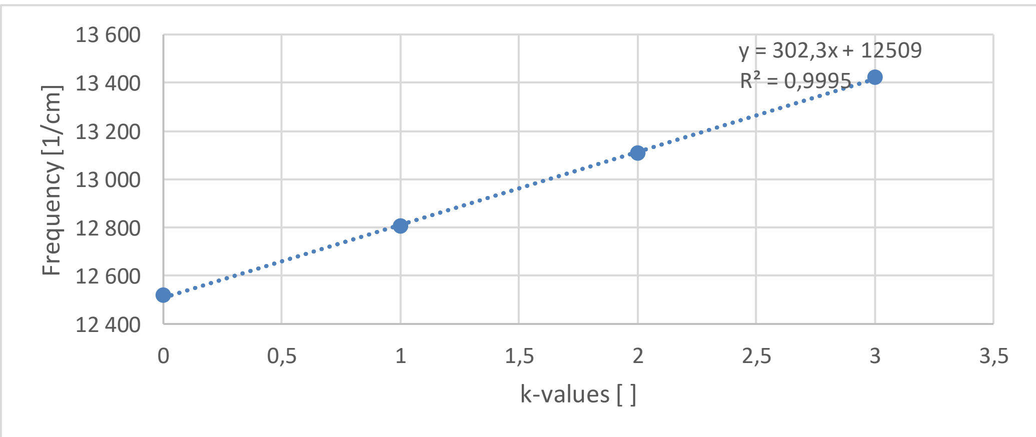

Figure 8: Plot of the frequencies of the determined maxima versus the k-values.

The equation of the linear fit shows that the slope 302,3 cm^{-1}. By placing this value into the aforementioned formula, and considering that n_p equals 1,516, a thickness of 0,0011 cm is calculated, which is not possible. This measurement is most likely wrong, and the error that was made arises from using the incorrect settings during the measurement. m_0 was determined to be equal to -41,7.

4 Summary

In the first and second experiment, the light intensities, transmission and extinction values of red and green light filters were measured separately as well as simultaneously, showing that the red filter transmitted light mostly above 600 nm, while the blue light filter transmitted mostly light with wavelengths less than 600 nm. Furthermore, from the figure 4, it could be seen that the extinction from both filters together was approximately equal to the sum of the extinction of the two filters separately, showing the additive nature of the extinction.

In the third experiment, the concentration of a methylene blue solution was determined by measuring the extinction of the solution relative to the reference spectrum, and is believed to be equal to (43,8 ± 1,7) $*10^8$ mol/L.

In the last experiment, the attempt was made to calculate the thickness of a glass plate. However, the wrong settings were used during the experiment and so a nonsensical value was achieved (0,0011 cm).

5 Bibliography

(1) Manual_transmission-Measurement.Pdf. https://www.mrc-systems.de/downloads/en/photo-activation/manual_transmission-measurement.pdf (accessed 2024-11-17).

(2) *UV-Vis spectrum of methylene blue solution, with maximum absorption at... | Download Scientific Diagram*. https://www.researchgate.net/figure/UV-Vis-spectrum-of-methylene-blue-solution-with-maximum-absorption-at-668-nm_fig6_41089542 (accessed 2024-11-17).