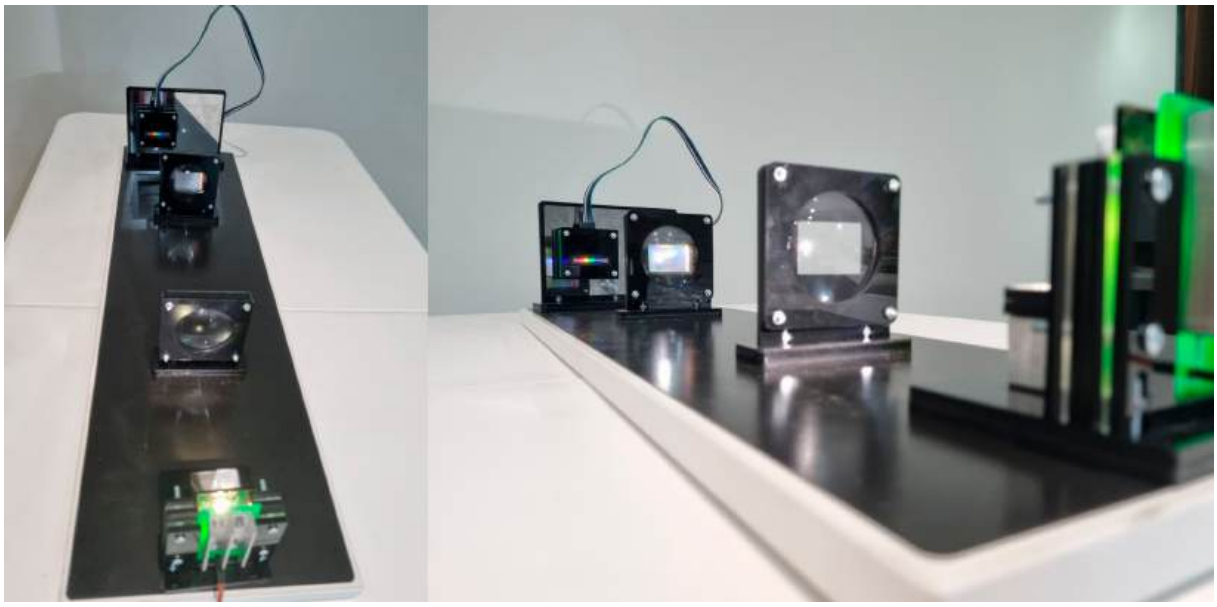
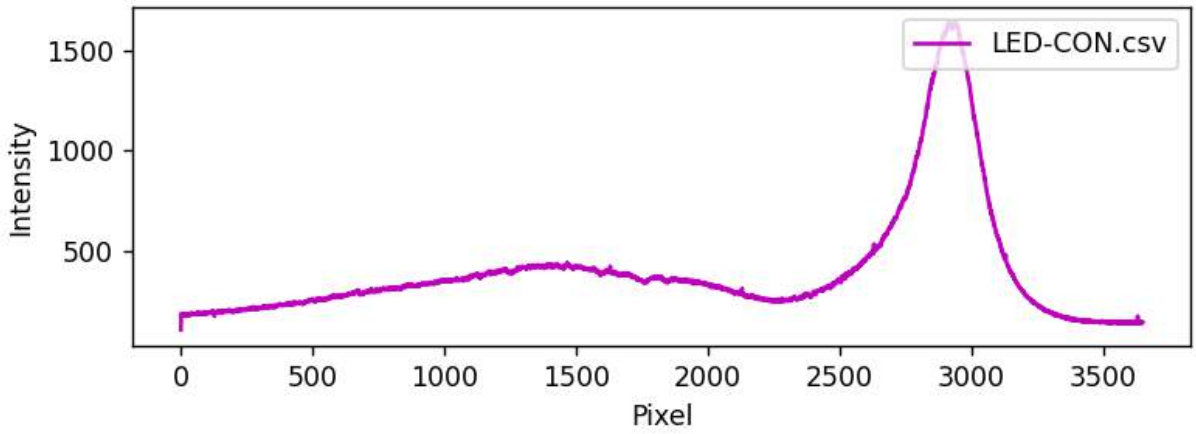
Solution

A1. For calibration, one needs to set the lens so that the source is in focus of the first lens and the screen is in focus of the second lens. A photo of the final installation is shown on the figure below.

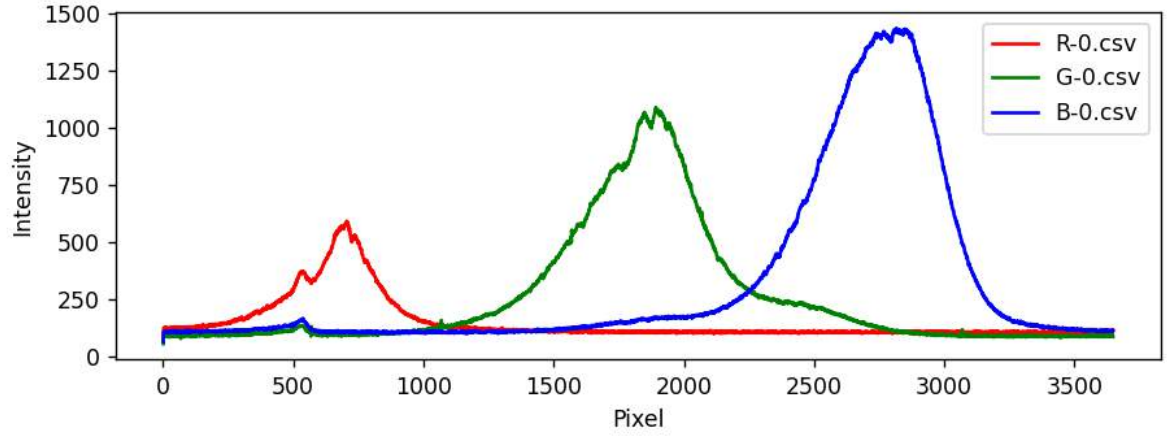


After adjusting the installation, it becomes possible to study the spectrum of the LED-CON. Note that this can be done using either of the two first-order diffraction patterns, since they are mirror-symmetric. A typical image of the LED-CON spectrum is shown on the figure below. At the edges of the LED-CON spectrum, the intensity is not zero, since there is background lighting from external sources. In the conditions of the Olympics, the background lighting could reach up to 1000. To reduce it significantly, one can use the "Sun Screen" as it suggested in the task.



A2. After turning off the LED-CON, one can get the spectrum of background lighting. The spectrum is not given here, because its type depends on the experimental conditions and is unique for each installation.

A3. Replace the LED-CON with LED-RGB and measure the spectra for all three colors of LEDs: red, blue and green. The characteristic graphs are shown in the figure below.



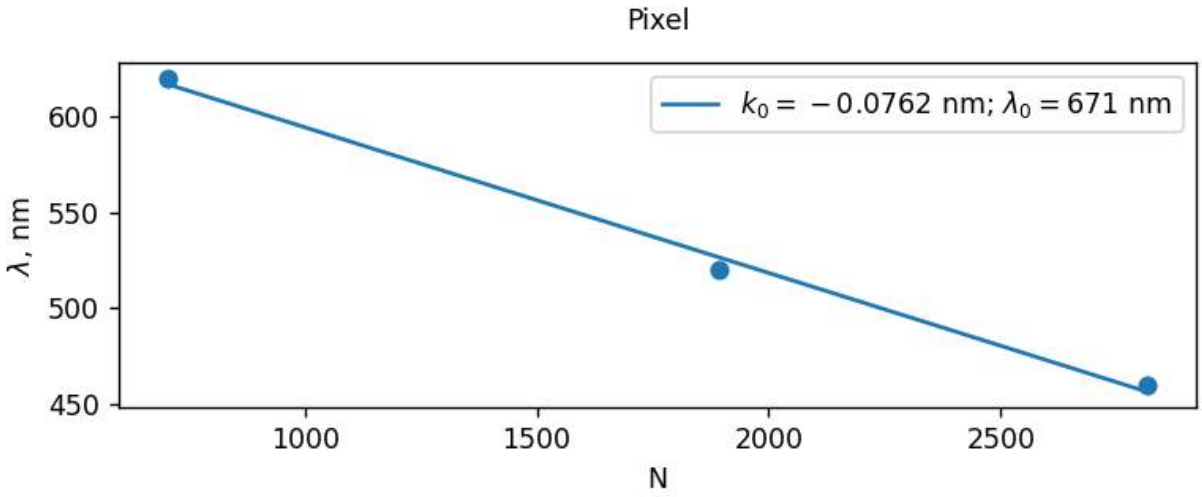
A4. As stated in the problem statement, the wavelength depends linearly on the pixel number:

$$\lambda = k_0 N + \lambda_0$$

Taking the pixel number corresponding to the maximum intensity value of each color, and the wavelength of that color, we get three points. By drawing the approximating line for these three points, we get the values of k_0 and λ_0.

Remarks:

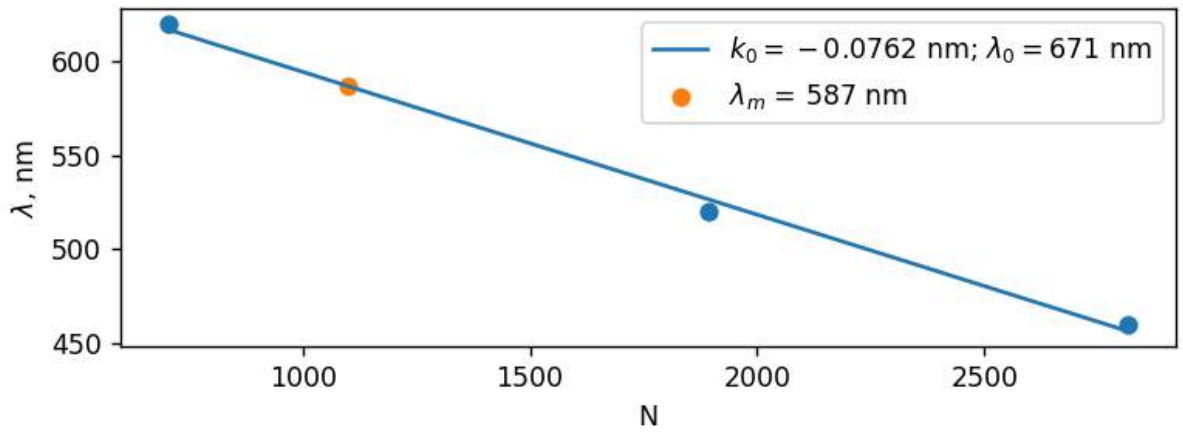
1. The value of k_0 could be either positive or negative depending on the installation constructed.
2. Shifting any element by a distance of the order of a millimeter can significantly change the coefficients k_0 and λ_0. Therefore, in case of a shift, a new calibration should be done.



$$\boxed{k_0 = -0.0752 \text{ nm}, \qquad \lambda_0 = 671 \text{ nm}}$$

A5. Using the formula from the previous paragraph, one can obtain the wavelength corresponding the pixel number of the maximum intensity of an unknown LED-UNK.

$$\lambda_{\text{max,UNK}} = 587 \text{ nm}.$$



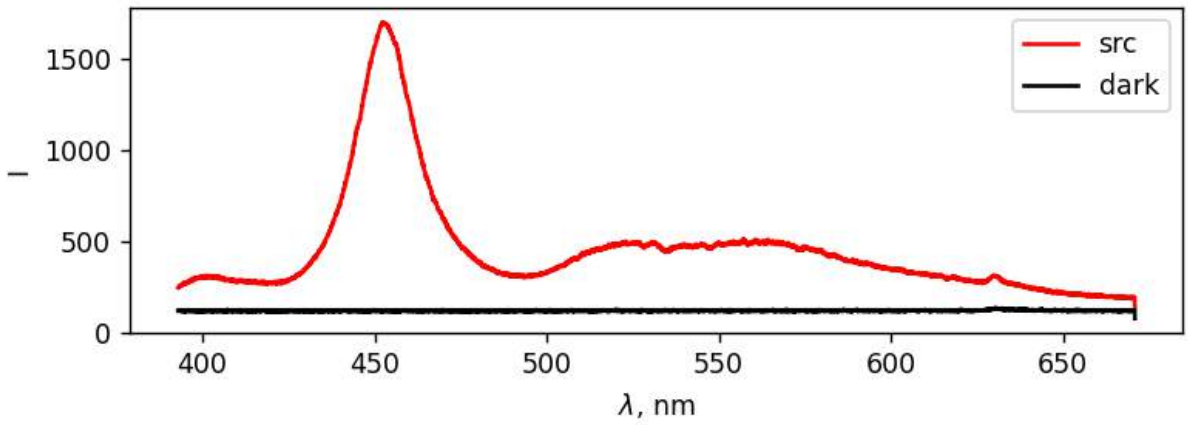
$$\boxed{\lambda_{\max} = 587 \text{ nm}}$$

B1. To find the average volume $V_{d,\text{IC}}$ of drops of fluid IC, one can slowly squeeze the fluid out of the syringe drop by drop and study the average volume change inside the syringe. There are approximately 100 drops per 0.5 ml of the fluid, and this value varies significantly from syringe to syringe. The phenomenon of the drop being held at the end of the needle is associated to the effects of surface tension, and its manifestation significantly depends on the geometry of the needle tip.

$$\boxed{V_{d,\text{IC}} = 5\ \mu\text{l}}$$

B2. In most cases, the optimal measurement parameters are the highest voltage on the LED-CON, such that the "src" spectrum does not go above "overflow", and the lowest "Sensitivity".

The spectrum of LED-CON light after passing through a cuvette with water is shown on the figure below.



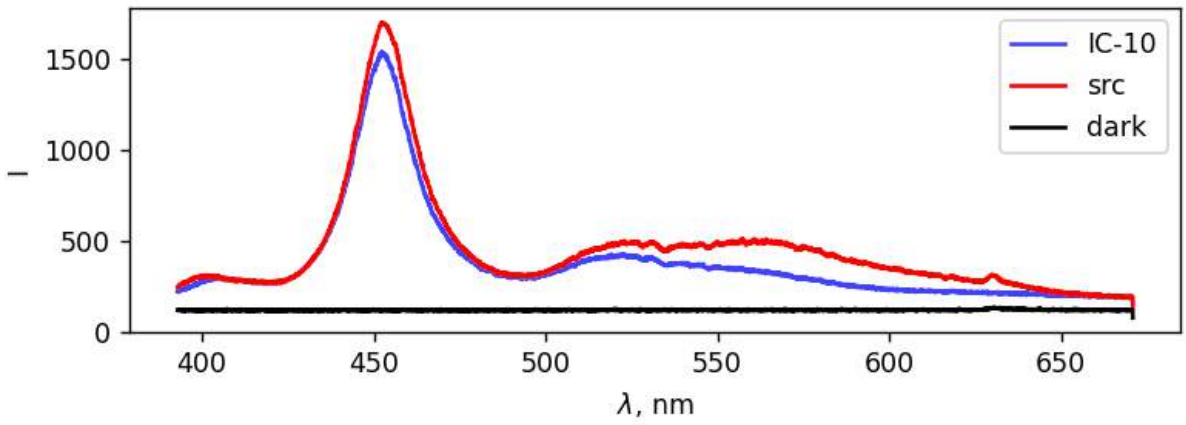
B3. The intensity of the source at each wavelength λ is equal to the difference between the intensities of 'src' and 'dark' at the same wavelength λ. By plotting the graph of the intensity of the source without background illumination, it is not difficult to obtain a wavelength range in which the dependence of $\beta(\lambda)$ can be studied.

$$\boxed{\lambda \in [420 \text{ nm}; 640 \text{ nm}]}$$

B4. By adding drops of the initial fluid to the water, we change the concentration of IC in the optical cuvette, which allows us to study the dependence of the intensity spectrum of light passed through the fluid on the concentration n. As marked in the the task statement, after adding drops the fluid should be

mixed. The easiest way to do it is to close the cover and shake the cuvette. If there are bubbles, one can get rid of them by tapping the finger on the walls of the cuvette.

The typical form of the IC spectrum, together with the 'src' and 'dark' spectra, is shown on the figure below. Significant absorption in the red region is observed in the obtained spectra, which explains the blue color of IC.



B5. Consider a layer of a substance with a thickness dl and a cross-sectional area S. It contains $dN = nS\,dl$ molecules. From the point of view of the described absorption mechanism, each of the molecules is an absorbing circle with the area $\sigma(\lambda)$, so in total they form the absorbing area $\sigma(\lambda)\,dN$.

The total power of the light entering the area S equals $P_\lambda = I_\lambda S$. The relative decrease in beam power after passing through the described layer is equal to the ratio of the absorbing area to the area S:

$$\frac{dP_\lambda}{P_\lambda} = \frac{dI_\lambda}{I_\lambda} = \frac{\sigma(\lambda)\,dN}{S} = \sigma(\lambda) n\,dl.$$

$$\boxed{dI_\lambda = I_\lambda \sigma(\lambda) n\,dl}$$

B6. After integration of the expression

$$\frac{dI_\lambda}{I_\lambda} = \sigma(\lambda) n dl$$

with appropriate limits

$$\int_{I_{0,\lambda}}^{I_\lambda} \frac{dI_\lambda}{I_\lambda} = -\int_0^l n\sigma(\lambda) dl,$$

where the negative sign in the right hand side corresponds the fact that dI_λ is the descease of the light intensity, we get

$$\ln \frac{I_\lambda}{I_{0,\lambda}} = -n\sigma(\lambda) l \quad \Rightarrow \quad \sigma(\lambda) = -\frac{1}{nl} \cdot \ln \frac{I_\lambda}{I_{0,\lambda}}.$$

$$\boxed{\sigma(\lambda) = -\tfrac{1}{nl} \cdot \ln \tfrac{I_\lambda}{I_{0,\lambda}}}$$

B7. Using the formula obtained in B7, express $\sigma(\lambda)$ in terms of the measured intensities:

$$\sigma(\lambda) = -\frac{1}{nL} \ln \left(\frac{I_{\text{IC}}(\lambda) - I_{\text{dark}}(\lambda)}{I_{\text{src}}(\lambda) - I_{\text{dark}}(\lambda)} \right),$$

where n is a concentration of IC in the fluid inside the optical cuvette, and L is the inner width of the optical cell.

We get the dependence of the concentration n on the number of added drops m. The mass concentration of IC in the initial solution equals $\rho = 0.70$ g/l. Let us find the concentration n_0 (its dimension is m^{-3}) of indigocarmine molecules in the initial fluid:

$$n_0 = \frac{N}{V} = \frac{\nu N_A}{m/\rho} = \frac{\nu N_A \rho}{m} = \frac{N_A \rho}{\mu_{\text{IC}}},$$

where N is the number of molecles of IC in the volume V of given fluid, N_A is the Avogadro constant, μ_{IC} is the molar mass of indigocarmine. Then the number of molecules N_m in m drops of indigocarmine equals

$$N_m = n_0 \cdot m V_{d,\text{IC}}.$$

Thus, the concentration n of indigocarmine in obtained fluid in the optical cuvette (the change $V_0 = 3.0$ ml in the volume of the fluid is negligible) equals

$$n = \frac{N_m}{V_0} = \frac{N_A \rho V_{d,\text{IC}}}{\mu_{\text{IC}}} \cdot m.$$

Substituting the concentration into the expression for $\sigma(\lambda)$, we get the expression

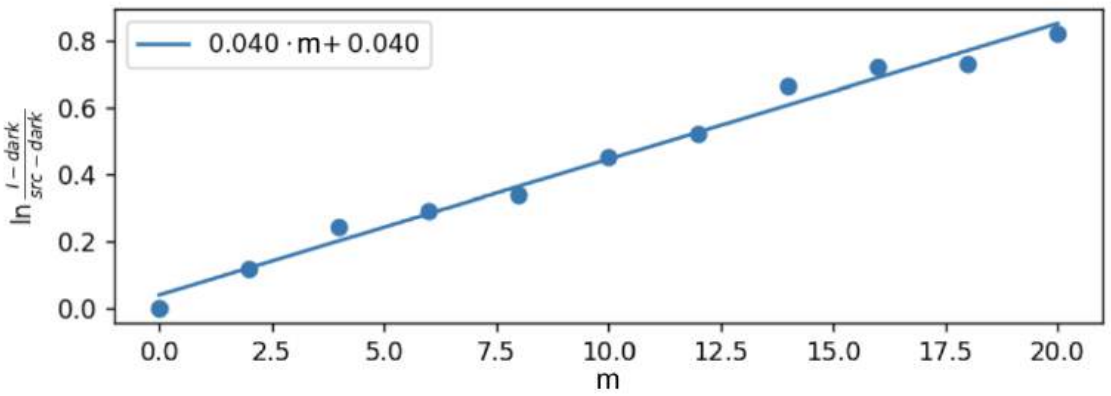
$$\sigma(\lambda) = -\frac{\mu_{\text{IC}}}{L N_A \rho V_{d,\text{IC}}} \cdot \frac{1}{m} \ln\left(\frac{I_{\text{IC}}(\lambda) - I_{\text{dark}}(\lambda)}{I_{\text{src}}(\lambda) - I_{\text{dark}}(\lambda)}\right).$$

Finally, linearized dependence of radiation intensity on the number of indigocarmine drops is the following:

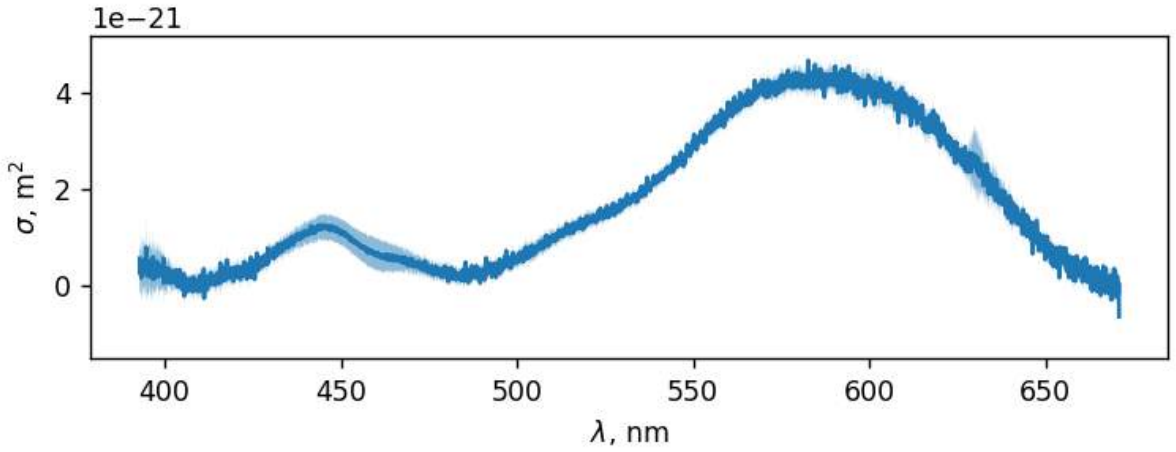
$$\ln\left(\frac{I_{\text{src}}(\lambda) - I_{\text{dark}}(\lambda)}{I_{\text{IC}}(\lambda) - I_{\text{dark}}(\lambda)}\right) = \sigma(\lambda) \cdot \frac{L N_A \rho V_{d,\text{IC}}}{\mu_{\text{IC}}} \cdot m.$$

It remains to process the received data. To do this, choose a certain wavelength and compute the value $Y_1 = \ln\left(\frac{I_{\text{src}}(\lambda) - I_{\text{dark}}(\lambda)}{I_{\text{IC}}(\lambda) - I_{\text{dark}}(\lambda)}\right)$ for different numbers m of added drops. Then one needs to construct the dependence of Y_1 on m and approximate it by linear regression with the coefficient slope $\varkappa$. By the previous formula:

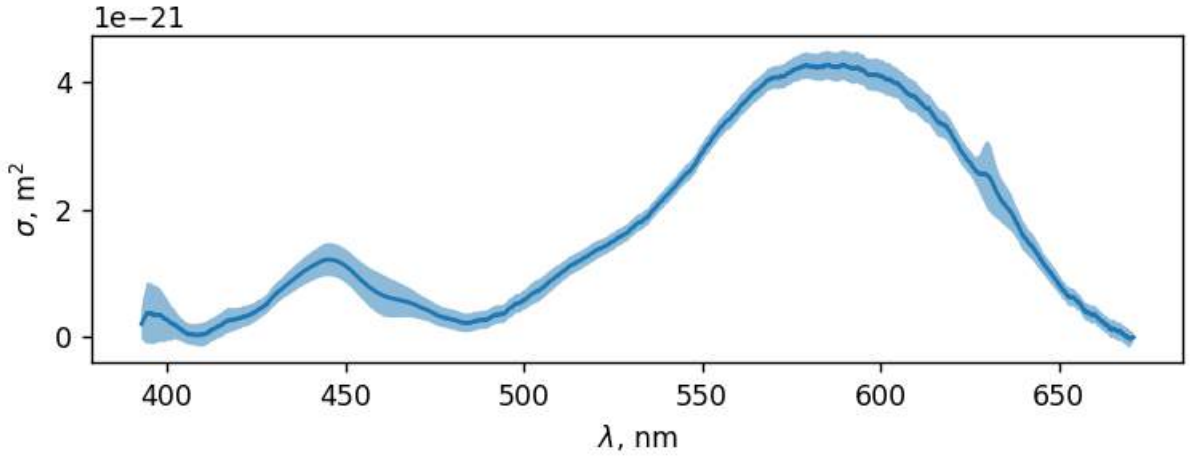
$$\varkappa(\lambda) = \frac{L N_A \mu V_{d,\text{IC}}}{\mu_{\text{IC}}} \cdot \sigma(\lambda).$$



Repeating the described procedure for 10 different wavelengths from the range found in B3, one can get 10 different linear regressions. Using their slope coefficients, one can compute the value of $\sigma(\lambda)$. Generally speaking, based on the data obtained, one can get the value of $\sigma(\lambda)$ for each pixel and the wavelength corresponding to it, not limited to 10 values. The graph $\sigma(\lambda)$ for all points calculated according to the described procedure is shown on the figure below. The width of the solid-colored area on the graph is the statistical error of the linear approximation of $Y_1(m)$.



Obtained graph should be smoothed so that it better reflects the shape of the final absorption cross-section spectrum $\sigma(\lambda)$.



The typical value of the maximum absorption cross section equals

$$\sigma \sim 5 \cdot 10^{-21} \text{ m}^2.$$

B8. The wavelength corresponding to the absorption maximum can be found from the graph obtained in B7.

$$\boxed{\lambda_{\text{max,IC}} = 590 \text{ nm}}$$

C1. Let us find the concentration of NaOH-solution of the molar concentration $c_0 = 0.30$ mol/l. There are two types of ions in the fluid.

Ion	i	Z_i	n_i
Na^+	1	1	$N_A c_0$
OH^-	2	-1	$N_A c_0$

$$\boxed{J_0 = 1.8 \cdot 10^{26} \text{ m}^{-3}}$$

C2. Since all the ions in the fluid have a charge number with the absolute value 1, and the concentration of each type of the ions coincides with the concentration of the corresponding dissolved substance, we can write:

Ion	i	Z_i	n_i
Na^+	1	1	$2N_Ac_1\frac{V_{\text{NaOH}}}{V_{\text{NaOH}}+V_{\text{NaOH}}+V_{\text{NaOH}}}+N_Ac_1\frac{V_{\text{NaCl}}}{V_{\text{NaOH}}+V_{\text{NaOH}}+V_{\text{NaOH}}}$
OH^-	2	-1	$2N_Ac_1\frac{V_{\text{NaOH}}}{V_{\text{NaOH}}+V_{\text{NaOH}}+V_{\text{NaOH}}}$
Cl^-	3	-1	$N_Ac_1\frac{V_{\text{NaCl}}}{V_{\text{NaOH}}+V_{\text{NaOH}}+V_{\text{NaOH}}}$

$$J_0=\frac{1}{2}\cdot 2\cdot\frac{2c_1V_{\text{NaOH}}N_A}{V_{\text{NaOH}}+V_{\text{NaCl}}+V_w}+\frac{1}{2}\cdot 2\cdot\frac{c_1V_{\text{NaCl}}N_A}{V_{\text{NaOH}}+V_{\text{NaCl}}+V_w}=N_A\cdot c_0$$

Simplifying the expression, we get the volume of distilled water, what should be added:

$$\boxed{V_{\text{w}}=\frac{2c_1V_{\text{NaOH}}+c_1V_{\text{NaCl}}}{c_0}-V_{\text{NaOH}}-V_{\text{NaCl}}}$$

C3. If we consider a fluid with the concentrations of NaCl and NaOH equal to c_0, then the relation obtained in C2 will be the following:

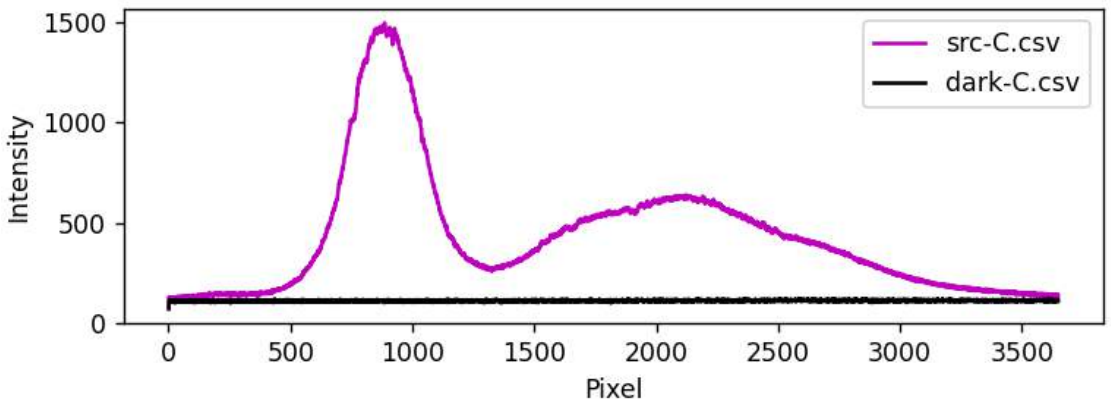
$$V_w=\frac{c_0V_{\text{NaOH}}+c_0V_{\text{NaCl}}}{c_0}-V_{\text{NaOH}}-V_{\text{NaCl}}=0.$$

From this expression, it can be concluded that the volume of distilled water added should be zero, and the ratio of volumes of NaCl and NaOH in the mixture can be arbitrary.

$$\boxed{V_{\text{w}}=0,\quad V_{\text{NaCl}},V_{\text{NaOH}}-\text{arbitrary}}$$

C4. Let us obtain the spectrum of LED-CON light that has passed through the cuvette, in order to take into account the absorption of the cuvette material and all kinds of reflections. Let us set such sensitivity so that the spectrum does not cross the "Overflow" level and does not change its characteristic shape when approaching it. Let us measure the spectrum of background lighting at the same sensitivity. The intensity of the background signal may differ from that obtained in the previous paragraphs.

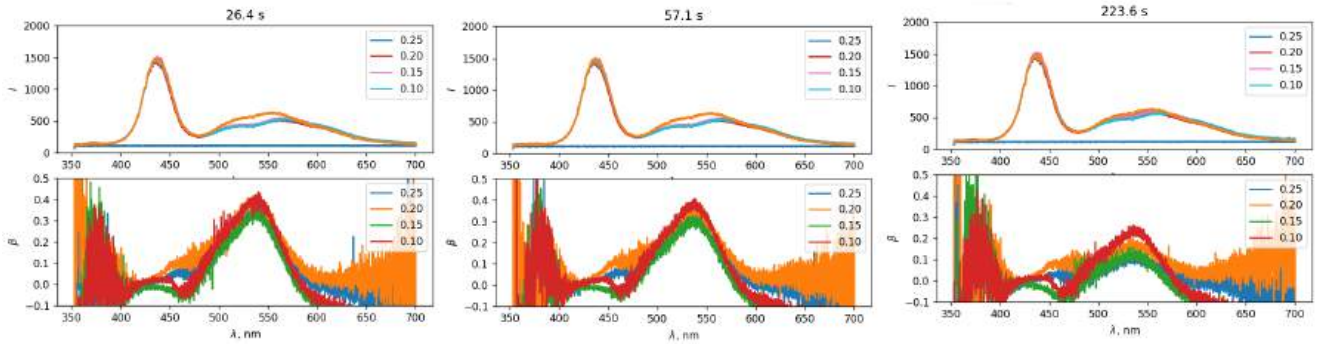
After passing through the cuvette with a mixture of NaOH- and NaCl-solutions, the light from the source loses intensity, but its spectrum keeps its typical form: narrow and high peak in the blue part of the spectrum, low and wide peak in the green-red part.



C5. Let us measure the dependence of transmission spectra on time for 5 fluids of different concentrations of $(OH)^-$ ions, as required in the task. We measure the intensity of background lighting before each dependence. The time of the experiment depends on NaOH concentration, and will increase as it decreases.

The difference in the shape of the spectrum obtained in this part of the task from the spectrum of the radiation source obtained in C4 is caused by the presence of absorption in the fluid inside the cuvette. The absorption leads to a significant decrease in the intensity of transmitted light in the wavelength range 500-600 nm.

Over time, the absorption will decrease, due to a decrease in the concentration of phenolphthalein In, until the concentration reaches an equilibrium state. The higher the initial concentration of $(OH)^-$, the faster the equilibrium state is being reached.



C6. In order to find the wavelength at which maximum absorption is achieved, one needs to plot $\beta(\lambda)$. Let us select the data that we will use in the process of plotting. We use an array of spectra obtained in the experiment using the $NaOH$-solution with the lowest concentration. This choice is caused by the fact that the concentration of $(OH)^-$ ions will always be excessive compared to the concentration of phenolphthalein, but the process will occur significantly slower than in a pure solution of NaOH. This will give more time and allow to measure the absorption before it would decrease by a significant amount after the reaction begins. Among all the time points at which the spectrum of this solution was measured, let us choose one close to the initial one, since the equilibrium state has not yet been reached, and therefore the absorption has not decreased.

For this data, we calculate the value of β using the information about background lighting:

$$\beta(\lambda) = \ln \frac{I_{\text{src}}(\lambda) - I_{\text{dark}}(\lambda)}{I_{\text{In}}(\lambda) - I_{\text{dark}}(\lambda)}$$

Let us plot the dependence of $\beta(\lambda)$. Based on the graph, we get the answer for $\lambda_{\text{max, In}}$.

$$\boxed{\lambda_{\text{max, In}} = 550 \text{ nm}}$$

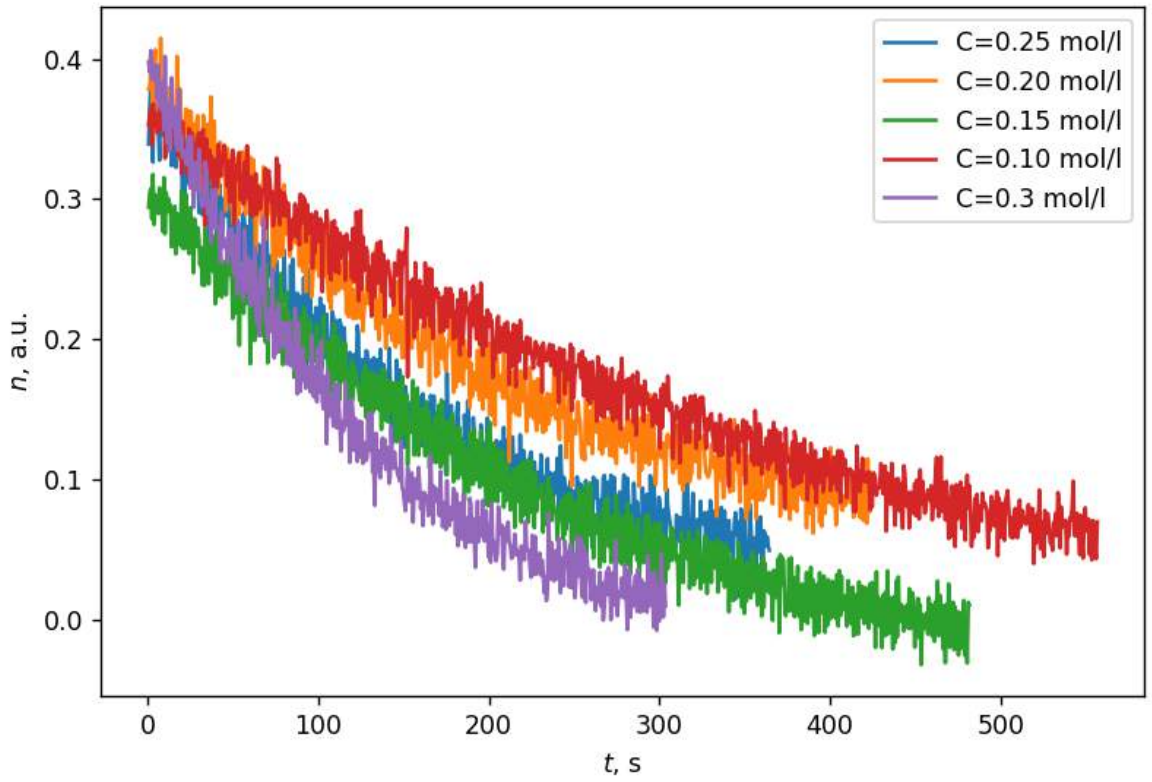
C7. The value $\beta(\lambda)$ measured in C6 can be expressed in terms of $\sigma(\lambda)$ and the concentration n:

$$\beta(\lambda) = \sigma(\lambda) n.$$

For the fixed wavelength holds $\sigma(\lambda) = \text{const}$, so $n \propto \beta$. Since we can compute the concentration of In in conventional units, we will use $\beta(\lambda)$ as these conventional units, which turns out to be directly proportional to the concentration of n.

Let us do our study for the wavelength $\lambda_{\text{max, In}}$.

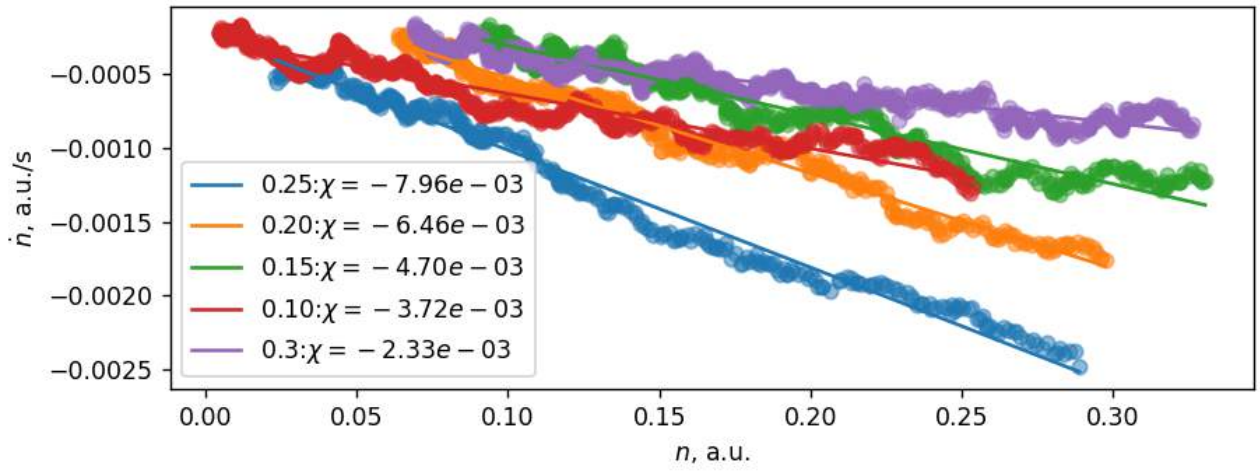
For each of the 5 ion concentrations $(OH)^-$ let us compute the dependencies $\beta(t)$ for the wavelength $\lambda_{\text{max, In}}$ and plot their graphs. The resulting graphs have the following form: these are decreasing dependencies that reach saturation, and the rate of decrease is higher, if the concentration of ions $(OH)^-$ is greater.



C8. In order to study the reaction rate as a function of concentration, one needs to find the derivative of concentration in time, instead of which we will use the derivative of β in time, since they are equal to each other with the accuracy of the multiplication by a constant. The numerical computation of the derivative is complicated by the significant noise of the signal from the CCD ruler. It is proposed to reduce the noise effect by calculating the derivative as follows:

$$\left.\frac{d\beta}{dt}\right|_N = \frac{\beta_{N+10} - \beta_{N-10}}{t_{N+10} - t_{N-10}}.$$

Let us compute the derivative $\dfrac{d\beta}{dt}$ for each of the concentrations and plot the dependence of $r(n)$ in conventional units (that is, $\dfrac{d\beta}{dt}(\beta)$) for each of the experiments.



Let us describe the kinetics of the chemical reaction theoretically.

$$r = -\frac{dn_{\mathrm{In}^{2-}}}{dt} = r_{\mathrm{com}} - r_{\mathrm{decom}}$$

.

As it is marked in the task,

$$r_{\text{com}} = \chi(n_{\text{In}^{2-}})(n_{(\text{OH})^-})^p, r_{\text{decom}} = \psi(n_{\text{In}^{2-}(\text{OH})_{\text{p}}^{\text{p}-}}),$$

where χ and ψ are constants.

Since the total number of phenolphthalein molecules in all states remains unchanged, one can say that:

$$n_{\text{In}^{2-}} + n_{\text{In}^{2-}(\text{OH})_{\text{p}}^{\text{p}-}} = const = n_0.$$

Then one can write the following expression for the reaction rate:

$$-\frac{dn_{\text{In}^{2-}}}{dt} = (n_{\text{In}^{2-}})(\chi(n_{(\text{OH})^-})^p + \psi) - \psi n_0.$$

According to the notations introduced in the task, we have $-\frac{dn_{\text{In}^{2-}}}{dt} = r$, $n_{\text{In}^{2-}} = n$

$$r = n(\chi(n_{(\text{OH})^-})^p + \psi) - \psi n_0.$$

Since hydroxyl ions are in the strong excess, it can be assumed that $n_{(\text{OH})^-} = const$. In this case, the dependence $r(n)$ turns out to be linear with a slope coefficient equal to $\chi(n_{(\text{OH})^-})^p + \psi$. The plotted graphs confirm the theoretical dependence we have obtained.

Based on the expressions obtained, it can be argued that the dependencies obtained in C7 are exponential, and their saturation output corresponds to the condition $r = 0$, or $r_{\text{com}} = r_{\text{decom}}$.

C9. Saturation condition is the following: $r_{\text{com}} = r_{\text{decom}}$, or

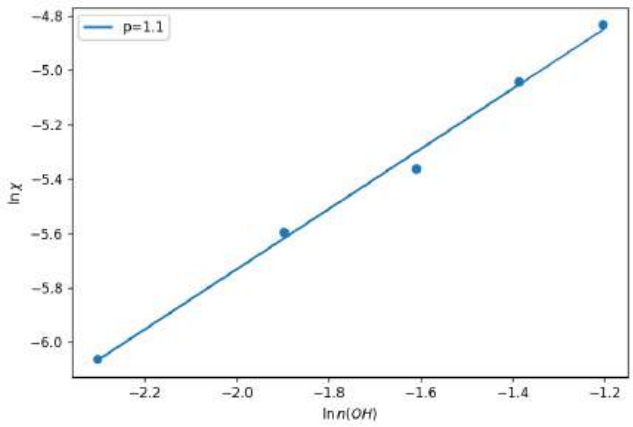
$$\chi(n_{\text{In}^{2-}})(n_{(\text{OH})^-})^p = \psi(n_{\text{In}^{2-}(\text{OH})_{\text{p}}^{\text{p}-}}).$$

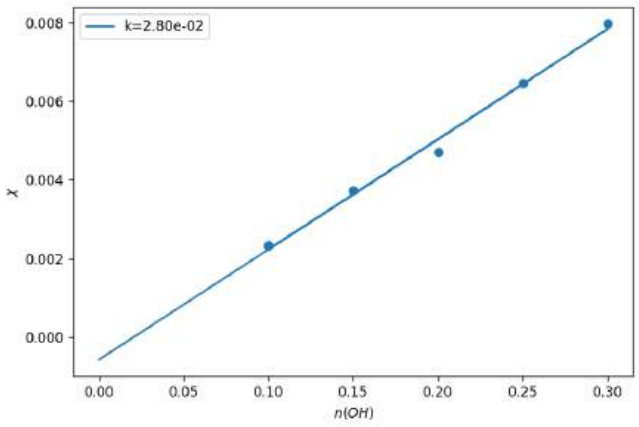
After the concentration reaches the stationary mode, the fluid turns out to be very weakly colored, which indicates that the final concentration of In^{2-} is small, that is, $n_{\text{In}^{2-}} \ll n_{\text{In}^{2-}(\text{OH})_{\text{p}}^{\text{p}-}}$. This means that $\psi \ll \chi(n_{(\text{OH})^-})^p$.

Using the graphs constructed in C8, let us calculate the slope coefficients k. If we assume that $k = \chi(n_{(\text{OH})^-})^p$ (still $\psi \ll \chi(n_{(\text{OH})^-})^p$), and plot the dependence $\ln(k)(\ln(n_{(\text{OH})^-}))$, we will get the value of p as the slope coefficient of the graph. The slope coefficient of the graph is equal to 1.1. Since p is obviously an integer, we can say that $p = 1$.

To check the assumption that $\psi \ll \chi(n_{(\text{OH})^-})^p$, one can plot the dependence of k on $n_{(\text{OH})^-}$. Since obtained dependence is linear and goes beyond zero, our assumption is correct.

Note that it was possible to obtain p by constructing other graphs and using other methods of analysis.





D1. At first the fluid has a green or blue-green color, then turns violet, then orange, and yellow at the end. The typical time of appearance of violet is $t_1 \in [30\,s; 90\,s]$, and the typical time of appearance of orange is $\Delta t \in [30\,s; 120\,s]$ later, and the transition from orange to yellow occurs smoothly. The transition to violet turns out to be faster when the concentrations of reagents are incorrect or when the reaction is "restarted".

Color	Green/Blue-green	Yellow	Red/Orange	Violet
Number	1	4	3	2
t, s	0.0	200+	60	40

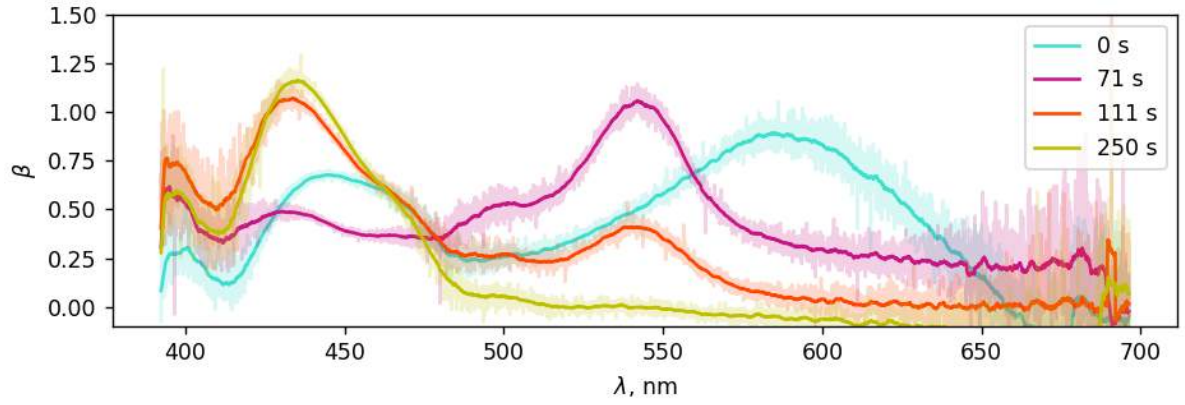
D2. The intensity of the background signal may differ from that obtained in the previous paragraphs. After passing through a cuvette with a mixture of NaOH and Gl solutions, the light from the source loses intensity, but its spectrum keeps its typical form: a narrow and high peak in the blue part of the spectrum, low and wide in the green-red part. The tops of the peaks are symmetrical. Initially, the spectrum of light transmitted through the fluid has a form similar to the form of the source spectrum, and then the following dynamics is observed:

- in the red area, the intensity decreases smoothly;
- in the green area, the intensity first increases smoothly, then decreases sharply, and then increases smoothly again;
- in the blue area, the intensity first increases smoothly, and then decreases smoothly.

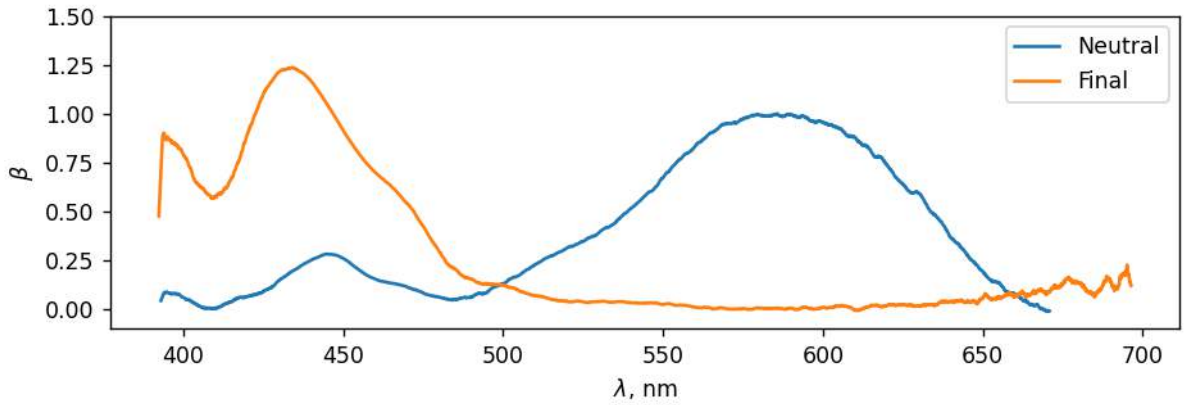
D3. According to the definition of β, which was given in Part B,

$$L\beta(\lambda) = \ln\left(\frac{I_{\text{src}}(\lambda) - I_{\text{dark}}(\lambda)}{I_{\text{IC}}(\lambda) - I_{\text{dark}}(\lambda)}\right).$$

Absorption spectrum graphs $\beta(\lambda)$ correspond to the dynamics of the spectrum described in task D2.



D4. At the time point t_1, the "neutral" state of IC prevails in the cuvette, that is, the state that indigocarmine has in a neutral medium. The absorption spectrum of the neutral state $\beta_n(\lambda)$ was received in part B. At the time point t_4, the state of IC in the cuvette was settled. Let us call this state the "finite". Its absorption spectrum $\beta_f(\lambda)$ can be calculated using the formula from **D3**. Let us plot $\beta_n(\lambda)$ and $\beta_f(\lambda)$ on a single graph.



Note that the envelope of these graphs differs from the envelope of the graphs obtained in **D3** only by the absence of a peak in the neighborhood of $\lambda = 540$nm. Therefore, IC molecules pass through three states.

3 states

D5. At each time point, a mixture of IC molecules in three states is in the cuvette: neutral (n), transitional (i), final (f). Denote the concentrations of these states by $n_n(t)$, $n_i(t)$, $n_f(t)$, and the corresponding absorption sections by $\sigma_n(\lambda)$, $\sigma_i(\lambda)$, $\sigma_f(\lambda)$. Then according to **B5**

$$L\beta(\lambda, t) = \sigma_n(\lambda)n_n(t) + \sigma_i(\lambda)n_i(t) + \sigma_f(\lambda)n_f(t),$$

where

$$L\beta(\lambda, t) = \ln\left(\frac{I_{\text{src}}(\lambda) - I_{\text{dark}}(\lambda)}{I_{\text{IC}}(\lambda, t) - I_{\text{dark}}(\lambda)}\right).$$

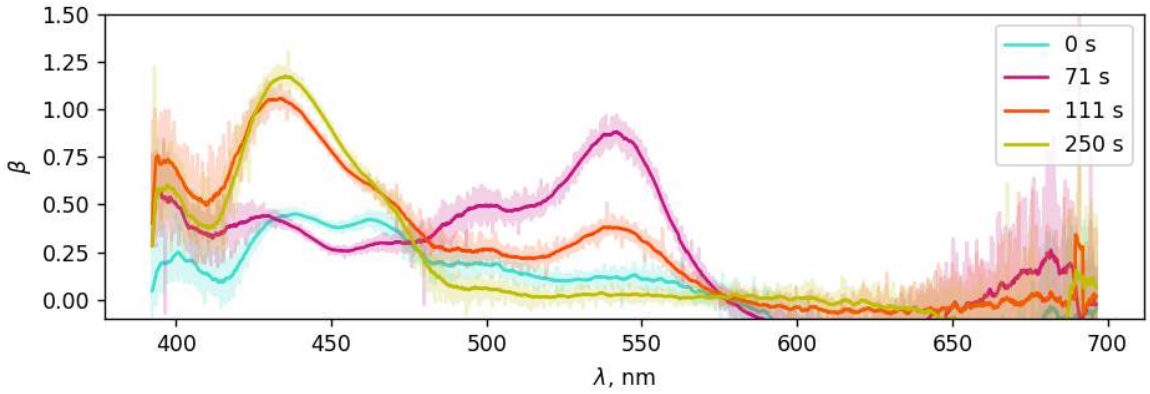
As follows from the graphs obtained in **D3**, the absorption at the wavelength $\lambda_n \approx 600$ nm is almost entirely caused by the presence of indigocarmine in the fluid in the first state. Therefore, the concentration of the neutral state IC, expressed in conventional units, can be computed using the formula

$$n_n^*(t) = L\beta(\lambda_n, t).$$

Subtract the contribution of the neutral state to absorption at other wavelengths and plot the functions

$$f_i(\lambda) = L\beta(\lambda, t_i) - n_n^*(t_i) \cdot \frac{\sigma_n(\lambda)}{\sigma_n(\lambda_n)},$$

where $\sigma_n(\lambda)$ is the absorption cross-section spectrum obtained in **B4**.

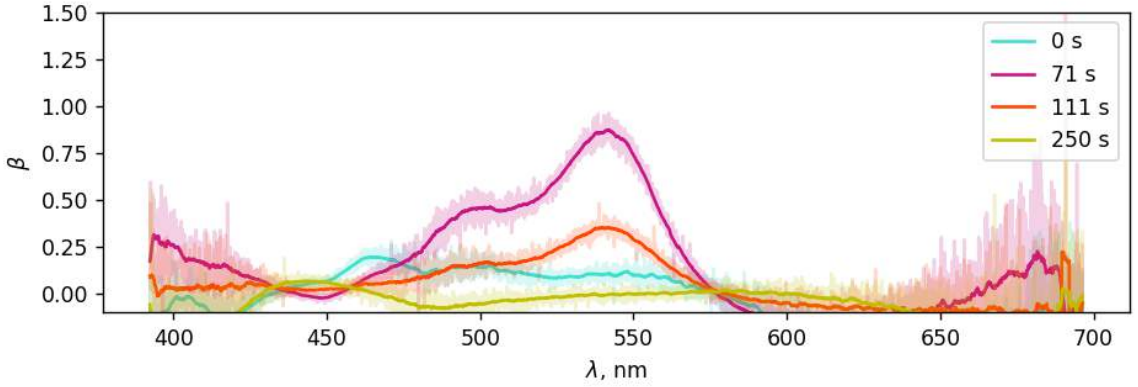


By the time point t_4, only the final state of IC remains in the cuvette. Therefore,

$$\sigma_f(\lambda) = \frac{l\beta(\lambda, t_4)}{n_f(t_4)}.$$

It allows us to subtract the contribution of the final state IC to the absorption spectrum. To do this, let us build the graphs of functions

$$g_i(\lambda) = f_i(\lambda) - n_f^*(t_i) \cdot \frac{\beta(\lambda, t_i)}{\beta(\lambda_f, t_i)}.$$



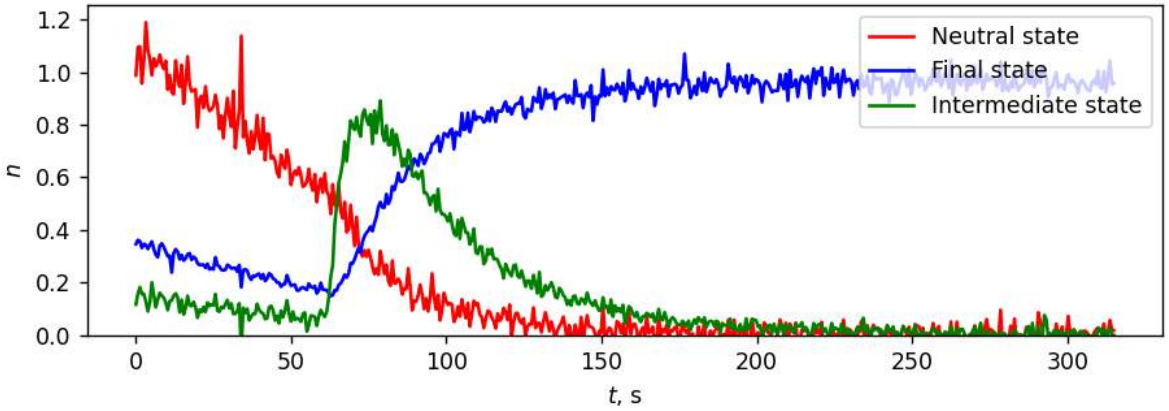
For similar reasons, the concentrations of each of the states can be computed using the formulas

$$n_n^*(t) = L\beta(\lambda_n, t).$$

$$n_i^*(t) = L\beta(\lambda_i, t) - n_n^*(t) \cdot \frac{\sigma_n(\lambda_i)}{\sigma_n(\lambda_n)} - n_f^*(t) \cdot \frac{\beta(\lambda_i, t)}{\beta(\lambda_f, t)}.$$

$$n_f^*(t) = L\beta(\lambda_f, t) - n_n^*(t) \cdot \frac{\sigma_n(\lambda_f)}{\sigma_n(\lambda_n)}.$$

The graphs of the functions $n_i^*(t)$ are shown on the figure below.


Neutral state
Final state
Intermediate state
n
t, s
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
50
100
150
200
250
300