E1. Absorption spectroscopy and chemical kinetics

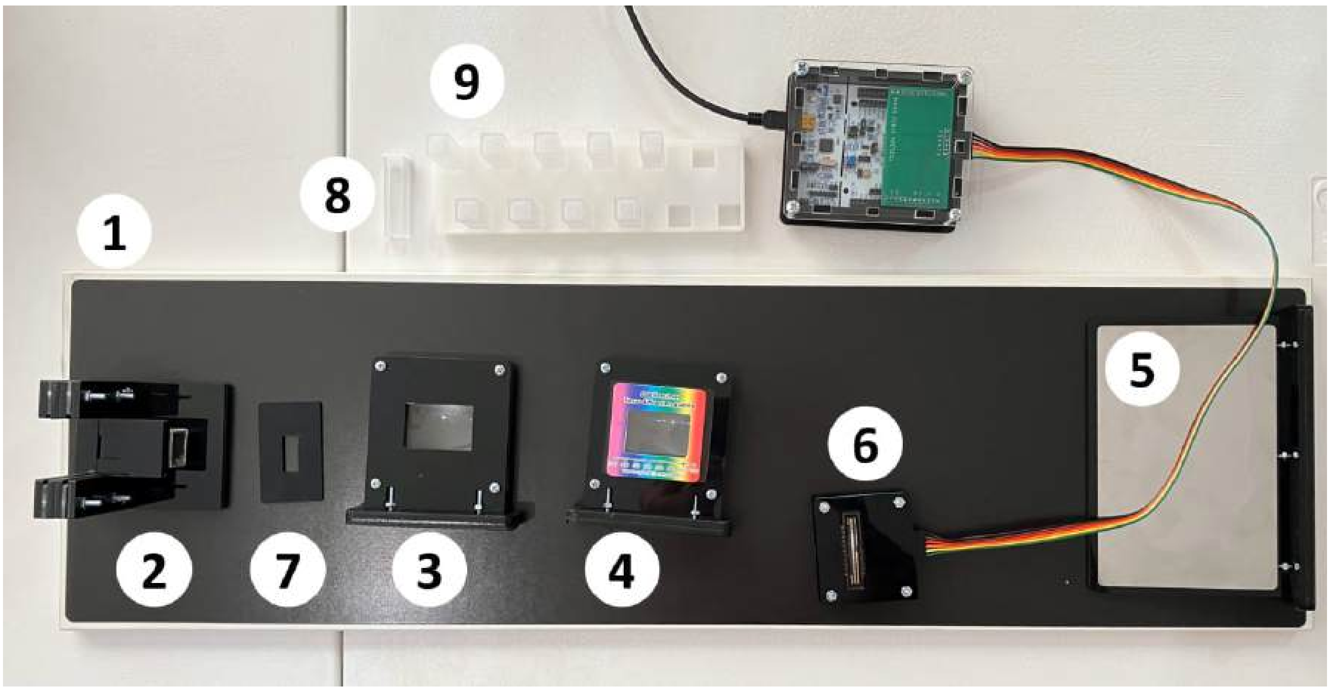
Chemical kinetics is a branch of physical chemistry that studies the rates of chemical reactions over time. The main purpose of chemical kinetics is to study all factors that affect the rate of both the overall process and all intermediate stages. There are many methods in this science that allow determining the chemical composition of substances and solutions based on indirect measurement results. The method used in this problem is called *absorption spectroscopy*. It involves investigating how light of different wavelengths is absorbed by a substance or solution.

ATTENTION! You have been provided with $NaOH$ ***granules! This substance is extremely caustic! Follow these safety rules when working with it:***

1. ***Do not touch*** $NaOH$ ***granules with naked hands!***
2. ***Avoid contact of*** $NaOH$ ***granules and solution with skin and face!***
3. ***Store*** $NaOH$ ***in containers with a closed tubes.***
4. ***If*** $NaOH$ ***comes into contact with skin or face, immediately contact the organizers!***

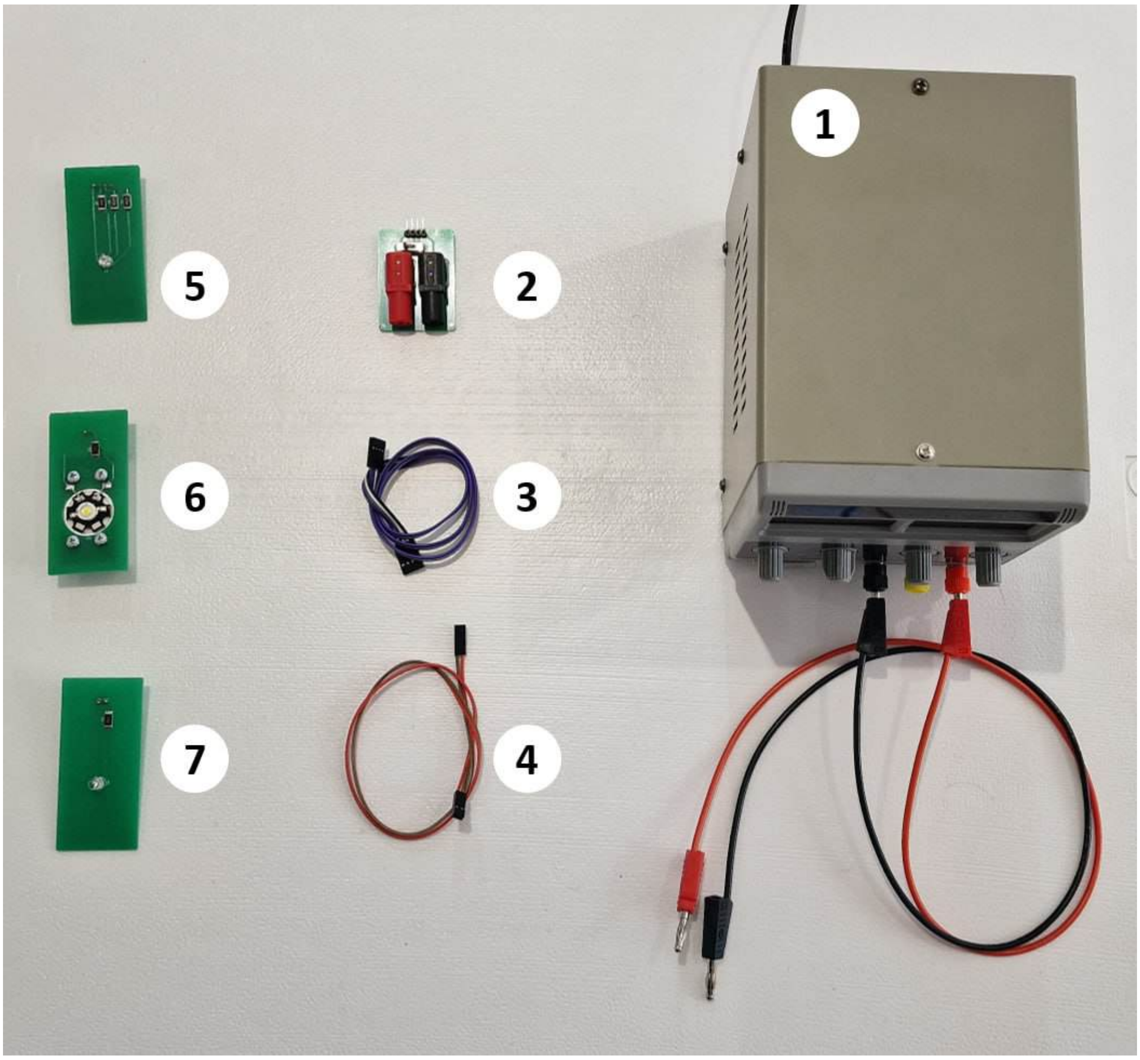
Equipment (optical)

1. Optical table.
2. Holder for light sorce.
3. Lens L_1.
4. Lens L_2 with diffraction grating G on a magnet.
5. Screen.
6. Photodetector CCD array connected to a computer (hereinafter - sensor).
7. Diaphragm.
8. Optical cuvette with cap - 10 pcs.
9. Holder for optical cuvettes.



Equipment (electrical)

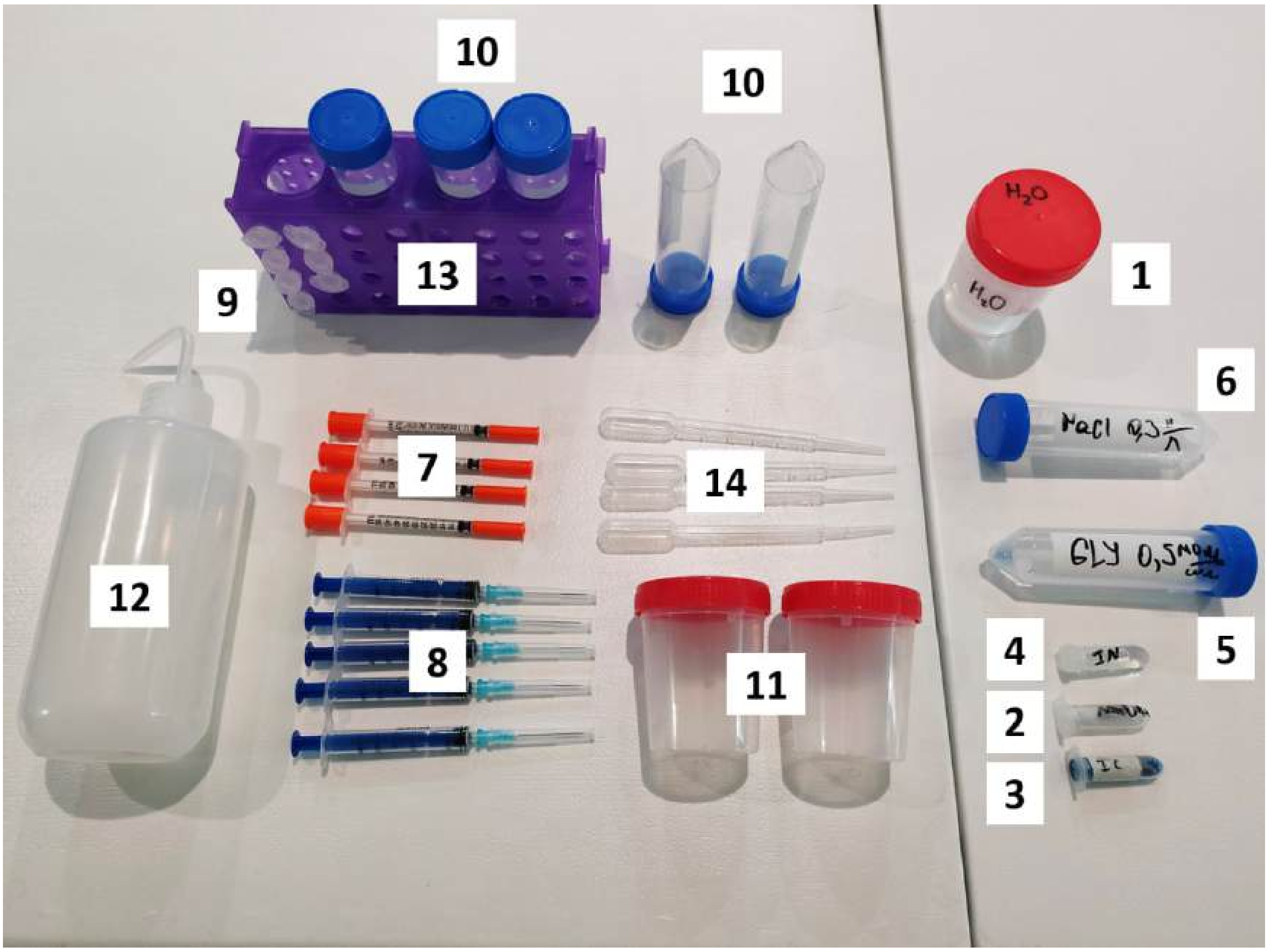
1. DC power supply up to 15 V.
2. Adapter with switch.
3. Connector with 4 outputs.
4. Connector with 2 outputs.
5. Three-color LED ”LED-RGB”.
6. Full spectrum LED ”LED-CON”.
7. Unknown color LED ”LED-UNK”.



Equipment (chemical)

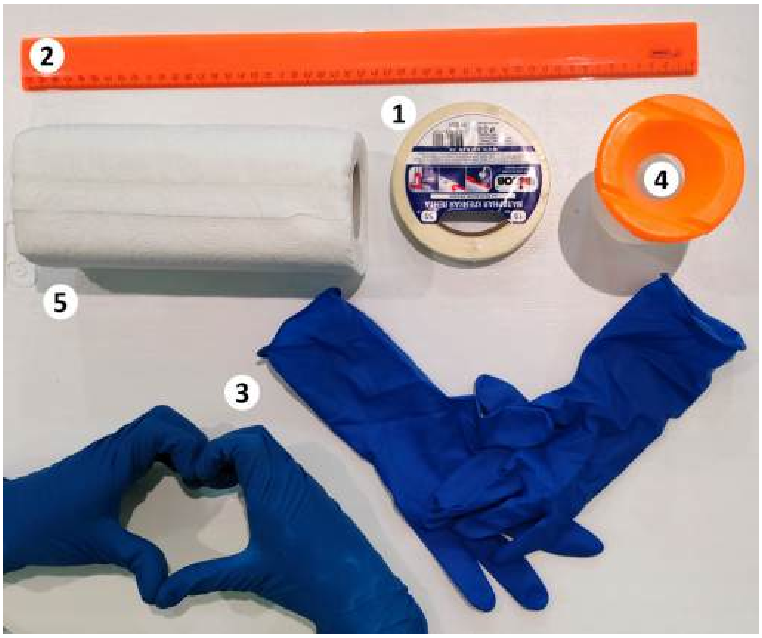
1. Distilled water H_2O.
2. Solid NaOH granules. The total mass of the provided NaOH is indicated on the microtube in grams.
3. Indigo carmine IC solution with concentration 0.70 mg/ml in a microtube.
4. Phenolphthalein In solution in a microtube.
5. Glucose Gl solution in a conical tube with concentration 0.50 mol/l.
6. Sodium chloride NaCl solution with concentration 0.30 mol/l in a conical tube.
7. Insulin syringe 0.50 ml - 4 pcs.

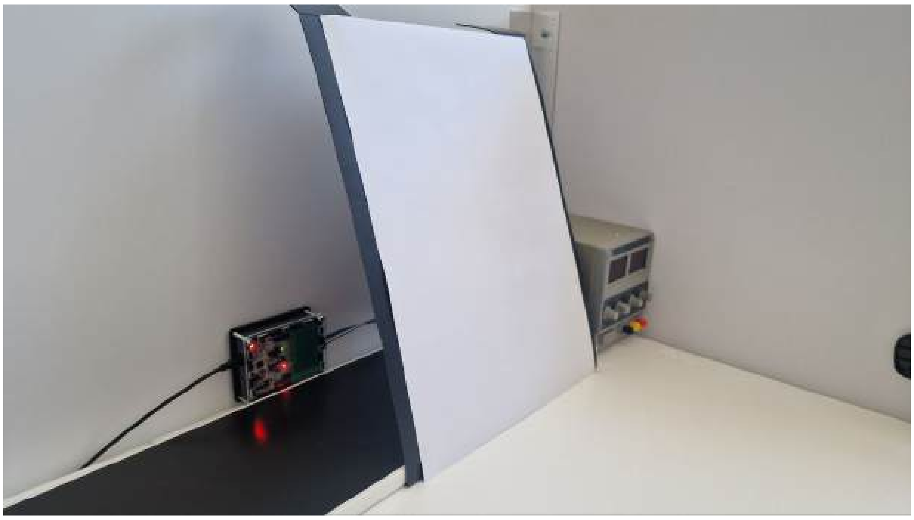
8. Syringe 3 ml - 5 pcs.
9. Microtube 2 ml with graduations - 7 pcs.
10. Conical tube 50 ml - 5 pcs.
11. Container 100 ml with screw cap - 2 pcs.
12. Wash bottle 500 ml.
13. Test tube rack.
14. Pasteur pipette - 5 pcs.



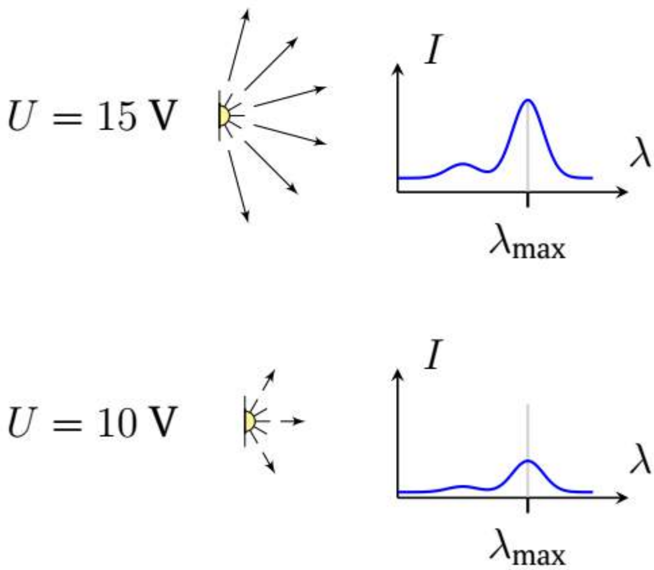
Equipment (other)

1. Masking tape.
2. Ruler 50 cm plastic.
3. Pair of gloves.
4. Container for used reagents.
5. Wipes.
6. Sunshield (shown in the extra image)





Note. Each of the light sources can be supplied with a voltage in the range $U \in [0, 15]$ V. Assume that when the voltage on the light source changes, its total light intensity changes, but the spectrum remains the same (see figure).



Attention! You are provided with three instructions that you should read before starting work:

1. Instructions for electrical equipment.
2. Instructions for chemical equipment.
3. Instructions for the Spectroscopy.bat program.

Note. A *mole* of a substance is the amount of a substance containing $N_A = 6.02 \cdot 10^{23}$ molecules. The *molar mass* μ is the mass of one mole of the substance. The required molar masses are listed below. The *molar concentration* c is the number of moles of a substance in a unit volume (its unit is mol/l).

Substance	μ, g/mol
NaOH	40.0
IC	466.4
Gl	180.0
NaCl	58.4

Note. It's strongly recommended to use a separate container for each solution (including separate syringes and pipettes). If you need to label a container, stick masking tape on it and make the necessary markings on the tape. If necessary, wash the used tubes with a wash bottle.

On the desktop of your computer, there is a folder "Results" with subfolders "Part A", "Part B", "Part C", "Part D", "Recalibrate". Save all files obtained during the work in the corresponding folders. Also, in the "Results" folder, there is a "Report.docx" file with a table. Save all graphs that are explicitly required to this table. You can also optionally add any other graphs to the report in the rows corresponding to the question items.

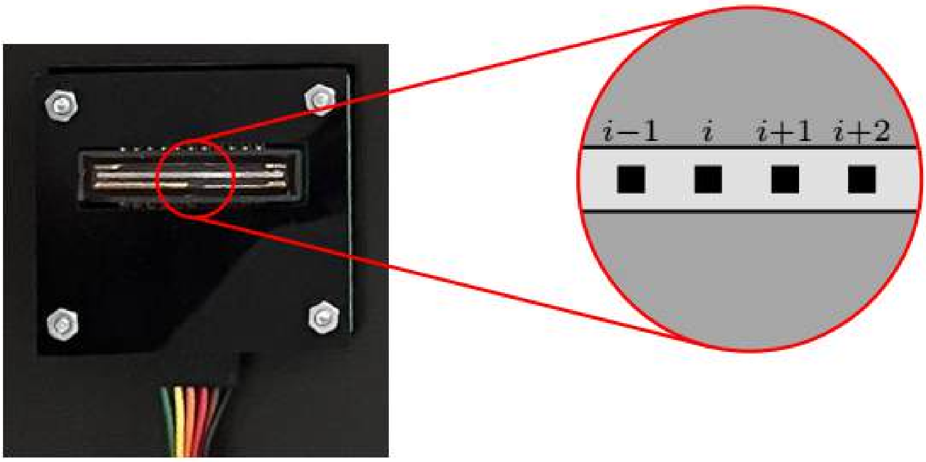
Error estimation is not required in the problem!

Part A. Calibration

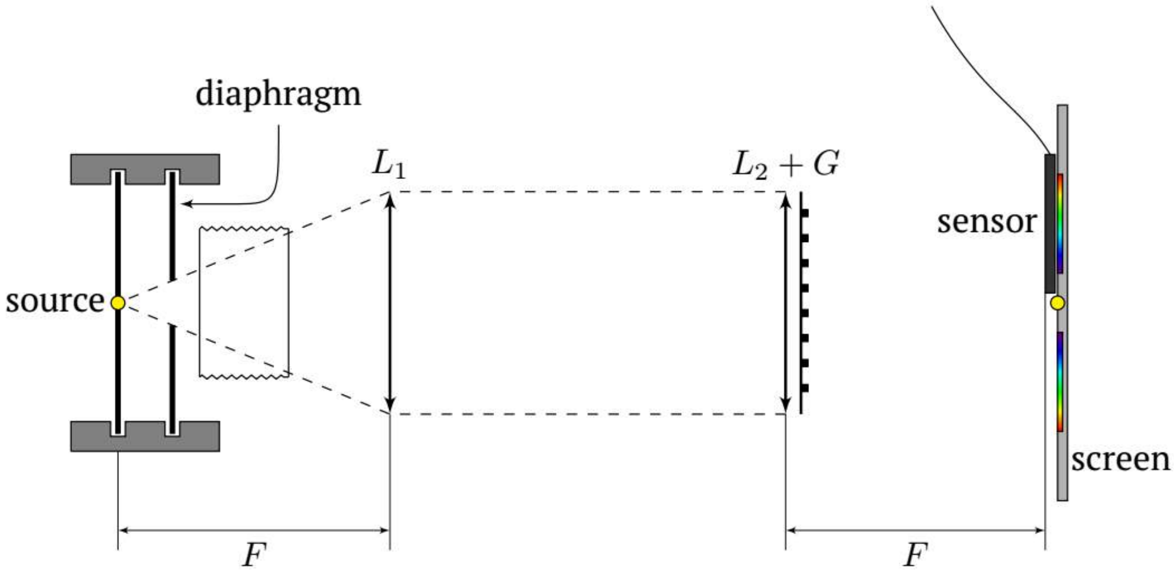
This part of the task requires assembling the optical setup according to the schematic (it is shown below) and calibrating the sensor.

The photosensitive part of the sensor consists of about 3650 of identical photodiodes called pixels (see Fig.). A computer program processes the data from the sensor and the result is the dependence of the illumination intensity of each pixel on its number. The intensity is measured by the sensor in arbitrary units.

The light of any real source consists of a continuous set of components of different wavelengths, called the *emission spectrum.* With the proposed optical scheme it is possible to "separate" the components of the spectrum spatially. In this way, it can be achieved that each pixel of the sensor receives almost monochromatic radiation. Calibration consists in matching the pixel number with its corresponding wavelength. After calibration, do not perform any operations on the setup other than inserting and removing the light source, the cuvette and the diaphragm. Moving other elements of the setup will cause the calibration to fail and the calibration must be repeated! Note that connecting wires to the light source while it is in the holder will also cause the calibration to fail. Assemble the setup so that the light source is in the focus of the first lens L_1. Place the screen with the sensor attached to it approximately in the focus of the second lens L_2. Place a cuvette with clean water in the holder.



Warning! Any light whose spectrum you are studying in this exercise must pass through the plane (not grooved) edges of the cuvette. Use the LED-CON as the light source. By slightly changing the position of the second lens and the sensor, achieve a clear diffraction pattern (" multicolored strip") on the sensitive part of the sensor.



A1	Save the obtained spectrum in the file "LED-CON.csv".

A2	Turn off the LED-CON and obtain the background spectrum. Save the result in the file "dark-A.csv".

A3	Change the source to LED-RGB and get the spectra of all three LEDs. Save the results in files "R-0.csv" "G-0.csv" and "B-0.csv" (R – red, G – green, B – blue).

Each LED-RGB LED emits at maximum intensity at a certain wavelength $\lambda_{\max}$. The values of $\lambda_{\max}$ values for all LED-RGB LEDs are shown in the table below.

LED color	$\lambda_{\max}$, nm
Red	620
Green	520
Blue	460

In the assembled optical setup, the wavelength of light λ corresponding to the sensor pixel with number N depends linearly on N:

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

A4	Using the results of A3, find the values of pixel numbers $N_{\max}$ corresponding to $\lambda_{\max}$. Calculate the parameters k_0 and λ_0.

A5	Change the source to LED-UNK, obtain its spectrum and save the result in the file ”unk.csv”. Find $\lambda_{\max}$ for this LED.

For all other parts, use only LED-CON as the light source.

If you change the position of any element of the setup while solving further tasks, you will need to recalibrate. When you run the calibration for the n-th time, be sure to save the spectra ”R-n.csv”, ”G-n.csv”, ”B-n.csv” in the ”Recalibrate” folder and find the values of k_n and λ_n. Also in the ”Calibration.docx” file, in the table, indicate which questions are made with the calibration number n! By default it is assumed that all questions are made with the original calibration.

Part B. Beer–Lambert law

To describe the adsorption of light by matter, the Beer–Lambert law is used: the intensity of each monocromatic component of the light decays exponentially with the path l in the matter:

$$\frac{I_\lambda}{I_{0,\lambda}} = e^{-\beta(\lambda)l},$$

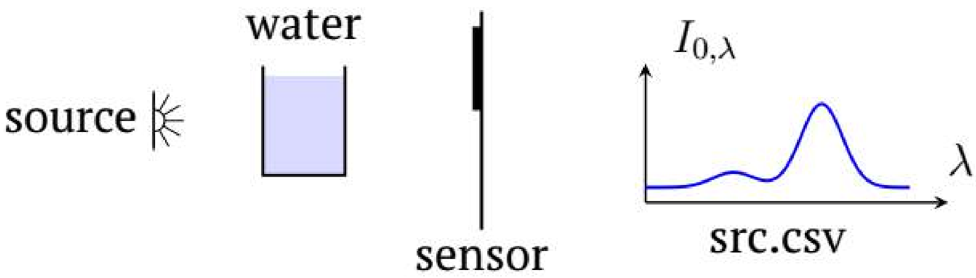
where $I_{0,\lambda}$ is the intensity of light of wavelength λ incident on the matter, I_λ is the intensity of light passed the distance l through the matter, β is some coefficient depending on the wavelength.

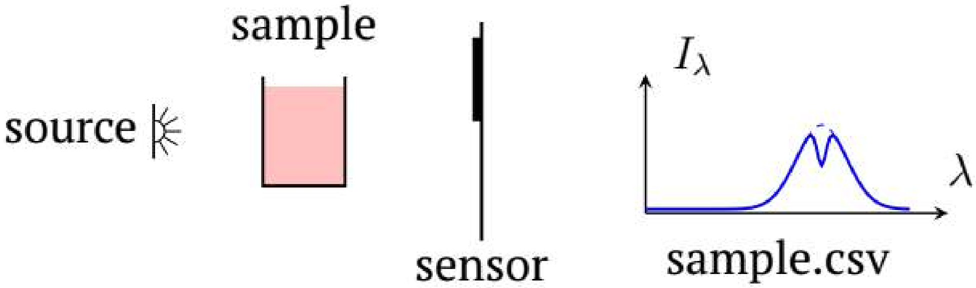
In this part we will study the adsorption of light of different wavelengths by indigo cramine IC. You have been provided a solution of IC with a concentration 0.70 mg/ml. You will need to get the droplets of IC solution with the same and known volume. If we hold the syringe with the volume 0.5 ml vertically and push the piston smoothly, the droplet will appear on the tip of the needle. This droplets comes off the needle after reaching some critical $V_{\mathrm{d,IC}}$

Use a 0.5 ml **syringe to obtain drops.**

B1	Determine the average volume $V_{\mathrm{d,IC}}$ of drops of the solution IC formed when it is squeezed through the needle of the syringe.

The values I_λ and $I_{0,\lambda}$ cannot be measured directly due to light reflections at the air-cuvette, cuvette-water boundaries and other factors. However, it can be assumed with a high degree of accuracy, that their ratio $I_\lambda/I_{0,\lambda}$ is equal to the ratio of the intensity of light that passed through **the cuvette containing the solution** to the intensity of light that passed through the **cuvette containing pure water**.





B2	Put 3.0 ml of water into the cuvette. Adjust the optimum voltage of LED-CON and Sensitivity. Measure the spectrum of the LED-CON light that passed through the cuvette with water and save the result in the "src-B.csv" file. Also measure background spectrum and save it in the file "dark-B.csv". For future measurements in this part do not change the voltage and Sensitivity! ***Note.*** If there are bubbles on the walls of the cuvette, remove them.

Measurements can only be made with acceptable accuracy in the wavelength range where the intensity of the source radiation is greater than 5% of the maximum.

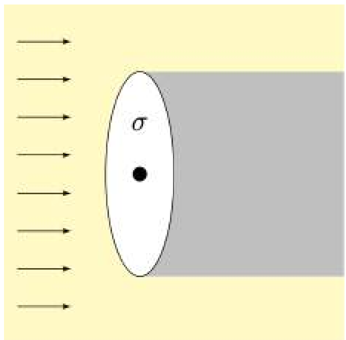
B3	Based on experimental data, indicate the wavelength range in which the $\beta(\lambda)$ dependence can be obtained with acceptable accuracy at your setup.

B4	By adding two drops of IC at a time to the cuvette, obtain the intensity spectra of the light passing through the solution for 10 different concentrations of IC. Save the results as multiple "IC-m.csv" files, where m is the number of drops of IC added to the cuvette. ***Note.*** Here and hereafter, after adding the test substance to the water, the solution should be stirred until it becomes homogeneous. If there are bubbles on the walls of the cuvette, remove them.



Let us describe the absorption of light theoretically.

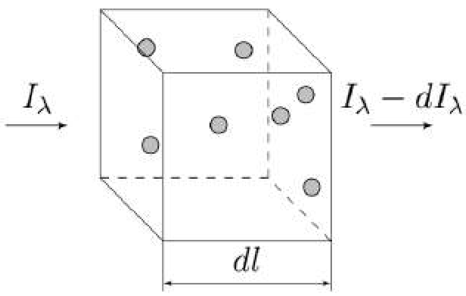
Let a solution of the investigated substance in a cuvette be illuminated by a parallel beam of monochromatic radiation with wavelength λ. The distance between the smooth inner walls of the cuvette is $L = 1.05$ cm. The concentration of the solution (the number of molecules of a substance per unit volume) is n (measured in 1/m^3).



Light is absorbed due to interaction with individual molecules of the substance under investigation. Let us determine the absorption cross section of a molecule σ, which has the dimension of area. Consider a circle of area σ centered on the center of the molecule. The plane of the circle is perpendicular to the direction of propagation of the light beam. Assume that all light hitting the σ circle is completely absorbed by the molecule (see figure).

The absorption cross section is different for different wavelengths, i.e., it is a function of the wavelength of the light $\sigma(\lambda)$.

Let a light of intensity I_λ incident on a thin layer of substance of thickness dl. After the light passes through the layer, the intensity decreases by dI_λ.



B5	Express dI_λ using the concentration of molecules of substance n, I_λ, $\sigma(\lambda)$, dl.

B6	Express $\sigma(\lambda)$ if the light intensity decreases from $I_{0,\lambda}$ to I_λ as it passes through a layer of matter with thickness l. Express the answer in terms of n, $I_{0,\lambda}$, I_λ and l.

Note. If you didn't get an expression for $\sigma(\lambda)$, you can investigate the dependency $\beta(\lambda)$ instead of $\sigma(\lambda)$ everywhere else. $\beta(\lambda)$ is defined at the beginning of this part.

B7	Plot the dependence graph $\sigma(\lambda)$ for at least 10 different wavelengths from the range found in question **B6**. Save the data for the graph as a table "IC-result.csv" in the "Part B" folder. Save the graph of this dependence in the "Report.docx" document in the line "IC-result".

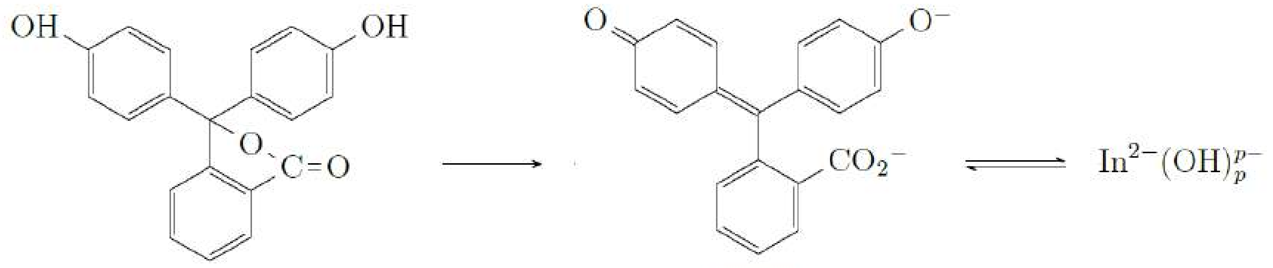
B8	Find $\lambda_{\max,\mathrm{IC}}$ – the wavelength of light that is absorbed the most by IC.

Part C. Phenolphthalein

Phenolphthalein is an organic dye that changes its color in an alkaline environment, therefore it is used as an acidity pH indicator. In an alkaline environment, the phenolphthalein molecule can exist in the following states:

- H_2In;
- In^{2-};
- $In^{2-}(OH)_p^{p-}$.

In the last of them p is a natural number ($p \in \{1, 2, 3, \dots\}$). Only one of these states (In^{2-}) has a typical pink color, the others are colorless.



H_2In In^{2-}

There are two reactions corresponding to the transitions between the indicated states of the molecules:

$$H_2In \rightarrow In^{2-} + 2H^+$$
$$In^{2-} + p(OH)^- \rightleftharpoons In^{2-}(OH)_p^{p-}$$

"Double arrow" in the second reaction means that the reaction can go both forward and backward. The first reaction is quite fast (phenolphthalein is instantly colored in an alkaline medium), and the second reaction is relatively slow. In this part of the problem it is required to calculate p by investigating the kinetics of the second reaction.

Ionic strength of a solution is the value J determined by the formula:

$$J = \frac{1}{2}\sum_i n_i Z_i^2.$$

Here summation is done over all types of ions in solution, n_i is a concentration of ions of a particular type i, Z_i is a charge number of a corresponding ion (it's a ratio of ion charge to elementary charge $e = 1.602 \cdot 10^{-19}$ C).

Rate of a chemical reaction is the number of elementary reactions occurring per unit time (measured in 1/s). The rate of each reaction depends on many factors, including the concentrations of the reagents at each time and the ionic strength of the solution.

Let us discuss the dependence of the rate of a chemical reaction on the concentrations of the reacting components. Consider a decomposition reaction in which a complex reagent $\mathrm{A}_\alpha\mathrm{B}_\beta$ is decomposed into simple reagents A and B:

$$\mathrm{A}_\alpha\mathrm{B}_\beta \to \alpha\mathrm{A} + \beta\mathrm{B}.$$

According to the theory, the rate of this reaction r_{decom} is proportional to the $\mathrm{A}_\alpha\mathrm{B}_\beta$ concentration in the solution:

$$r_{\text{decom}} \propto n_{\mathrm{A}_\alpha\mathrm{B}_\beta}$$

The reverse reaction (composition) is also possible:

$$\alpha\mathrm{A} + \beta\mathrm{B} \to \mathrm{A}_\alpha\mathrm{B}_\beta.$$

According to the theory, the reaction rate of the composition r_{com} is proportional to a power expression of the concentrations of the respective substances n_A, n_B:

$$r_{\text{com}} \propto n_\mathrm{A}^\alpha n_\mathrm{B}^\beta.$$

In this part it is required to investigate the dependence of the reaction rate on the concentration of ions $(\mathrm{OH})^-$, keeping the ionic strength of the solution constant. To satisfy the last requirement, we will also use table salt NaCl solution. We will assume that NaOH and NaCl dissociate completely in water, i.e. they decompose into ions according to the reactions:

$$\mathrm{NaOH} \to \mathrm{Na}^+ + \mathrm{OH}^-$$
$$\mathrm{NaCl} \to \mathrm{Na}^+ + \mathrm{Cl}^-$$

Note. Under the conditions of the experiment, it is possible to assume that the concentrations of all states of In are much smaller than the concentrations of other ions and substances. Therefore, you can assume that the concentration of $(\mathrm{OH})^-$ ions does not change much during the reactions. You can also neglect the contribution of all the ionic states of In to the ionic strength of the solution.

C1	Calculate the ionic strength J_0 of the NaOH solution, the concentration of which is $c_0 = 0.30$ mol/l.

C2	Let us consider the mixture of three components: 1. NaOH solution, concentration $2c_1$, volume V_{NaOH}; 2. NaCl solution, concentration c_1, volume V_{NaCl}; 3. Distilled water, volume V_w. Obtain the relationship between V_{NaOH}, V_{NaCl}, V_w, c_0, c_1 which gives the ionic strength J_0 of the solution.

Further it will be necessary to prepare solutions with different concentrations of $(\mathrm{OH})^-$ ions, but with the same ionic strength J_0. For this purpose it's convenient to use when solutions of NaOH and NaCl with the same concentration $c_0 = 0.30$ mol/l are used.

C3	Let us consider the mixture of three components: 1. NaOH solution, concentration c_0, volume V_{NaOH}; 2. NaCl solution, concentration c_0, volume V_{NaCl}; 3. Distilled water, volume V_w. Obtain the relationship between V_{NaOH}, V_{NaCl}, V_w, which gives the ionic strength J_0 of the solution.

Before operating with NaOH ***reread the warning at the beginning of the problem text.***

Prepare the NaOH solution with the concentration $c_0 = 0.30$ mol/l using the given grains.

C4	Prepare 5 solutions with different concentrations of $(\mathrm{OH})^-$ ions in different optical cuvettes. The ionic strength of all the solutions has to be the same and equal to J_0. Label all the cuvettes to make sure that you don't mix them up. Place one of the cuvettes in the holder. Adjust the optimal LED-CON voltage and Sensitivity. Measure the spectrum of the LED-CON light that has passed through the cuvette and save it in the file "src-C.csv". Do not change the LED-CON voltage and Sensitivity in future measurements in this part! Obtain the background spectrum and save it in the file "dark-C.csv".

Next, you will study the dependence of the spectrum of the light passed through the cuvette with the solution over time after some In has been added. There is the order of experiment for each solution:

1. Measure the background and save it in "dark-OH-c.csv", where c is the concentration of ions OH^- in the solution in mol/l units
2. Add **two** droplets of In to the optical cuvette with insulin syringe (syrenge's volume is 0.5 ml).
3. Stir to homogenize the contents of the cuvette.
4. Place the cuvette in the holder.
5. Start the spectrum measurements ("Time series").
6. Conduct measurements during 5-10 minutes.
7. Save the results in "In-OH-c.csv", where c is the concentration of ions OH^- in the solution in mol/l units.

C5	Conduct measurements according to the instructions above for all five solutions prepared in the cuvettes.

C6	Based on the experimental data, determine which light wavelength $\lambda_{\mathrm{max,In}}$ is most strongly absorbed by phenolphthalein.

The absolute value of phenolphthalein In^{2-} concentration (measured in $1/\mathrm{m}^3$) cannot be determined from the data obtained. However, the time dependence of the relative change of concentration is enough for further calculations. This means that you can express the required concentration in any arbitrary units.

C7	Plot the graphs of the concentration n of In^{2-} versus time. Save your graphs on the lines "C-OH-c-t" in the file "Report.docx", where c is the concentration of $(\mathrm{OH})^-$ ions in your solution expressed in mol/l.

C8	Plot the graphs of the reaction rate r (it can be expressed in any convenient arbitrary units identical for all concentrations) versus In concentration n for all optical cuvettes. Save your graphs on the lines "C-OH-c-r" in the file "Report.docx", where c is the concentration of $(OH)^-$ ions in your solution expressed in mol/l. ***Note.*** The next question **C9** can be solved without solving question **C8**.

C9	Using the experimental data obtained, determine the value of p (p is defined at the beginning of this part).

Part D. Chemical traffic light

As you observed in part **B**, indigo carmine IC is blue in pure water. However, if we add some IC to the solution of glucoze Gl with ions OH^-, the solution will be green at the beginning and will change color later. This behavior is a consequence of the chemical reactions present in the mixture.

Use the solution of NaOH prepared in part **C**.

In an optical cuvette prepare the solution in which the concentration of NaOH is 0.15 mol/l and the concentration of Gl is 0.25 mol/l.

D1

Color	Green/ Blue-green	Yellow	Red/Orange	Purple
Number	1			
t, s	0.0			

D2	Prepare a new solution of NaOH and Gl in an optical cuvette and place the cuvette in the holder. Find the optimal voltage on LED-CON and Sensitivity. Obtain the spectrum of the LED-CON light passing through the cuvette and save it in "src-D.csv". Don't change the voltage and Sensitivity during the next questions of this part! Obtain the spectrum of the background and save it in "dark-D.csv". After adding 0.15 ml of indigo carmine IC obtain the dependence of the spectrum of the light passing through the solution over time and save the obtained data to the file "IC-1.csv". "Restart" the reaction and save the obtained data to "IC-2.csv".

D3	Calculate four spectrums of $\beta(\lambda)$ for the moments when each of the four colors appears brightest. Save the result in "IC-n-result.csv", where n - is the order number of the color. Plot each $\beta(\lambda)$ and save the graph in "Report.docx" in rows "IC-n-beta", where n - is the order number of the color.

D4	Study the change in the spectrum over time and find the number of different states of the moleclus that are present during chemical reactions in visible wavelengths. There are no transparent (colorless) states of the IC moleclus in visible light.

D5	Plot the dependence of the concentrations of each state of the molecule IC over time on the single graph. Save the result in the "Report.docx" file in the "IC-t" row.