ANALYSIS OF ABSORPTION SPECTRA OF CHEMICAL COMPOUNDS

OUTLINE

In this experiment absorption spectra of some organic dyes and metal ion-based complex compounds are to determined.

INTRODUCTION

Electromagnetic radiation

Electromagnetic radiation in certain phenomena shows properties typical of waves (e.g. diffraction, interference), while in others - those types of individual particles (e.g. the photoelectric effect). For this reason, electromagnetic radiation is of dual nature, which means that we describe it as a wave or individual particles stream (photons or light quanta).

The propagation velocity of the electromagnetic wave in a vacuum is constant, it does not depend on its frequency or the reference system. It is a physical constant and its value is approx. $c = 3 \cdot 10^8$ m/s. In material media, this velocity is lower than in vacuum.
Depending on wavelength λ (or frequency ν), taking into account interactions with the environment different ranges of electromagnetic radiation can be distinguished: radio wave (the greatest wavelength), microwaves, visible infrared (VIS/IR), ultraviolet (UV), Roentgen (X) and gamma radiation.

The energy of the electromagnetic wave

The energy of one quantum of electromagnetic radiation is proportional to its frequency ν and inversely proportional to wavelength λ:

$$E = h \cdot \nu = h \cdot c/\lambda \qquad (1)$$

where proportionality factor h, called Planck's constant, is:

$h = 6.63 \times 10^{-34}$ J·s

Chemical reactions, including also photochemical reactions, are described using the amounts of reagents in moles. The energy of one mole of photons is called 1 einstein (E):

$$1\ E = N_A \cdot h \cdot \nu = 6.02 \times 10^{23}\ \text{mol}^{-1} \cdot \ 6.63 \times 10^{-34}\ \text{Js} \cdot \nu \ = 3.99 \times 10^{-10}\ \text{J·s·mol}^{-1} \cdot \nu$$

where N_A is the Avogadro constant (the number of constituent particles in 1 mole)

Absorption of electromagnetic radiation (UV-Vis) by matter

Electromagnetic radiation may be absorbed by matter, with the system being raised to the excited state (with an elevated energy level):

$AB + hv \rightarrow AB^*$ (excitation) (2)

Absorption of UV-Vis radiation leads to particle AB being raised to its excited state AB^*. Energy absorbed in this range corresponds to the electron transition from the basic state, with a lower energy level, to the excited state of higher energy. The distance between the energy levels quantified, i.e. photons of particular energy may be absorbed, which energy corresponds to the difference between energies of successive potential electron levels.

The transition (return) of the system excited to the basic state may take place as a result of various mechanisms.

Photoluminescence
It is an opposite process to excitation, i.e. it is re-emission of the previously absorbed quantum of light with the transition to the ground state:

$AB^* \rightarrow AB + hv$ (photoluminescence) (3)

Photoluminescence may be the result of two mechanisms:

- *Fluorescence* occurs when the emission is immediate (particles of the system after the cessation of the excitation factor immediately return to the ground state).
- *Phosphorescence* is when emission lasts for a relatively long time (even many hours after the cessation of the excitation process).

The conversion consists of the transfer of the electron excitation energy to several other lower energy states (vibrations, rotations and translations, i.e. thermal energy) within the same molecule.

Energy transfer consists of the transfer of excitation energy to other objects (molecules):

$A^* + B \rightarrow A + B^*$ (4)

Ionisation consists of the removal of an electron from the excited molecule.

The photochemical reaction consists of the conversion of the excited state to the activation energy required for the formation of an active complex, which results in a chemical reaction (in this case called the photochemical reaction).

$A + hv \rightarrow A^*$
$A^* + B \rightarrow AB^{\#} \rightarrow$ Product

Radiation spectrum
Visible radiation is contained in the range from approx. 400 nm to 780 nm. A mixture of all wavelengths is perceived by the eye as white. Emission of an incomplete visible range or absorption of a portion of radiation by an object results in the vision of complementary colours, which produces the sensation of colour. The dependence of the flux of radiated energy or the amount of absorbed energy (absorbance) on wavelength is referred to as the spectrum.

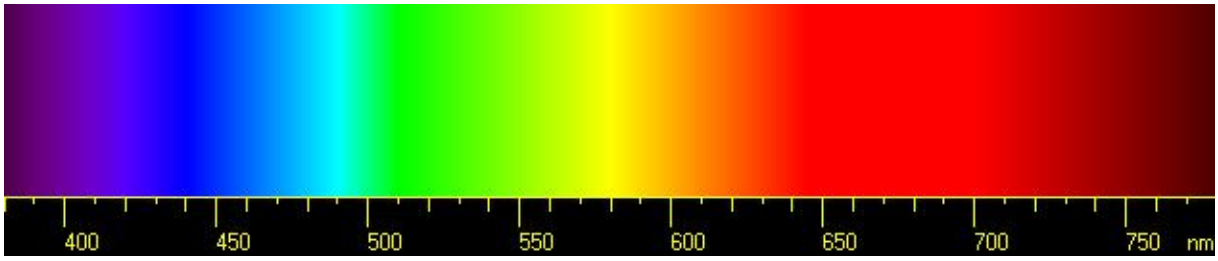


Fig. 1 The spectrum in the visible (VIS) range

Primary colours, colour mixing

The occurrence of all wavelengths leads to the perception of white light. The absence of radiation (of all wavelengths) in the visible range leads to the perception of black. These effects (white and black) are jointly referred to as **achromaticity.**

Minimal sets of colours, which when mixed produce any given colour (in the case of the human eye) are termed **primary colours**. It is generally assumed that the three primary colours are red, blue and yellow (as historically determined in art).

In the case of mixing the colours of emitted radiation (e.g. LEDs, computer monitors, television sets) we talk of additive mixing. In this method, it is assumed that primary colours are red, blue and yellow, or red, green and blue (in the RGB colour model). In this case, as a result of colour mixing the complementary colours provide the perception of white (light interference). When radiation unabsorbed by a filter is mixed, then it is referred to as subtractive mixing, used e.g. in printing (waves of a certain length are subtracted from white light, while the others are mixed). In this method the colour mixing effect yields black (filter interference), while magenta (purplish red), cyan (blue) and yellow are primary colours.

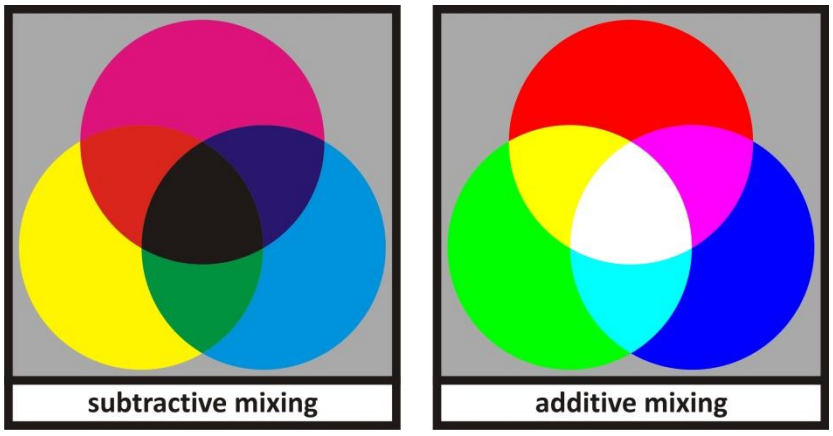


Fig. 2 Subtractive and additive mixing of colours

Principles of colour mixing and formation are explained by graphical models: the Newton disc and the Maxwell colour triangle. In the colour circle, the continuous spectrum of white light was drawn clockwise along the centre so that violet is transformed smoothly into red and in this way the spectrum is combined into the closed cycle of colour change. Colours located at the opposite sides of the circle centre are called complementary colours, e.g. yellow and violet or green and red.

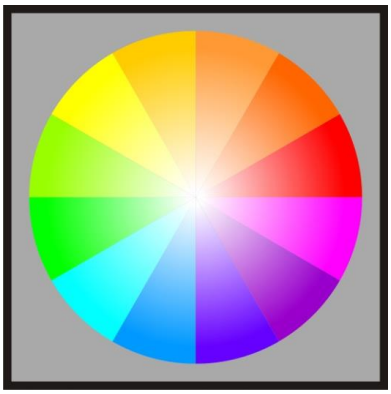


Fig. 3. The colour disc (the Newton disc)

Black body radiation

According to the black body mode, at a given temperature T the surface of this body radiates a flux of energy ϕ [W/m^2] proportional to the fourth power of temperature (the Stefan–Boltzmann equation):

$$\phi = \sigma T^4 \qquad (5)$$

All bodies at a temperature above zero (T > 0K) emit some of their internal energy in the form of radiation, called boson gas (photons are bosons). Figure 4 presents the radiation spectrum of a complete radiator depending on temperature. At lower temperatures around 300 K (invisible in the Figure) radiation is within the range of infrared (IR, invisible to the human eye).

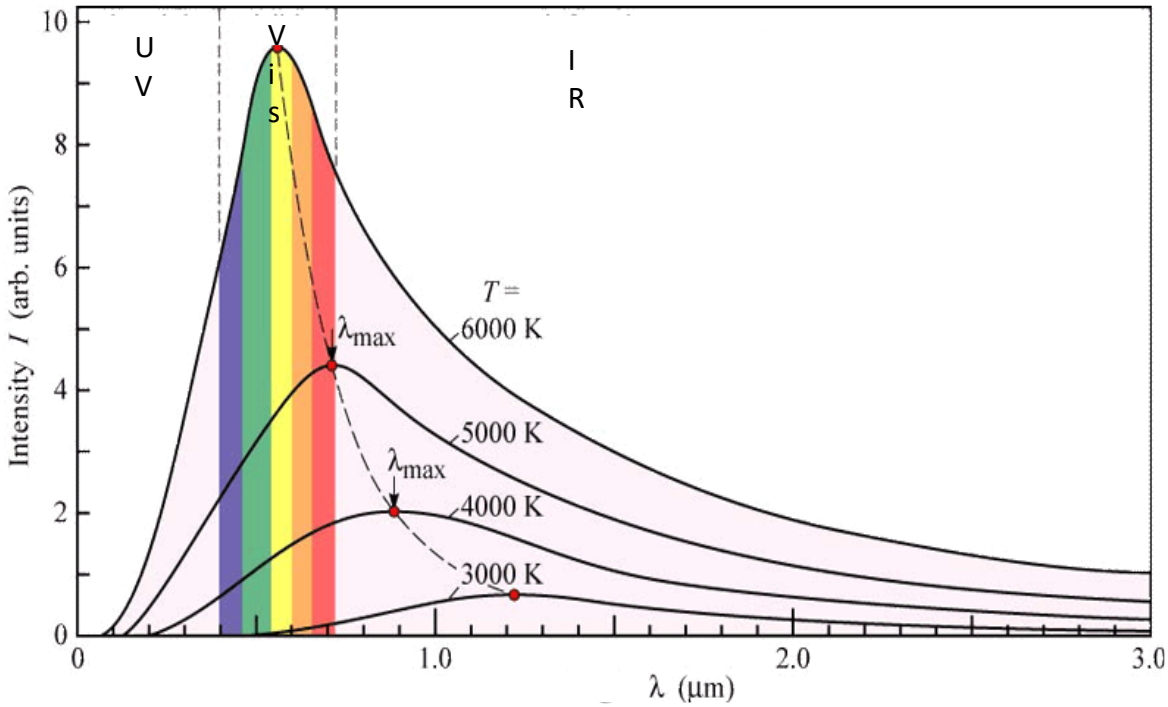


Fig. 4 The spectrum of radiation of a complete radiator depending on temperature.

With an increase in temperature not only does the flux of energy increase, but also the spectrum maximum moves towards the visible range (VIS) and ultraviolet (UV). Bodies at high temperatures radiate within the entire range of visible light, thus we perceive radiation as white (e.g. the surface of the Sun, which temperature is approx. 6000 K).

UV-VIS absorption spectrum, dyes

Dyes are inorganic or organic compounds, providing the surface of objects with specific colours. Their action is based on the absorption of electromagnetic radiation, as a result of which electrons of particular energies are exited and raised to higher energy states, with conversion to thermal energy.

Inorganic compounds (pigments, dyes)

Inorganic compounds are typically composed of crystals containing transition metals bound with ligands (complex bonds). Absorption of radiation is possible here by hybridization of electron levels of the central ion. In quantum physics, the term degeneracy refers to a phenomenon, in which many quantum states may correspond to some value of the energy level. The concept of degeneracy is generally connected with symmetric systems. By changing physical conditions, e.g. placing the system in a magnetic or electric field, energies of quantum states may change to a varying degree, splitting one energy level into several levels. Quanta of electromagnetic radiation with energy corresponding to the difference in energy between these states may thus be absorbed.

The effect of degeneracies of electron levels is connected with the **crystal field theory** and **ligand field** theory or the Jahn-Teller effect. This is connected with the proposal of removal of the degeneracy of electron levels as a result of symmetry breaking due to distortion in the symmetry of the magnetic and electric field by the geometry of a crystal or a complex. The Jahn-Teller effect is typically considered for complexes or crystals of transition metals (degenerate orbitals *d*) with octahedral geometry. Transferring such an atom from a completely symmetric system (degenerate orbitals *d*) to octahedral symmetry results in the formation of a non-zero electric and magnetic field, which leads to the removal of degeneracy. For this reason, many complexes or crystals of such transition metals as Cu, Co, Ni or Fe are capable of absorbing radiation in the visible spectrum.

Other inorganic compounds may also be coloured, e.g. blue ultramarine, which is an aluminosilicate ($Na_{8\text{-}10}Al_6Si_6O_{24}S_{2\text{-}4}$).

Organic compounds (dyes)

The colour of an organic compound is caused by the presence of conjugated electron systems π within its molecule, which is excited absorbing radiation in the visible range of the spectrum. Such dyes are divided into carbocyclic and heterocyclic. The colour of many organic systems depends on the pH of the medium.

An example of a carbocyclic system may be alizarin, while azorubine is an example of a heterocyclic system:

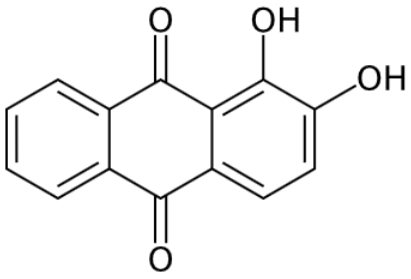


Fig. 5 Alizarine (a carbocyclic system).

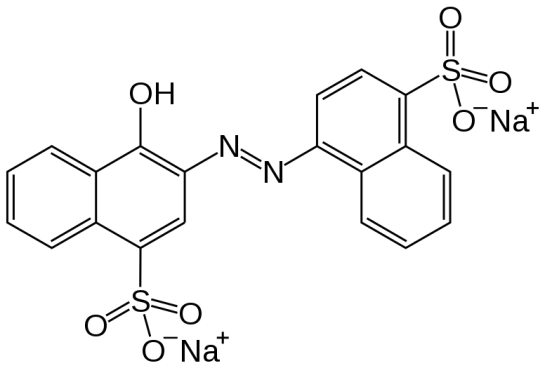


Fig. 6 Azorubine (an azo heterocyclic system).

One of the optical methods applied in analytical chemistry is absorption spectrophotometry, including UV-vis spectrophotometry (in the ultraviolet and visible range of the spectrum) and IR spectrophotometry (in the near-infrared region). Absorption spectrophotometry in the visible range (colourimetry) is the most extensively applied instrumental method. The basic criteria in this method are connected with selective absorption of light radiation by a solution of the tested substance.
The colour of a body indicates that it transmits or absorbs radiation in the visible range selectively. The observed colouring is a complementation of the colour of absorbed radiation. For the experiment, the table below lists selected colours with the respective wavelength ranges.

Absorbed radiation		**Complementary colour (observed colouring)**
wavelength [nm]	**colour**	
380-430	violet	yellow
430-450	indigo (navy blue)	yellow-orange
450-500	blue	orange
500-520	blue-green (cyan)	orange-red
520-560	green	red
560-570	yellow-green	red violet (purple)
570-595	yellow	violet
595-605	yellow-orange	indigo (navy blue)
605-615	orange	blue
615-635	orange-red	blue-green (cyan)
635-680	red	green
680-780	red violet (purple)	yellow-green

OUTLINE
The task aims to prepare and analyse the absorption spectra of organic dyes and metal complexes

APPARATUS

- a computer.
- an SP-880 Spectrophotometer.

GLASSWARE

- a porcelain cuvettes

1. Glass set for organic dyes:
- a 75 cm^3 beaker – 3 piece.
- a 250 cm^3 beaker – 1 piece.
- a 25 cm^3 measuring cylinder - 1 piece
- 1 cm^3 one-mark pipettes – 4 pieces.

2. Glass set for nonorganic dyes:
- a 75 cm^3 high beaker – 1 piece.
- a 50 cm^3 high beaker – 1 piece.
- a 250 cm^3 beaker – 1 piece.
- a 25 cm^3 measuring cylinder.
- a 2 cm^3 pipette – 1 piece.
- 10 cm^3 pipettes – 3 pieces.
- a laboratory spatula
- a weighing boat

REAGENTS

- Solutions of organic dyes:
  - eriochromocyanine
  - bromocresol green
  - bromophenol blue
  - bromothymol blue
- Solutions of metal ions: Cu^{2+}, Ni^{2+}, Co^{2+}
- 1:1 ammonia solution
- 0.1 M HCl solution
- 0.1 M NaOH solution
- Solid NaCl

HOW TO PERFORM THE TASK

- The task is divided into two stages, in each after solutions have been prepared according to the data in the tables below the absorption spectra are prepared. After the first part has been completed (when organic dyes are tested), used laboratory glassware is washed and then replaced to respective containers. The same procedure is followed in the second stage (when spectra of metal ions are examined).
- Glassware used to prepare solutions is washed after contact with each dye or metal ion in order to prepare it for use in the next series.
- Pipettes used to measure dyes are kept in bottles with reagents both during and after the experiment.

I. Preparation of solutions for spectrophotometric analysis:

A. Organic dyes:

1) Eriochromocyanin

	Beaker 1	Beaker 2	Beaker 3
HCl	10 cm^3	-	-
NaOH	-	10 cm^3	-
H_2O	-	-	10 cm^3
eriochromocyanin	3 drops	1 drop	3 drops

2) bromocresol green

	Beaker 1	Beaker 2	Beaker 3
HCl	10 cm^3	-	-
NaOH	-	10 cm^3	-
H_2O	-	-	10 cm^3
bromocresol green	9 drops	3 drops	3 drops

3) bromophenol blue

	Beaker 1	Beaker 2	Beaker 3
HCl	10 cm^3	-	-
NaOH	-	10 cm^3	-
H_2O	-	-	10 cm^3
bromophenol blue	6 drops	2 drops	3 drops

1) bromothymol blue

	Beaker 1	Beaker 2	Beaker 3
HCl	10 cm^3	-	-
NaOH	-	10 cm^3	-
H_2O	-	-	10 cm^3
bromothymol blue	15 drops	9 drops	20 drops

B. inorganic dyes:

1) copper ion solution

	Beaker 1	Beaker 2	Beaker 3
NaCl	-	4 g	-
ammonia	-	-	1,5 cm^3
Cu^{2+}	10 cm^3	10 cm^3	10 cm^3

2) cobalt ion solution

	Beaker 1	Beaker 2
NaCl	-	3 g*
ammonia	-	-
Co^{2+}	10 cm^3	10 cm^3

***Measurement is taken approx. 10 minutach after the solution has been prepared.**

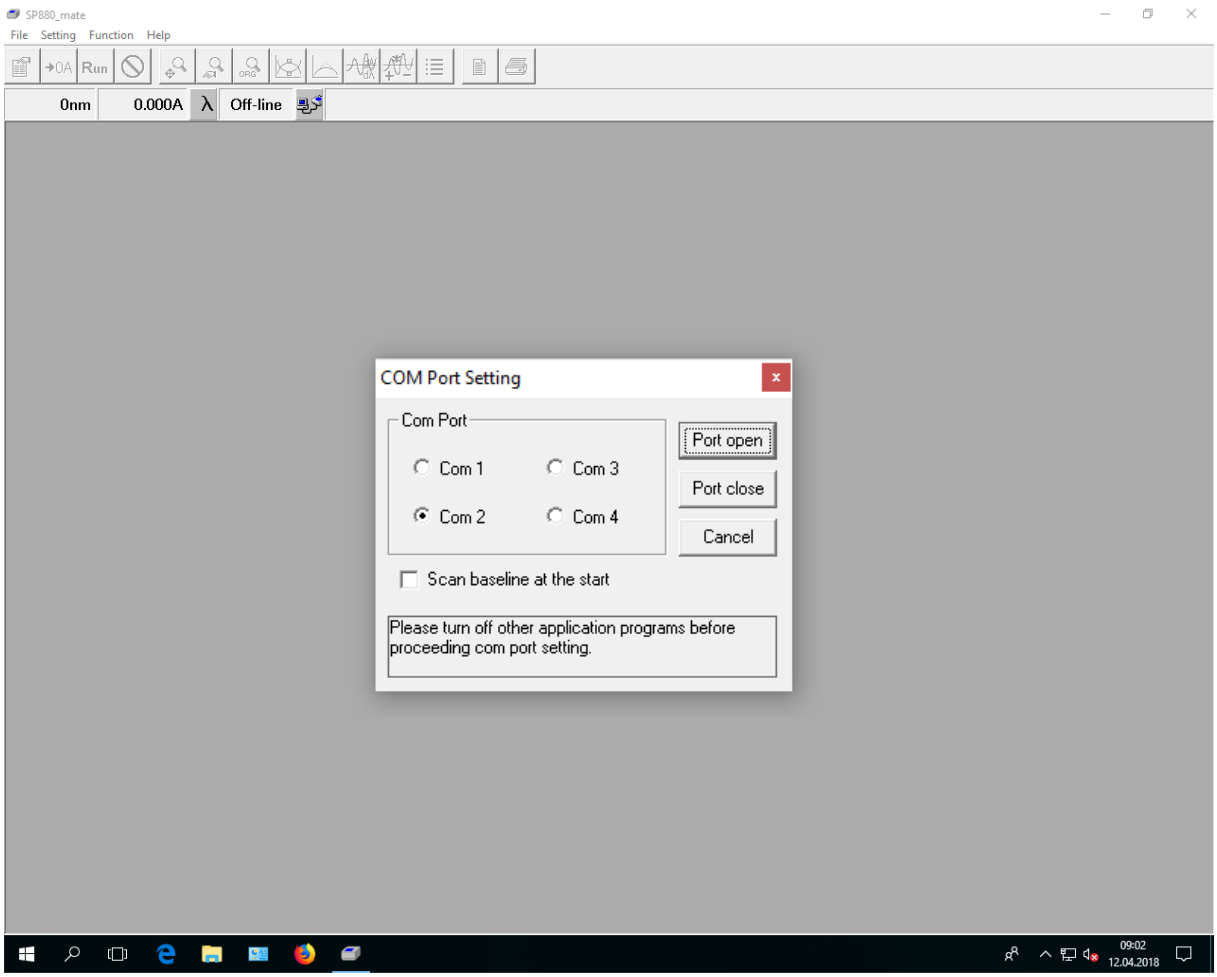
3) nickel ion solution

	Beaker 1	Beaker 2
NaCl	-	-
ammonia	-	10 cm^3
Ni^{2+}	10 cm^3	10 cm^3

II Preparation and recording of absorption spectra for prepared solutions using an SP-880 spectrophotometer, which instruction manual is given below.

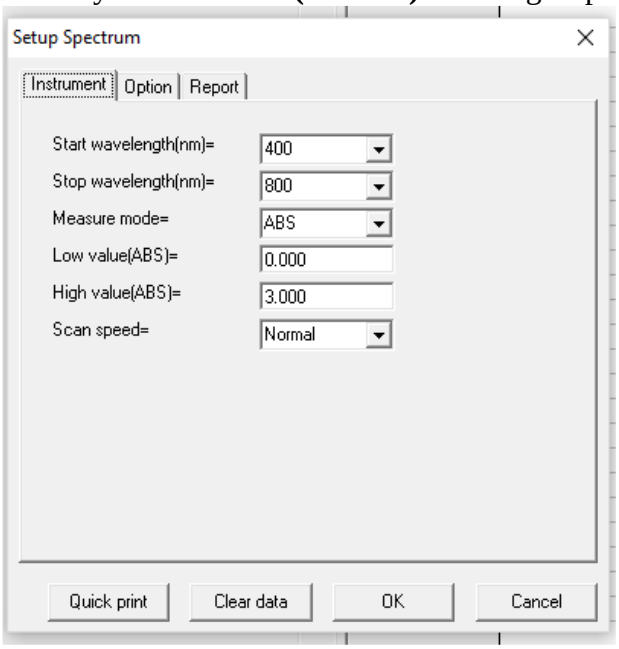
Operational manual of SP-880 Spectrophotometer

1. Check the contents of the measuring chamber, it should be empty.
2. Run the spectrophotometer software by clicking the **SP880mate** shortcut, which is located on the monitor's desktop.
3. After the program executed, a dialog box **COM Port Setting** wil show up (fig.1). The default setting is **COM2** and this setting should.

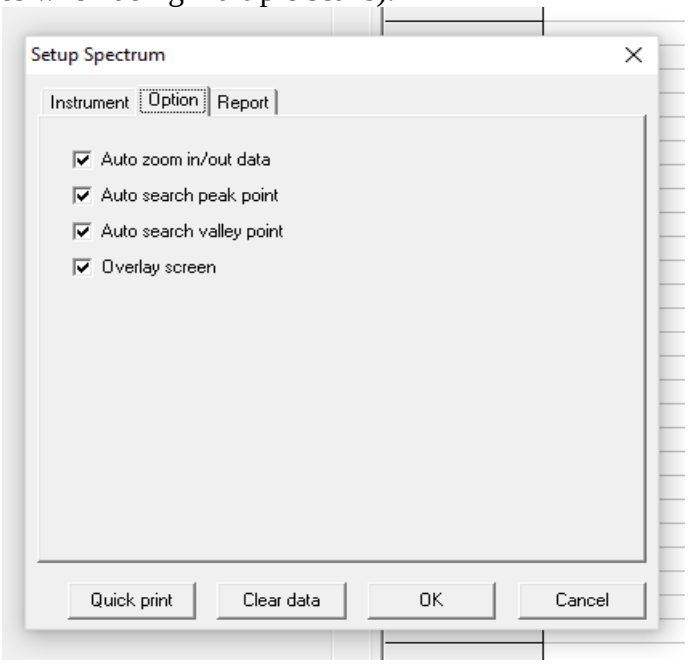


4. Press **Port Open** buton and the status bar will change ‘’Off-line” into ‘’On-line”. The SP880 machine is starting to find optical zero position. After reaching final position, users can see ‘’OK” showing in the status bar and can start to execute measurement functions.
5. Choose **Spectrum** from **Function** of menu bar and a dialog box of **Setup Spectrum** will show up. There are three tabs for setting in this screen:
   a) Tab ‘’**Instrument”:**
   -Start wavelength(nm), enter the initial value of the spectrum (380 nm).
   -Stop wavelength(nm), enter the final value of the spectrum (780 nm).
   -Measure mode, remain with the absorbance measurement option (ABS).
   -Low value (ABS)- users can set up the low value in scale graph (remain the default value).

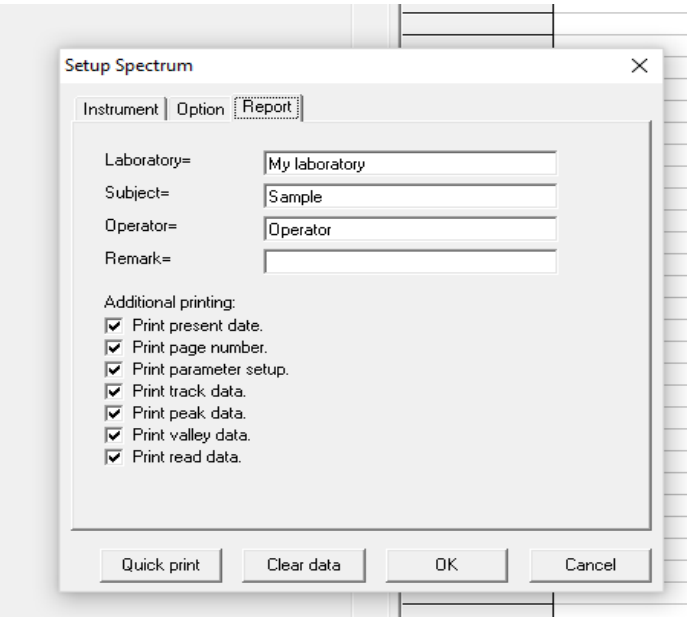
-High value (ABS)- users can set up the high value in scale graph (remain the default value).
-Scan speed- you should stay at the normal **(Normal)** scanning swpeed (600 nm / min).



b. In the Option tab, select all proposed options: **Auto zoom in / out data** (used to fit in the optimal scale automatically after reading data), **Auto search peak point** (will search for local maximum automatically after reading data, and display their values), **Auto search valley point** (will search for local minimum automatically after reading data, and display their values), **Overlay Screen** (will not clear previous read curves when doing multiple scans).



c. Tab **Report** is to set up options for printing reports in this function. Remain the default selection in this tab.



6. After completing above parameter setup, press icon →0A in the toolbar for baseline scanning.
7. Then put in sample and press icon **Run for sample** scanning.Program will start reading data and show those in a graph.
8. After measuring in the **File** menu, select **Date export to Excel** and export the measurement data to the excel file. In the window that appears enter the proper name of the tested sample. Note the file saving path.
9. After changing the solution in the cuvette, repeat the measurement by pressing the **Run** icon without repeating the baseline.

PREPARATION OF RESULTS:

1. Prepare graphs for the dependence of absorbance on wavelength for all analysed systems.
2. Convert absorbance to transmittance and prepare the graph for the dependence on wavelength.
3. Plot formed peaks on the graphs and determine the respective wavelengths and corresponding colours.
4. Analyse the cause for changes in the form of the spectrum and thus also the colour of analysed systems: in the case of organic dyes on changes in pH, while in the case of inorganic dyes on the structure of the formed complex. Draw structures of formed compounds.

Attention!
We re-make the baseline only if we change the spectrum or turn off the software.

Template of the table and draft of the study

…….. *Faculty* …….. *Field of study* *Full-time/ part-time studies*	…… *Name and surname*	…….... *Date:*
Group no.: …… *Team no.:* ……	……..…… *Exercise no.:*	…….. *Instructor:*

…….. *Wydział* …….. *Kierunek* *Studia stacjonarne/niestacjonarne*	…… *Imię i Nazwisko studenta*	…….... *Data wykonywania ćwiczenia:*
Nr grupy: ……... *Nr zespołu:* ……..	……..…… *Nr ćwiczenia:*	…….. *Nazwisko Prowadzącego:*

1. Temat ćwiczenia
2. Cel ćwiczenia:
3. Wstęp teoretyczny:
4. Pomiary:
5. Obliczenia:
6. Wykresy:
7. Wnioski

1. Exercise title:
2. The aim of the exercise:
3. Theoretical introduction:
4. Results:
5. Calculations:
6. Graphs:
7. Conclusions: