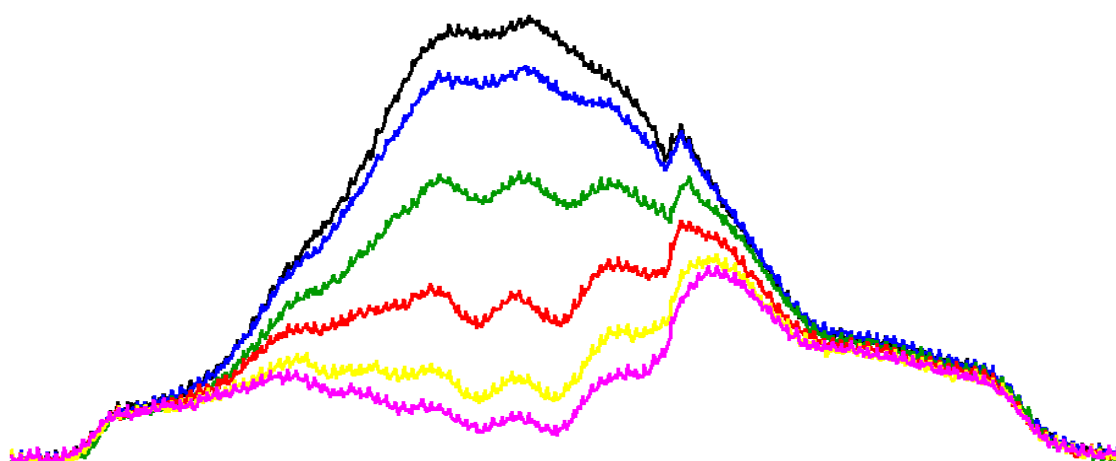
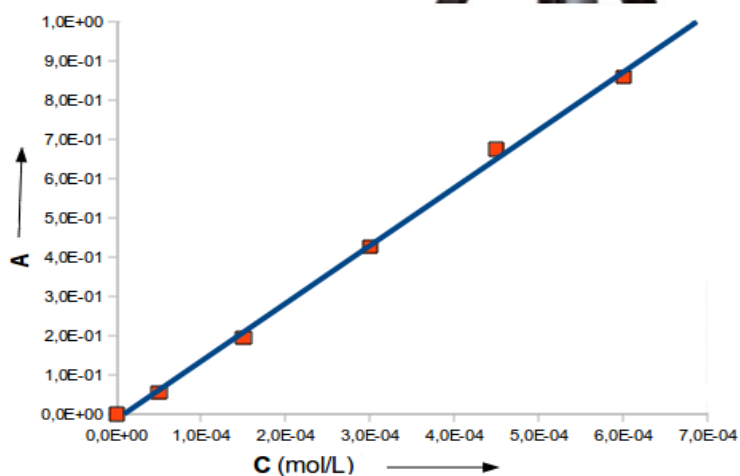


# Construction of a simple spectroscope

## Application in Chemistry

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### **Abstract**

This paper presents the construction of a simple spectroscope and explores its usefulness in the area of chemistry. The spectroscope is in fact a construction made of materials of zero value that is adapted to a camera. To exploit this construction to the spectroscopy, free software/open source software is used. The spectroscope presented here and the method that support its functionality are suitable for use in secondary education and early years of university education.

**Keywords:** spectroscope, spectroscopy, chemistry, diffraction grating, simple constructions, *Lambert – Beer Law, chemical kinetics, chemical equilibrium, stoichiometry, complexometry, water quality.*

### ***1. Introduction***

Spectroscopy and spectroscopic analysis is an area of the science that has offered much to the understanding of our world and our culture. It applies from the smallest (atoms) to the largest objects (galaxies). Dealing with spectroscopy requires the use of spectroscopes, simple or complex instruments, worth tens of euros to several thousand of euros. But the magic of spectroscopy can be revealed using simple tools that can be easily constructed by anyone willing to devote some free time and using simple materials of everyday life and a camera.

A basic component of the spectroscope introduced here, is the part of the optical disc in which the data are recorded and act as diffraction grating. Due to diffraction and interference phenomena, the light that strikes on the surface of an optical disk is analyzed and its spectrum is formed. Then the spectrum captured by a camera and the photo is processed by proper software for conclusions to be drawn.

The purpose of this work is to show the construction of an inexpensive spectroscope and the method that help us to use it in chemical teaching and chemical analysis.

## 2. Construction of the spectroscope

### 2.1 Materials that needed

1. A cylinder from towel paper about 6 cm in diameter
2. A cylindrical plastic bottle of mineral water 0.5L
3. A blank DVD
4. A shaving razor
5. A piece of hard cardboard
6. Aluminum tape
7. Adhesive tape
8. A scissor
9. A thin blade (cutter)
10. A digital camera with its lens hood

### 2.2. Instructions

#### 2.2.1 Preparation of diffraction grating

##### Step 1

*Using a thin blade, carefully depart the upper disk (cover) from the bottom disk (the one the data are recorded). Keep the bottom disk*



**Picture 2.1**

##### Step 2

*Using adhesive tape thoroughly clean the remains of mirror left on the disk.*



**Picture 2.2**

##### Step 3

*Finally you have a clear disk with some color on it. Remove the color by sinking the disk into a plate with some alcohol.*



**Picture 2.3**

#### Step 4

With the help of the scissor, cut a piece of about, 4cmX4cm as it is shown in pict. 2.4. This will serves as diffraction grating.



Picture 2.4

#### 2.2.2 Preparation of the body cylinder

With the help of the thin blade we cut the paper cylinder at one end obliquely about 45 degree to fit the camera lens hood. It is recommended to paint the cylinder interior black to reduce reflections on the cylinder walls.

#### 2.2.3 Preparation of the head

With the help of the thin blade we cut the plastic bottle about 8 cm from the base and we keep the piece with the base. In the center of the base we open a window about 2cmX1cm to fit the thin slit.

#### 2.2.4 Construction of the thin slit

1. We make a frame from hard cardboard dimensions of 4cmX2cm and open window of 3cmX0.5cm in the center of it.
2. We brake the razor to make two blades.
3. We fit the blades on the frame's window with the sharp sides faving each other. We can easily make slits of 0.1mm – 0.2mm in width.
4. We cover the slit with aluminum tape, leaving a central opening of 8mm in length. The reason we do this, is that we have in mind to fit in the front of the slit a cuvette that is 10mm in width.

#### 2.2.5 Preparation of the lens hood

1. We make a circular disk from hard cardboard sized to fit well in the lens hood.
2. We open a window in the center of disk with dimensions 3cmX2cm.
3. Using adhesive tape, we fit the diffraction grating on the disk's window.
4. Using adhesive tape, we fit the disk in the lens hood.

#### 2.2.6 Assembly of the head

1. We fit the thin slit frame on the top of the plastic bottle's window.
2. We cover the the set with aluminum tape, taking care to avoid entering light, except the thin slit.
3. We put in front of slit a hand made base for the cuvettes.

#### 2.2.7 Fitting the cylinder to the lens hood

1. We fit the cylinder to the lens hood.
2. We cover the set with aluminum tape, taking care to avoid entering light and for stabilization.

#### 2.2.8 Assembly of the spectroscope

We join the head with the cylinder, inserting the cylinder in the head. If the application is poor, we increase the thickness of the cylinder wrapping tape around it. So, we finalize the spectroscope that we will adjust on the camera. If we turn the spectroscope to a light source and look through the diffraction grating, we should see the light source spectrum. We may need to turn the head left –

right for better results..



*Picture 2.5: Some aspects of the spectroscope*

### 2.2.9 Final assembly

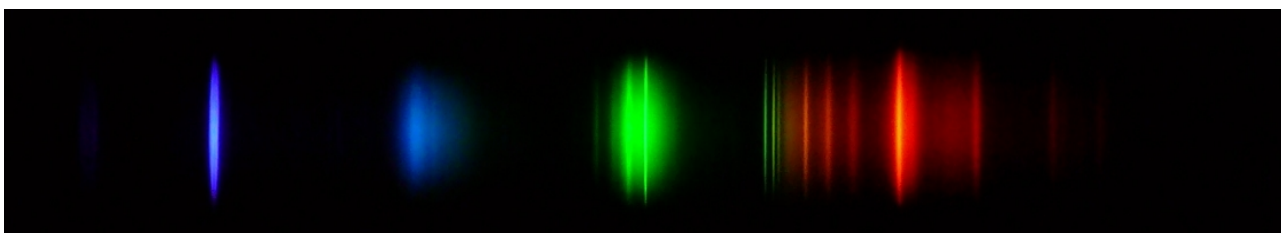
We now fit the spectroscopy to the camera and take photos of light sources. The light entering the slit, forms its spectrum on the camera's CCD.



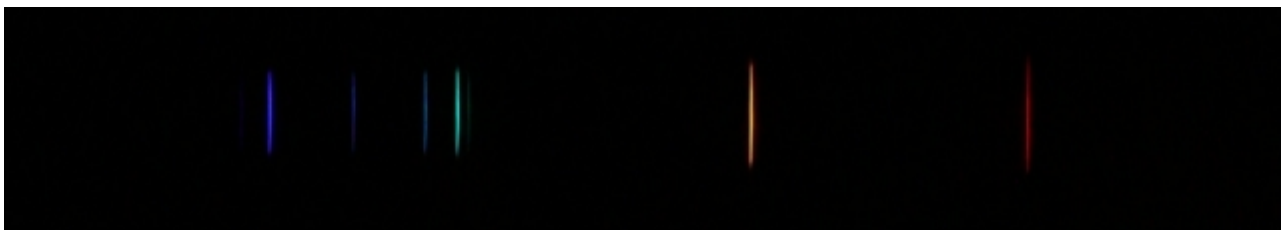
*Picture 2.6: The spectroscope ready for action*

### 2.2.10 The results

In the next pictures some photos of spectra taken with the spectroscope – camera are shown:



*Picture 2.7: CFL lamp spectrum (energy saver lamp)*



*Picture 2.8: Helium lamp spectrum*



*Picture 2.9: Daylight spectrum*



*Picture 2.10: KMnO<sub>4</sub> solution spectrum*



*Picture 2.11: Diode laser spectrum*

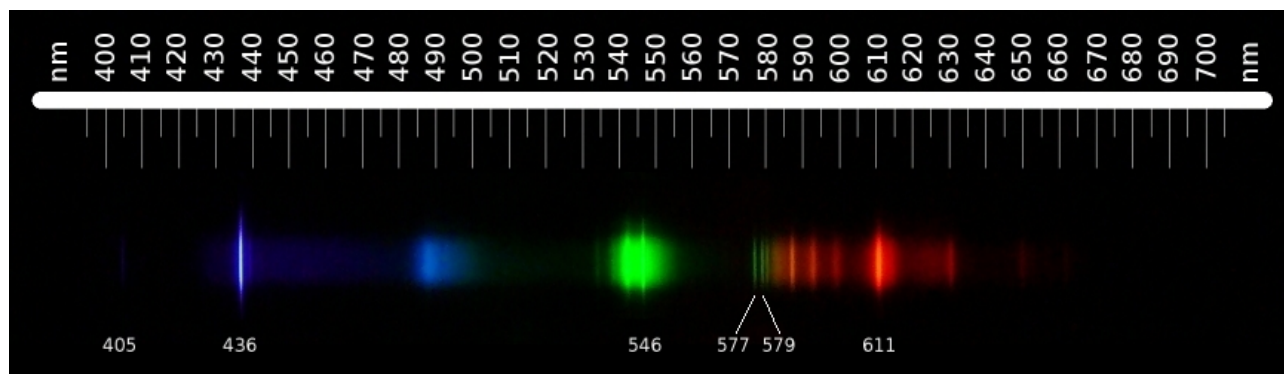
### 2.3 Suppling a scale

The above pictures look pretty impressive, but it would be better if there was a scale to be able to identify various characteristics of the spectra, as the position of the emission and absorption lines.

It is easy to make a scale using an image editing software (e.g The Gimp, Photoshop) and a reference lamp (e.g hydrogen lamp, CFL lamp). The procedure is as follow:

1. Select the image resolution (i.e the image size) in which we work. Each scale applies to a specific image size. This will be clear below.
2. Take a photo of the reference lamp's spectrum. The spectrum shows spectral lines at specific wavelengths that are positioned in specific point on the picture.
3. Open the picture with the image editing software.
4. Choose two spectral lines of known wavelength, preferable at the ends of the spectrum and match the known wavelengths to their coordinates on the picture (x position or y position depending of the spectrum orientation).
5. Add a transparent layer on which the scale is to be painted.
6. Having to pairs of position and wavelength and having in mind that diffraction grating produce linear spectra over wavelength, paint the scale on the transparent layer.
7. Delete the layer with the spectrum, so the scale will be left on the transparent layer.
8. Save the scale in a file type that supports transparency.

Having an image scale, one can easily add it on an image spectrum by copying and pasting.



**Picture 2.12:** *The CFL lamp spectrum (OSRAM DULUX S 11W/840)*

The above picture shows a CFL lamp spectrum and a scale attached to it. CFL lamps (energy saving lamps) are widely used in our homes and on our desktops. The spectrum of this lamp can be used as reference spectrum because it gives spectral emission lines of known wavelengths.



### ***3. Application in Chemistry – Spectroscopic measurements***

Using appropriate software and bases on spectra photos, we can do spectroscopic measurements similar to those made by spectrophotometers used in scientific laboratories.

The software we are using for the needs of this work is the following:

- ***The Gimp*** ([www.gimp.org](http://www.gimp.org)). It is an image processing software. The Gimp is free software/open source software of professional level. We use it for basic image processing of spectra images as the scale pasting or cropping, but mainly to convert the image files usually in JPEG or TIFF format to FIT file format.

- ***Fv*** (<http://heasarc.nasa.gov/lheasoft/fvtools/fv/>). It is free software/open source software that was developed and is freely available by NASA. It is used for processing astronomical data in FIT file format.

- ***Calc*** (<http://www.openoffice.org/product/calc.html>). It is a spreadsheet software in the category of free software/open source software. We use it to process the measurements.

#### **3.1 Taking the spectra**



***Picture 3.1: How to take photos of spectra***

The above picture shows how to take photos of the spectra that are used in the experiments. The assembly contains:

- The handmade spectroscope attached on the camera
- PANASONIC LUMIX DMC FZ-50 (camera)
- PHILIPS KRYPTONE 40watt (light source)
- A CFL lamp to adjust the wavelength scale (because the device is sensitive to geometry)
- Light source – spectroscope distance 1m
- Shooting conditions: aperture f2.8, exposure time 1s, manual focus, remote control for stabilization, lamp warming half an hour before taking photos.

### 3.2 Experiments

The value of the spectroscope and the method will be tested in some areas of chemistry, by performing representative experiments. More accurately, there will be experiments in the following areas of chemistry:

1. **Lambert – Beer Law:** *Determination of concentration of  $KMnO_4$  solution.*
2. **Chemical kinetics:** *Determination of fading rate of phenolphthalein in alkaline solution.*
3. **Chemical equilibrium:** *Determination of ionization constant of methyl orange.*
4. **Stoichiometry:** *Determination of ions ration in  $Ag_2CO_3$ .*
5. **Complexometry:** *Determination of instability constant of  $FeSCN^{2+}$ .*
6. **Water quality:** *Determination of chlorine in water.*

#### 4. Lambert – Beer Law: Determination of concentration of $\text{KMnO}_4$ solution

When light passes through a solution containing a colored (absorbing) substance, the intensity of the light decreases gradually along the route. The reduction of intensity depends on the concentration of the substance and the distance the light travel through the solution. These are expressed in the law of Lambert – Beer and reflected in the form:

$$A = \log \frac{P_o}{P} = \epsilon bc \quad (4.1)$$

όπου:

- A light absorption
- $P_o$  intensity of the incident radiation
- P intensity of the outgoing radiation
- $\epsilon$  constant called molar absorptivity that depends on the substance (solvent) and expressed in  $\text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{L}$
- b length traveled by the light in the solution in cm
- c solution concentration in  $\text{mol} \cdot \text{L}^{-1}$

The law of Lambert – Beer, as given in the above equation, is not directly applicable to chemical analysis, because it is practically impossible to measure  $P_o$  and P. In fact, the intensity of the outgoing radiation from the sample is compared to the outgoing radiation from the blank, so we have:

$$A \cong \log \frac{P_{blank}}{P_{sample}} \cong \log \frac{P_o}{P} = \epsilon bc \quad (4.2)$$

Theoretically, it is possible to calculate the concentration of a solution from equation 4.2, based on the measured values of A and b and  $\epsilon$  from literature. But this is impracticable, because different values for  $\epsilon$  are taken with different spectrophotometers. Even for the same spectrophotometer, the  $\epsilon$  values are depended on the width of the spectrophotometer's slit., So practically, a calibration curve is used.

#### 4.1 Experiment: Determination of concentration of $\text{KMnO}_4$ solution

##### Objectives:

- To verify the Lambert – Beer law.
- To calculate the molar absorptivity of  $\text{KMnO}_4$ .
- To calculate the concentration of an unknown aqueous solution of  $\text{KMnO}_4$ .
- To assess the detection limit of  $\text{KMnO}_4$  with this method.

**Method:**

- Spectrophotometric with calibration curve

**Equipment and materials:**

- The handmade spectroscope
- 40 watt light bulb (brilliant white lamp)
- Volumetric flask 1L
- Volumetric flasks 100mL
- Measuring pipettes 1mL, 2mL, 5mL, 10mL
- Pipette 10mL
- Balance  $\pm 0,01\text{g}$
- Cuvettes 1cm
- Potassium permanganate (solid)
- Deionized water

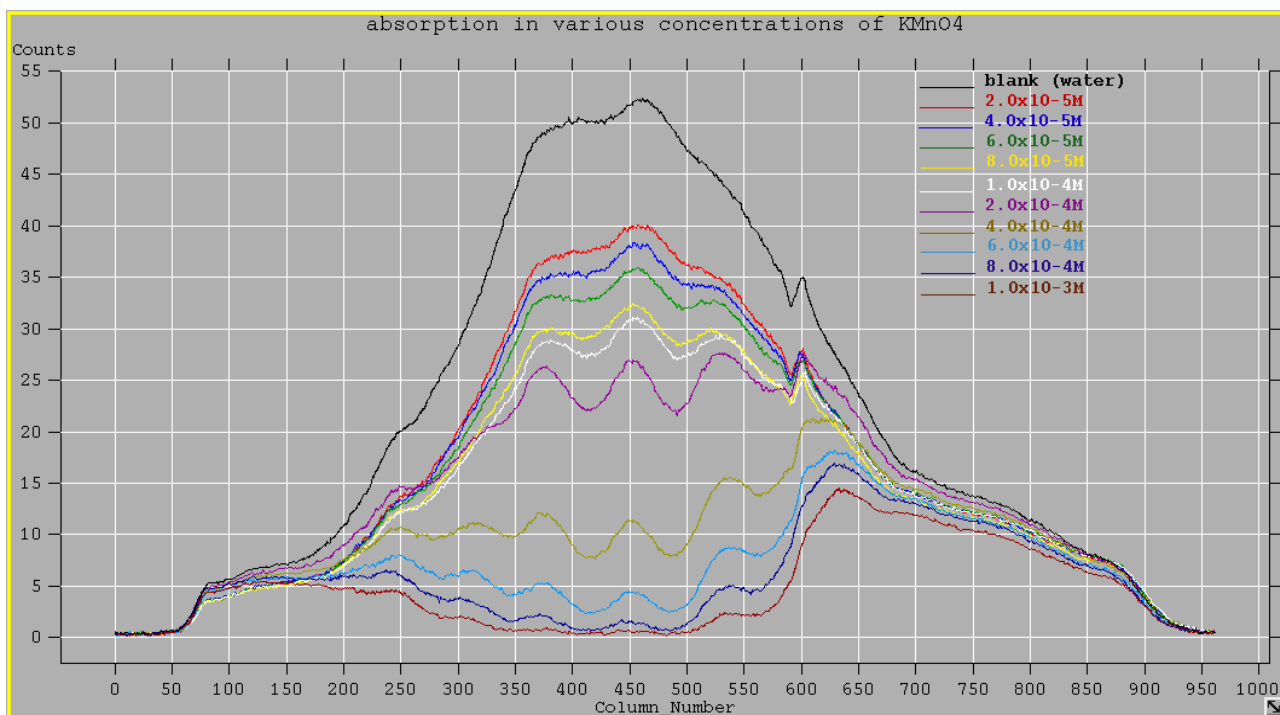
**Process:*****4.1.1 Estimation of the response range of the instrument (first trials)***

To determine within limits of concentration the instrument can properly function, a series of measurements originally were performed. Initially, 1.58g of solid  $\text{KMnO}_4$  was weighted. The amount was transferred to a flask of 1L and diluted to the mark. So a solution of  $1.0 \times 10^{-2}\text{M}$  was formed (stock solution). From the stock solution, amounts of 0.2mL, 0.4mL, 0.6mL, 0.8mL and 1.0mL were transferred to flasks of 100mL using measuring pipette and diluted to the mark. Next from the stock solution, amount of 2.0mL, 4.0mL, 6.0mL, 8.0mL and 10.0mL were transferred to flasks of 100mL and diluted to the mark. So, 10 solutions of  $2.0 \times 10^{-5}\text{M}$ ,  $4.0 \times 10^{-5}\text{M}$ ,  $6.0 \times 10^{-5}\text{M}$ ,  $8.0 \times 10^{-5}\text{M}$ ,  $1.0 \times 10^{-4}\text{M}$ ,  $2.0 \times 10^{-4}\text{M}$ ,  $4.0 \times 10^{-4}\text{M}$ ,  $6.0 \times 10^{-4}\text{M}$ ,  $8.0 \times 10^{-4}\text{M}$  and  $1.0 \times 10^{-3}\text{M}$  were formed. Then the spectra of the above solutions were taken using apparatus of picture 3.1.

The pictures of spectra processed with the Gimp as follow:

- a) Turn left  $90^\circ$  for most relevant position.
- b) Crop around the spectrum to reduce the file size and easier to process.
- c) Desaturate based on luminosity.
- d) Save as FIT file type.

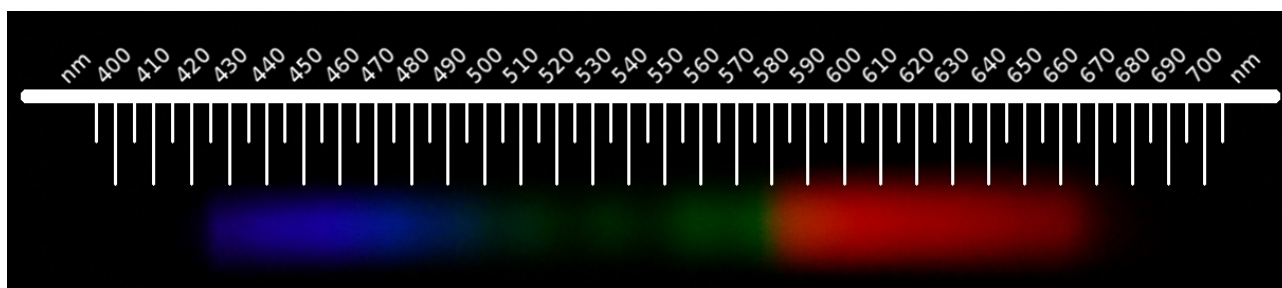
Finally, the Fv software was used to take the spectral profiles, that are shown in the next picture.



**Picture 4.1:** Spectra profiles of  $KMnO_4$  solutions in various concentrations

From the picture 4.1, it follows that the ideal concentration range is about  $6.0 \times 10^{-5}M$  to  $6.0 \times 10^{-4}M$ , because for these concentrations clear absorption bands are formed. (the two last profiles fall in the “noise” area, but the two upper profiles seem two work well).

To calculate the wavelength of the absorption bands, the scale was pasted on the pictures.



**Picture 4.2:** A  $KMnO_4$  solution spectrum with scale

The above picture shows that the  $KMnO_4$  solution strongly absorbs at 525nm and 545nm. Therefore our calculations will be made at these wavelengths, that correspond to the two main minima of the spectral profiles of figure 4.1.

#### 4.1.2 Preparation of the standard solutions

1.58g of solid  $KMnO_4$  was weighted. The amount was transferred to a flask of 1L and was diluted to the mark. So a solution of  $1.0 \times 10^{-2}M$  was formed (stock solution). From the stock solution, amounts of 0.5mL, 1.5L, 3.0mL, 4.5mL and 6.0mL were transferred to 100mL flasks and were diluted to the mark. So, five solutions of  $5.0 \times 10^{-5}M$ ,  $1.5 \times 10^{-4}M$ ,  $3.0 \times 10^{-4}M$ ,  $4.5 \times 10^{-4}M$  and  $6.0 \times 10^{-4}M$  were formed (standards solutions). Next an “unknown” solution was formed, by mixing 10mL of  $5.0 \times 10^{-5}M$  solution and 10mL of  $4.5 \times 10^{-4}M$  solution. Deionized water was used as blank.

#### 4.1.3 Taking the absorption spectra of standard solutions

From the standards solutions, the proper amount of solutions were transferred to cuvettes and their absorption spectra were taken, as well the blank and unknown spectra, according the apparatus shown in picture 3.1 and the conditions mentioned in that paragraph. The photos were taken with care not to disturb the geometry of the apparatus (ie. the parts not to moved from their initial positions, until the end of taking photos). In this way, it is assured that the light intensity reach the cuvettes is the same for all samples and the spectra are formed in the same place of photos, differing only in the light intensity. For each standard solution, as well the blank and unknown solution, five photos were taken in order to use the average. Also, photos of light source and “dark” (ie. with covered lens) were taken, the last for noise estimation.

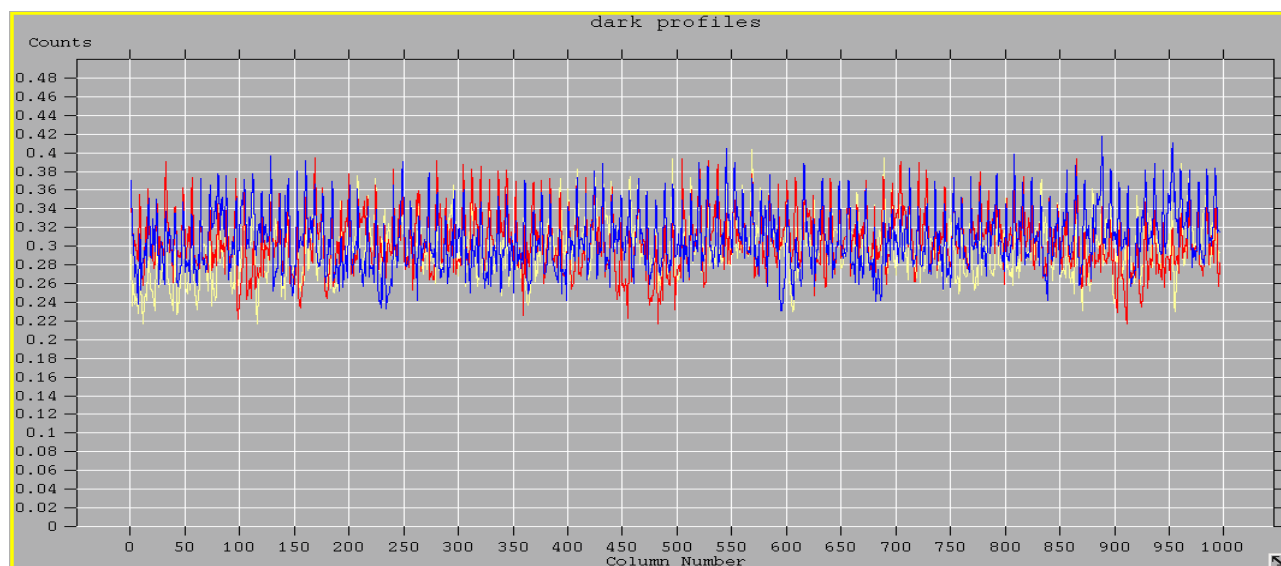
#### 4.1.4 Processing the photos of spectra with the Gimp

The pictures of spectra processed with the Gimp as follow:

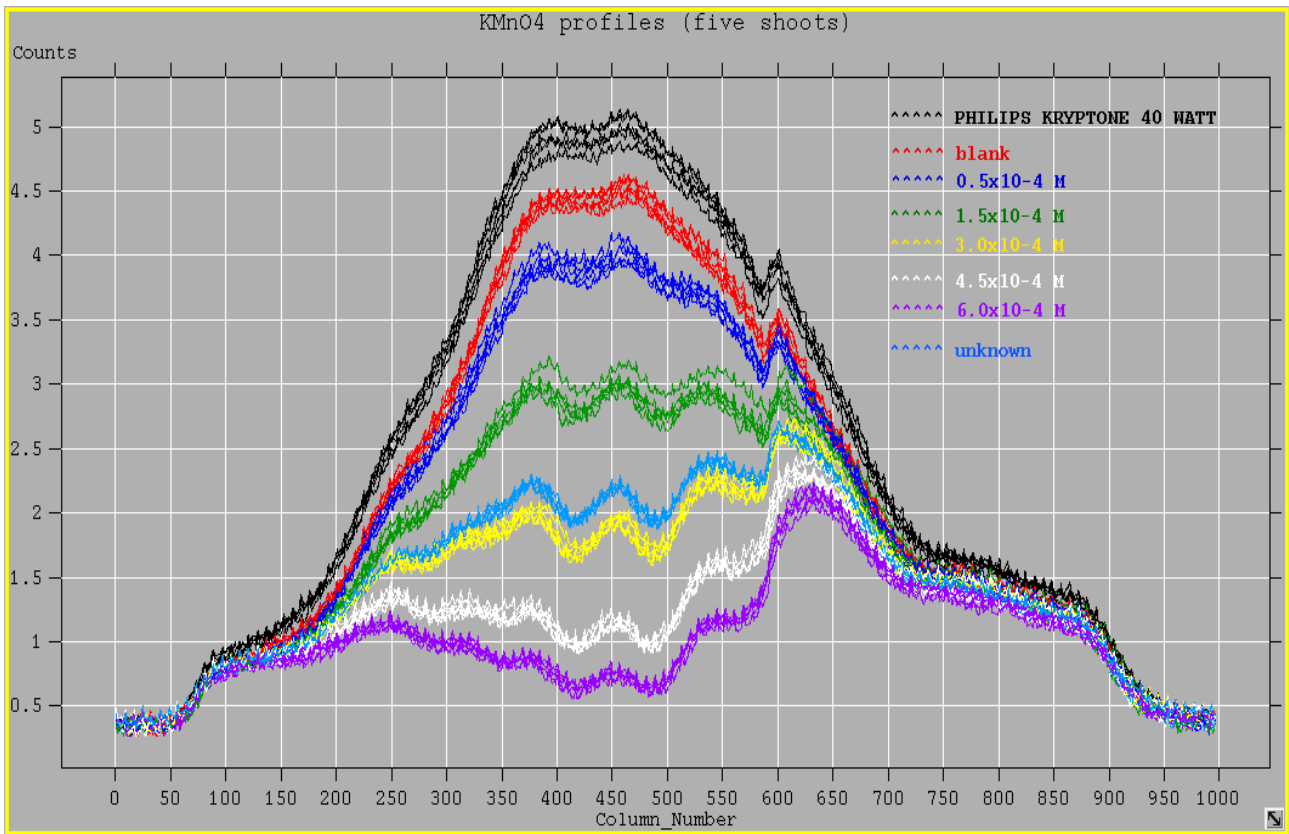
- Turn left to obtain the spectrum a more relevant position (ie. from low to high wavelengths).
- Crop the left and right black areas of the photos in such a way that the spectra to stay in the same place for all photos. Cropping only serves to reduce the size of files produced.
- Desaturate based on luminosity.
- Save as FIT file type.

#### 4.1.5 Taking the spectral profiles with Fv

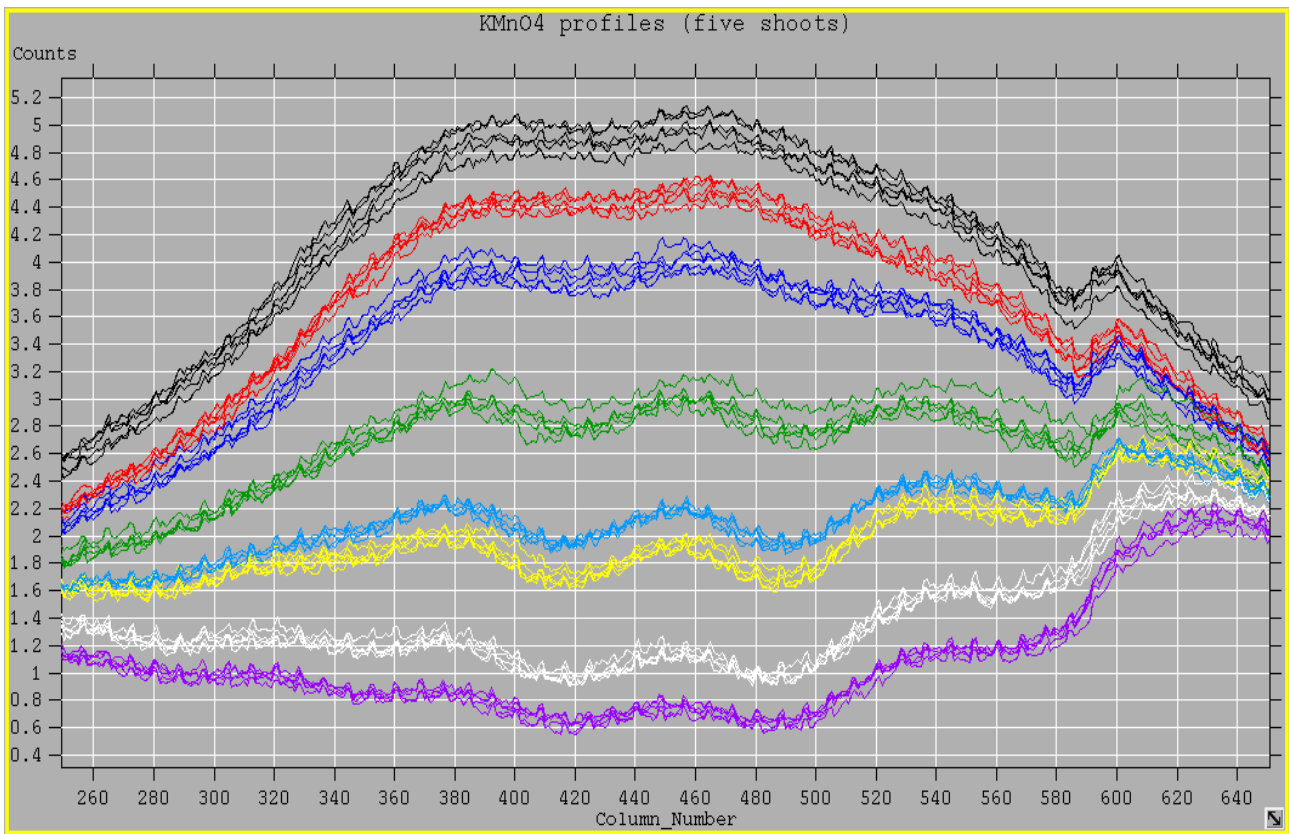
Using Fv, the spectral profiles were formed, that are shown in the next pictures.



**Picture 4.3:** Spectral profiles of “dark” (3 shoots)



**Picture 4.4:** Spectral profiles of standard solutions, light source, blank and unknown solution (5 shoots in each case)



**Picture 4.5:** Zoom to the central area of previous picture

Inspection of picture 4.4 and 4.5 shows that:

1. There are two regions of intense absorption around Column\_Number = 420 and Column\_Number = 490 corresponding to wavelenths 525nm and 545nm respectively (see pict. 4.2).
2. The spectra profiles of solutions varies 0.1 – 0.2 counts (see pict. 4.5).

To use the above pictures 4.4 or 4.5 in the Lambert – Beer law, the data presented should be properly interpreted.

So:

1. **Column\_Numbers** identify the location of pixels in the horizontal direction (image width) and can be matched to wavelenths, if two points are known.
2. **Counts** is considered to be proportional to the intensity of the outgoing radiation that captured by the camera's CCD.

So, according to this interpretation, equation 4.2 converts to:

$$A \cong \log \frac{P_{blank}}{P_{sample}} = \log \frac{\alpha * Counts_{blank}}{\alpha * Counts_{sample}} = \log \frac{Counts_{blank}}{Counts_{sample}} = \epsilon bc = kc \quad (4.3)$$

As it seen from pictures 4.4 and 4.5, the absorption depends on the light wavelength. Theoretically we can work at any wavelength, but it is preferable to work at the wavelength of maximum absorption. This is for Column\_Number = 420 and Column\_Number = 490, where the difference  $Counts_{blank} - Counts_{sample}$  maximum (a careful observer can see that the absorption is slightly higher for Column\_Number = 420) . Also, because the photos were taken under the same conditions, there is no need for any kind of “normalization”.

#### 4.1.6 Processing with the Calc

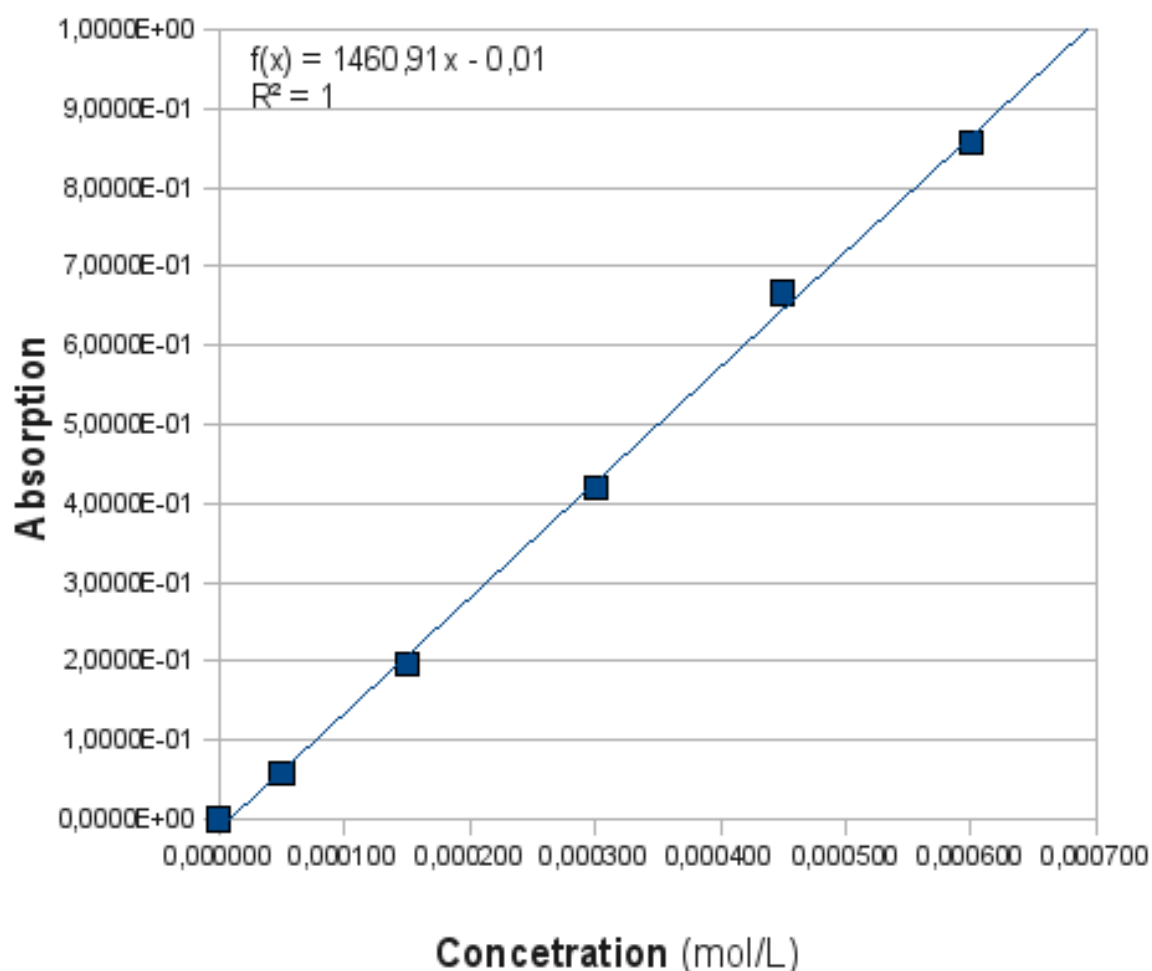
Based on the graphs of spectral profiles of  $KMnO_4$  solutions, the average values of Counts for the standards, the blank and the unknown are found for Column\_Number = 420 and Column\_Number = 490. Then using equation 4.3, the absorption is computed and the graphs absorption vs concentration are made. Usinig these graphs, the concentration of the unknown is found. The entire process is facilitated using a spreadsheet, which provides all necessary tools for the work.

In the next pictures, the data tables and the curves generated by the Calc are shown:



Column\_Number            420  
 Counts\_blank            4,40

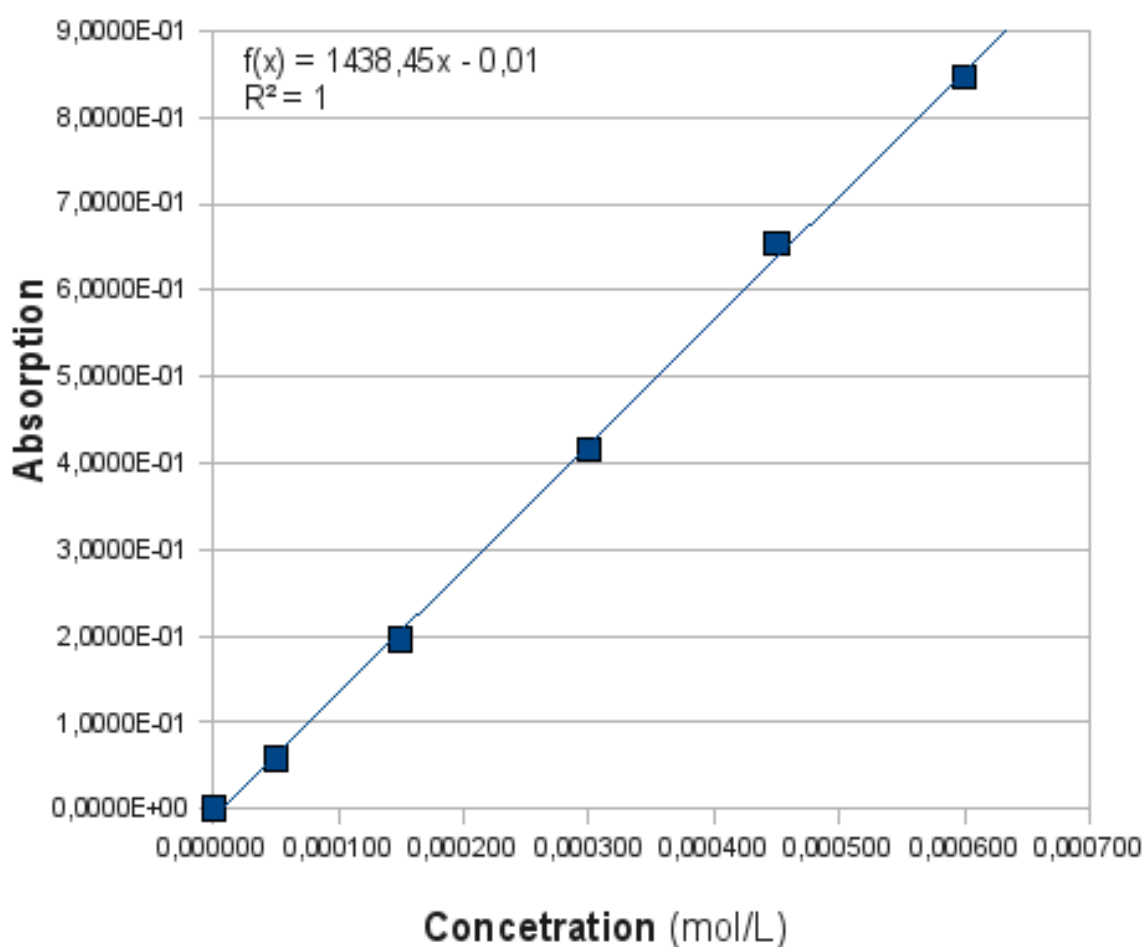
c (mol/L)	Counts	A =log(Counts_blank/Counts)
0,000000	4,40	0,0000E+00
0,000050	3,85	5,7950E-02
0,000150	2,80	1,9638E-01
0,000300	1,67	4,1954E-01
0,000450	0,95	6,6601E-01
0,000600	0,61	8,5758E-01



*Picture 4.6: Calibration curve of KMnO<sub>4</sub> solutions at 525nm*

Column\_Number            490  
 Counts\_blank            4,35

c (mol/L)	Counts	A =log(Counts_blank/Counts)
0,000000	4,35	0,0000E+00
0,000050	3,80	5,8000E-02
0,000150	2,77	1,9536E-01
0,000300	1,67	4,1607E-01
0,000450	0,97	6,5353E-01
0,000600	0,62	8,4650E-01



*Picture 4.7: Calibration curve of KMnO<sub>4</sub> solutions at 545nm*

#### 4.1.7 Verification of Lambert – Beer law

From the graphs of pictures 4.7 and 4.8 it is quite clear that the absorption is proportional to concentration for the chosen range.

#### 4.1.8 Determination of the molar absorptivity of $KMnO_4$ solution

From the graphs of pictures 4.7 and 4.8, the constant  $k$  (see eq. 4.3) is determined from the slopes of the lines for wavelengths 525nm (Column\_Number = 420) and 545nm (Column\_Number = 490).

$$k_{525} = 1460.91$$

$$k_{545} = 1438.45$$

and because the cuvettes used were 1cm in thickness, the molar absorptivity should be given (restricted to three significant digits) as:

$$\varepsilon_{525} = 1460 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{L}$$

$$\varepsilon_{545} = 1440 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{L}$$

#### 4.1.9 Determination of the concentration of the unknown solution

From the spectral profiles of picture 4.5, the average of Counts of the unknown solution was calculated for wavelengths 525nm and 545nm and based on equation 4.3 the absorptions in that wavelengths were calculated. Finally, the concentration of the unknown was calculated from the experimentally found equations of the form  $A = b \cdot c + a$ .

The whole process of the calculations done by the Calc which gave:

For 525nm:  $c = 2.5126 \times 10^{-4} \text{ M}$

For 545nm:  $c = 2.5436 \times 10^{-4} \text{ M}$

If we give the result with two significant digits, we should give it as:

$$c = 2.5 \times 10^{-4} \text{ M}$$

(Note that the “unknown solution” was prepared by mixing equal volumes of solutions  $5.0 \times 10^{-5} \text{ M}$  and  $4.5 \times 10^{-4} \text{ M}$ , so it will be  $2.5 \times 10^{-4} \text{ M}$ ).

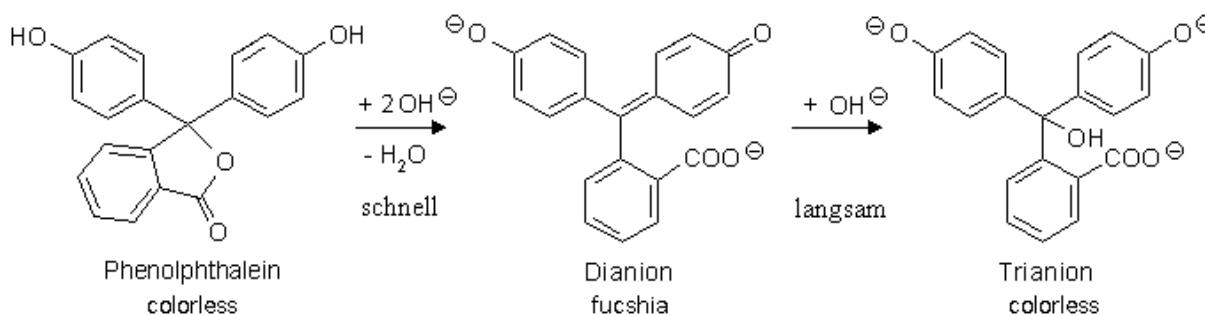
#### 4.1.10 Estimation of detection limit

Looking at the picture 4.4, it is clear that the values of Counts for a sample solution with concentration been at detection limit, should be in an area approximately 0.2 Counts (equal to the noise) in range just below the blank area. The center of that area would correspond to approximately 4.2 Counts for Column\_Number = 420 and approximately 4.1 Counts for Column\_Number = 490. Based on these values, it is calculated, that the detection limit for this method is approximately  $2.0 \times 10^{-5} \text{ M}$ .

## 5. Chemical kinetics: Determination of fading rate of phenolphthalein in alkaline solution

The rate of a chemical reaction depends on several factors. In the experiment presented below, the effect of concentration on the fading rate of phenolphthalein in strongly alkaline solution of NaOH is examined.

When phenolphthalein is added to strongly alkaline solution, first it converts quickly to a colored (fuchsia) dianion, which then reacts slowly with the excess of hydroxides to a colorless trianion.



**Picture 5.1:** The reaction of phenolphthalein in strongly alkaline solution

The kinetics of fading can be studied by monitoring the discoloration with a spectrophotometer. The change in concentration of dianion is recorded by monitoring the change in absorption over the time, assuming that the Lambert – Beer law is applied.

The rate law for the fading of phenolphthalein is expressed by the equation:

$$v = k \cdot [P^{2-}]^a \cdot [OH^-]^b \quad (5.1)$$

Όπου:

- v: reaction rate
- k: reaction rate constant
- $[P^{2-}]$ : concentration of phenolphthalein (dianion)
- $[OH^-]$ : concentration of hydroxides
- a: order of  $P^{2-}$
- b: order of  $OH^-$

The classical treatment of the issue, requires the execution of a series of experiments, where keeping constant the concentration of one substance and varying the concentration of the other, somehow the speed of reaction is calculated. Next, using the equation 5.1, The reaction constant and the orders are calculated.

In this case, because the alkaline solution is concentrated and the phenolphthalein is added in a little amount (a few drops), it can be assumed that the concentration of hydroxides remain constant during the reaction, while changing only the concentration of phenolphthalein. With these assumptions the equation 5.1 simplifies to:

$$v = k' \cdot [P^{2-}]^a \quad (5.2)$$

όπου:  $k' = k \cdot [OH^-]^b$

Under these conditions it is possible to run only an experiment to find the pseudo-low (eq. 5.2) of the fading rate of phenolphthalein.

### 5.1 Experiment: Determination of the fading rate of phenolphthalein in alkaline solution

#### Objectives:

- To find the pseudo-low of the reaction rate of fading of phenolphthalein.
- To find the half-life of phenolphthalein during the reaction.
- To calculate the molar absorptivity of phenolphthalein.

#### Method:

- Spectrophotometric

#### Equipment and materials:

- The handmade spectroscope
- 40 watt light bulb (brilliant white lamp)
- Volumetric cylinder 100mL
- Volumetric flask 100mL
- Measuring pipettes 1mL, 10mL
- Balance  $\pm 0,1g$
- Bakers 50mL
- Cuvettes 1cm
- Phenolphthalein
- 0,357M NaOH solution (stock solution for olive oil acidimetry)
- Ethanol 95°
- Deionized water

#### Process:

##### 5.1.1 Preparation of 0.1% phenolphthalein in 50% ethanol solution

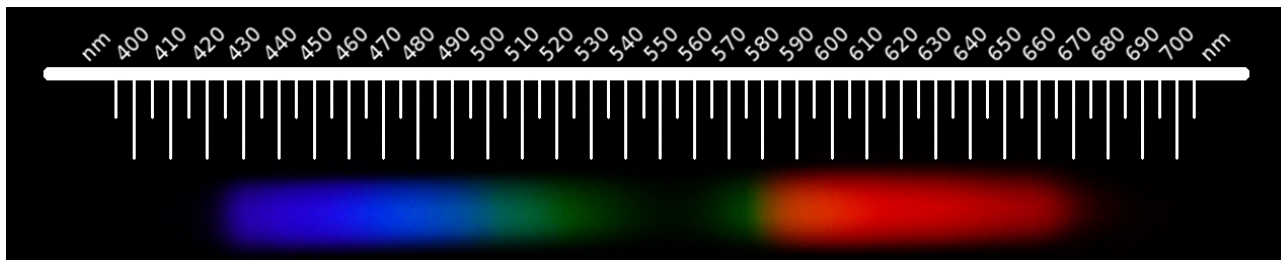
Firstly an alcoholic solution of 50% is prepared, by mixing 53mL of ethanol and 47mL deionized water. Next, 0.1g of phenolphthalein is weighted and transferred to a 100mL volumetric flask and dissolved with 50% alcoholic solution to the mark. In this solution the concentration of phenolphthalein is  $0.3 \times 10^{-2}M$ .

##### 5.1.2 Formation of colored dianion and taking of spectra during fading.

9.7mL of 0.357mL NaOH solution was transferred to a 50mL baker using a measuring pipette of 10mL. In the same baker, 0.3mL of phenolphthalein solution was transferred too, using a measuring

pipette of 1mL (so, the concentration of phenolphthalein was  $0,9 \times 10^{-4} \text{M}$ ). The timing of the addition of phenolphthalein in the NaOH solution was taken as the zero time. Next, without delay, the proper amount of colored solution was transferred in a cuvette which was attached to the spectroscope and pictures of the spectra were taken per minute. As blank sample, the NaOH solution was used. The temperature during exoeriments was  $25^{\circ}\text{C}$  (ambient temperature).

In the next picture, the absorption spectrum of a colored phenolphthalein solution is shown at some time.



**Picture 5.2:** Absorption spectrum of phenolphthalein in alkaline solution.

The above picture shown that phenolphthalein strongly absorb at about 555nm. Therefore absorption computations will be made this wavelength (Column\_Number).

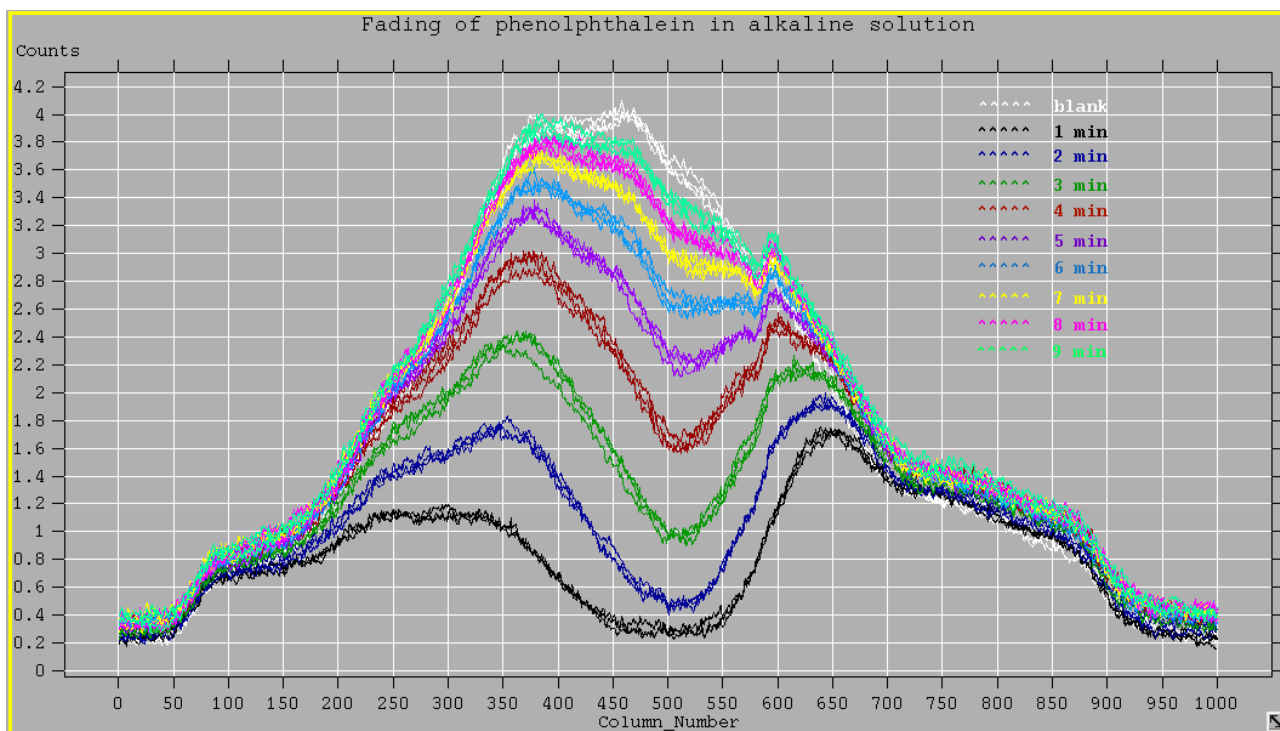
### 5.1.3 Processing the photos of spectra with the Gimp

The pictures of spectra processed with the Gimp as follow:

- Turn left to obtain the spectrum a more relevant position (ie. from low to high wavelengths).
- Crop the left and right black areas of the photos in such a way that the spectra to stay in the same place for all photos. Cropping only serves to reduce the size of files produced.
- Desaturate based on luminosity.
- Save as FIT file type.

### 5.1.4 Taking the spectral profiles with Fv

Using Fv, the spectral profiles were formed, that are shown in the next pictures.



**Picture 5.3:** Spectral profiles of phenolphthalein in alkaline solution at various times (3 shoots each time).

Inspection of picture 5.3 shows that:

1. There is an intense absorption around Column\_Number = 510 corresponding to 555nm (εικόνα 5.2).
2. Spectral profiles at time 1min should be excluded from calculations, because they fall in the noise area (the concentration of phenolphthalein is out the range of instrument). Also, the spectral profiles at time 10min were excluded, because they fell in the blank area.

#### 4.1.5 Processing with the Calc

Based on the graphs of spectral profiles of alkaline solutions of phenolphthalein, the averages of Counts for the blank and the solution were calculated at times 2min, 3min, 4min, 5min, 6min, 7min, 8min και 9min for Column\_Number= 510. Next, using the Lambert – Beer law (eq. 4.3), the absorptions are calculated and the graphs of absorption vs time is made. The entire process is done by the Calc spreadsheet.

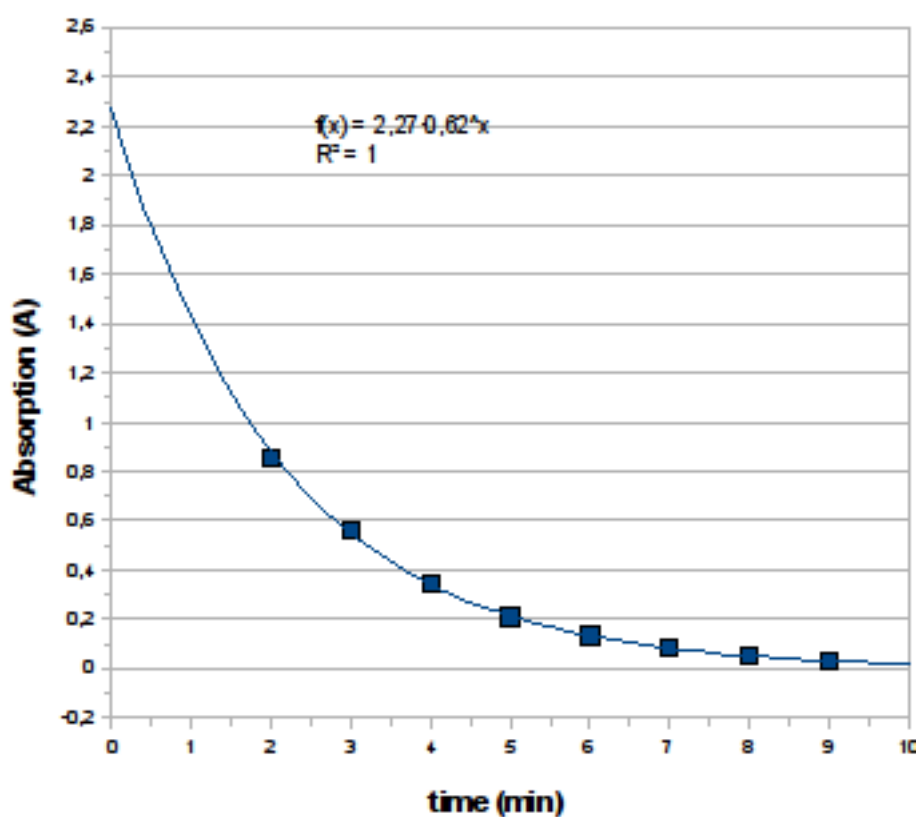
In the next pictures, the data table and the graphs are shown, that are created using the Calc.

Column\_Number            510  
Counts\_blank                3,58

t (min)	Counts	A	Ln (A)
1	0,27	1,12	0,11
2	0,50	0,85	-0,16
3	0,98	0,56	-0,58
4	1,63	0,34	-1,07
5	2,22	0,21	-1,57
6	2,64	0,13	-2,02
7	2,94	0,09	-2,46
8	3,16	0,05	-2,93
9	3,34	0,03	-3,51

*Picture 5.4: Data table.*

*The first row of the table has been eliminated, because it falls in the noise area.*



*Picture 5.4: The graph of absorption vs time.*

*The Calc have also produced the analytical function.*

The graph of picture 5.4 gives all information required for the export of results.



Provided that the Lambert – Beer law is applicable, it applies:

$$v = -\frac{dc}{dt} = -\frac{1}{\varepsilon \cdot b} \cdot \frac{dA}{dt} = -\frac{c}{A} \cdot \frac{dA}{dt} \quad (5.3)$$

Όπου:

$v$ :	reaction rate
$dc/dt$ :	concentration change over time
$\varepsilon$ :	molar absorptivity of phenolphthalein
$b$ :	cuvette width
$dA/dt$ :	absorption change over time
$c$ :	concentration of phenolphthalein
$A$ :	absorption of solution

The change in absorption over time can be calculated from the graph of picture 5.4 by calculation the slope at various points. Following this procedure, it can be shown that the change in absorption over time is proportional to absorption and therefore the rate of reaction is proportional to the concentration.

But, as long as an analytical function for the change in absorption over time is available, it is preferable an algebraic manipulation of the issue:

$$\begin{aligned} A &= 2.27 \cdot 0.62^t \\ \frac{dA}{dt} &= 2.27 \cdot \ln(0.62) \cdot 0.62^t \\ \frac{dA}{dt} &= -0.47 \cdot A \end{aligned} \quad (5.4)$$

The combination of equations 5.3 and 5.4 results:

$$\begin{aligned} v &= -\frac{c}{A} \cdot (-0.47) \cdot A \\ v &= 0.47 \cdot c \end{aligned} \quad (5.5)$$

The equation 5.5 is the pseudo-law of fading rate of phenolphthalein in alkaline solution. From this equation it appears that the rate of reaction is first order to the concentration of phenolphthalein.

A feature of first order reaction is the constant half-life (ie the time at which the amount of reactive substance is half of the original). In the graph of the picture 5.5 it seems that the time interval that the absorption to take  $\frac{1}{2}$  of the initial value, to change from  $\frac{1}{2}$  στο  $\frac{1}{4}$  of initial value etc. is constant and equal to about 1.4min.

The same result gives the algebraic manipulation of the absorption – time equation:

$$\frac{A_o}{2} = 2.27 \cdot 0.62^{t_{1/2}}$$

$$\frac{2.27}{2} = 2.27 \cdot 0.62^{t_{1/2}}$$

$$t_{1/2} = 1.4 \text{min} \quad (5.6)$$

To calculate the molar absorptivity of phenolphthalein, the initial condition of the experiment will be used:

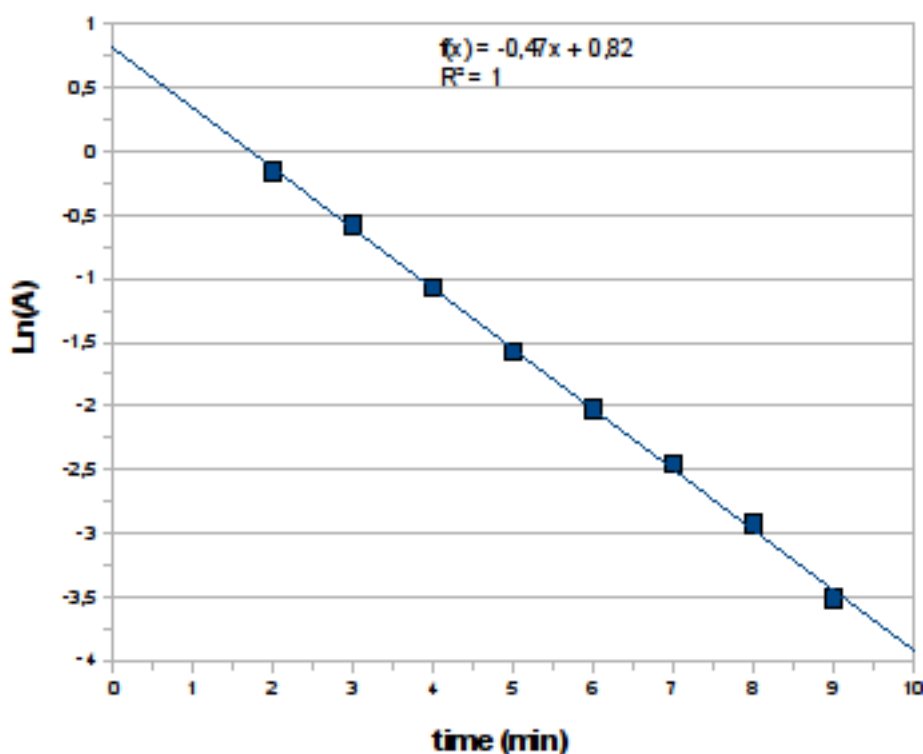
For  $t = 0$ ,  $A = 2.27$   $c = 0.9 \times 10^{-4} \text{M}$

$$A = \varepsilon \cdot b \cdot c$$

$$2.27 = \varepsilon \cdot 1 \cdot 0.9 \cdot 10^{-4}$$

$$\varepsilon = 2,5 \times 10^4 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1} \quad \sigma_{\alpha} 555 \text{nm} \quad (5.7)$$

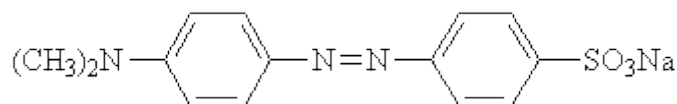
A similar process for conclusions can be made based on the graph of logarithm of absorption vs time that is shown below:



**Picture 5.6:** The graph of logarithm of absorption vs time.  
The Calc have also produced the analytical function.

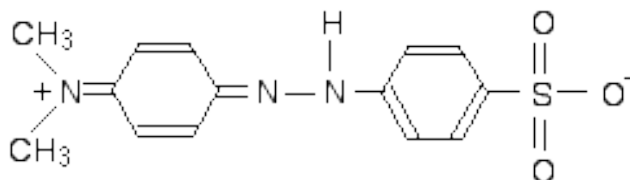
## 6. Chemical equilibrium: Determination of ionization constant of methyl orange

Methyl orange is a weak organic acid, whose acid and base forms are different in color. The color of a solution that contains methyl orange depends on the ratio of species in acid and base form and it changes by changing the pH getting colors from red (acid form) to yellow (base form). For this reason, methyl orange is used as indicator in acid – base titrations.



**Picture 6.1:** The chemical formula of methyl orange.

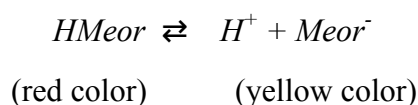
As shown in the above picture, methyl orange is actually a sodium salt of an organic acid – which has come to be called methyl orange – whose hydrolysis gives anions and undissociated molecules in equilibrium..



**Picture 6.2:** The protonated form of methyl orange.

The change in equilibrium between acid/base forms of methyl orange can be studied spectroscopically by measuring the absorption of methyl orange solutions of various pH values. This study leads to the determination of the ionization constant.

Suppose methyl orange (regarded as acid) ionized according the equation:



From the above equilibrium it applies:

$$K_a = \frac{[\text{H}^+] \cdot [\text{Meor}^-]}{[\text{HMeor}]} \quad (6.1)$$

and

$$pK_a = pH - \log \frac{[\text{Meor}^-]}{[\text{HMeor}]} \quad (6.2)$$

From the equation 6.2 it is obvious that pK<sub>a</sub> of methyl orange equals to pH of the solution where the undissociated molecules are 50% of the total molecules.

## 6.1 Experiment: Determination of ionization constant of methyl orange

### Objective:

- To determine the dissociation constant of methyl orange

### Μέθοδος:

- Spectrophotometric

### Equipment and materials:

- The handmade spectroscope
- 40 watt light bulb (brilliant white lamp)
- Volumetric cylinder 100mL
- Volumetric flask 100mL
- 4 volumetric flasks 250mL
- Measuring pipettes 1mL, 2mL, 5mL
- Pipette 25mL
- Balance  $\pm 0.01\text{g}$
- Plastic bottles 100mL
- Cuvettes 1cm
- Methyl orange powder (sodium salt)
- HCl 37% w/w (stock solution, about 11.5M)
- Deionized water

### Process:

#### 6.1.1 Preparation of 0.1% w/v methyl orange solution

Using a balance  $\pm 0.01\text{g}$ , 0.1g of methyl orange (sodium salt) is weighted. The amount is transferred to a 100mL volumetric flask and diluted with deionized water to the mark. So, a methyl orange solution of  $3.1 \times 10^{-3}\text{M}$  was formed.

#### 6.1.2 Preparation of hydrochloric acid solutions of known concentration

Using a measuring pipette of 5mL, 2.2mL of HCl 37% w/w transferred to a 250mL volumetric flask and diluted to the mark. So, a solution of  $1.0 \times 10^{-2}\text{M}$  is formed. Next, using the pipette of 25mL and the volumetric flasks of 250mL, four solutions of  $1.0 \times 10^{-2}\text{M}$ ,  $1.0 \times 10^{-3}\text{M}$ ,  $1.0 \times 10^{-4}\text{M}$  and  $1.0 \times 10^{-5}\text{M}$  are formed by successive dilutions. Finally, 32mL from each of the previous solutions are transferred to a volumetric cylinder of 100mL and diluted to 100mL. Thus, four more solutions are formed with concentrations of  $1.0 \times 10^{-2.5}\text{M}$ ,  $1.0 \times 10^{-3.5}\text{M}$ ,  $1.0 \times 10^{-4.5}\text{M}$  and  $1.0 \times 10^{-5.5}\text{M}$ . Totally, there are eight solutions that have pH values: 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 and 5.5. Using a 100mL volumetric cylinder, amounts of 90mL of these solutions are transferred to 100mL plastic bottles and the pH values are printed on.

#### 6.1.3 Preparation of acidic solutions of methyl orange

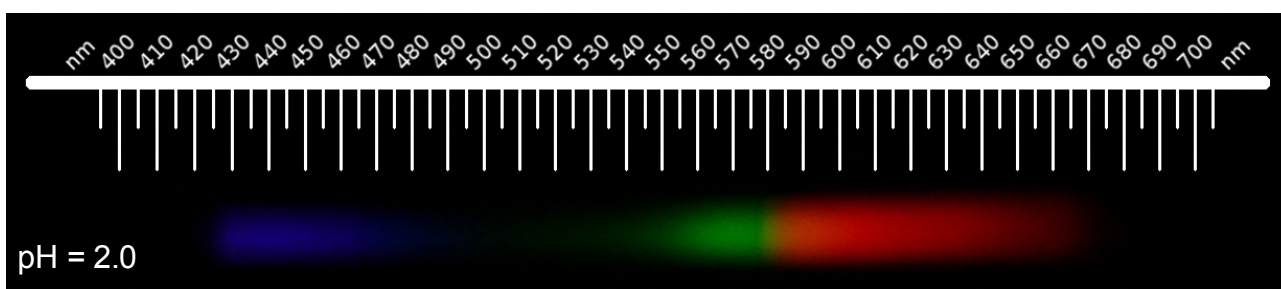
In the above plastic bottles, 1.5mL of methyl orange solution is poured using a measuring pipette of 2.0mL. These solutions are shown in the next picture.



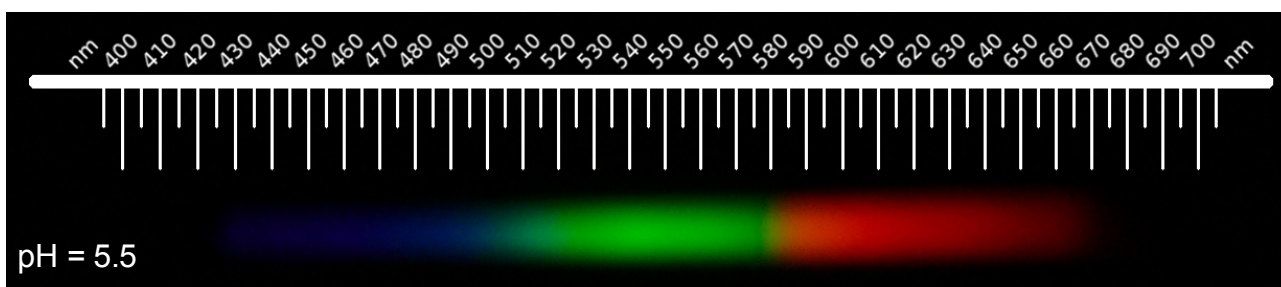
*Picture 6.3: Acidic solutions of methyl orange.*

#### 6.1.4 Taking the spectra of solutions

From the acidic solutions of methyl orange, the proper amounts are transferred to the cuvettes and the spectra of solutions are taken. The ambient temperature was 28°C. Next pictures show the spectra of red and yellow forms of methyl orange.



*Picture 6.4: The spectrum of methyl orange solution at pH = 2.0 (red).*



*Picture 6.5: The spectrum of methyl orange solution at pH = 5.5 (yellow).*

In the picture 6.4 it is seen to be a maximum absorption at about 510nm, while in the picture 6.5 there is an absorption in the blue region without a clear maximum. Thus, the measurements will be made at 510nm.

(Note: It is recommended a second set of measurements to be done in the blue region, but this is impossible, as it is shown in picture 6.6)

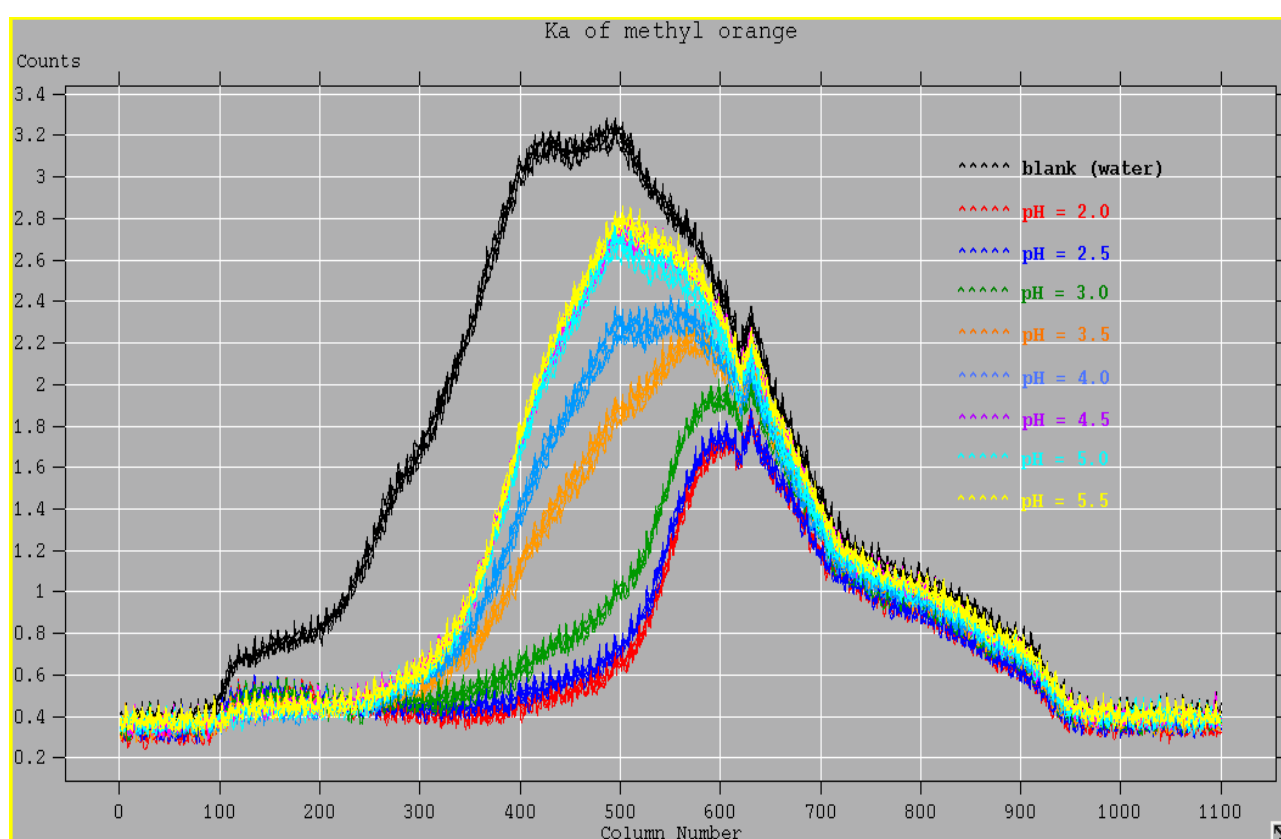
### 6.1.5 Processing the photos of spectra with the Gimp

The pictures of spectra processed with the Gimp as follow:

- Turn left to obtain the spectrum a more relevant position (ie. from low to high wavelengths).
- Crop the left and right black areas of the photos in such a way that the spectra to stay in the same place for all photos. Cropping only serves to reduce the size of files produced.
- Desaturate based on luminosity.
- Save as FIT file type.

### 6.1.6 Taking the spectral profiles with Fv

Using Fv, the spectral profiles were formed, that are shown in the next picture.



**Picture 6.6:** Spectral profiles of acidic solutions of methyl orange (5 shoots in each case).

From the above picture it is seems that the absorption of 510nm is located at about Column\_Number = 350.

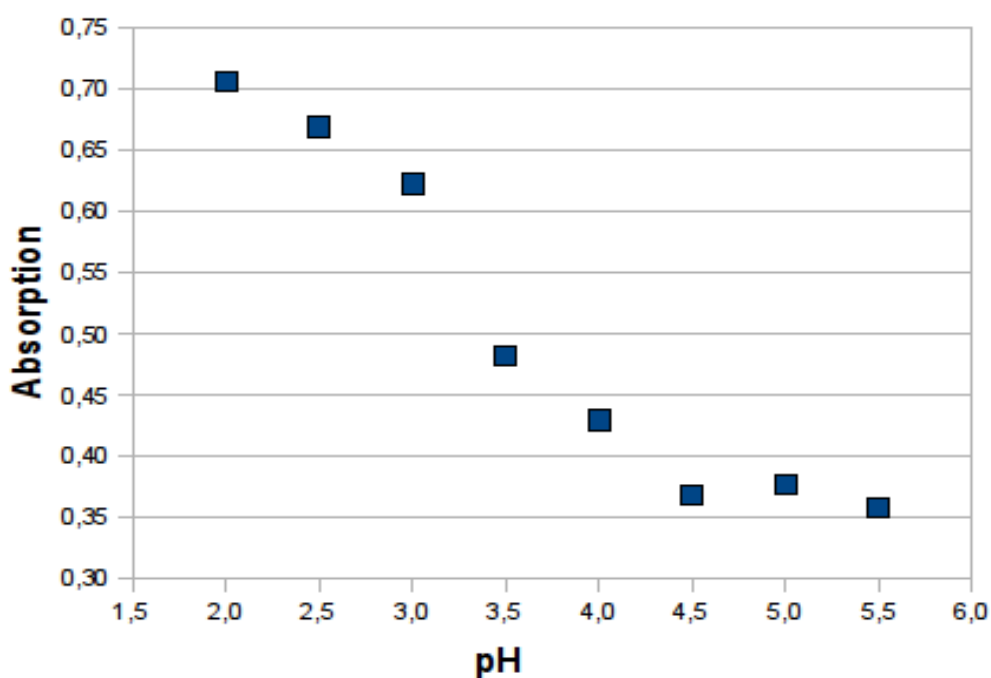
### 6.1.7 Processing with the Calc

Based on the spectral profiles of methyl orange solutions, the average Counts for the blank and for the solutions are calculated at Column\_Number = 350. Next, using the Lambert – Beer law (eq. 4.3), the absorptions are calculated and the graph of absorption over pH is plotted. The entire process is done easily by the spreadsheet.

The data table and the graph made by Calc is shown in the next picture.

Column\_Number                      350  
Counts\_blank                        2,30

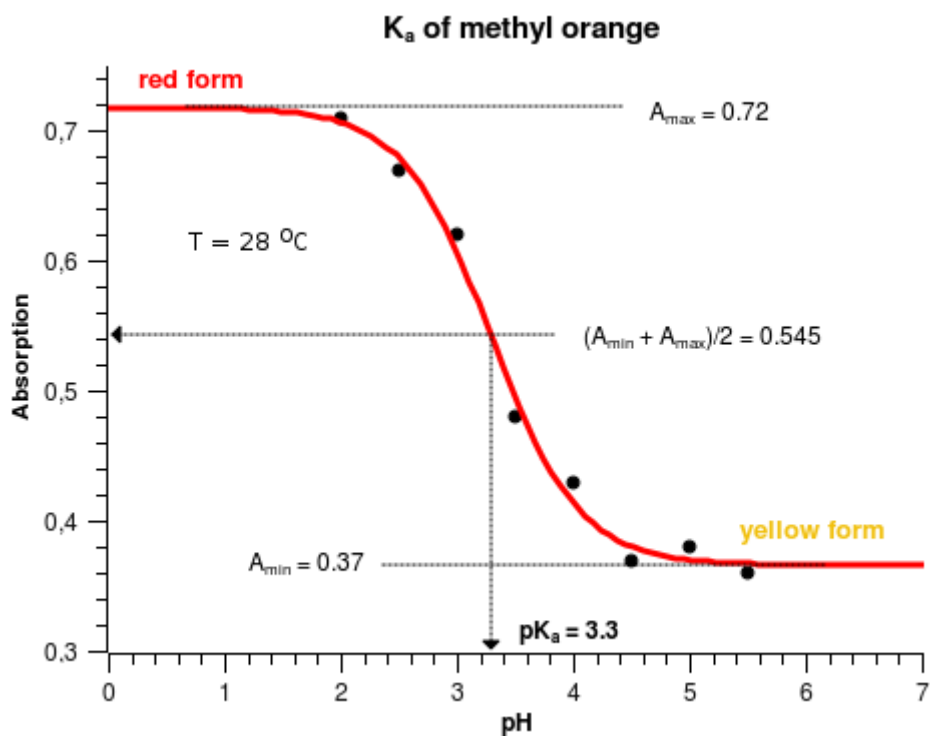
pH	Counts	A
2,0	0,45	0,71
2,5	0,49	0,67
3,0	0,55	0,62
3,5	0,76	0,48
4,0	0,85	0,43
4,5	0,98	0,37
5,0	0,96	0,38
5,5	1,01	0,36



*Picture6.7: Data table and graph of absorption over pH*

According to the equation 6.2, it should be calculated the pH at which the undissociated molecules (red) are 50% of the total concentration, therefore they absorb half. This is midway between the maximum absorption (almost 100% undissociated molecules) and the minimum absorption (almost 100% anions).

The further processing of the data was done using the more specific software QtiPlot (free software/open source software) and the results are shown in the picture below.



**Picture 6.8:** The absorption over pH at 510nm and at temperature 28°C for acidic solutions of methyl orange.

From the above graph, it is graphically calculated that the ionization constant of methyl orange is:

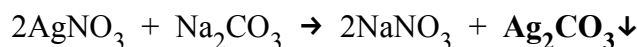
$$pK_a = 3,3 \text{ and}$$

$$K_a = 5,0 \times 10^{-4} \text{ at } 28 \text{ }^\circ\text{C}$$



## 7. Stoichiometry: Determination of the ions ration in $\text{Ag}_2\text{CO}_3$

Silver carbonate is an insoluble yellow salt, which can be formed by mixing solutions of silver nitrate and sodium carbonate according the following equation:



Spectroscopy can be used to calculate the ration of ions in an insoluble salt (precipitate). The measurements based on the fact that the formation of precipitate blurs the solution in which it is formed, so the light that captured by the spectrophotometer is decreased with increasing turbidity. Provided that the Lambert – Beer law is applied in this case, it follows that the turbidity is proportional to the amount of precipitate formed. Applying a technique of continuous change, where the relative proportion of ions changes, it can be found the proportion that the turbidity takes its maximum value, which coincides with the ration of ions in the precipitate.

### 7.1 Experiment: Determination of ion ration in $\text{Ag}_2\text{CO}_3$

#### Objective:

- To determine the ions ration in  $\text{Ag}_2\text{CO}_3$

#### Method:

- Spectrophotometric

#### Equipment and materials:

- The handmade spectroscope
- 40 watt light bulb (brilliant white lamp)
- Volumetric cylinder 100mL
- 2 volumetric flasks 1L
- 2 measuring pipettes 10mL
- Balance  $\pm 0.1\text{g}$
- 9 Erlenmeyer flasks 100mL
- Cuvettes 1cm
- Solid silver nitrate
- Solid sodium carbonate
- Deionized water

#### Process:

##### 7.1.1 Preparation of 0.01M silver nitrate solution

Using a  $\pm 0.1\text{g}$  balance, 1.70g of solid silver nitrate is weighted. Then the amount is transferred to a volumetric flask of 1L and it is diluted to the mark.

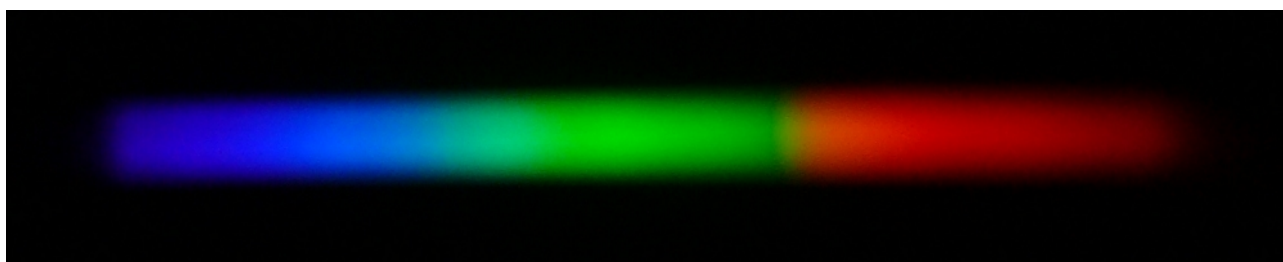
##### 7.1.2 Preparation of 0.01M sodium carbonate solution

Using a  $\pm 0.1\text{g}$  1.06g of solid sodium carbonate is weighted. The amount is transferred to

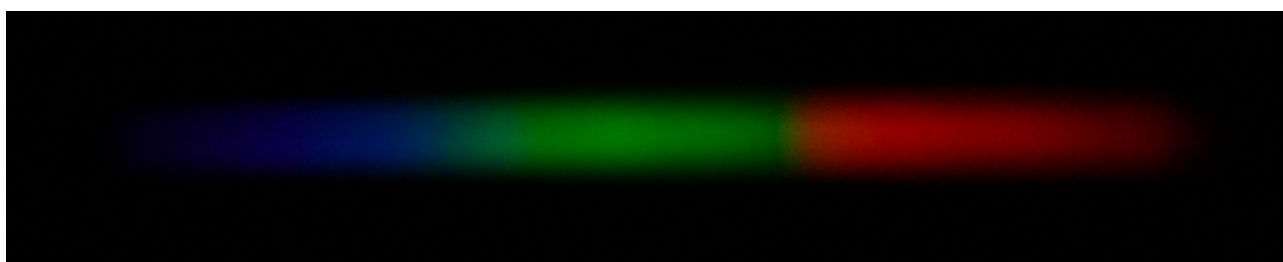
volumetric flask of 1L and it is diluted to the mark.

### 7.1.3 Preparation of solutions and taking their spectra

In each of 9 Erlenmeyer flasks of 100mL, it is added 30mL of deionized water. Next, in each flask, it is added 4.5mL, 5.0mL, 5.5mL, 6.0mL, 6.5mL, 7.0mL, 7.5mL, 8.0mL and 8.5mL of silver nitrate solution using a measuring pipette of 10mL. Next, in each flask, it is added 5.5mL, 5.0mL, 4.5mL, 4.0mL, 3.5mL, 3.0mL, 2.5mL, 2.0mL and 1.5mL using a measuring pipette of 10mL, with the same order as previously. Thus, nine solutions are formed, where ratio of ions of  $\text{Ag}^+$  and  $\text{CO}_3^{2-}$  is 0.8, 1.0, 1.2, 1.5, 1.9, 2.3, 3.0, 4.0 and 5.7 respectively. The formation of the solution was made in a manner that the turbidity to be in a level to allow the light to be recorded by the camera's CCD and the formation of  $\text{AgOH}$  due to hydrolysis of  $\text{CO}_3^{2-}$  not to be apparent, so the measurements not to be affected. Finally from each flask, the proper amount of solutions are transferred to cuvettes, having shaken well, and the spectra was taken. As blank, the silver nitrate solution was used which showed a very slight white turbidity. For each case, five spectra was taken.



*Picture 7.1: The spectrum of blank*



*Picture 7.2: The spectrum of a solution.*

Inspecting the two pictures above, it is shown a decrease of outgoing light due to formation of  $\text{Ag}_2\text{CO}_3$  precipitate and a absorption in the blue region, which gives a slightly yellowish tinge to precipitate.

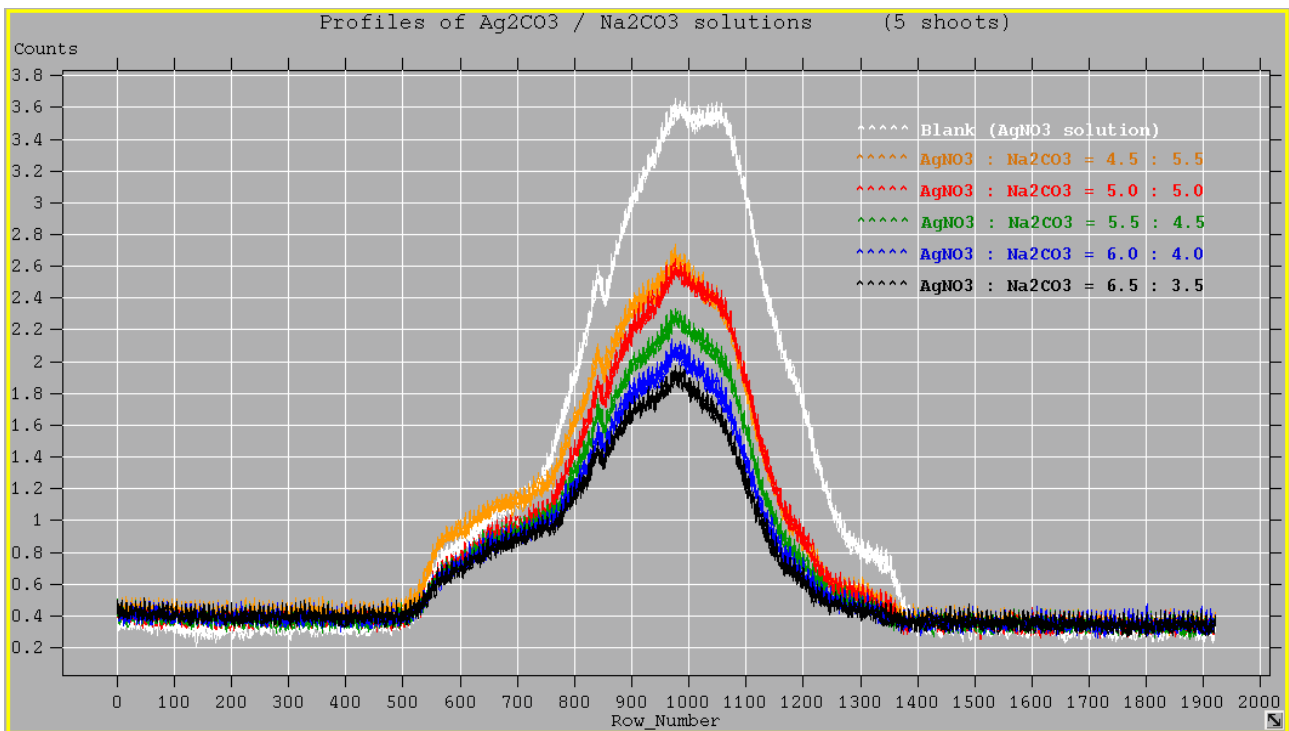
### 7.1.4 Processing the photos of spectra with the Gimp

The pictures of spectra processed with the Gimp as follow:

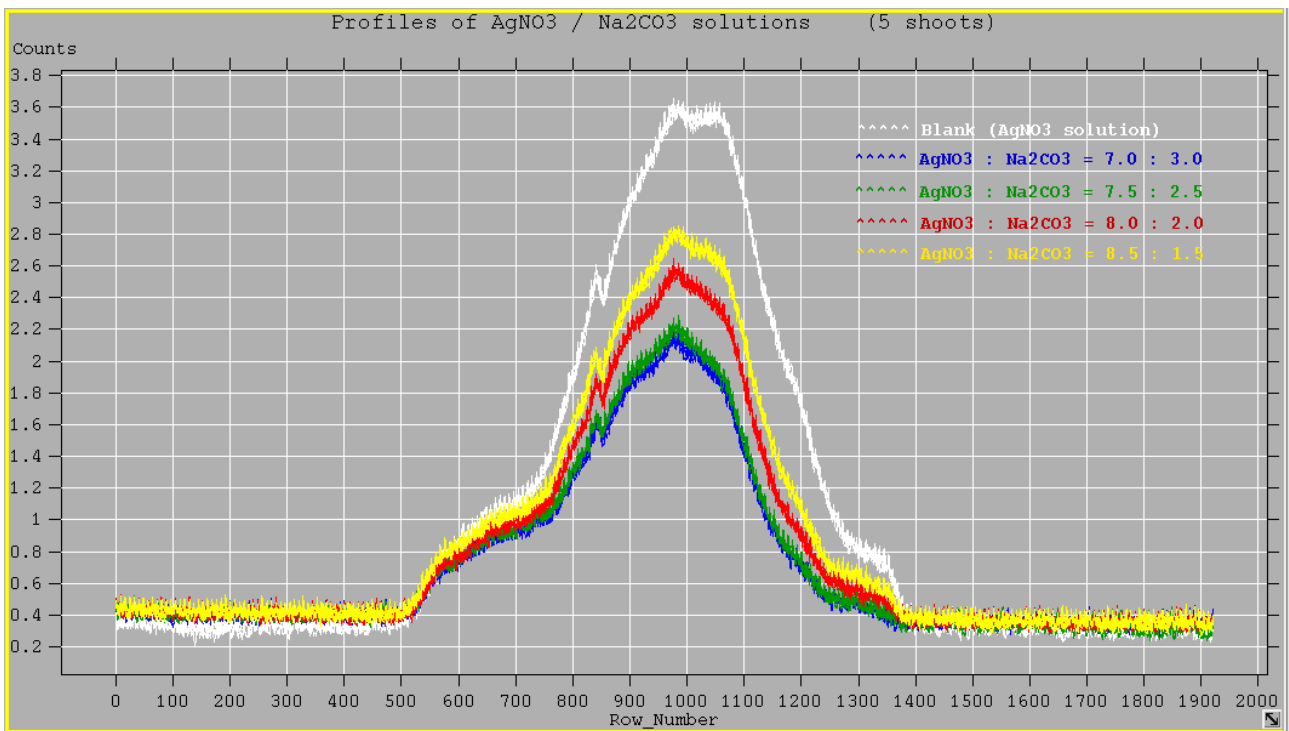
- a) Desaturate based on luminosity.
- b) Save as FIT file type.

### 7.1.5 Taking the spectral profiles with Fv

Using Fv, the spectral profiles were formed, that are shown in the next picture.



**Picture 7.3:** Spectral profiles of solutions with ions ratio  $Ag^+ : CO_3^{2-}$  from 4,5:5,5 to 6,6 : 3,5 (5 shoots)



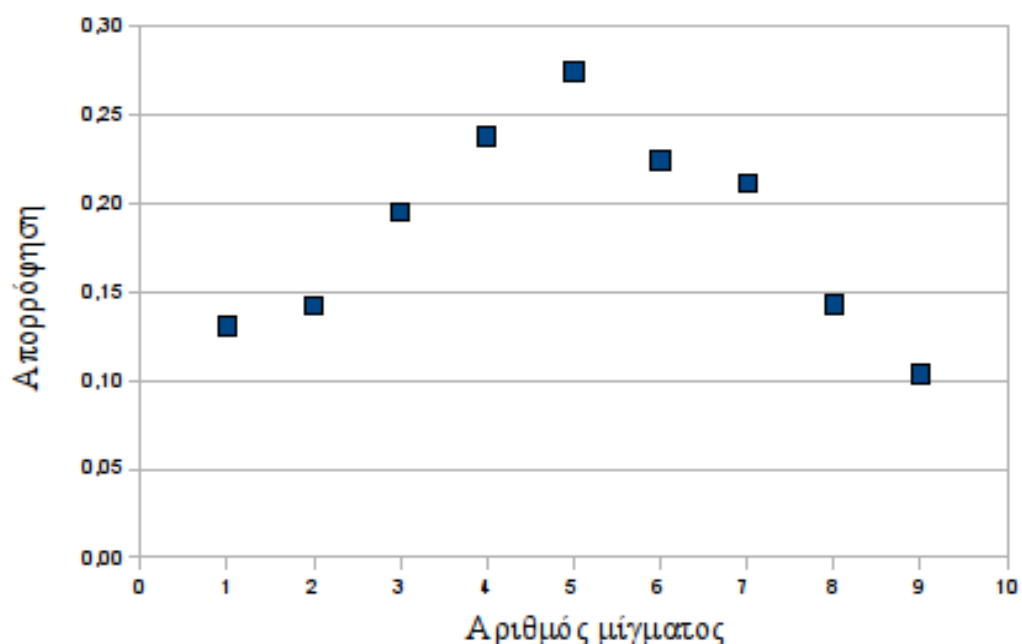
**Picture 7.4:** Spectral profiles of solutions with ions ratio  $Ag^+ : CO_3^{2-}$  from 7,0:3,0 to 8,5 : 1,5 (5 shoots)

### 7.1.6 Processing with the Calc

Based on the graphs of the spectral profiles, the average of Counts for the solutions and for the blank are calculated at Column\_Number = 980. Next, using the Lambert – Beer law (eq. 4.3), the absorptions are calculated and the graph of absorption over the ions ration is plotted. All the process is easily done by the spreadsheet.

Column\_Number            980  
Counts\_blank            3,55

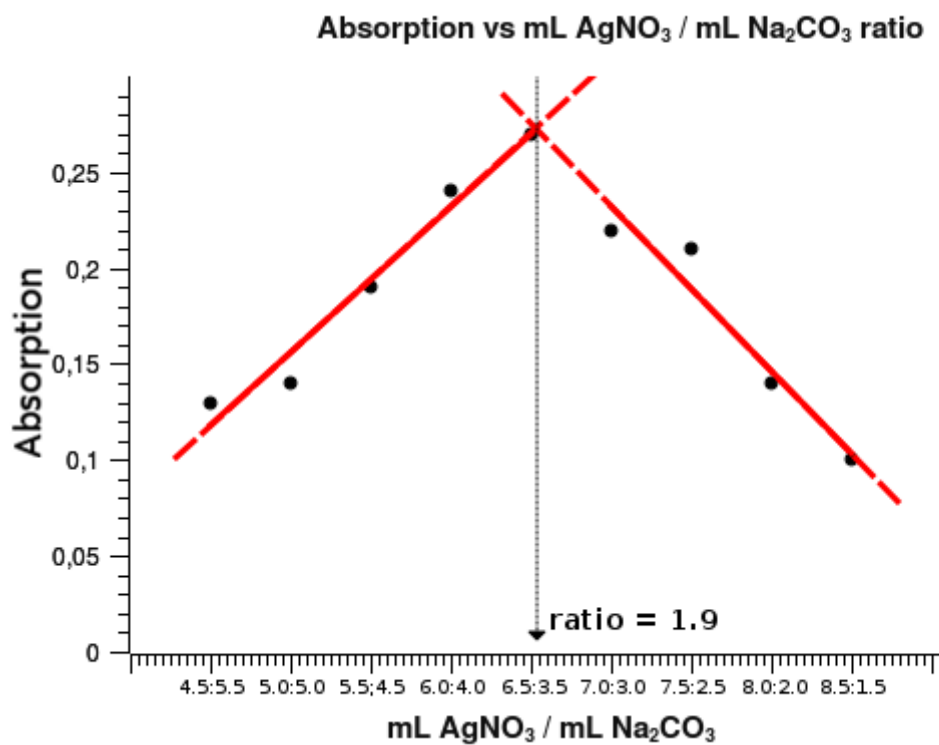
Mixture	mL AgNO <sub>3</sub> : mL Na <sub>2</sub> CO <sub>3</sub>	Counts	A
1	4,5 : 5,5	2,63	0,13
2	5,0 : 5,0	2,56	0,14
3	5,5 : 4,5	2,27	0,19
4	6,0 : 4,0	2,05	0,24
5	6,5 : 3,5	1,89	0,27
6	7,0 : 3,0	2,12	0,22
7	7,5 : 2,5	2,18	0,21
8	8,0 : 2,0	2,55	0,14
9	8,5 : 1,5	2,79	0,10



Picture 7.4: Data table and graph Absorption – mL AgNO<sub>3</sub> : mL Na<sub>2</sub>CO<sub>3</sub>

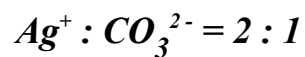
From the graph of picture 7.4 it is shown that the absorption is maximum for the ions ratio that corresponds to the fifth mixture, which is  $1,89 \cong 2$ . This can be made more obvious by using the more specific software QtiPlot (free software/open source software) and the results are shown in the

next picture.



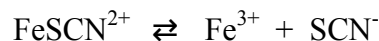
**Picture 7.4:** The graph of Absorption – mL AgNO<sub>3</sub> : mL Na<sub>2</sub>CO<sub>3</sub>

From the previous graphs and taking account that the terms of the ratio must be small natural numbers, it is concluded that the ratio of ions Ag<sup>+</sup> and CO<sub>3</sub><sup>2-</sup> in Ag<sub>2</sub>CO<sub>3</sub> is:



## 8. Complexometry: Determination of instability constant of $FeSCN^{2+}$

Transition metals forms many complex ions that are colored in solutions. Such complex ion is  $FeSCN^{2+}$ , that gives a reddish brown color in aqueous solutions in relatively high concentrations. This complex is in equilibrium with the ions  $Fe^{3+}$  and  $SCN^-$  according the equation:



For the above equation it is applies:

$$K_{inst} = \frac{[Fe^{3+}] \cdot [SCN^-]}{[FeSCN^{2+}]} \quad (8.1)$$

To determine the thermodynamic instability constant, activities should be used instead concentrations, so equation 8.1 will be:

$$K_{inst}^o = K_{inst} \cdot \frac{[f_{Fe^{3+}}] \cdot [f_{SCN^-}]}{[f_{FeSCN^{2+}}]} \quad (8.2)$$

where:

$$a = f \cdot C$$

$a$ : activity of ion

$f$ : activity factor of ion

$$-\log f = A \cdot z^2 \cdot \sqrt{\mu}$$

$C$  ( $c_1, c_2, \dots$ ): molarity of ion

$A$ : constant, for water  $A = 0.51$  ( $25^\circ C$ )

$$\mu = \frac{1}{2} \cdot \sqrt{c_1 \cdot z_1^2 + c_2 \cdot z_2^2 + \dots}$$

$z$  ( $z_1, z_2, \dots$ ): charge of ion

$\mu$ : ionic strength of solution (eq. Debye - Hückel)

Of course, there are some others equilibria in the solution, but they can be ignored because the conditions of the experiment. Besides, iron can form many complex with thiocyanate ( $Fe(SCN)_2^+$ ,  $Fe(SCN)_3$ ,  $Fe(SCN)_4^-$ ,  $Fe(SCN)_5^{2-}$ ,  $Fe(SCN)_6^{3-}$ ), but in solution with  $Fe^{3+}$  in excess and low concentration of  $SCN^-$ , complex  $FeSCN^{2+}$  almost exclusively is formed.

Due to the formation of colored ion, it is possible to determine spectroscopically the concentration of ion aqueous solution and using equations 8.1 and 8.2 to determine the instability constant of the complex ion.

### 8.1 Experiment: Determination of instability constant of $FeSCN^{2+}$

#### Objective:

- To determine the instability constant of  $FeSCN^{2+}$  in aqueous solution

#### Method:

- Spectrophotometric

### Equipment and materials:

- The handmade spectroscope
- 40 watt light bulb (brilliant white lamp)
- Volumetric flasks of 250mL and 100mL
- Measuring pipettes of 10mL, 5mL και 1mL
- Balance  $\pm 0.1\text{g}$
- Erlenmeyer flasks 100mL
- Cuvettes 1cm
- Solid  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
- Solid NaSCN
- HCl 0,1M
- Deionized water

### Process:

#### 8.1.1 Preparation of stock solutions of $\text{Fe}^{3+}$ and $\text{SCN}^-$

Using a balance of  $\pm 0.1\text{g}$ , it is weighted 6.8g of solid  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and transferred to a volumetric flask of 250mL where dissolved to the mark using 0.1M solution of HCl. The use of HCl solution ensures that precipitate of  $\text{Fe}(\text{OH})_3$  will not be formed. So, a solution of  $\text{Fe}^{3+} 1.0 \times 10^{-1} \text{ M}$  (*stock solution of  $\text{Fe}^{3+}$* ) is formed. Next, it is weighted 2.1g of solid NaSCN and transferred to a volumetric flask of 250mL where dissolved to the mark using deionized water. So, a solution of  $\text{SCN}^- 1.0 \times 10^{-1} \text{ M}$  (*stock solution 2 of  $\text{SCN}^-$* ) is formed. Finally, amount of 1mL is transferred to a volumetric flask of 100mL and diluted to the mark with deionized water. So, a solution of  $\text{SCN}^- 1.0 \times 10^{-3} \text{ M}$  (*stock solution 1 of  $\text{SCN}^-$* ) is formed.

#### 8.1.2 Preparation of standards solutions of $\text{FeSCN}^{2+}$

For the preparation of standards solutions of  $\text{FeSCN}^{2+}$ , the stock solution of  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  were used. For this purpose, the amounts that referred to the table below (table 1) were transferred to Erlenmeyer flasks of 100mL. Because the concentration of  $\text{Fe}^{3+}$  is much greater than that of  $\text{SCN}^-$ , the equilibrium is practically shifted 100% to the side of  $\text{FeSCN}^{2+}$ .

**Table 1: Preparation of standards solutions of  $\text{FeSCN}^{2+}$**

$\text{Fe}^{3+} 1.0 \times 10^{-1} \text{ M}$	$\text{SCN}^- 1.0 \times 10^{-3} \text{ M}$	HCl 0.1M	$[\text{FeSCN}^{2+}] \text{ (M)}$
5mL	0mL	5mL	blank
5mL	1mL	4mL	$1.0 \times 10^{-4}$
5mL	2mL	3mL	$2.0 \times 10^{-4}$
5mL	3mL	2mL	$3.0 \times 10^{-4}$
5mL	4mL	1mL	$4.0 \times 10^{-4}$

### 8.1.3 Preparation of equilibrium solutions

For the calculation of the instability constant of the complex ion, we need solutions where the ions  $\text{FeSCN}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  are in equilibrium. Also, in these solutions, the concentration of  $\text{Fe}^{3+}$  has to be much greater than that of  $\text{SCN}^-$ , to ensure the formation only the  $\text{FeSCN}^{2+}$ . But the instability constant is affected by the ionic strength of the solution to. The presence of HCl in the solutions at high concentrations compared to the concentrations of other ions, ensures that the ionic strength is the same to all solutions ( $\mu \approx 0.2$  according to Debye – Hückel equation and ignoring the contribution of other ions).

From the solution of  $\text{Fe}^{3+}$   $1.0 \times 10^{-1}$  M there were transferred 10mL of solution to a volumetric flask of 100mL and diluted to the mark with HCl 0.1M forming a solution of  $\text{FeSCN}^{2+}$   $1.0 \times 10^{-2}$  M. From the solution of  $\text{SCN}^-$   $1.0 \times 10^{-1}$  M there were transferred 10mL of solution to a volumetric flask of 100mL and diluted to the mark with deionized water forming a solution of  $\text{SCN}^-$   $1,0 \times 10^{-2}$  M.

Next, the equilibrium solutions were formed in Erlenmeyer flasks of 100mL according the table below (table 2).

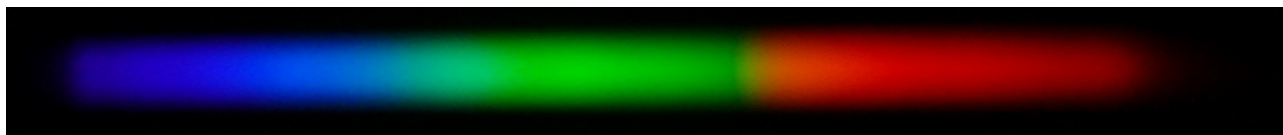
**Table 2: Preparation of equilibrium solutions**

$\text{Fe}^{3+}$ $1.0 \times 10^{-2}$ M	$\text{SCN}^-$ $1.0 \times 10^{-2}$ M	HCl 0.1M	equilibrium solution
15mL	0mL	25mL	blank
15mL	1mL	24mL	solution 1
15mL	2mL	23mL	solution 2
15mL	3mL	22mL	solution 3

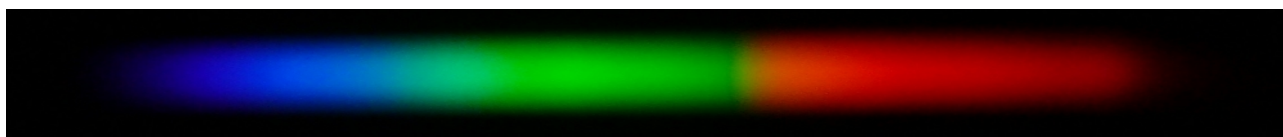
### 8.1.4 Taking the spectra of solutions

From the above solutions (standards and equilibrium), the required amounts were transferred to cuvettes of 1cm and their spectra were taken, after having previously left on rest for about an hour to take place chemical and thermal equilibrium. Also, the spectra of deionized water was taken. The ambient temperature was 20 °C.

In the below pictures, same spectra are shown.



**Picture 8.1: The spectrum of deionized water**



**Picture 8.2: The spectrum of the blank of standards solutions**





*Picture 8.3: The spectrum of blank of equilibrium solutions*



*Picture 8.4: The spectrum of a standard solution*



*Picture 8.5: The spectrum of an equilibrium solution*

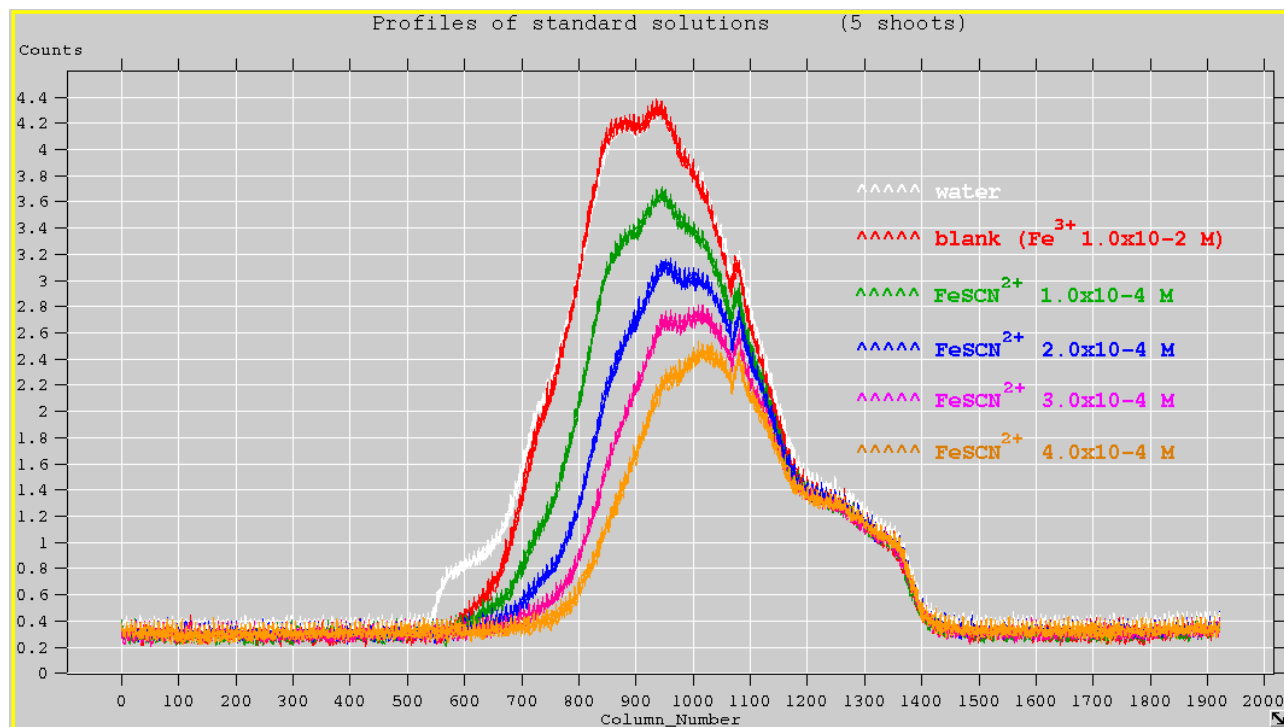
### 8.1.5 Processing the photos of spectra with the Gimp

The pictures of spectra processed with the Gimp as follow:

- Turn left 90°.
- Desaturate based on luminosity.
- Save as FIT file type.

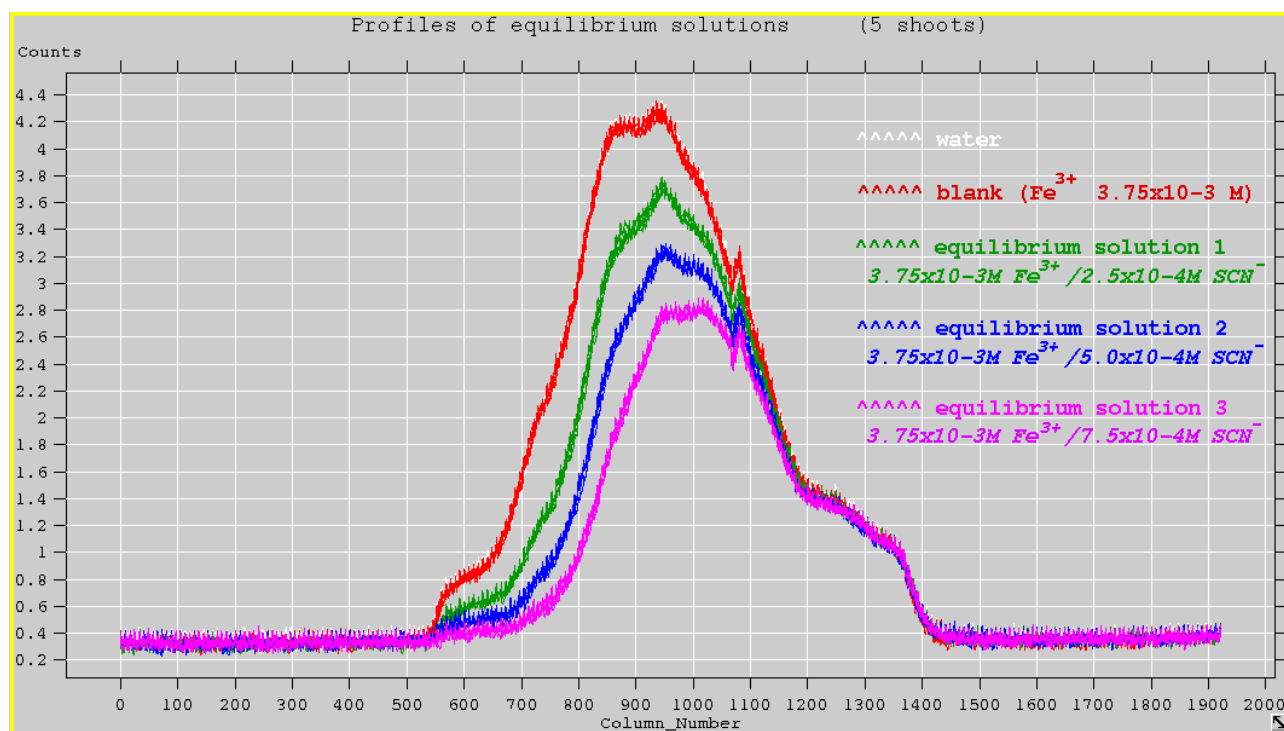
### 8.1.6 Taking the spectral profiles with Fv

Using Fv, the spectral profiles were formed, that are shown in the next picture.



*Picture 8.6: The spectral profiles of standard solutions of  $\text{FeSCN}^{2+}$  (5 shoots)*

The above picture shows that  $\text{FeSCN}^{2+}$  absorbs strongly at about Column\_Number = 750. But the absorption of the fourth solution falls in the noise area, so there will be error in the measurement. Therefore the measurements of absorption have to be done in a little longer wavelength, at Column\_Number = 800.



**Picture 8.7:** The spectra profiles of equilibrium solutions (5 shoots)

Inspecting the pictures 8.6 and 8.7 it seems that the absorption of blank is the same for the standard and equilibrium solutions at Column\_Number = 800, so we can safely use the curve resulting from the standard solutions to calculate the concentrations of  $\text{FeSCN}^{2+}$  in equilibrium solutions.

### 7.1.7 Processing with the Calc

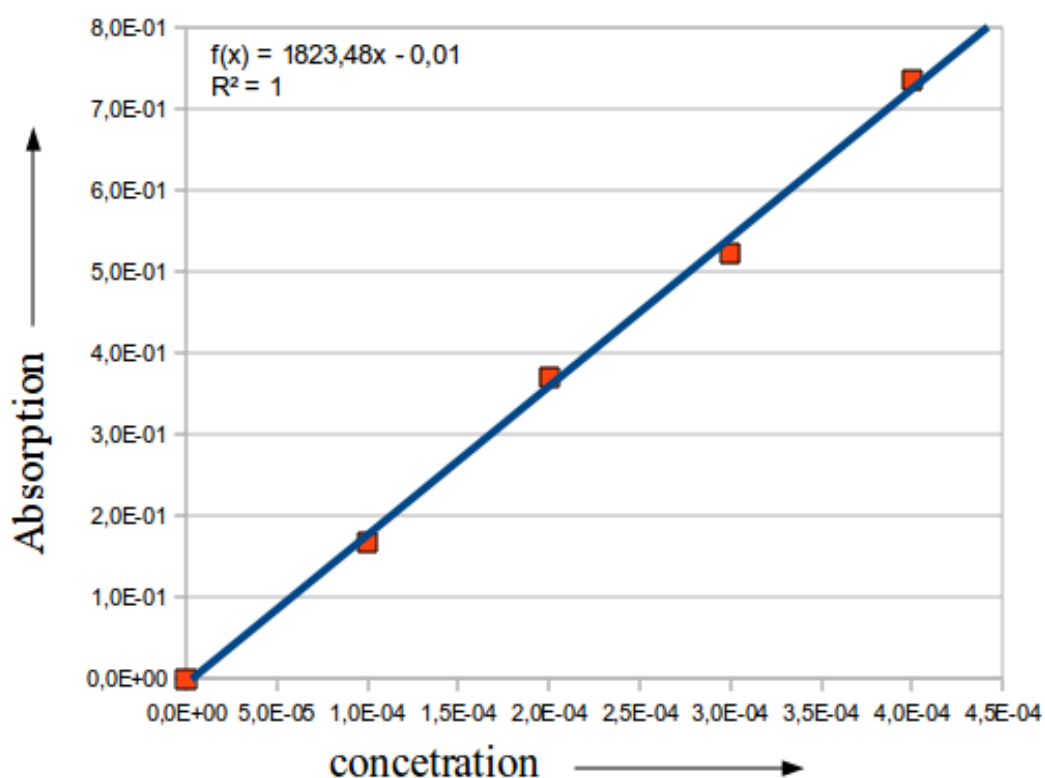
Based on the graphs of spectral profiles of the standard solutions of  $\text{FeSCN}^{2+}$ , the average of Counts is calculated for the solutions and the blank at Column\_Number = 800. Then, using the Lambert – Beer law (eq. 4.3), the absorptions are calculated and the calibration graph of absorption over concentration is plotted.

Next, the absorptions of equilibrium solutions are calculated and with the aim of the calibration graph the concentrations of  $\text{FeSCN}^{2+}$  ions are calculated. The entire process is easily done by the spreadsheet.

Tables and graphs are given below.

Column\_Number                      800  
 Counts\_blank                         3,07

c (mol/L)	Counts	A =log(Counts_blank/Counts)
0,0E+00	3,07	0,0E+00
1,0E-04	2,09	1,7E-01
2,0E-04	1,31	3,7E-01
3,0E-04	0,92	5,2E-01
4,0E-04	0,57	7,3E-01



*Picture 8.8: Data table and graph of Absorption - Concentration*

**Table3: Data for equilibrium solutions**

solution	counts	A	C <sub>FeSCN<sup>2+</sup></sub> (mol/L)
1	2.06	1.7x10 <sup>-1</sup>	1.0x10 <sup>-4</sup>
2	1.49	3.1x10 <sup>-1</sup>	1.8x10 <sup>-4</sup>
3	1.02	4.8x10 <sup>-1</sup>	2.7x10 <sup>-4</sup>

From the fourth column of table 3 and using the the chemical equation, the equations 8.1 and 8.2, the instability constant and the thermodynamic instability constant are are calculated for each solution. The value of ionic strength set equal to 0.2 (only the contribution of HCl).

The result of calculations are listed to the table below.

**Table 4: Values of  $K_{inst}$  and  $K^0_{inst}$  for the equilibrium solutions**

<b>solution</b>	<b><math>K_{inst}</math></b>	<b><math>K^0_{inst}</math></b>
1	$5.5 \times 10^{-3}$	$2.4 \times 10^{-4}$
2	$6.3 \times 10^{-3}$	$2.7 \times 10^{-4}$
3	$6.2 \times 10^{-3}$	$2.7 \times 10^{-4}$

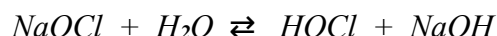
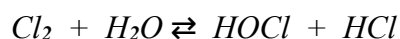
From the last column of the above table, the average of thermodynamic instability constant is calculated:

$$K^0_{inst, FeSCN^{2+}} = 2.6 \times 10^{-4} \quad \text{at } 20 \text{ } ^\circ\text{C}$$

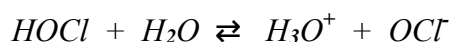
## 9. Water quality: Determination of chlorine in water

Chlorination is so far the most popular and most effective method for water disinfection. But, because the chlorine reactivity and warnings of the chlorine effects on the public health, we have to be aware for the proper use of chlorine. Usually the chlorination of water is done by adding to it gaseous chlorine or sodium hypochlorite in such quantities to be able to disinfect the water, but also to maintain a reasonable amount of chlorine for protection.

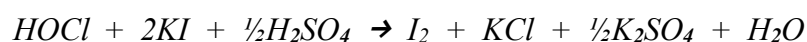
If chlorination compounds are added to water, hypochlorous acid is produced according the equations below:



Hypochlorous acid is a weak acid that is partially ionized according the equation:

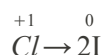


The degree of ionization of hypochlorous acid depends on pH and temperature. At pH values less than 4, the degree of ionization is practically 0% irrespective of temperature. The residual chlorine (total chlorine) in water can be detected from the yellow hue that is derived after adding potassium iodide.



(yellow hue)

If there are chloramines in water, they react with potassium iodide, in the same way as above, liberating iodine:



Due to the formation of colored potassium triiodide, it is possible to be determined spectroscopically the concentration of iodine in the water and finally the concentration of chlorine.

### 9.1 Experiment: Determination of chlorine in water

#### Objectives:

- To determine the chlorine concentration of Milton solution
- To determine the chlorine concentration of household water and estimate the ability to detect chlorine in urban water supply.

#### Method:

- Spectrophotometric

**Equipment and materials:**

- The handmade spectroscope
- 40 watt light bulb (brilliant white lamp)
- Volumetric flasks of 100mL and 1L
- Measuring pipette of 1mL
- Volumetric cylinder of 10mL
- Balance  $\pm 0.1$ g
- Cuvettes 1cm
- Iodine solution 5% w/v (Lugol)
- Milton solution
- Household bleach
- Solid potassium iodide
- Sulfuric acid 1M
- Deionized water
- Tap water

**Process:****9.1.1 Preparation of standard iodine solutions**

Amounts of 0.1mL, 0.2mL, 0.3mL, 0.4mL and 0.5mL of iodine solution (Lugol) are transferred to volumetric flasks of 100mL using measuring pipette of 1mL and diluted to the mark with deionized water. So, 5 standard solutions are formed containing iodine 50mg/L, 100mg/L, 150mg/L, 200mg/L and 250mg/L respectively.

**9.1.2 Preparation of Milton solution**

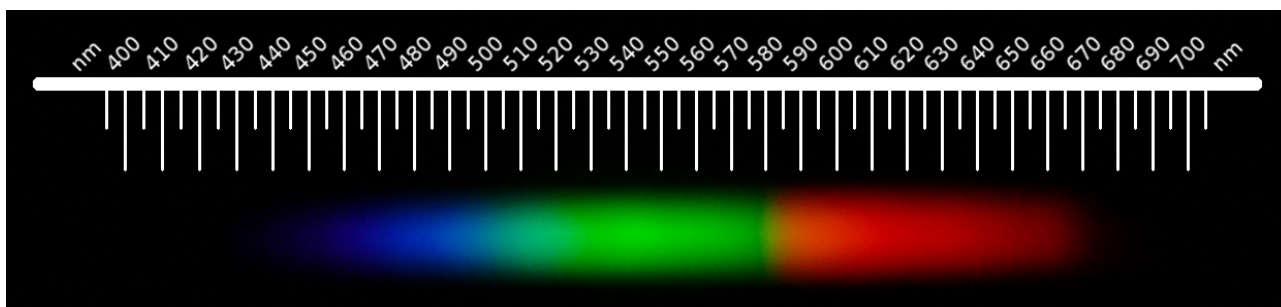
The Milton solution in the market contains 2%w/w that is high enough for the experiment. So, using measuring pipette of 1mL, 0.1mL of Milton solution are transferred to a volumetric flask of 100mL and 0.1g of solid KI and 10 drops of 1M sulfuric acid are added. The solution is diluted to the mark with deionized water. Thus it is formed a colored (yellow – brown) solution corresponding to sodium hypochlorite concentration of 100mg/L. This solution will be used to test the accuracy of the method (test solution).

**9.1.3 Preparation of household water solution**

In a volumetric flask of 1L, it is added tap water below the mark and then added 0.1mL of household bleach, 1g of solid potassium iodide and 5mL sulfuric acid 1M. The final solution is diluted to the mark with tap water. Thus it is formed a colored (yellow) solution corresponding approximately to 5mg/L of sodium hypochlorite. This solution will be used to test the accuracy of the method (test solution), but also it will be used to estimate the ability of the method to determine chlorine in the urban water supply.

### 9.1.4 Taking the spectra of solutions

From the above solutions (standards, tests and blank) were transferred to cuvettes the required amounts and their spectra were taken. As blank solution, deionized water was used.



*Picture 9.1: The spectrum of a standard solution*

The above picture shows that the iodine solutions absorb in the blue region of the visible spectrum.

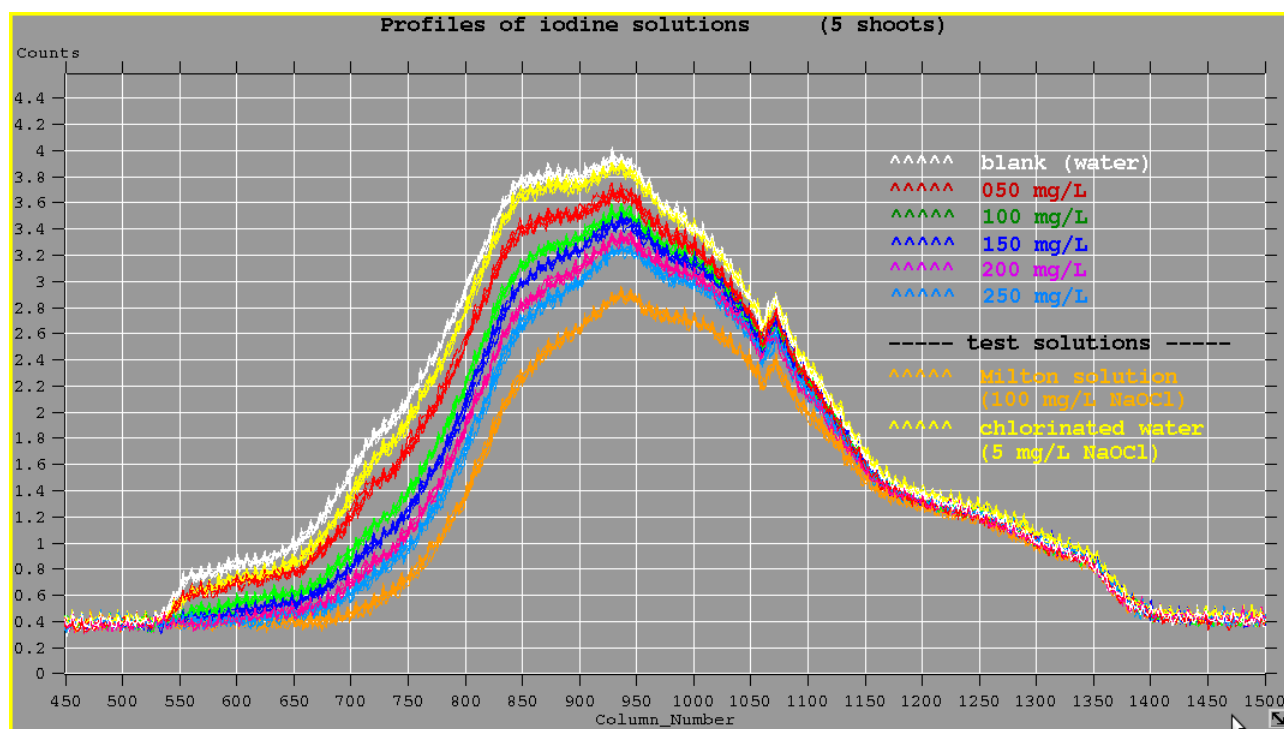
### 9.1.5 Processing the photos of spectra with the Gimp

The pictures of spectra processed with the Gimp as follow:

- Turn left 90°.
- Desaturate based on luminosity.
- Save as FIT file type.

### 9.1.6 Taking the spectral profiles with Fv

Using Fv, the spectral profiles were formed, that are shown in the next picture.



*Picture 9.2: Spectral profiles of standard and test solutions*

The above picture shows that the maximum absorption is located at about Column\_Number = 720.

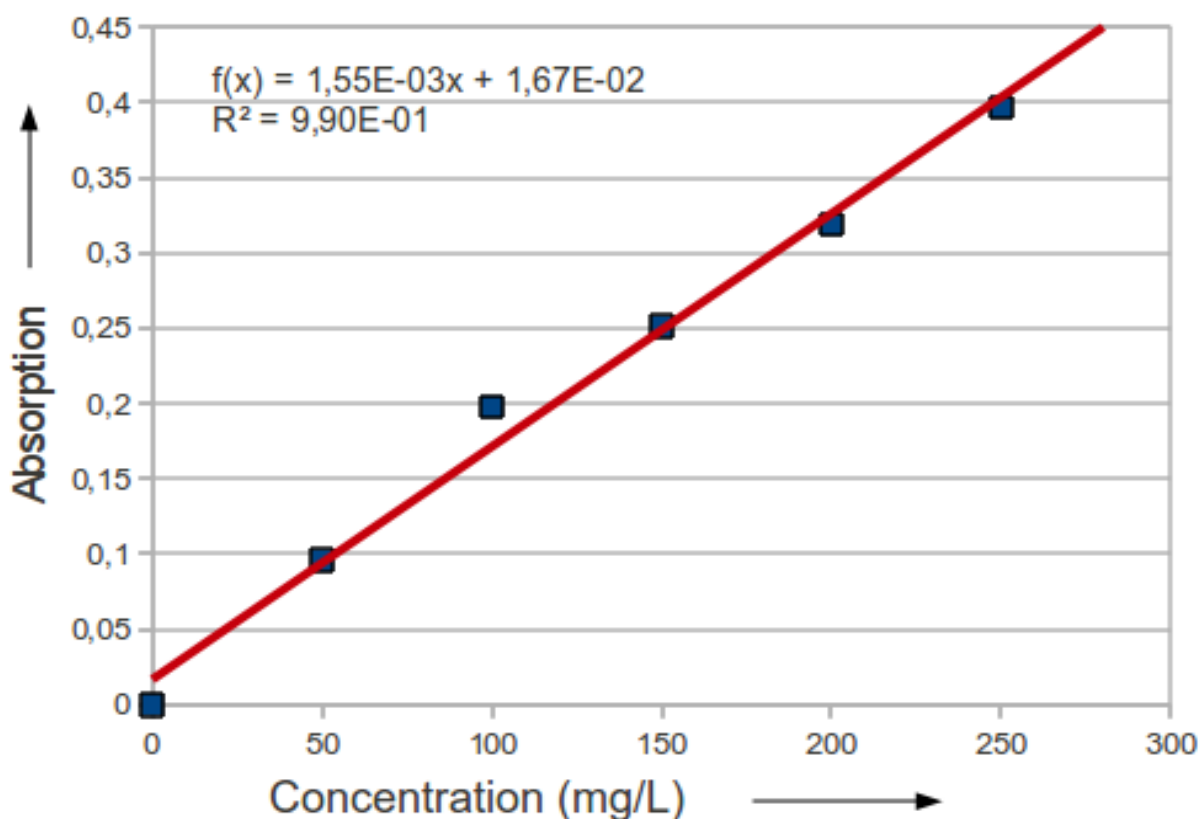
### 9.1.7 Processing with the Calc

Based on the spectral profiles of standard iodine solutions, the average of Counts for the solutions and the blank are calculated at Column\_Number= 720. Next using the Lambert – Beer law (eq. 4.3), the absorptions are calculated and the graph of absorption over concentration is constructed. The entire process is easily done by the spreadsheet.

The following picture shows the data table and graph that made the Calc.

Column\_Number = 720  
Counts\_blank = 1,85

C (mg/L)	Counts	A = log(Counts_blank/Counts)
0	1,85	0
50	1,48	0,10
100	1,17	0,20
150	1,04	0,25
200	0,89	0,32
250	0,74	0,40



Picture 9.3: Calibration curve of standard iodine solutions



### **9.1.8 Determining the chlorine**

Based on the spectral profiles of test solutions, the averages of Counts for the Milton solution and the tap water were calculated at Column\_Number=720. Next, using equation 4.3 the absorptions of Milton solution and chlorinated tap water were calculated. Finally the concentration of iodine was calculated using the equation of the form  $A = b \cdot c + a$  found experimentally.

The entire process of calculations made by the Calc which gave:

*Concentration of  $I_2$  in Milton solution:*      **310 mg/L**    και

*Concentration of  $I_2$  in tap water:*              **18 mg/L**

*Concentration of NaOCl in Milton solution:* **91 mg/L**    και

*Concentration of NaOCl in tap water:*        **5 mg/L**

*Concentration of  $Cl_2$  in Milton solution:*    **43 mg/L**    και

*Concentration of  $Cl_2$  in tap water:*         **2,5 mg/L**

### **9.1.8 Estimating the ability of method to detect chlorine in urban water supply**

The allowable chlorine concentration in urban water supplies is 0.1mg/L – 1.0mg/L, so the sample of tap water used was overchlorinated enough to be considered as urban tap water. However, inspecting the spectral profiles (pict. 9.2) it seems that there is a little room between the spectral profiles of blank and chlorinated tap water. So, concentrations of chlorine less than 2,5mg/L can be determined. Perhaps the upper limit of allowable chlorine concentration can be determined with reasonable certainty.

## ***Comments***

1. The method is based on photography, so great importance should be given in taking photos. Before the experiment, the investigator should have take a sufficient number of photos, with different values for aperture and shutter speed, to produce photos that show best the changes in absorption of solutions. Special care should be taken that photographs do not contain overexposed (burned) areas, because the intensity values that taken are wrong.
2. Caution must be given to focus. In a particular position, a clear photo is taken, but there are not absorption areas. The position of appropriate focus should be based on clear details of the spectrum not on clear photos.
3. All photos should be taken in one stage. If during taking photos, the luminosity of the lamp changes or the items move, the process should be repeated from the beginning.
4. It is good practice to crop only the left and right portion of the photos to reduce the file size. If crop around the spectrum, this increases the relative effect of noise in the absorption areas and therefor to worse results.

## ***Handling chemicals, precautions and disposal***

Chemical can be hazardous to health and release into enviroment may cause impacto to it. Therefore a particular attention in their use and disposal is required. As general rules can be the following:

- Good ventilation of the workspace
- Using gloves and goggles
- Do not mix substances, unless sure it is safe
- Disposal according the national and local laws

More specific information can be found on the website:

- Material Safety Data Sheet (MSDS): <http://msds.chem.ox.ac.uk/#MSDS>

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