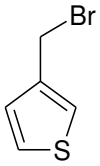
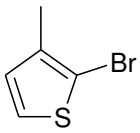
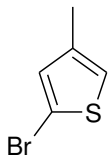
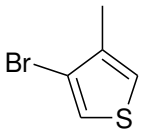
PRACTICAL PROBLEMS

PROBLEM 1P (Practical)

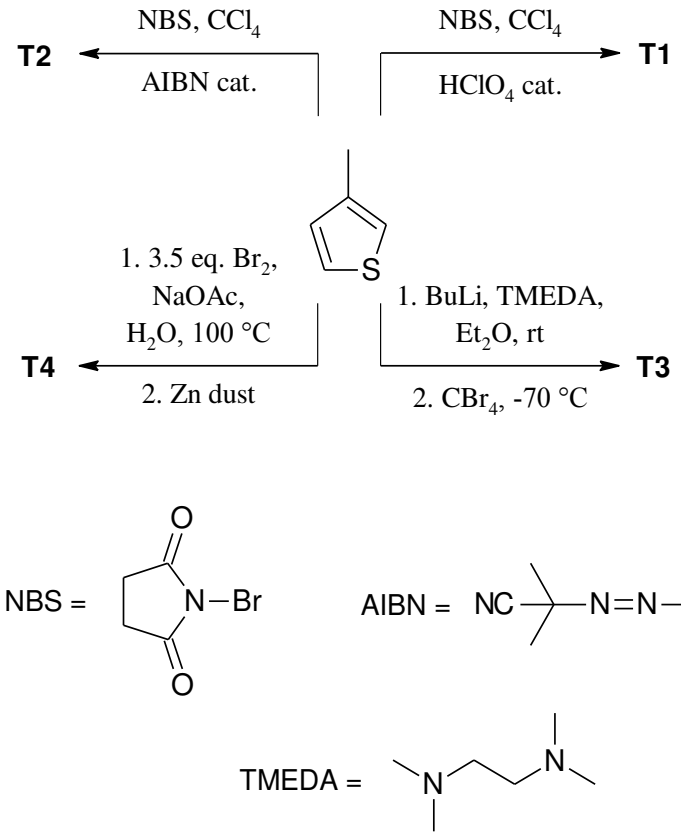
Tuning bromination selectivity by catalysis

Selectivity of chemical reactions is one of the most challenging problems of contemporary research. In many cases, reaction conditions and the catalysts applied are keys to achieving high selectivity of organic reactions. In this problem, you will study one of such cases. 3-Methylthiophene can theoretically be transformed into four monobrominated derivatives **T1–T4**, which have been actually synthesized and characterized in detail. Structures of **T1–T4** and the values of refractive indexes are given in Table 1.

Table 1. Structures and refractive indexes of monobrominated thiophenes.

Designation	**T1**	**T2**	**T3**	**T4**
Structure				
n_D^{20}	1.5961	1.5706	1.5786	1.5795

The selective synthesis of each of **T1-T4** can be performed using 3-methylthiophene as the starting material. **T1** and **T2** can be obtained by direct bromination using different catalysts, whereas **T3** and **T4** are the products of “one pot” multistep synthesis (see Scheme 1).



Scheme 1. Selective synthesis of monobrominated thiophenes.

Task 1.1 Assign the structures given in Scheme 1 with **T1, T2** to the structures given in the Table 1. Fill in the boxes below with one of A - B.

☐ **T1** ☐ **T2**

In this problem you will:

- synthesize a monobrominated thiophene derivative using one of the catalysts from the list below,
- measure the product refractive index (n_D),
- compare the results obtained with literature data and decide on the structure of the product and the catalysts given.

List of possible catalysts

- $HClO_4$ in CCl_4
- AIBN in CCl_4

Chemicals

- 3-Methyl-thiophene, solution in CCl_4, 4g / 8 cm^3
- 1-Bromo-2,5-pyrrolidinedione (NBS), solid, 7.3 g

- Carbon tetrachloride, liquid, 24 cm^3
- Unknown catalyst in CCl_4, in plastic vial, 4 cm^3
- Potassium carbonate, solid, 0.02 g

Chemical Glass and Equipments

- 2 Laboratory stands
- Round-bottom three-necked flask, 100 cm^3
- Reflux condenser, connected to water supply
- 6 Glass ground joint stoppers
- Dropping funnel, 50 cm^3
- Oval magnetic stir-bar (big)
- Pear-shaped round-bottom flask for distillation, 50 cm^3
- Claisen distillation adapter
- Thermometer with fixed ground joint tube
- Buchner type fritted glass filter
- Rubber spacer for vacuum filtration
- Liebig (downward) condenser
- Distilling receiver cow
- 4 Receiver flasks, 10 cm^3
- Receiver flask, 50 cm^3
- Adjustable lab jack lift support
- Oval magnetic stir-bar (small)
- Plastic beaker, 50 cm^3
- Teflon sleeves for ground tapered joints
- Large funnel, 65 mm, with short stem
- 5 Joint clips
- Grey clamp
- Red clamp
- Permanent marker
- Glass beaker, 25 cm^3
- Plastic container labeled “Used glassware”
- Plastic container labeled “Ice bath”
- Digital manometer
- Spatula
- Glass rod

PROCEDURE

Note!

- *Apparatuses used in this problem are shown in Fig. 1 and 2.*
- *Always equip every joint with the Teflon sleeve. Immediately place every piece of the used glassware in the corresponding container. Always keep the container tightly closed.*
- *You can use cotton gloves when handling hot things!*

Step 1. Clamp the three-necked flask on the laboratory stand on top of the hot-plate magnetic stirrer. (Fig.1). Apply the dropping funnel and the reflux condenser to the corresponding necks and put the big magnetic stir-bar into the flask through the open neck. Ask your lab assistant to switch on water supply in the reflux condenser (**Do not do it yourself!**). Transfer NBS quantitatively into the flask using spatula and big plastic funnel. Transfer ~15 cm^3 of CCl_4 into the 25 cm^3 glass beaker. Pour ~2/3 of the solvent volume from the beaker into the flask. Shake the Catalyst and quantitatively add it through the same plastic funnel into the flask. Add the rest of the solvent from the beaker to the flask. Close the open neck with the stopper. Put the flask into the ice bath filled with water and ice to ~ 2/3 of its volume. Start stirring the mixture.

Step 2. Using the big plastic funnel quantitatively transfer the solution of 3-methyl-thiophene to the dropping funnel with **tap closed**. Apply a piece of the cotton wool to the open end of the dropping funnel and reflux condenser. Under vigorous stirring, add the solution of 3-methylthiophene dropwise during ~ 3 min. Replace the dropping funnel by a glass stopper. Use the Teflon sleeve. Remove the ice bath. Dry the plate and bottom of the flask with napkin.

Step 3. Wrap up the flask with aluminum foil. Switch on the heater (position 3). Bring up the mixture to boiling and boil it for 10 min. Prepare the ice bath (~2/3 of the volume) while the mixture boils.

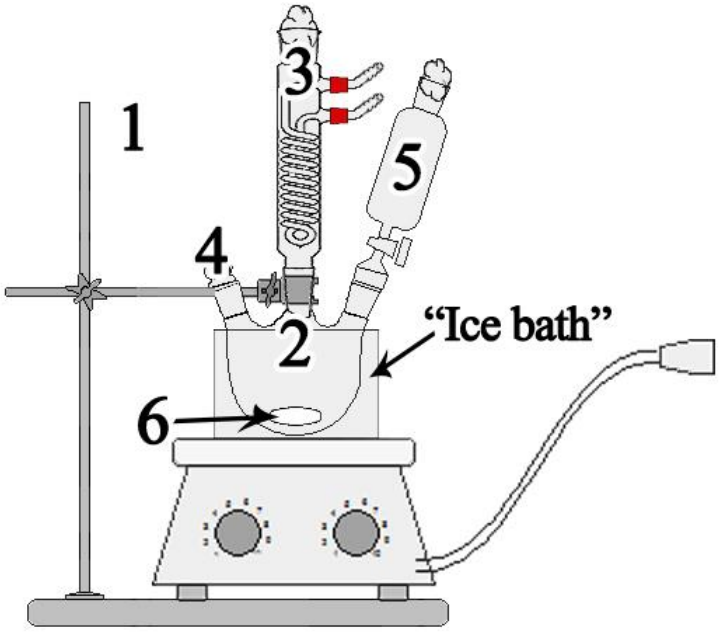


Fig. 1. Set up needed to implement Steps 1-4 of the synthesis.

The particular parts of the apparatus: 1 - laboratory stand, 2 - round-bottom three-necked flask, 3 - reflux condenser, connected to water supply, 4 - glass ground joint stopper, 5 - dropping funnel, 6 - oval magnetic stir-bar (big).

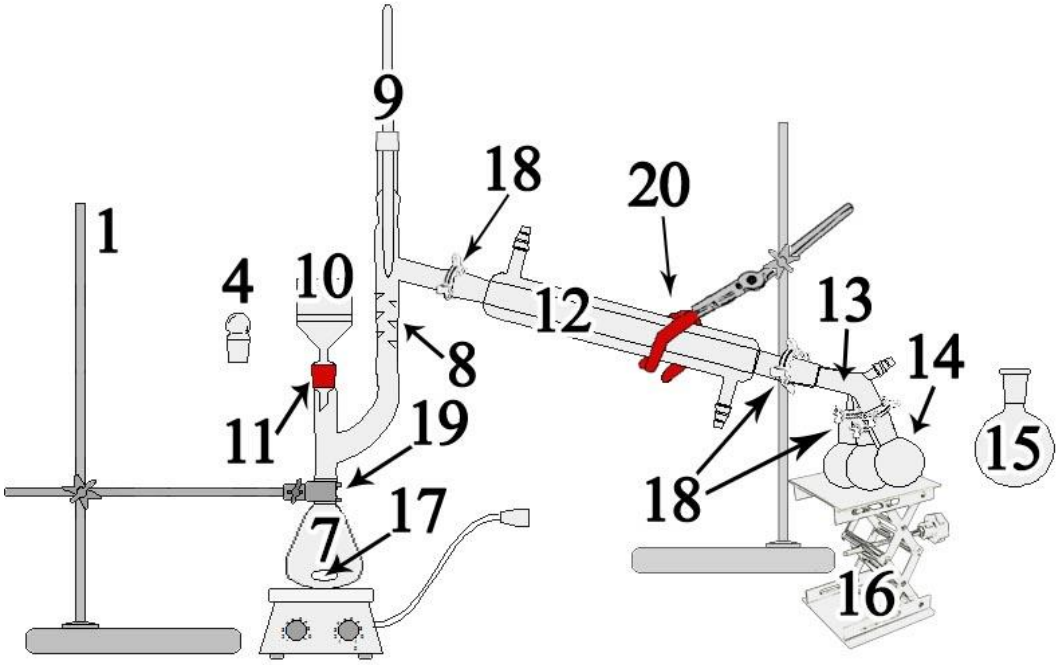


Fig. 2. Set up needed to implement Steps 5-10 of the synthesis.

The particular parts of the apparatus: 1 - laboratory stand, 4 - glass ground joint stopper, 7 - pear-shaped round-bottom flask, 8 - Claisen distillation adapter, 9 - thermometer with fixed ground joint tube, 10 - Buchner type fritted glass filter, 11 - rubber spacer for vacuum filtration, 12 - Liebig condenser, 13 - distilling receiver cow, 14 - receiver flask, 10 cm^3, 15 - receiver flask, 50 cm^3, 16 - lift support, 17 - oval magnetic stir-bar, 18 - joint clips, 19, 20 – clamps.

Step 4. Switch off the heater and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Dip the flask equipped with the condenser and stoppers into the ice bath for 3-5 min. Keep gently swirling the flask from time to time to provide the faster cooling. Then remove the reflux condenser and load 0.02 g of K_2CO_3 using the big funnel applied to the open neck. Close the neck with a glass stopper and shake the flask several times. Turn off the water supply and unscrew the adaptors of the tubings from the reflux condenser. Let the residual water leak out of the condenser and immediately place it into the container for the used glassware. Remove the clamp keeping the flask in the ice bath.

Step 5. Weigh the 10 cm^3 receiver flask for product with the glass stopper, both marked with your student code. Write down the value in the answer sheet. Put the small magnetic stir-bar in the 50 cm^3 pear-shaped distillation flask. Screw on the adaptors with tubings to the Liebig condenser and fix it on the stand with the red clamp. Turn on the water supply yourself and make sure there is no water leakage.

Step 6. Assemble the distillation apparatus as shown on Fig. 2 supplying all the joints with the teflon sleeves and clips. First, attach two 10 cm^3 and one 50 cm^3 receiver flasks to the distilling receiver cow. Then connect the vacuum hose to the cow and complete assembling. Fix the apparatus over the magnetic stirrer to adjust it on height. Use the adjustable lab jack lift support.

Step 7. Remove the hot-plate magnetic stirrer aside. Insert the fritted glass filter into the Claisen distillation adapter using the rubber spacer. Turn on the water-jet pump and switch on the digital manometer. Remove the three-necked flask from the ice bath and dry it with a napkin. Carefully transfer the reaction mixture from the three-necked flask to the filter (**Attention! If you do it too fast, the mixture can be partially sucked into the curved part of the adaptor**). When finished, turn off the pump and replace the filter with a glass stopper, use the teflon sleeve.

Step 8. Tightly wrap up the flask and distillation adaptor with aluminum foil up to the thermometer joint. Bring back the magnetic stirrer and turn on stirring and heating (position 6). **Do not turn on the water-jet pump!** Collect the distilled solvent into the 50 cm^3 receiver. When the solvent distillation is over, turn off heating and stirring and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Replace the receiver flask containing the distilled solvent by a new 10 cm^3 receiver. Close the 50 mL flask with a glass stopper and deliver it to your lab assistant.

Step 9. Remove the foil and put the pear-shaped bottom flask into the ice bath for 2-3 min to bring the temperature below ambient. Remove the ice bath; dry the flask with a napkin. Bring back the magnetic stirrer under the flask **(Attention! The hot-plate may be still hot!).** Turn on stirring. Wrap up the flask tightly with aluminum foil. Switch on the water-jet pump. When vacuum is stabilized (follow the reading of the digital manometer), turn on the heater (position 6). Observe the initial stage of the targeted product distillation and collect the first 3-5 drops into an attached receiver flask not labeled with your student code. Then rotate the cow and collect the targeted product into the receiver flask with your student code. Write down the product boiling point and pressure reading from the digital manometer into the answer sheet.

Step 10. When the targeted product is collected, turn off the heater, remove the foil and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Cool down the apparatus to ambient temperature using the ice bath. **Ask your lab assistant to disconnect the vacuum line.** Disconnect the receiver flask with the targeted product and **immediately** close it with the glass stopper labeled with your student code. Do not attempt to drag the teflon sleeve out if it remains in the receiver. Place the flask into the 50 cm^3 plastic beaker labeled "For the receiver with the product". Immediately attach a new receiver instead of the removed one and apply the joint clip. **Leave the apparatus as it is.**

Step 11. Measure the refraction index **(before weighing)** following the instruction below. Record the temperature from the refractometer.

Weigh the receiver with the targeted product closed with the labeled stopper. Calculate the mass and yield of the product (take the mass of the teflon sleeve equal to 149 mg). The molar masses of 3-metylthiophene and the product equal 98 and 177 g mol^{-1}, respectively.

Task 1.2 Write down all the results in the hereunder Table.

#	Parameter /Characteristics	Value	Units
1	Mass of the receiver flask with the glass stopper, both marked with student code		g
2	Mass of the product		g
3	Yield of the product		%
4	Refraction index for the product		-
5	Temperature recorded from the refractometer		°C

Table continued:

6	Boiling point of the product		°C
7	Pressure at the boiling point		mmHg

Task 1.3 By comparing the obtained and literature data, draw the structure of the product and catalyst given.

Task 1.4 Draw the structure of the 3-methylthiophene-based reactive intermediates behind the selectivity in the case of **T1** and **T2**.

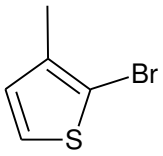
Task 1.5 Write down the product (**T1** or **T2**) formed as a result of direct bromination of 3-methylthiophene with NBS under the given conditions / catalyst used.

Task 1.6 In the synthetic pathways to **T3** and **T4**, draw the structures of the compounds formed in the first steps of each pathways shown on Scheme 1.

SOLUTION

1.1 T1 [B] T2 [A]

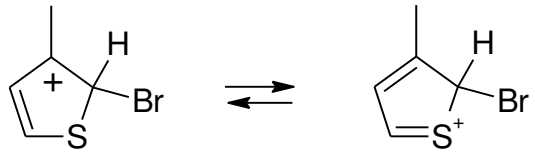
1.3 The product obtained:



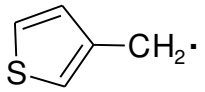
The catalyst given: $HClO_4$

1.4

T1



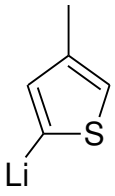
T2



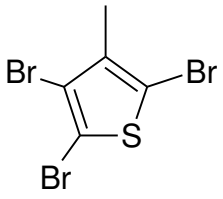
1.5

$ZnBr_2$	**T1**
Dibenzoyl peroxide	**T2**
LiBr in AcOH	**T1**
Visible light or UV light	**T2**

1.6 **T3**



T4



PROBLEM 2P (Practical)

Analysis of the solution of a chromium – vanadium alloy

Antiferromagnetic materials show a good prospect in the development of memory devices for ultra-high-density data storage, the world's smallest magnetic memory bit using only 12 atoms being one of prime examples. Vanadium – chromium alloys exhibit antiferromagnetic properties at subzero temperatures. It is obvious that composition of alloys used in various hi-tech applications should be accurately controlled.

In this problem you will analyze an aqueous solution simulating the product of digestion of vanadium – chromium alloy sample. The task consists of two parts:

I. Oxidation of vanadyl (VO^{2+}) to vanadate (VO_3^-) in the test solution using potassium permanganate, followed by determination **of vanadium** (note that chromium (III) is not oxidized under these conditions).

II. Oxidation of the test solution with ammonium persulfate, followed by titrimetric determination of the total content of vanadium and chromium with Mohr's salt (Ammonium iron(II) sulfate).

Chemicals

- Test aqueous solution containing VO^{2+} and Cr^{3+} (to be determined), 100 cm^3,
- Sulfuric acid, aq., (c = 1 mol dm^{-3}), ~ 500 cm^3,
- Potassium permanganate, aq., (c = 0.03 mol dm^{-3}), 15 cm^3,
- Oxalic acid, aqueous solution, (c = 0.03 mol dm^{-3}), 30 cm^3,
- Phenylanthranilic acid, aqueous solution, 0.1 %, 5 cm^3, indicator in a dropper,
- Ammonium iron(II) sulfate, Mohr's salt, aqueous solution, 100 cm^3, (concentration given on the label),
- Silver nitrate, aqueous solution, 0.3 %, 5 cm^3 in a dropper,
- Ammonium persulfate, aqueous solution, 10 %, 70 cm^3.

Chemical Glass and Equipments

- Laboratory stand
- Clamp for burette
- Plastic beaker, 100 cm^3,
- Glass beaker, 150 cm^3
- Volumetric flask with a stopper, 100 cm^3

- Small funnel, (45 mm)
- Medium-size funnel, (55 mm)
- Watch glass
- Burette, 25.00 cm^3, clamped in the stand
- Volumetric pipette, 10.00 cm^3
- Graduated pipette, 5.00 cm^3
- 2 Erlenmeyer flasks, 150 cm^3
- Graduated cylinder, 100.0 cm^3
- 2 Pasteur pipettes
- White paper sheet
- Refractometer and its operating instructions
- Balances

Procedure

Note!

- The amount of vanadium and chromium should be calculated and reported in mg per 100 cm^3 of the test solution.
- Start doing this task with Part A, since you will need time to oxidize the test solution to be analyzed in Part C.

Part A. Preparation of the solution for determination of vanadium and chromium total content

1. Transfer a 10.00 cm^3 aliquot of your test solution into the 150 cm^3 beaker and add 20 cm^3 of sulfuric acid (c = 1 mol dm^{-3}) using the 25 cm^3 graduated cylinder.
2. Add 6–8 drops of the 0.3% solution of silver nitrate (the catalyst) and heat the mixture on the hotplate to 70 – 80 °C (position 3), until condensate on the beaker wall appears.
3. Add 20 cm^3 of the 10% ammonium persulfate solution to the heated mixture using the 100 cm^3 graduated cylinder.
4. Continue heating and observe the appearance of yellow color, indicating the formation of dichromate.

Note! You can perform the determination of vanadium (Part B, 1 – 6), while the mixture is being heated.

5. Keep heating the mixture for 10 - 15 min (position 3) after appearance of the yellow color to decompose the excess of ammonium persulfate (the decomposition is over when you see no small bubbles in the solution).

6. Cool the solution to ambient temperature.
7. Transfer quantitatively the solution from the 150 cm^3 beaker into the 100 cm^3 volumetric flask, dilute to the mark with distilled water, stopper the flask and mix thoroughly.

Part B. Titrimetric determination of Vanadium

1. Transfer a 5.00 cm^3 aliquot of the test solution into an Erlenmeyer flask using the graduated pipette.
2. Carefully add potassium permanganate solution (c = 0.03 mol dm^{-3}) dropwise, shaking the flask after adding each drop until light pink color appears. Make sure that the light pink color is stable. Remove the excess of potassium permanganate by adding oxalic acid solution (0.03 mol dm^{-3}) dropwise. Shake the flask after each drop until the light pink color changes to pale blue. Let the solution stand for about 1 min to make sure that the pink color has disappeared completely.
3. Transfer 10 cm^3 of H_2SO_4 solution (c = 1 mol dm^{-3}) into the Erlenmeyer flask using the 25 cm^3 graduated cylinder.
4. Add 2–3 (not more!) drops of the indicator into the Erlenmeyer flask and shake it vigorously. Let the flask stand for 2–3 min and observe the purple color appearance.
5. Fill the burette with the Mohr's salt solution. Use the 100 cm^3 plastic beaker labeled "Waste" to drain the excess of Mohr's salt solution from the burette, record the initial reading.
6. Titrate the solution in the Erlenmeyer flask with the Mohr's salt solution until the color changes to pure light green through brownish-grey one.
7. Take the final reading of the burette. Repeat as necessary.

Task 1. Fill in Table 2.

Table 2. Determination of vanadium

Titration №	1	2	3			
Initial reading of the burette, cm^3						
Final reading of the burette, cm^3						
Consumed volume, cm^3						

Accepted volume, V_1 _____cm^3

Part C. Titrimetric determination of vanadium and chromium total content in the test solution

1. Wash the 10.00-cm^3 volumetric pipette with distilled water, rinse with the solution prepared in 100-cm^3 volumetric flask (obtained in part A).
2. Pipette a 10.00-cm^3 aliquot into an Erlenmeyer flask, add 10 cm^3 of H_2SO_4 solution (c = 1 mol dm^{-3}) using the 25-cm^3 graduated cylinder.
3. Add 3–4 drops of the indicator. Vigorously shake the flask and let it stand for 3–4 min. Observe appearance of red color.
4. Fill the burette with the Mohr's salt solution. Use the 100-cm^3 plastic beaker labeled "Waste" to drain the excess of Mohr's salt solution from the burette, record the initial reading.
5. Titrate the solution in the flask with the Mohr's salt solution until the color changes to light yellow-green.
6. Take the final reading of the burette. Repeat as necessary.

Task 2 Fill in Table 3.

Table 3. Determination of vanadium and chromium total content

Titration No	1	2	3			
Initial reading of the burette, cm^3						
Final reading of the burette, cm^3						
Consumed volume, cm^3						

Accepted volume, V_2 _____ cm^3

Part D. Tasks and Data Analysis

Task 3. Write down the balanced chemical equations for the reactions that take place upon:

a) oxidation of the test solution with potassium permanganate
b) titration of vanadate with Mohr's salt

Task 4. Write down the balanced chemical equations for the reactions that take place upon**:**

a) oxidation of the test solution with ammonium persulfate

b) titration of the oxidized test solution with Mohr's salt

Task 5 Calculate the concentrations of

a) V(IV),

b) Cr(III)

in the test solution.

c) Calculate the mass of the metals in mg per 100 cm^3 of test solution.

Task 6 This protocol can not be applied to the determination of vanadium and chromium in steels, if the steel was digested by conc. HCl. Give equations of two reactions to explain the reasons behind**.**

_____

SOLUTION

Task 3 a) $2\ KMnO_4 + 10\ VOSO_4 + 12\ H_2O = 2\ MnSO_4 + 10\ HVO_3 + K_2SO_4 + 7\ H_2SO_4$

b) $2\ HVO_3 + 2\ FeSO_4 + 3\ H_2SO_4 = 2\ VOSO_4 + Fe_2(SO_4)_3 + 4\ H_2O$

Task 4 a) $Cr_2(SO_4)_3 + 3\ (NH_4)_2S_2O_8 + 7\ H_2O = H_2Cr_2O_7 + 3\ (NH_4)_2SO_4 + 6\ H_2SO_4$

$2\ VOSO_4 + (NH_4)_2S_2O_8 + 4\ H_2O = 2\ HVO_3 + (NH_4)_2SO_4 + 3\ H_2SO_4$

b) $H_2Cr_2O_7 + 6\ FeSO_4 + 6\ H_2SO_4 = Cr_2(SO_4)_3 + 3\ Fe_2(SO_4)_3 + 7\ H_2O$

$2\ HVO_3 + 2\ FeSO_4 + 3\ H_2SO_4 = 2\ VOSO_4 + Fe_2(SO_4)_3 + 4\ H_2O$

Task 5 a) Calculation for vanadium:

$$c(VO^{2+}) = \frac{V_1(Fe^{2+}) \times c(Fe^{2+})}{V(VO^{2+})}$$

$$m(V) = 0.1 \times c(VO^{2+}) \times M(V) \times 1000 \quad (mg)$$

b) Calculation for chromium:

$$n(Fe^{2+} \text{ on } Cr_2O_7^{2-}) = \frac{V_2(Fe^{2+})\, c(Fe^{2+})}{1000} - 2 \times \frac{V_1(Fe^{2+})\, c(Fe^{2+})}{1000} \times \frac{10}{100}$$

$$n(Cr_2O_7^{2-}) = \frac{1}{6}\left(n(Fe^{2+}) \text{ on } Cr_2O_7^{2-}\right) \text{ mol}$$

$$c(Cr^{3+}) = 2 \times \frac{n(Cr_2O_7^{2-}) \times 100}{10} \times \frac{1000}{100} \text{ mol dm}^{-3}$$

$$m(Cr) = 0.1 \times c(Cr^{3+}) \times M(Cr) \times 1000 \quad (mg)$$

Task 6 $Fe + 2\ HCl \rightarrow FeCl_2 + H_2\uparrow$

$2\ FeSO_4 + (NH_4)_2S_2O_8 \rightarrow Fe_2(SO_4)_3 + (NH_4)_2SO_4$

$2\ Cl^- + S_2O_8^{2-} \rightarrow Cl_2 + 2\ SO_4^{2-}$

(decrease of the amount of ammonium persulfate due to its reaction with excess of iron(II) in steels)

$Ag^+ + Cl^- \rightarrow AgCl\downarrow;\ AgCl + Cl^- \rightarrow AgCl_2^-$

(reaction between the catalyst and chloride)

PROBLEM 3P (Practical)

Kinetic determination of diclofenac (DCF)

Kinetic methods with spectrophotometric detection for assaying drugs have been intensively developed during the last decade due to a number of obvious advantages, including inherent simplicity, cost-effectiveness, availability in most quality control laboratories, and improved selectivity. In this task you will:

- perform kinetic determination of Diclofenac (DCF) in a medicine by following the progress of the drug oxidation reaction,
- determine the reaction order with respect to DCF.

Task 1. Spectral changes in the course of DCF oxidation with $KMnO_4$ are given in Fig. 1, (1 to 10 reflects the reaction progress). Complete table 1 below suggesting which wavelengths can be applied for photometric kinetic determination of DCF. In each case, indicate the direction of the absorbance changes (denote increasing with ↑ and decreasing with ↓).

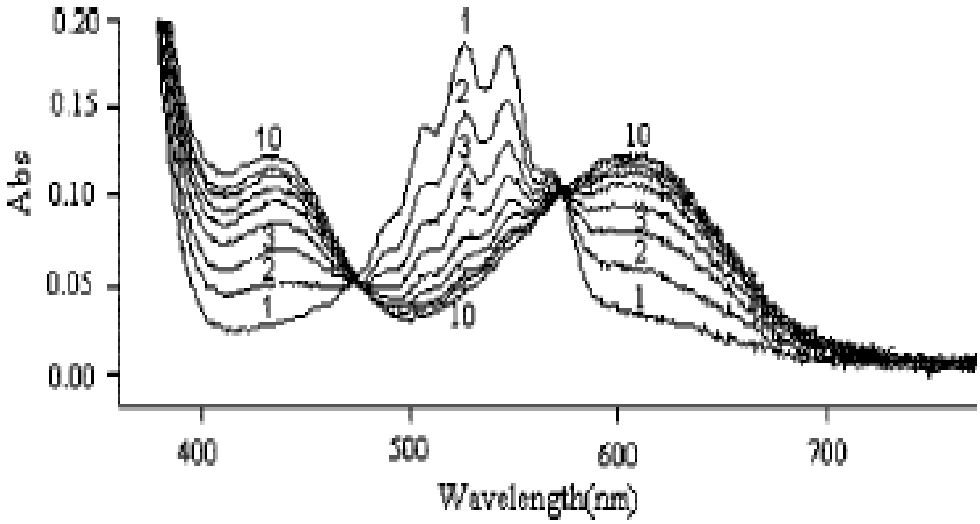


Fig. 1. DCF oxidation with $KMnO_4$

Table 1

#	Wavelength, nm	Yes or No and direction
1	420	
2	480	
3	520	
4	580	
5	610	

Chemical Glass and Equipments

- Photometer, 525 nm
- Thermostat with adaptor
- 2 spectrophotometer cells with a 3.5 cm optical path length
- Magnetic stirrer
- Magnetic stir-bar (medium-size)
- Netbook with adaptor and mouse
- Volumetric flask with a stopper, 100 cm^3
- 2 Graduated pipettes, 2 cm^3
- Memory stick 8 Gb
- Black magnet

Procedure

Part A. Assembling of laboratory equipment

Assemble the laboratory equipment as shown in Fig. 2. Connect the photometer (1), 525 nm (fixed wavelength) and thermostat (2) to the Netbook via USB slots. Connect the thermostat to the cable labeled “Thermo” to the power supply at your work place via the power adapter. Put the optical cuvette (3) on top of the magnetic stirrer (4), pass the cuvette through the photometer from aside (not possible from top down) and place the thermostat over the cuvette from top down (Fig. 2b).

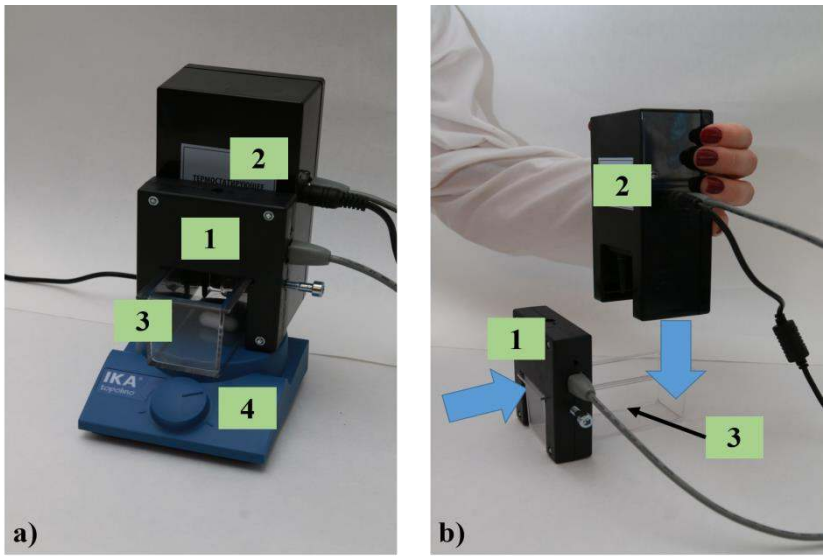


Fig. 2. Laboratory equipment

Hints:

- Plug in your Netbook to the mains before switching on.

- Plug in all the equipment (the photometer and thermostat) before switching on the Netbook. Switch on the mouse.
- If only one window (hereafter referred to as Pattern) instead of two appears after launching the software, quit and re-launch the program.
- Do not unplug ANY device from the USB slot while carrying out the measurements. If it still happens, you will see a warning on the screen. Quit and re-launch the program.
- If your Netbook falls asleep, click the «Setup» button in the Measurements window on the absorbance plot pattern when reverting to the measurements.
- In case you see chaotic temperature changes on the screen, stop and re-start the measurement.

Part B. Plotting of the calibration curve

All measurements needed to plot the calibration curve are carried out at 30 °C with constant initial concentrations of $KMnO_4$ and H_2SO_4. The DCF concentration is varied by using four different aliquots (0.2, 0.4, 0.6, and 0.8 cm^3) of the DCF stock solution.

1. Transfer 5 cm^3 of the H_2SO_4 solution (c = 1 mol dm^{-3}) with a graduated cylinder and 0.2 cm^3 of DCF stock solution using the 2 cm^3 pipette into a 100 cm^3 volumetric flask, dilute up to the mark with distilled water, stopper the flask and mix thoroughly.
2. Carry over the flask contents into the cuvette, put the medium-size stir-bar and switch on the magnetic stirrer. Adjust the stirring speed regulator to the mark shown on Fig. 2a to provide for intensive mixing.
3. Launch the «Chemistry-Practicum» software on the Netbook. The software will detect the external devices (sensors) automatically. You will see two plot patterns (that of absorbance/extinction/optical density, D *vs.* *t*, (s); and that of temperature, *T* (°C) *vs.* *t*, (s) on the display.
4. Set the following parameters in the Menu bars of the corresponding plot patterns (Fig. 3):

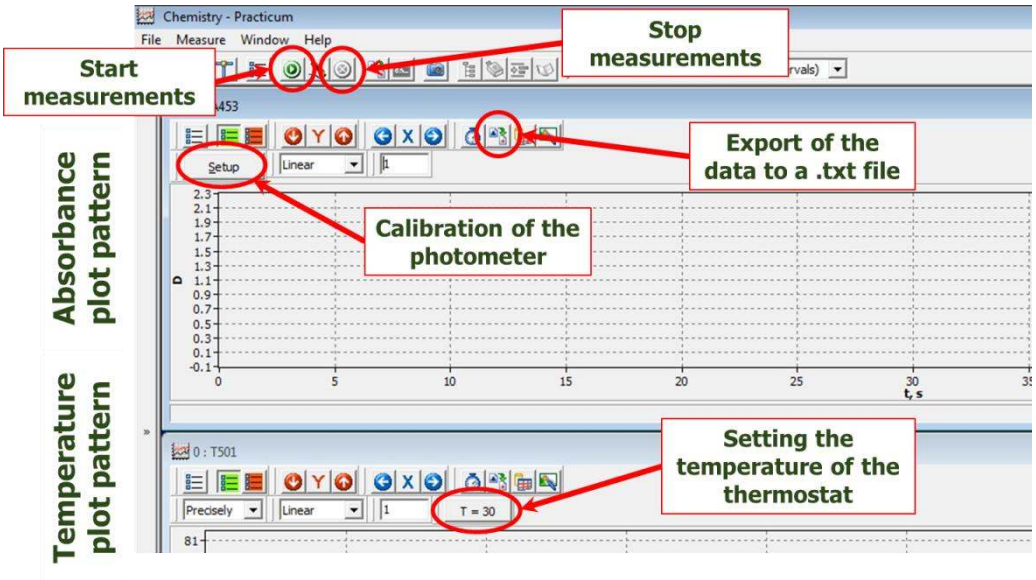


Fig. 3 "Chemistry-Practicum" software interface

- Click the  icon next to the  button («Fixes X-axis maximum on screen») on the absorbance plot pattern. The entire plot will always fit to the screen;
- Click the  button («Sets the Y range») on the absorbance plot pattern and set the absorbance range (the ordinate axis) from -0.1 to 1.1.
- Type "2" (instead of "1") in the box of the measurements interval on the absorbance plot pattern.
- Choose «Precisely» in the «Precisely/Roughly» window on the temperature plot pattern, then click on the «T = X» button and set the required temperature of 30 °C in the pop-up window.
- Calibrate the photometer by clicking the «Setup» button in the Measurements window on the absorbance plot pattern.

Note! Setting the parameters (step 4) is needed only prior to the first measurement.

5. Click the  button («Start measure for chosen sensors») to switch on the thermostat and observe the lamp heating up the solution in the cuvette. Follow the current temperature reported in the line above the plot. Wait until the thermostat lamp switches off, reflecting the set up temperature is attained. Stop the measurements by clicking  button (is activated and turns to red-orange when the measurement is on).

6. Click any part of the absorbance plot pattern to activate it. Take 2 cm^3 of the $KMnO_4$ solution using the 2 cm^3 pipette. Click the  button («Start measure for chosen

sensors») in the Menu bar of the Measurements window and quickly blow out (press the pipette piston) the permanganate solution from the pipette into the cuvette.

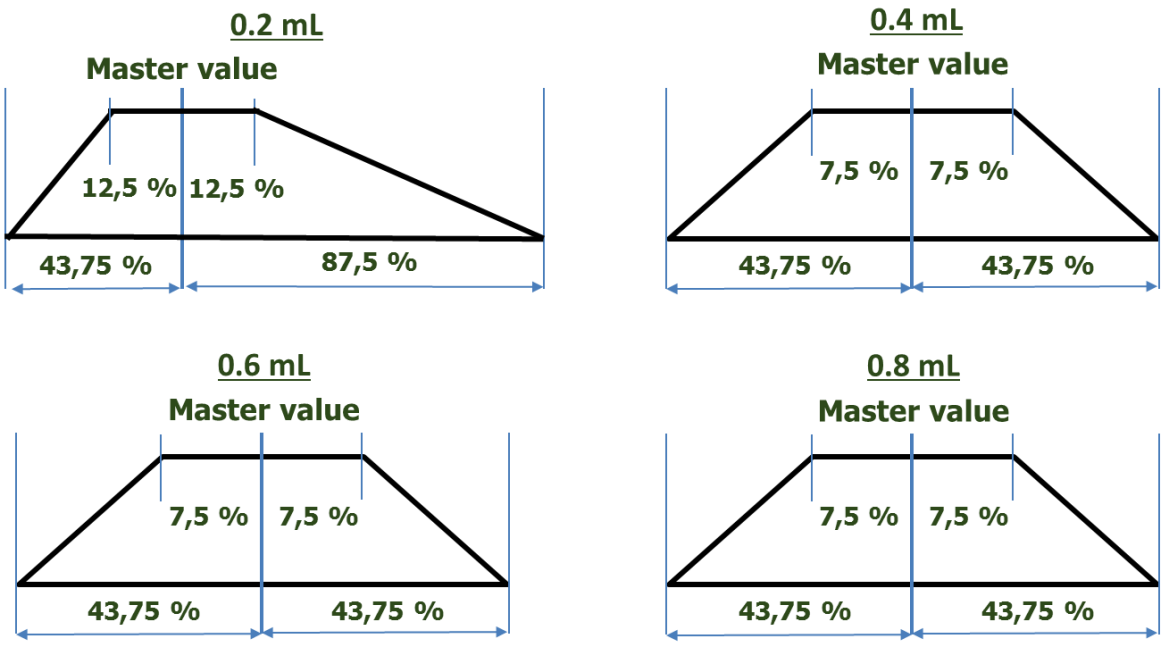
Note! Make sure the temperature in the cuvette equals 30 °C before adding the $KMnO_4$ solution!

7. Observe the progress of the kinetic curve on the screen. Continue measurement for 50 s after adding the $KMnO_4$ solution, then terminate the measurement by clicking the «Stop measurements»  button.
8. Save the data by clicking the  button («Export all the data collected in an external file») in the Menu bar of the absorbance plot pattern, choose the **Desktop** and type the file name “DCF2” (change the name to “DCF4”, or “DCF6”, or “DCF8” in the subsequent experiments).

Note!

- Use only the names of the given format!
- Always save the data on your Desktop before starting the next experiment, otherwise the current data set will be lost after the next click on the  button.
- Make sure absorbance plot pattern is active when exporting the data. Otherwise, you will export invalid results. In case no pattern is chosen, you will get a warning.

9. Empty the cuvette into the Waste bottle, wash thoroughly the cuvette with distilled water. Use black magnet from the outer side of the cuvette to avoid your stir-bar being dropped into the Waste bottle while washing. Wipe carefully the external surfaces of the cuvette with the napkin. Also, use the napkin to dab the thermostat lamp.
10. Repeat the steps 1, 2, 5 - 9 with the other volumes of the DCF stock solution.



Part C.

I. Studying of the DCF containing medicine ("Control")

i) Wash the volumetric flask and prepare the mixture as described above using a 0.4 cm^3 aliquot of the medicine ("Control") instead of the DCF stock solution.

ii) Repeat the steps 1, 2, 5 - 9 described in Part B. When saving the data, name the file "DCFmed".

iii) Repeat the measurement of the "Control" as necessary.

II. Experimental data analysis

i) Open the Excel file on your memory stick in Excel. One by one open your saved data files in Notepad by double clicking on them on Desktop. Choose Edit/Select All in the Menu bar, then right click and copy the selected data into the Excel sheet with the corresponding name (the volume of DCF added or "DCFmed") and choose Edit/Paste in the Menu bar. You will see the experimental data on the Excel sheet (time, s, in column A, and absorbance in column B).

ii) Ignore the values before the maximum. Select columns A and B, and plot the data. Use the "Insert Scatter" icon shown on Fig 4.

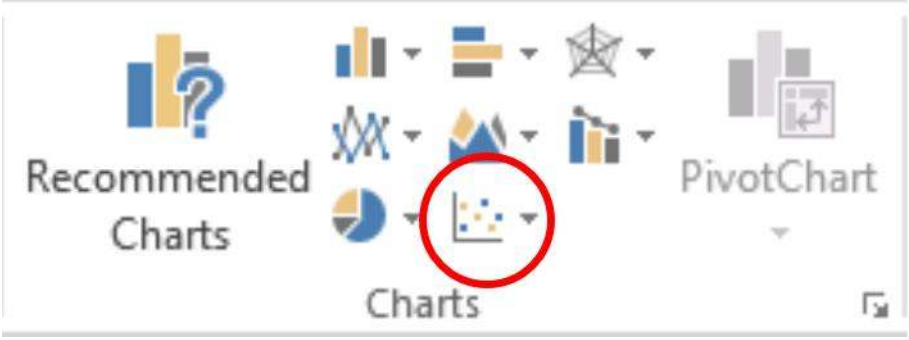


Figure 4. Position of the “Insert Scatter” icon

iii) Choose the initial linear section of the remaining curve (15 to 20 data points), apply linear approximation by adding the linear trend line and bring the parameters to the chart area. Make sure that the R^2 value exceeds 0.98. If needed, decrease the number of the experimental data points plotted removing later data points. Still always search for the most wide range of the experimental data providing for the target R^2 value. Determine the value of the initial rate of absorbance change, v_0.

Note! You will get zero point for this part of the task if less than 12 values are included in the plotted data range.

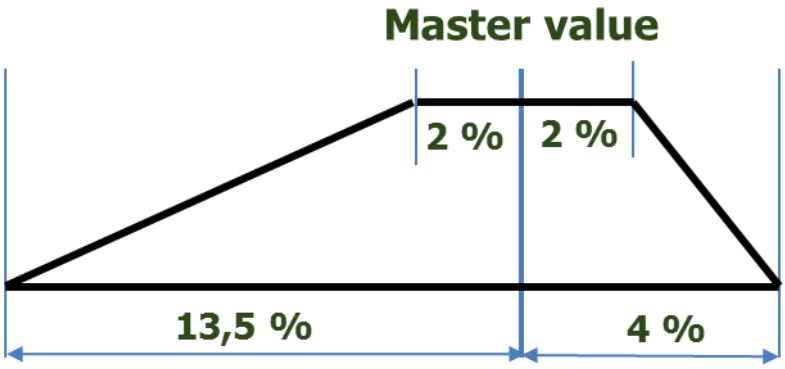
iv) Analyze similarly the experimental data obtained with the other DCF concentrations and with the medicine solution “Control” (“DCFmed” file).

v) Calculate the DCF concentrations in the reaction mixtures (in mg/L). Write down the DCF concentrations and initial rates in appropriate cells of the “Results” Excel sheet.

vi) Plot the calibration graph on the “Results” sheet and use it to determine the DCF concentration in the analyzed mixture prepared from the medicine (“Control”). Fill in the appropriate cells of the “Results” Excel sheet with the coefficients of linear approximation of the calibration graph. Calculate the DCF concentration in the medicine.

vii) Write down the accepted value in the cell F10 of the “Results” sheet.

viii) On the “Results” Excel sheet, graphically determine the reaction order with respect to DCF and write down the exact obtained value in the cell I3.



ix) Once finished, save your file and invite your Lab assistant to demonstrate that you have got experimental data in the Excel file. Sign and get the Lab assistant's signature.

SOLUTION

#	Wavelength, nm	Yes or No and direction
1	420	Yes ↑
2	480	No
3	520	Yes ↓
4	580	No
5	610	Yes ↑