

43rd Austrian Chemistry Olympiad

National Competition

Practical Tasks

2017-05-26

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| Name |  | Nr. |

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| --- | --- | --- | --- | --- | --- | --- |
|  |  | bp | / | rp | / | rpmax |
| 8 | Synthesis |  | / |  | / | 16 |
| 9 | Qualitative Analysis |  | / |  | / | 8 |
| 10 | Quantitative Analysis |  | / |  | / | 16 |
| Total points: | | | |  | / | 40 |

Hints

* You have 5 hours to solve the tasks and may use the following tools:
  + a non-programmable pocket calculator
  + Concept Paper
  + writing utensils (pencil, pen blue or black, ruler or triangle, eraser)
* Only the answers in the boxes or the evaluation sheet for task 3 are used
* Where calculations are required, these have to be written into the boxes in a comprehensible manner.
* If you do not have any space left in a reply box, write the answer on concept paper. Mark the answer with your name and with the task number x.xx.

**When using an open flame, be sure to keep flammable solvents (ethyl ethanoate) closed and at a safe distance.**

**Material list**

**Used in several examples**

1 marker

1 kitchen roll

1 bottle deionized water

1 magnetic stirrer with magnetic stir bar

20 plastic pasteur pipettes in a beaker (used in task 8 and 9)

1 small spatula

1 tweezers

2 cryorack

1 test tube rack

1 small funnel (used in task 9 and 10)

Task 8 – Synthesis (red color code)

1 100 mL Erlenmeyer flask with 3.00 g vanillin

1 plastic dish for cooling with water and ice

1 small flask with 20 mL NaOH (5% (w/w))

1 test tube with 1g NaBH4

1 small flask with approx. 30 mL HCl 3M

1 small flask with approx. 20 mL ethyl acetate

1 thermometer

1 glass rod

1 Eppendorf tube with a small amount of vanillin (labelled „E“)

2 empty Eppendorf tubes (labelled „RP“ and „P“)

1 TLC chamber

3 capillaries 2µL in Eppendorf tube

1 pH paper

1 Buchner funnel

1 Beaker 400 mL for recrystallization

2 watch glasses, one with student number

1 triangle

available from the lab assistant

1 TLC plate (a second one if necessary)

available in the lab

2 vacuum flasks with Büchner ring

2 water aspirators with vacuum tube

2 flasks with acetone

2 lab balances

2-3 ice crates

1-2 Kofler benches

1-2 UV lamps

1 lab oven (70°C)

Task 9 – Qualitative Analysis (yellow color code)

1 Bunsen burner

1 matchbox

1 magnesia stick

1 spot test grid

10 test tubes 12x100mm, one with plug

4 filter paper sheets

1 test tube holder

1 dropper bottle with approx. 20 mL nitric acid 2M

1 plastic pasteur pipette with approx. 2 mL sodium sulfide solution 0.5M

1 plastic Pasteur pipette with approx. 2 mL silver nitrate solution 0.1M

1 test tube with approx. 7 mL sodium hydroxide solution 2M

Task 10 – Quantitative Analysis (blue color code)

1 burette with holder and support stand

1 pipette filler

1 volumetric pipette 25 mL

1 graduated pipette 10 mL

6 test tubes with screw cap

1 test tube 16x160mm with markings at 5mL and 10mL

1 Erlenmeyer flask 200 mL

1 watch glass as a cover for the Erlenmeyer flask

1 beaker 600mL

6 cuvettes in rack

1 brown glass flask with a solution of KMnO4 (

1 flask with H2SO4 5M

1 flask with 100mL solution of FeCl3

3 Eppendorf tubes with 1 g zinc powder each

1 flask with 10 mL solution of KSCN (

1 flask with 45 mL dilute nitric acid 0.2M

1 flask with sodium oxalate solution (concentration on label)

available in the lab

1-2 photometers

Task 8 16 points

Synthesis of a white powder out of the natural identic compound „vanillin“

**Principle:**

In this reaction vanillin (4-Hydroxy-3-methoxybenzencarbaldehyd, *M* = 152,15 g/mol) reacts with sodium borohydride (NaBH4). The resulting product has a molar mass of *M* = 154,17 g/mol.

Synthesis of the crude product:

* In a 100 mL Erlenmeyer flask there are 3.00 g vanillin.
* Add 20 mL NaOH (5% (w/w)) and stir until the starting material has dissolved completely.
* The temperature of the reaction mixture is kept between 20-25°C during the synthesis. For this, a plastic dish filled with water is used for cooling. As required ice cubes can also be used for this purpose.
* Permanent temperature control and the use of the magnetic stirrer are necessary during the synthesis. **When planning the experiment, remember that you need a cold heating plate!**
* Then the NaBH4 tablet is added and the reaction mixture is stirred for about 25 minutes.
* Especially during dissolution of sodium borohydride a permanent temperature control is of importance. NaBH4 takes about 5 mins to dissolve.
* Add the HCl (3M) **drop by drop** in this step (the Erlenmeyer flask is still in the plastic dish filled with water). Before you add the next drop of HCl, wait until the gas evolution has stopped. When the gas evolution is finished, measure the pH of the reaction mixture. The pH-value must be acidic (total necessary volume of HCl about 22 mL).
* The reaction mixture is left standing at room temperature until crystals are formed, then it is cooled in the ice / water bath (if the crystallization does not start, you might scratch with the glass rod on the bottom of the flask).
* Filter off the precipitated crude product through a Buchner funnel using suction.
* For TLC analysis put material of the crude product into an Eppendorf-reaction tube („RP“)

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| 8.1 Show the lab assistant the crude product and wait for confirmation. |
| Crude product was present: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (signature) |

**Work-up and purification:**

* Recrystallize the crude product in ethyl ethaneoat. For this purpose it is transferred into the cleaned Erlenmeyer flasks. Add 4 mL ethyl ethaneoat and heat it in the boiling water bath until the material has dissolved completely.
* The hot solution is taken from the heating plate, cooled to room temperature and finally placed in an ice-water bath (10-15 minutes).
* In case of no crystallization despite scratching, some solvent must be removed.
* Filter the product through the Büchner funnel using suction and then draw air through the solid (3 mins, first drying step).
* Transfer the product to the pre-weighed petri-dish labelled with the number of your laboratory place and hand it over to the lab assistant for drying (at 70°C for 30 minutes).
* Before handing in the product place a small amount of it in the Eppendorf tube (**„P“**). Use the same amount of the product like the one of the educt that exists in tube „**E**“.
* Ask the lab assistant for your dried product after 30 minutes.

Analysis and purity control:

* Determine **yield** and **melting point** of your product.
* Purity control:

The educt, the crude product and the product are dissolved in the Eppendorf tubes with 10 drops ethyl ethaneoat respectively. Prepare and develop a TLC in the usual way. Use ethyl ethaneoat as mobile phase.

**Give your prepared and (in a usual way) analysed TLC plate (with your laboratory place number in the upper right corner) to the lab assistant.**

If the DC does not succeed in the desired form, one (!) additional DC plate can be requested (without points deduction) from the hall supervisor.

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| 8.2 Write down the equation for the synthesis. Use constitutional formulae for this purpose. |
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| 8.3 Calculate your yield in g and % of the theoretical mass. |
| *mass tara:\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ mass product: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_* |

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| 8.4 Determine and write down the melting point. |
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| 8.5 Determine and write down your Rf values.... |
| Rf-value starting material: Rf-value product: |
| 8.6 Explain verbally and with an equation why the use of NaOH in the first step is necessary. |
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| 8.7 Explain the reason for the different Rf-values between starting material and product. |
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Task 9 8 points

Qualitative Analysis

You have obtained 6 samples, all of which are salts. One sample is a mixture of two salts which can be separated by different solubility behavior.

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| 9.1 Complete the table according to your analysis results. | | |
| sample no. | formula | reasons |
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Task 10 16 Points

Quantitative Analysis: Determination of a complex formation constant

In this task you should determine the complex formation constant and the molar extinction coeffizient *ε* of the complex [Fe(SCN)]2+ using photometry.

In a first step you have to use manganometric titration.

Manganometric titration is applied to establish the concentration of the Iron(III) chloride stock solution in a first step. For this purpose iron(III) is reduced with zinc powder in acidic solution leading to iron(II) species.

You determine the exact concentration of the permanganat solution by titration with sodium oxalate with a known concentration. The reaction between oxalate and permanganate proceeds slowly at low temperature and is catalyzed by manganese(II) ions. Thus the hot solution is titrated. After addition of the first milliliters of permanganate you have to wait until the reaction has started.

Keep in mind to **wash and to condition volumetric glass dishes** if it is necessary.

**Disposal** permanganate containing solutions (you identify them because of the pink color). All other solutions can be washed into the sink.

Determination of the exact permanganat concentration

25.0 mL of the sodium oxalate solution were pipetted into the 200 mL Erlenmeyer flask.

Dilute with deionized water up to 50 mL and add 5 mL 5 M H2SO4 (use the test tube with the marking).

Heat the solution until a temperature of 70°C is reached. Titrate the solution while it is still hot with the potassium permanganate solution until a stable but soft pink color is reached. If necessary repeat the titration.

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| 10.1 Write down your titration volume (average value). |
| V = |
| 10.2 Calculate the concentration of your potassium permanganate solution. |
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Determination of the Iron(III) concentration:

Pipette 25.0 mL of the Iron(III) chlorid stock solution in the erlenmeyer flask. Add 10 mL 5M H2SO4 (use the test tube with the marking). Then add 1 g zinc powder (it is preweighted in a eppendorf test tube) **in two portions**.

Stir the solution and close the Erlenmeyer flask with a watch glass.

When the gas evolution becomes weaker, put the flask on to the heat plate until the whole zinc powder has dissolved.

Titrate the cooled solution (room temperature) until a stable but soft pink color is reached.

If necessary repeat the titration with the cleaned Erlenmeyer flask.

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| 10.3 Write down your titration volume (average value). |
| V = |
| 10.4 Calculate the concentration of your iron(III) chloride solution. |
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Theoretical background for evaluation of the photometrical measurements

Formation of the iron(III) complex:

The complex formation constant:

The Lambert-Beer law () was applied and the equation was transformed as described[[1]](#footnote-1).

The equation contains two unknowns () and provides one result only, when several measurements were proceed. For this purpose againsted were plotted respectively. You obtain a straight line with a **slope** of and a **y-intercept** of

The thickness of the cuvette is known (1 cm), thus *ε* and *Kβ* can be calculated.

The slope and the y-intercept will be calculated by the lab assistent using a computer.

Preparation of the solutions, the photometrical measurement and their evaluation

Lable the closable test tubes with the numbers in the given table below. Pipette using a graduated pipette the given volumina of the FeCl3 stock solution, of the 0.2M HNO3 and the KSCN solution in to the test tubes. Close the test tubes and homogenize them by shaking.

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|  | volumina in mL | | | |
| No | *V*(FeCl3) | *V*(KSCN) | *V*(HNO3) | V(ges) |
| **B** | 3 | 0 | 7 | 10 |
| **1** | 1 | 1 | 8 | 10 |
| **2** | 2 | 1 | 7 | 10 |
| **3** | 3 | 1 | 6 | 10 |
| **4** | 4 | 1 | 5 | 10 |
| **5** | 5 | 1 | 4 | 10 |

Fill the solutions in to the cuvettes respectively and measure the absorptions (*A*) using a wavelength of *λ* = 457nm. Notice, the solution of test tube marked with **B** is used as the blank.

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| 10.5 Write down the measured absorption values and the calculated concentrations of FeCl3 on the evaluation sheet and hand it over to the lab assistant. |

You get the evaluation sheet and the computer evaluation. This contains a graphical representation and numeric values for and

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| 10.6 Calculate and using these numeric values. |
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1. Frank, H. S.; Oswalt, R. L. *J. Am. Chem. Soc.* **1947**, *69,* 1321 [↑](#footnote-ref-1)