

44th Austrian Chemistry Olympiad

Federal Competition

Practical Part

June 1st, 2018

|  |  |  |
| --- | --- | --- |
| Name |  | Desk Nr. |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  |  | bp | / | rp | / | rpmax |
| 6 | Synthesis |  | / |  | / | 16 |
| 7 | Qualitative Analysis |  | / |  | / | 8 |
| 8 | Quantitative Analysis |  | / |  | / | 16 |
| Sum of points: |  | / | 40 |

**Please note:**

* You have five hours to solve the problems and may use the following tools:
	+ Non-programmable calculator
	+ Concept paper
	+ Writing utensil (pencil, blue- or black-coloured pen, ruler or set square, eraser)
* You are not allowed to separate the parts of this booklet.
* Only **answers written into the boxes** will be used for scoring.
* Wherever you ***need to calculate*** („Calculate…“), write the respective calculus into the corresponding boxes ***in a COMPREHENSIBLE way.***
* If you run out of space in an answer box, write the solution to the problem on concept paper. Write your ***name*** on top of that paper. *Clearly and unmistakably* mark the answer with the corresponding problem number x.xx

**Plan your work carefully.**

**When using the magnetic stirrer / hot plate, give special consideration to the necessary temperatures and in which order you can reach them.**

List of Materials

|  |  |  |
| --- | --- | --- |
|  |  | To be used in problem |
| 1 |  | Bottle containing deionized water | 6, 7, 8 |
| 1 |  | Kitchen roll | 6, 7, 8 |
| 1 |  | Marker pen | 6, 7, 8 |
| 1 |  | Tweezers | 6, 7, 8 |
| 1 |  | pH indicator paper in a test tube | 7, 8 |
| 1 |  | Color scale | 7, 8 |
| 1 |  | Beaker glass 400mL for waste | 7, 8 |
| 1 |  | Spatula | 7, 8 |
| 1 |  | Magnetic stirrer + hot plate | 7, 8 |
| 1 |  | Magnetic stirring bar | 7, 8 |
| 1 |  | Cryo rack | 6, 8 |
|  |  |  |  |
| 1 |  | Glass rod | 6 |
| 1 |  | Glass frit | 6 |
| 1 |  | Test tube with marking for 5 mL | 6 |
| 1 |  | Bowl for ice bath | 6 |
| 3 |  | Empty plastic pasteur pipets (PPP) | 6 |
| 2 |  | Empty Eppendorf vials | 6 |
| 1 |  | TLC plate silica gel | 6 |
| 1 |  | Jar containing mobile phase for TLC (10mL ethyl acetate) | 6 |
| 1 |  | Medium-sized watch glass | 6 |
| 1 |  | Petri dish annotated with desk number | 6 |
| 3 |  | TLC capillaries in small snap-on lid vial | 6 |
| 1 |  | 25mL volumetric flask | 6 |
| 1 |  | Pencil | 6 |
| 1 |  | Set square | 6 |
| 1 | ⚫ | 100mL Erlenmeyer flask containing 1.70 g phenetidine | 6 |
| 1 | ⚫ | PE bottle containing 30 mL isopropanol | 6 |
| 1 | ⚫ | Snap-on vial containing 1.4 g KOCN | 6 |
| 1 | ⚫ | 100mL PE bottle containing 50 mL acetic acid 10% | 6 |
| 1 | ⚫ | Eppendorf vial containing acetone „Ac“ (for TLC) | 6 |
| 1 | ⚫ | Eppendorf vial containing educt „E“ (dissolved in acetone for TLC) | 6 |

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|  |  | vorgesehen für Aufgabe |
| 1 |  | Spot test plate | 7 |
| 5 |  | Toothpicks | 7 |
| 1 |  | Test tube 12x100 + plug | 7 |
| 1 |  | PPP „S“ sodium sulfide solution | 7 |
| 1 |  | PPP „Na“ potassium hydroxide solution | 7 |
| 1 |  | PPP „Ag“ silver nitrate solution | 7 |
| 1 |  | PPP „Ba“ barium nitrate | 7 |
| 8 |  | Samples | 7 |
|  |  |  |  |
|  |  |  |  |
| 1 |  | Spatula | 8 |
| 2 |  | Watch glasses small | 8 |
| 1 |  | 10mL volumetric pipette | 8 |
| 1 | ⚫ | Eppendorf vial containing 3-5 boiling stones „S“ | 8 |
| 1 |  | Rubber bulb | 8 |
| 3 |  | Erlenmeyer flask 250mL | 8 |
| 1 |  | Stand + buret | 8 |
| 1 |  | Test tube 16x160 | 8 |
| 1 |  | PPP empty „HNO3“ | 8 |
| 1 | ⚫ | 100mL volumetric flask + sample (desk number) | 8 |
| 1 | ⚫ | Dropper bottle containing 150mL ZnSO4 | 8 |
| 1 | ⚫ | Dropper bottle containing 200mL EDTA | 8 |
| 1 | ⚫ | Dropper bottle containing 10mL Sulfosalicylsäure | 8 |
| 1 | ⚫ | Screw cap bottle containing 20mL 1M HNO3 | 8 |
| 1 | ⚫ | Eppendorf vial containing xylenol orange indikator „X“ | 8 |
| 1 | ⚫ | Powder bottle containing 20g sodium acetate „NaAc“ | 8 |
|  |  |
| **For joint use in the room** |
|  |  | Container with washing acetone |  |
|  |  | Büchner flasks |  |
|  |  | Aspirator pumps |  |
|  |  | Container with deionized water |  |
|  |  | Ice cube stock |  |
|  |  | Scales |  |
|  |  | Kofler bench |  |
|  |  | Hairdryer |  |
|  |  | UV lampDrying cabinet |  |

Problem 6 16 Points

Synthesis of a Sweetener

Background:

Many derivatives of urea are important due to their physiological or pharmaceuticyl activity. *p*-Phenetidine-urea („Dulcin“) is a 200 times more intensive sweetener than saccharose. Therefore it was frequently used as a sweetener together with saccharine. However, due to its damaging properties to health it has been banned in Europe and the USA several years ago. The aim of this problem is to synthesize this sweetener by converting *p*-phenetidine with potassium cyanate in aqueous acetic acid.



Synthesis of the Raw Material:

* You find 1.70 g *p*-phenetidine (4-ethoxyaniline) in the 100 mL Erlenmeyer flask.
* Add 50 mL acetic acid (10% (*w*/*w*)) to *p*-phenetidine followed by stirring rapidly for a short period of time.
* Dissolve 1.40 g potassium cyanate („K“) in 5 mL water.
* Add the potassium cyanate solution dropwise within 7-10 min while vigorously stirring with the magnetic stirrer.
* Continue stirring for 15 minutes at room temperature.
* Then place the flask into an ice/water bath for 45 min. Occasionally stir vigorously with a glass rod.
* Finally, filtrate the solid raw product by suction through a glass frit. Wash it by adding about 40 mL cold water in several portions.
* Transfer a small amount of the raw product into an Eppendorf vial for TLC analysis.

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| 6.1 Present your raw product to the supervisor to obtain confirmation. |
|  Raw product was obtained: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (paraph) |

**Work-up and Purification:**

* Recrystallize the raw product with propan-2-ol. Use the cleaned Erlenmeyer flask for that purpose.
* Cool the solution to room temperature and place the flask into an ice/water bath for 10 minutes.
* Finally, filtrate the product by suction on the cleaned frit and wash with a small amount of cold water.
* Transfer a small amount of the product into an Eppendorf vial for TLC analysis.
* Transfer the product onto the tared watch glass and hand it over to the lab supervisor for drying (80°C, ca. 20 minutes).
* Fetch the product from lab supervisor after 20 minutes.

Analysis and Assessing Purity:

* Determine **yield** and **melting point**.
* Analysis:

During drying you can analyze your products by TLC.

 Dissolve both raw product (RP) and purified product (P) in acetone (taken from the Eppendorf vial „Ac“), respectively. The educt (E) is already dissolved in acetone.

 Prepare and develop a TLC plate following the usual procedeures. Use ethyl acetate (=ethyl ethanoate) as the mobile phase.

 **Develop und evaluate the TLC plate following the known procedures. Then hand it over to the lab supervisor. For that purpose mark the upper right-hand corner of the TLC plate with your desk number.**

 Should your TLC not have succeeded in the desired way, you may obtain **one more TLC** plate without losing points.

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| 6.2 Caclulate your yield in g and % of theory. |
|  *Mass Tara:\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ Mass Product: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_* |

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| 6.3 Give the melting point of your product: |
|  |
| 6.4 Give the Rf values: |
| Rf value educt: Rf value raw product: Rf value product: |
| 6.5 Briefly explain the reason for the different Rf values of educt and product. |
|  |

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| 6.6 Tick all correct ways of interpreting the thin layer chromatogramme. You will lose points for ticking wrong boxes. However, you cannot reach a negative number of points within 6.6. |
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|  | Two substance spots for RP indicate complete reaction. |
|  | Two substance spots for RP indicate a high yield. |
|  | Two substance spots for RP indicate contamination by a side product. |
|  | Two substance spots for RP indicate contamination by the educt. |
|  | Two substance spots for the RP and one substance spot for P indicate further reaction during work-up. |
|  | Two substance spots for the RP and one substance spot for P indicate that the contamination has been removed during work-up. |

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Problem 7 8 Points

Qualitative Analysis

You have received 8 liquid samples. Those are either aqueous solutions of salts or acids, or pure substances. Four samples contain salt solutions comprising sodium as a cation.

**Furthermore, you have at your disposal:**

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| --- | --- |
| * Sodium sulfide solution (0,1 M) - „**S**“
* Sodium hydroxide solut. (2M) - „**Na**“
* Silver nitrate solution (0,1 M) – „**Ag**“
* Barium nitrate solution (0,1 M) – „**Ba**“
 | * pH indicator paper
* 1 empty test tube 12x100 with plug
* Toothpicks
* Spot test plate
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| Complete the table based on the results of your analyses. |
|  | Formula | Justification |
| 1 |  |  |
| 2 |  |  |
| 3 |  |  |
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| 5 |  |  |
| 6 |  |  |
| 7 |  |  |
| 8 |  |  |

Problem 8 16 Points

Quantitative Analysis: Iron and Aluminum in a Sample

Complexometric titrations allow for determining Fe3+ and Al3+ present in the same sample. For that purpose, one titrates Fe3+ at *pH* = 2 - 3 directly with EDTA. Then excess EDTA is added to coordinate Al3+. Remaining EDTA is then re-titrated with Zn2+ at pH 5-6. Before doing so, one needs to determine the exact concentration of Zn2+ in the solution used.

Do not forget to clean and condition volumetric instruments when necessary.

If it turns out that you do not have enough sodium acetate (“NaAc”), you can receive **one** refill without losing points.

**Disposal**: All solutions can be disposed of via the sink.

A. Determining the exact concentration of zinc sulfate

Add 40 ml (2 test tubes full) of distilled water and 1 mL nitric acid *c*=1M (PPP) to 10.00 mL ZnSO4 solution. Adjust to pH 5-6 by adding a spoonful of NaAc. Then add a tip of a spatula xylenol orange indicator poweder (“X”) and titrate with EDTA - solution (*c* = 0.0500 mol/L) purple red to yellow (“*V*Zn“).

B. Determining the concentration of Fe3+

After making up the sample to the mark, transfer 10.00 mL of the solution into an Erlenmeyer flask and add ca. 20 mL (one full reaction tube) deionized water. Then add 1 M nitric acid (PPP) dropwise to reach a pH between 2 and 3. Now add a few drops of sulfosalicylic acid indicator solution and titrate with EDTA (*c* = 0.0500 mol/L) from deep purple to light yellow. Just before reaching the end point (“*V*Fe“), you need to titrate **very slowly**! Considering the next step, it is important **not to overtitrate** the solution!

C. Determining the concentration of Al3+

Add 30.00 mL EDTA (from the burette – be careful that the flow is not too fast) to the titrated sample from (B). After adding 3 mL (PPP) 1 M nitric acid and 1-2 boiling stones let the solution boiling for 30 minutes; cover the flask with a watch glass during this time. You can place **up to two flasks** onto the hot plate! Add solid sodium acetate to the hot solution until pH is between 5 and 6. Then add the tip of a spatula of xlyenol orange indiactor powder (“X“) and titrate the still warm solution with zinc sulfate solution from yellow to orange-red (“*V*Al“).

Hint: In this case the color change can be more easily seen **from the side**.

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| 8.1 Report your titration volumes. |
| “VZn“ =  | “VFe“ =  | “VAl“ =  |
| 8.2 Calculate the concentrations: |
| c(Zn2+) =  | c(Fe3+) =  | c(Al3+) =  |
|  |