
# 19th Chemistry Olympiad of the Baltic States

Vilnius, Lithuania, 2011

## Practical examination

# Introduction

## General information

• Keep your safety or optical glasses on, while working in laboratory. Fill pipettes only with a bulb. Food is strongly prohibited in the laboratory.
• Participants must follow safety rules, be polite and keep instruments and your working place in neat order. Do not hesitate to ask laboratory assistant about safety.
• You can only start to work once the starting command is given.
• You are given 5 hours to complete your experimental work and fill the answer sheets. You will be notified 15 before the end of practical examination. You must stop working once the "stop" signal is given. If you are late 5 min or more, your work will be disqualified and you will be given 0 points for practical examination.
• Write your last name and code (found on your working place) in designated areas on your answer sheets.
• All results should be written in boxed areas in answer sheets. Information written in other parts of answer sheets will not be graded. Do not write on the other side of answer sheets. Ask laboratory assistant, if you need paper for calculations or clean answer sheet.
• Do not leave the laboratory without permission.
• You can only use materials given to you in the laboratory.
• Number of decimal places in calculations must be in accordance with experimental error and data analysis principles. You will be penalized for inaccurate calculations, even if your experimental skills are faultless.

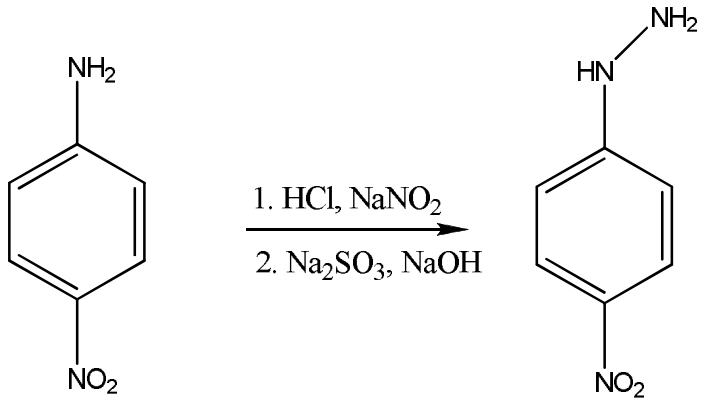
**Utilization of spilled chemicals and broken glassware**

- All filtrates of organic compounds, washing liquids and other waste materials should be placed in waste containers.
- When disposing waste, look for the appropriate waste container.
- Broken glassware should be placed in waste basket.

## Problem 1. *p*-nitrophenylhydrazine synthesis

Diazotization reaction was discovered in 1858 by Peter Griess. It has been immediately noted that diazonium compounds are quite reactive and can be a valuable reagent in organic synthesis. Substituted aromatic hydrazines can be prepared by reducing the corresponding diazonium salts. Hydrazines can react with aldehydes and ketones resulting in formation of the corresponding hydrazones, which have been used for the determination of the carbonyl compound by measuring the melting point of the hydrazone. This method has fallen out of use due to advancement of spectroscopic techniques. However reactions with diazonium compounds are still used.

In this task you will attempt to produce *p*-nitrophenylhydrazine by preparing *p*-nitrophenyldiazonium salt from *p*-nitroaniline and reducing it with sodium sulphite in basic media.



**Apparatus and glassware**
10 mL beaker (2)
25 mL beaker (1)
Pasteur pipett (4)
Plastic Pasteur pipett (2)
2 mL pipett
3-way bulb
Glass rod
Spatula
Ice bath
Warm water bath (in hood)
Thermometer
Graduated cylinder (10-20 mL)
Magnetic stirer with hot plate
Magnetic stiring rod
Vacuum filtration set
Petri dish
Beaker for TLC
TLC plate
Eluent (EtOAc and PE (1:1))
Capillars for TLC
Tweezers
Vials for standart solution
Filter papper
Cotton
Ruler
Pencil
Wire
Testtube

**Chemicals and reagents:**
*p*- nitroaniline labeled as PNA (250 mg in vial)
$NaNO_2$ (nearby the balance)
$Na_2SO_3$ (nearby the balance)
NaOH (nearby the balance)
Concentrated HCl (in hood)
Saturated sodium acetate
Ethanol
Ethyl acetate

# Synthesis

You can use time gaps in this synthesis to perform tasks for Problem 2.

1. At first you will have to prepare three separate solutions:

**Solution A.** All your p-nitroaniline sample (labeled PNA) is mixed with 0.5 mL of HCl and 0.5 mL of $H_2O$ in a 10 mL beaker. Mixture is heated until *p*-nitroaniline is dissolved and then by transferring the beaker to an ice bath *p*-nitroamonnium chloride precipitate is obtained as fine crystals. The mixture is left to stand in an ice bath.

**Solution B.** 0.13 g of $NaNO_2$ is dissolved in 0.5 mL of water in a 10 mL beaker and is also cooled in an ice bath.

**Solution C.** A solution of 0.70 g $Na_2SO_3$ and 0.13 g of NaOH in 3 mL of water is prepared in a 25 mL beaker by heating the mixture on a hotplate. After the materials have dissolved the solution is also cooled in an ice bath.

2. By keeping the temperature below 5 °C and with constant stirring **solution B** is slowly added to **solution A**. The resulting solution is left to react for a few minutes.

3. The resulting solution of *p*-nitrophenyldiazonium salt is added dropwise to the **solution C** with constant stirring. The resulting mixture is left to stand in an ice bath for at least 10 minutes.

4. The resulting solution is acidified by the addition of 6 mL of concentrated HCl (in hood) and heated to 30-40 °C (water bath in hood) for about 5 min and then it is left to stand for at least 40 minutes in room temperature.

5. Mixture is heated to boiling and boiled for 5 min. Then it is gradually cooled down and put into ice bath and left to stand for about half an hour.

6. The precipitate is filtered off (vacuum filtration) and transferred to a beaker with about 5 mL of water. By heating the beaker some of the precipitate is dissolved. The insoluble part is filtered off by using the Pasteur pipette and some cotton (you can use a piece of wire for pushing small amount of cotton into the Pasteur pipette), filtrate is collected in a separate clean beaker.

7. Saturated sodium acetate solution (approximately the same volume of this solution as volume of the filtrate) is added to the filtrate. After a short while *p*-nitrophenylhydrazine precipitates. It is filtered off (vacuum filtration) and transferred to the numbered Petri dish (together with the filter paper that was used for filtration).

## Analysis

You have to prepare a solution of a small amount of your reaction product by dissolving it in ethyl acetate (if you have failed to synthesize the product you should ask for a prepared sample). A solution of *p*-nitroaniline is given to you. By using a glass capillary a small amount of both solutions is placed on a startline at separate places.
Small amount of eluent is added to a beaker (the level of the eluent must be lower than the startline) and the TLC plate is placed vertically in it. Cover beaker by lid. When the eluent has traveled about 90 percent of its path the plate is removed and the finish line is marked.

*Hint. p-nitrophenylhydrazine is more polar then p-nitroaniline.*

## Problem 2. Determination of purity of potassium bisoxalatocuprate(II) dihydrate

### Apparatus and glassware

Graduated cylinder (10-20 mL) (1)
Burette (2)
Funnel for burette (2)
Laboratory stand with clamps (1)
3-way bulb
Volumetric pipette (20.00 mL) (1)
Erlenmeyer flask (1)
Glass rod (1)

### Chemicals and reagents

Sample that was obtained by dissolution of mixture of $K_2Cu(C_2O_4)_2 \cdot 2H_2O$ and $K_2C_2O_4 \cdot H_2O$
0.03 M $KMnO_4$ solution (exact concentration will be given in the laboratory)
0.02 M $Na_2S_2O_3$ solution (exact concentration will be given in the laboratory)
2 M $H_2SO_4$
Starch indicator
Distilled water
10% acetic acid solution with dropper (in hood)
Solid $Na_2CO_3$ (in hood)
pH indicator paper (in hood)
Solid KI (nearby the balance)
Solid KSCN (nearby the balance)
10% $MnSO_4$ solution with dropper

Student tried to synthesise potassium bisoxalatocuprate(II) dehydrate $K_2Cu(C_2O_4)_2 \cdot 2H_2O$, but due to some errors his product was contaminated with potassium oxalate monohydrate $K_2C_2O_4 \cdot H_2O$. Trying to determine purity of his product he dissolved some amount of his product in water. You have got a sample of this solution and your task is to determine the mass percent of $K_2Cu(C_2O_4)_2 \cdot 2H_2O$ in mixture of $K_2Cu(C_2O_4)_2 \cdot 2H_2O$ and $K_2C_2O_4 \cdot H_2O$ that have been dissolved. You can do this by two different titrations. Amount of oxalate ions can be determined by titration with permanganate solution. Amount of copper can be determined by iodine-thiosulfate titration.

**Attention**. It will be necessary reuse some glassware, so take care for appropriate procedures to avoid contamination or dilution of your solutions.

## A. Determination of oxalate

Take 20.00 mL of the given sample and transfer it into Erlenmeyer flask. Add approximately 10 mL of 2 M $H_2SO_4$. Heat the solution to about 80 °C. Then add 10 drops of 10% $MnSO_4$ and titrate with 0.03 M $KMnO_4$ solution (exact concentration will be presented in the laboratory) until the colour of the solution becomes pink persistent for 1 min. Record the volume of $KMnO_4$ solution used.

**Attention.** Do not discard your solution in the Erlenmeyer flask. You will need the same solution in step B.

Chemical equation of the titration reaction:

$16\ H^+(aq) + 2\ MnO_4^-(aq) + 5\ C_2O_4^{2-}(aq) \rightarrow 10\ CO_2(g) + 2\ Mn^{2+}(aq) + 8\ H_2O(l)$

## B. Determination of copper

Carefully add solid $Na_2CO_3$ to the solution that was obtained in previous step. Continue adding $Na_2CO_3$ until a precipitate appears. Then add 10% acetic acid until pH is about 5. Finally add about 1 g of solid potassium iodide into the solution. Titrate the liberated iodine with 0.02 M $Na_2S_2O_3$ solution (exact concentration will be presented in the laboratory). Use starch solution indicator. When you are very close to the endpoint, add 1 g of solid KSCN (this will release iodine adsorbed on the solid CuI). Record the volume of $Na_2S_2O_3$ solution used.

Chemical equations:

$2\ Cu^{2+}(aq) + 5\ I^-(aq) \rightarrow 2CuI(s) + I_3^-(aq)$
$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow 3I^-(aq) + S_4O_6^{2-}(aq)$

Repeat your titrations as many times as you think is necessary.

Calculate mass percent of $K_2Cu(C_2O_4)_2 \cdot 2H_2O$ in mixture of $K_2Cu(C_2O_4)_2 \cdot 2H_2O$ and $K_2C_2O_4 \cdot H_2O$