# 24th BChO, 2016, Tartu, Estonia

Problem 1 – APPLIED, ELECTRO – Lead-acid battery

The lead-acid rechargeable battery is still one of the most common car batteries at the beginning of the 21st century. It has some superior characteristics, and it could be almost completely recycled. During the discharge process, the lead of one electrode and lead(IV) oxide of the other electrode are converted into lead sulfate. The sulfuric acid is used as the electrolyte.

a) Write the anode, cathode and total reactions of the lead-acid battery during the discharge process.

The solubility product of $PbSO_4$ is K_{sp} = 1.6·10^{-8}. The Latimer diagram of lead (in acid) is:

$$PbO_2 \xrightarrow{\ E^0 = 1.454\ V\ } Pb^{2+} \xrightarrow{\ E^0 = -0.126\ V\ } Pb$$
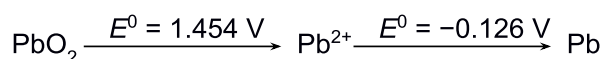
b) Is the disproportion reaction of lead(II) ions a spontaneous process? Justify the answer using calculations.

c) Calculate the open circuit potential $E_{cell}°$ of one cell of the fully charged battery.

d) Calculate the open circuit potential (E_{cell}) of one cell of the fully charged lead-acid battery (at 25 °C) which contains sulfuric acid with density of 1.275 g cm^{-3}.

%$_{wt}$	ρ (g cm^{-3})	%$_{wt}$	ρ (g cm^{-3})	%$_{wt}$	ρ (g cm^{-3})
2	1.0104	34	1.2479	66	1.5602
4	1.0234	36	1.2647	68	1.5829
6	1.0367	38	1.2818	70	1.6059
8	1.0502	40	1.2991	72	1.6292
10	1.0640	42	1.3167	74	1.6526
12	1.0780	44	1.3346	76	1.6761
14	1.0922	46	1.3530	78	1.6994
16	1.1067	48	1.3719	80	1.7221
18	1.1215	50	1.3911	82	1.7437
20	1.1365	52	1.4109	84	1.7639
22	1.1517	54	1.4310	86	1.7818
24	1.1672	56	1.4516	88	1.7968
26	1.1829	58	1.4726	90	1.8091
28	1.1989	60	1.4940	92	1.8188
30	1.2150	62	1.5157	94	1.8260
32	1.2314	64	1.5378	96	1.8305

The open circuit potential of one cell of a lead-acid battery is $E_{cell}°$ = 2.033 V at 5 °C.

e) Calculate the temperature coefficient (d$E_{cell}°$/dt) of one cell of the lead-acid battery in this temperature region.

f) Calculate the reaction enthalpy of the discharging process in the battery.

g) During the discharging of the battery:

- ☐ The temperature of the battery increases;
- ☐ The temperature of the battery decreases;
- ☐ The temperature of the battery does not change;
- ☐ The water could evaporate from the battery because of the overheating;
- ☐ The output voltage of the usual lead-acid battery is 12 V, and it consists of several cells.

h) How many cells should be used to get a 12 V battery?

i) Draw an electrical circuit demonstrating how the individual cells are connected in the 12 V lead-acid battery.

j) Calculate the theoretical output voltage of 12 V lead-acid battery, i.e. use the open circuit potential E_{cell} calculated in **d)**.

The weight of the commercial lead acid battery is 4.05 kg (9.75×9.8×15.1 cm), the capacity is 12 A h, and the internal resistance of the battery is 100 mΩ.

k) Calculate the charge which could be withdrawn from the battery that is fully charged.

The battery was discharged, and the density of the electrolyte measured was 1.195 g cm^{-3}. The fully charged battery contained 580 cm^3 of sulfuric acid.

l) Calculate how many hours it would take to fully charge the battery using average current 3 A. The efficiency of the charging process is 65%. Assume that the amount of water is constant.

m) During discharging, the internal resistance of the battery:

☐ Increases;
☐ Decreases;
☐ Decreases drastically;
☐ Does not change.

n) The open circuit potential of the battery:

☐ Does not change during charging;
☐ Does not change during discharging;
☐ Increases during discharging;
☐ Increases during charging;
☐ Decreases during charging.

The efficiency of the charging process is much lower than 100% because high overvoltage is applied to the electrodes and instead of charging, also side reactions could occur: hydrogen evolution and oxygen evolution.

o) Write the equations of side reactions on the anode and cathode during the charging process.

The performance of various energy-storing devices could be compared using maximum energy density $W_{max} = qE/m$, where q is the charge stored in the device, E – operation voltage window, and m – weight of the device. Maxwell ultracapacitor BCAP3000 has the following characteristics: capacitance – 3000 F, voltage window – 2.7 V and mass of the device – 510 g.

p) For which energy storage device the maximum energy density (Wh kg^{-1}) is higher? During the discharge of the battery, the potential does not change but during the discharge of the capacitor, the potential decreases almost linearly, i.e. the average potential should be used.

**q)** The energy density of the lead-acid battery:

☐ Increases with the temperature;
☐ Decreases with the temperature;
☐ Does not change with the temperature;
☐ Increases during discharging;
☐ Increases during charging.

Problem 2 – CRYSTAL, THERMO – Fullerenes

Some of the alkali metal-doped fullerenes have a superconducting state. In these compounds, the alkali metal atoms fill the holes in a face-centered cubic lattice formed by the molecules of fullerene. Molecules in the fullerene crystal are also arranged in the face-centered cubic lattice.

a) Calculate the lattice parameter (a) of the fullerene crystal with a density of 1.67 g cm^{-3}.

b) Estimate the radius of the fullerene molecule, assuming that the distance between the neighboring molecular spheres is d = 1.42 Å, i.e. one C–C bond length.

c) Estimate the radii of spheres (r_{oct} and r_{thd}) that can fit the octahedral and tetrahedral holes of the fullerene crystal. The radius of a tetrahedron circumsphere is given as $r_{thd} = \sqrt{3/8} \cdot t$, where t is the length of the tetrahedron edge.

The figure below shows the crystal structure of face-centered cubic A_nC_{60}, where A = Li, Na, K, Rb, Cs, and n is an integer number.
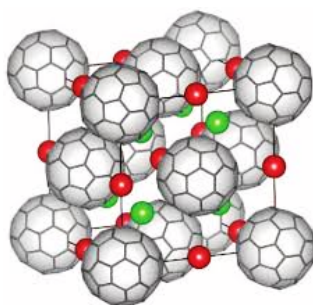
d) Prove that n = 3 for the illustrated crystal structure. Note that all tetrahedral and octahedral holes are occupied by the alkali metal atoms.

In the Table below are given atomic ($r(A^0)$) and ionic ($r(A^+)$) radii of Li, Na, K, Rb and Cs, metal vaporization enthalpies ($\Delta H_{vap}(A)$) and ionization energies (IP(A)), as well as lattice parameters of corresponding fullerides.

	$r(A^0)$, Å	$r(A^+)$, Å	$\Delta H_{vap}(A)$, kJ mol^{-1}	IP(A), kJ mol^{-1}	$a(A_nC_{60})$, Å
Li	1.52	0.76	136	520	–
Na	1.86	1.02	108	496	14.191
K	2.27	1.38	90	419	14.240
Rb	2.48	1.52	69	403	14.384
Cs	2.65	1.67	66	376	14.761

e) Calculate r_{thd} values for each of the alkali metal-doped fullerenes. Compare the calculated values with the $r(A^0)$ and $r(A^+)$ values from the table and prove that the alkali metal atoms are charged.

f) Calculate the lattice energy for Li_3C_{60} using the Kapustinskii equation: $\Delta U_{lattice} = -107000 \cdot v \cdot |z_+| \cdot |z_-|/(r_+ + r_-)$, where v is the total number of ions in the empirical formula, z_+ and z_- are the charges of the individual ions, r_+ and r_- are the ionic radii in pm, and the result is given in kJ mol^{-1}. Assume, $r_+ + r_- \approx r_{thd}(Li_3C_{60})$ + 4.31 Å.

The first reported superconductor in the fulleride family was K_3C_{60}. In a year, Rb_3C_{60} and Cs_3C_{60} were synthesized. The preparation of Na_3C_{60} was more difficult and took longer. So far, it has

not been possible to produce Li_3C_{60}. There is a correlation between the formation enthalpy values and the sequence of the A_3C_{60} studies.

g) Write the A_3C_{60} formula in ascending order of the corresponding formation enthalpy absolute values. You may estimate the relative values using the data from the table.

Problem 3 – SYNTH – The Great Drug of China

Artemisinin is a drug that possesses the most rapid action of all of the drugs used to treat Malaria. It was discovered in the 1970s by Tu Youyou, a Chinese scientist, who was awarded a Nobel Prize in 2015. She was the first Chinese Nobel Prize laureate. Initially, artemisinin was obtained by isolation from the plant *Artemisia annua*. Unfortunately, no significant quantities of this plant are being grown, so in 1992, Avery et al. published a synthetic route to the Artemisinin shown below.
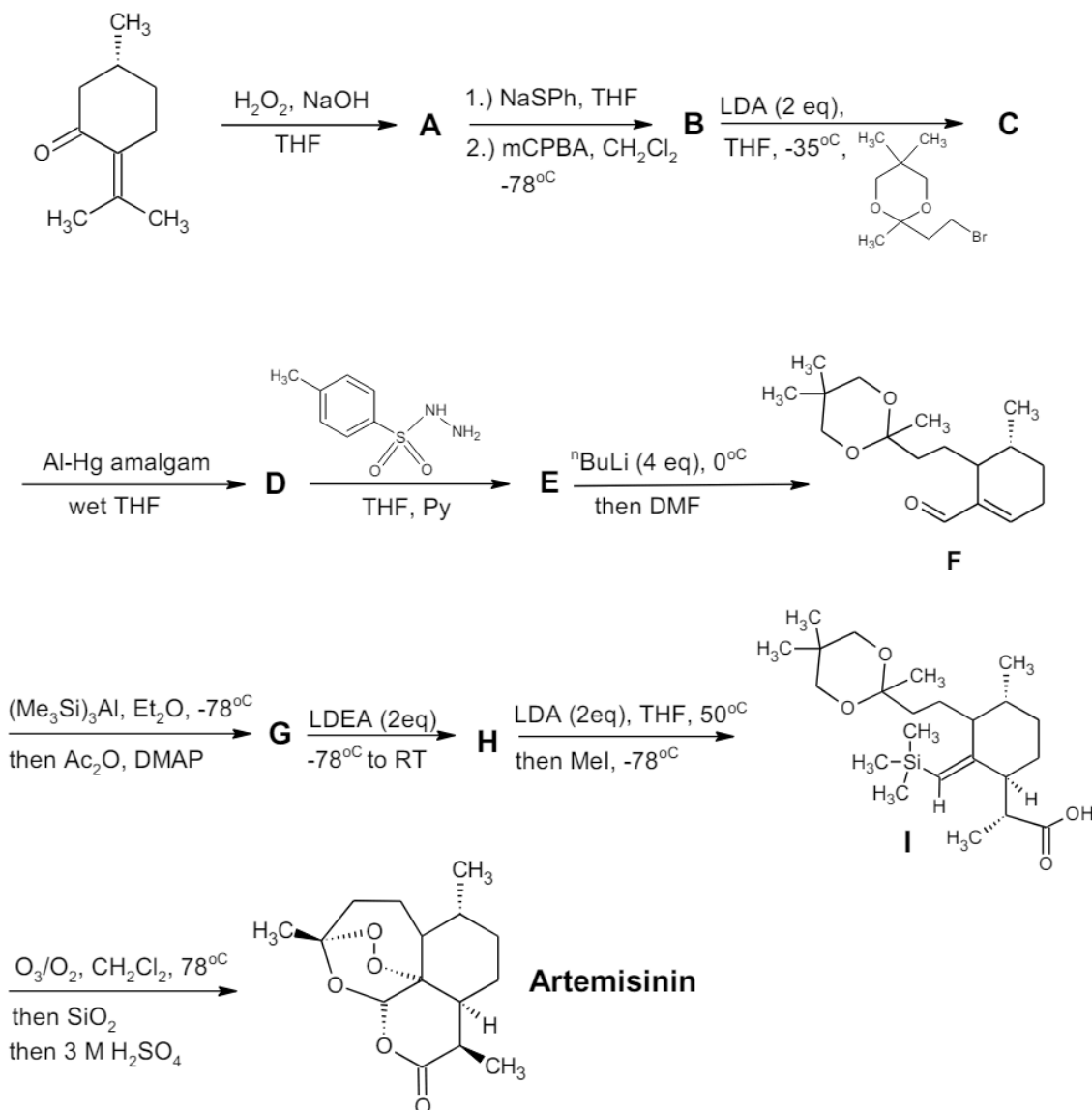
- The empirical formulas of compounds are: **B** – $C_{13}H_{16}O_2S$, **D** – $C_{16}H_{28}O_3$, **G** – $C_{22}H_{40}O_4Si$
- All steps from **B → I** are stereoselective. Thus, you must draw the major enantiomers of all the intermediates from **C** to **I**.
- LDA and LDEA are bulky bases.
- Conversion **G** to **H** is the Claisen rearrangement reaction.

a) Draw the structural formulas of the compounds **A–E** with stereochemistry.

b) Propose a reaction mechanism for the conversion **A → B**.

c) Propose a mechanism for converting **E** to **F**. Note that DMF (dimethylformamide) is not the solvent of the reaction and that there is no racemization.

d) What is the major driving force of the reaction **E → F**?

    A. The product can form hydrogen bonds with the solvent.

    B. Having three oxygen in the molecule is better than having two.

    C. Nitrogen is produced and released during the reaction.

    D. The product is more conjugated than the starting material.

    E. Compound **E** is harmful, but compound **F** is not.

e) Draw the structural formulas of the compounds **G** and **H**. Pay attention to the stereochemistry.

f) Propose a reaction mechanism for the conversion **G → H**.

g) Assign the configuration (*R* or *S*) for all of the stereocenters of compounds **G** and **I**.

Problem 4 – CRYSTAL, THERMO – The biggest coins in the world

The beginning of the 17th century was a turning point in Sweden's economics as it lost control over silver mines in Norway but added the Baltic region (including Tartu and Riga) to their territories. The Mine of Falun had rich stores of raw material, and the Swedish king decided to produce copper coins (plates) of value close to the value of silver coins. The first copper coins were issued in 1624, the weight of one coin was 19.7 kg and the volume of 2205 cm^3. Copper has a face-centered cubic lattice (FCC) with a lattice parameter of 361.5 pm. In nature, copper is usually found as sulfide minerals, for example – chalcopyrite (contains 35% of copper by mass and iron) and chalcocite (contains 80% of copper by mass).

a) Calculate the chemical formulas of chalcopyrite and chalcocite.

Nowadays, copper is extracted from ores, where the copper content is as small as 0.60%.

b) Write equations showing the extraction of copper from ore containing chalcocite when copper(I) oxide forms as an intermediate.

c) Calculate the mass of the ore to be recycled to produce copper that is necessary to make one Swedish coin.

Copper(I) oxide is a reddish-brown substance used as a component of some antifouling paints. Copper(I) oxide is reduced when it is mixed with chalcocite, free copper and sulfur dioxide are formed.

Substance and its state	Cu$_2$O (s)	Chalcocite (s)	Cu (s)	SO$_2$ (g)
ΔH_f° [kJ mol^{-1}]	−168.6	−79.5		−296.8
S° [J mol^{-1} K^{-1}]	93.1	120.9	33.2	248.2
Melting point [°C]	1232	1130	1084	
ΔH_{fus}° [kJ mol^{-1}]			13	

d) Calculate Gibbs energy of copper(I) oxide reduction reaction at **i)** 25 °C and **ii)** 1100 °C.

Young chemist Grzegorz decided to reuse copper coins; he made up the electrolytic cell, attached Swedish copper coin and almost pure copper wire as electrodes, and used copper(II) nitrate as the electrolyte.

e) Which electrode (anode/cathode) was made from Swedish copper coin? Write the corresponding half-reaction.

f) How long (in hours) does it take to recycle all Swedish coins if electrolysis is performed with 1.00 A current?

g) Nowadays, copper is used to prepare internet cables. Calculate the length of copper fiber of diameter 0.1 mm which can be produced from Swedish copper coins.

h) How many copper coins are needed to recycle to produce a copper fiber with a length of 600 km (distance from Tallinn to Vilnius via Riga)?

Most of the used copper is recycled. Another recycling process includes the dissolution of copper in nitric acid. Nitric acid reacts with copper in two ways giving NO and NO_2.

i) Complete and balance both oxidation-reduction reaction equations.

Scientific papers state that complete oxidation of carbon monoxide can be achieved at room temperature over unsupported copper(II) oxide catalyst by a careful and controlled generation of the oxide. The Figure below shows the natural logarithm of the oxidation reaction rate as a function of $1/T$, where T is the temperature in Kelvin (K).
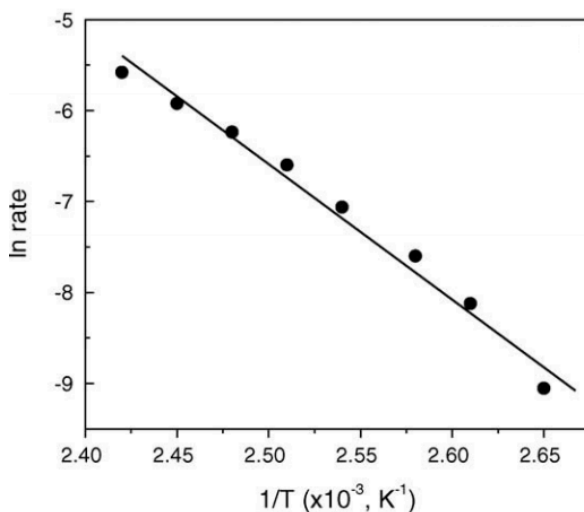

j) Calculate the activation energy for the oxidation of carbon monoxide.

The enthalpy of the complete combustion of carbon (in the solid state as graphite) is −393 kJ mol^{-1}, but the standard enthalpy of the formation of carbon monoxide is −111 kJ mol^{-1}.

k) Sketch the energy diagram of the carbon monoxide oxidation reaction and state exact energy difference values where possible.

Copper is still used in the production of coins. Young chemist Grzegorz decided to prove it and analyzed a 2 EUR coin by X-ray diffraction. The diffraction pattern for the analyzed coin is shown below.
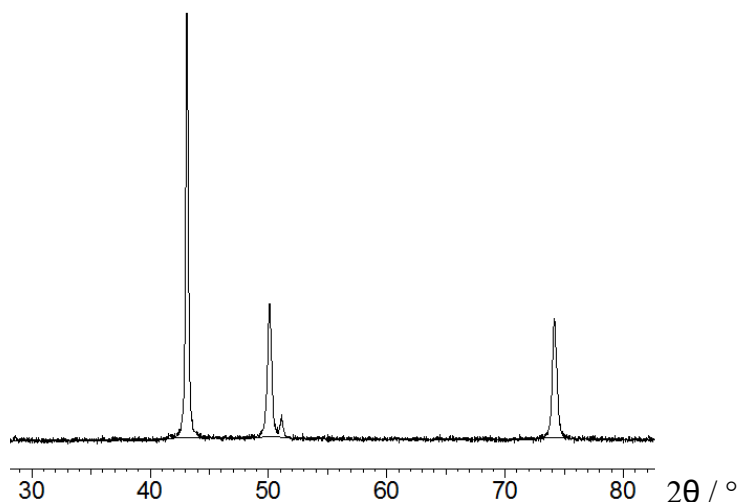
Use Bragg's law: $\lambda = 2d \cdot \sin(\theta)$, where d is the distance between diffraction planes (nm, $d = a/\sqrt{h^2 + k^2 + l^2}$); λ is the wavelength of X-rays (0.15408 nm), θ is the diffraction angle, a is the lattice parameter, h, k, and l are Miller indices. For the face-centered cubic lattice (FCC), only diffraction peaks where all Miller indices are odd numbers or all Miller indices are even numbers are allowed.

l) Indicate in diffraction pattern which peak(s) correspond to copper and state, at least, one set of Miller indices for each copper peak.

Problem 5 – CALC, SPECTRA – "My precious"

Silver jewelry is seldom made of absolutely pure silver. Different alloys are usually used instead of pure silver. Chemistry student Grzegorz decided to analyze his mom's silver ring and find out how much copper it contained because he knew that this ring had some copper impurity. So, Grzegorz dissolved 1.00 g of that ring in a small volume of concentrated nitric acid and diluted the solution to 25 ml. Let's call it solution **A**. It was colored, and because of that, the student decided to calculate the amount of copper in the solution using its feature to absorb visible light. He measured the absorbance of the solution using the photometer. Usually, molar extinction coefficients of metal salt solutions are less than 1000 M^{-1} cm^{-1}. In this problem, use the Bouguer-Beer-Lambert law: $A = \log(I_0/I) = \varepsilon c l$. In his measurements, Grzegorz used the photometer, which can measure the smallest value of absorption $A = 0.001$.

a) Calculate the smallest concentration of hypothetical substance **X** that can be measured by this device when $\lambda = 600$ nm, $\varepsilon_{600} = 3.25$ M^{-1} cm^{-1}, and $l = 1.000$ cm.

Light filters are usually used in photometers to generate the monochromatic light beam.

b) What is the color of the filter if it absorbs only violet (390 nm) light?

The absorbance spectrum of hypothetical substance **X** is given in the figure below.

111
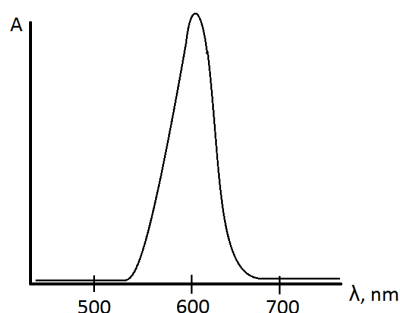
c) Draw the absorbance spectrum of the best suitable filter for the substance **X** analysis. "Best suitable" means that when that filter is used, Lambert-Beer law holds the smallest possible substance **X** concentrations can be measured, and the most accurate results are obtained.

To find out the copper concentration in solution **A**, he used the "addition method". In the beginning, Grzegorz measured the absorbance of solution **A** in a 3.00 cm cuvette at λ = 700 nm wavelength. The photometer showed 0.240. Assume that silver ions do not absorb visible light.

d) Calculate the fraction (in percent) of initial light intensity that is transmitted through the sample.

After that, Grzegorz weighed 5.12 g of copper sulfate pentahydrate, dissolved it in a 20 cm^3 volumetric flask, and diluted it to the mark (solution **B**). Then he mixed 15 cm^3 of solution **A** and 1 cm^3 of solution **B** and also measured the absorbance of this mixture in a 1.00 cm cuvette at λ = 700 nm wavelength. The photometer showed the value A = 0.694.

e) Calculate the mass fraction (in percent) of copper in the ring.

Grzegorz was so interested in his mom's jewelry analysis that he measured the quantitative composition of his mom's earring, which was made from Monel metal (copper-nickel alloy). So, the student dissolved a piece of that earring in concentrated nitric acid (let us call it solution **C**) and measured the absorbance of solution **C** in a 1.00 cm cuvette at λ_1 = 400 nm wavelength and at λ_2 = 800 nm wavelength. He also measured the absorbance of earlier prepared standard solution **D** in which $[Cu^{2+}]$ = 0.025 M and $[Ni^{2+}]$ = 0.055 M. The results he got are listed in the Table below. The Figure below shows the molar extinction coefficient dependence on wavelength for copper and nickel. The molar extinction coefficient for nickel at wavelength 800 nm ε_{800} = 4.41 M^{-1} cm^{-1}.
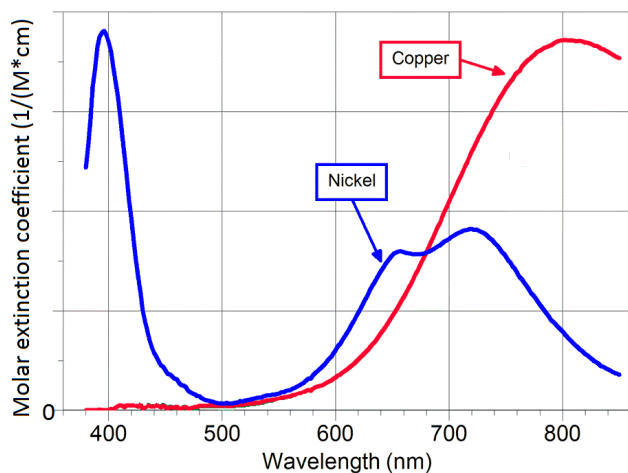
λ [nm] Solutions	400	800
C	0.765	0.548
D	0.894	0.638

Table. Absorbance dependence on solution and λ.

f) Determine the composition (in mass percent) of the earring.

Grzegorz's friend Piotr told Grzegorz about metal complexes. Piotr pointed out that it is better to evaluate metal concentrations in solutions using organic compounds that make complexes with metal ions. Due to recent changes in safety rules, Grzegorz's school has been trying to eliminate carcinogenic cobalt(II) chloride. So Grzegorz waited for the right moment and deliberately took the salt as he devised an idea to analyze cobalt(II) complex formation reaction.

| Conc. **R** [M]·10^{-5}	Absorbance (A)
1.50	0.106
3.25	0.232
4.75	0.339
6.25	0.441
7.75	0.500
9.50	0.523
11.5	0.529
12.5	0.531
16.5	0.529
20.0	0.530

The complex between Co(II) and the ligand **R** was investigated photometrically. A green filter at 550 nm (the wavelength of absorbance maximum for the complex) was used for the measurements. Assume that only the complex absorbs the light. The initial cation concentration was $2.5 \cdot 10^{-5}$ M in solutions with different concentrations of **R**. The absorbance data (1 cm cell) were obtained as follows:

g) Draw a graph of absorbance versus **R** concentration and determine the ligand-to-cation ratio for the complex.

h) Determine the value of molar extinction coefficient ε_{550} for the complex from question **g)**.

i) Which one of the following statements best describes the advantage of using complexes in photometry?

  i) To increase the molecular mass of the analyst;

  ii) To enhance the solubility of the analyst;

  iii) To increase the molar extinction coefficient of the analyst;

  iv) All of the above.

## Problem 6 – BIO, SPECTRA, SYNTH – Ayahuasca

Ayahuasca is a brew made out of *B. caapi* vine. This brew is used orally as a traditional spiritual medicine in ceremonies in South America. It can be mixed with leaves containing DMT for a significantly different – psychedelic effect. *N,N*-dimethyltryptamine (DMT) is a psychedelic compound of the tryptamine family, and it is a structural analog of serotonin and melatonin. It is interesting to notice that DMT taken orally is broken down by the enzyme monoamine oxidase through a process called deamination and is quickly inactivated orally unless combined with a monoamine oxidase inhibitor.

Harmala alkaloids are monoamine oxidase-inhibiting *beta*-carbolines. Two of the three most studied harmala alkaloids in the *B. caapi* vine are harmine and harmaline. In this problem, you have to complete the synthesis of harmine and harmaline given below.
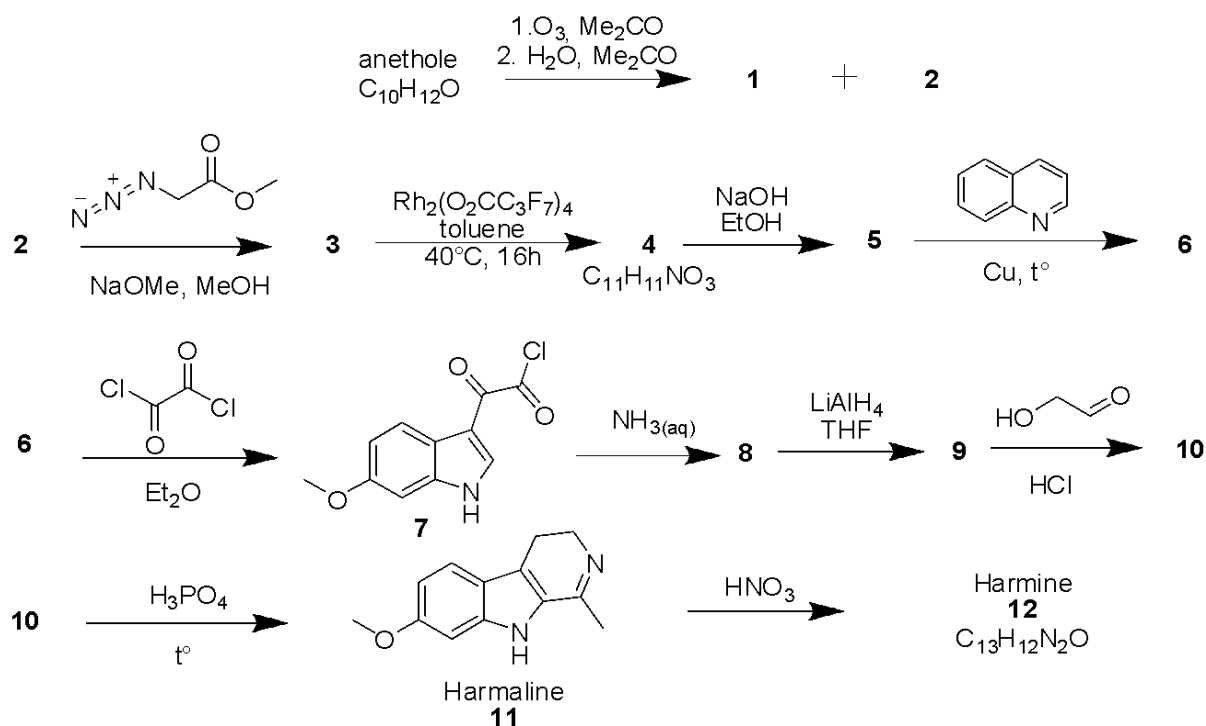
*Hints: anethole exhibits cis/trans isomerism; products **1** and **2** are both aromatic compounds; $Rh_2(O_2CC_3F_7)_4$ is used as an intramolecular reaction catalyst; compound **5** has broad signal in IR spectra (~3000 cm^{-1}) whereas compound **6** does not.*

a) Investigate a ^{1}H NMR spectrum (which is given below) of the starting material – anethole. Draw the molecule, assign the peaks to the protons, and mark signal multiplicity (s for singlet, d for doublet, dd for doublet of doublets, etc.).
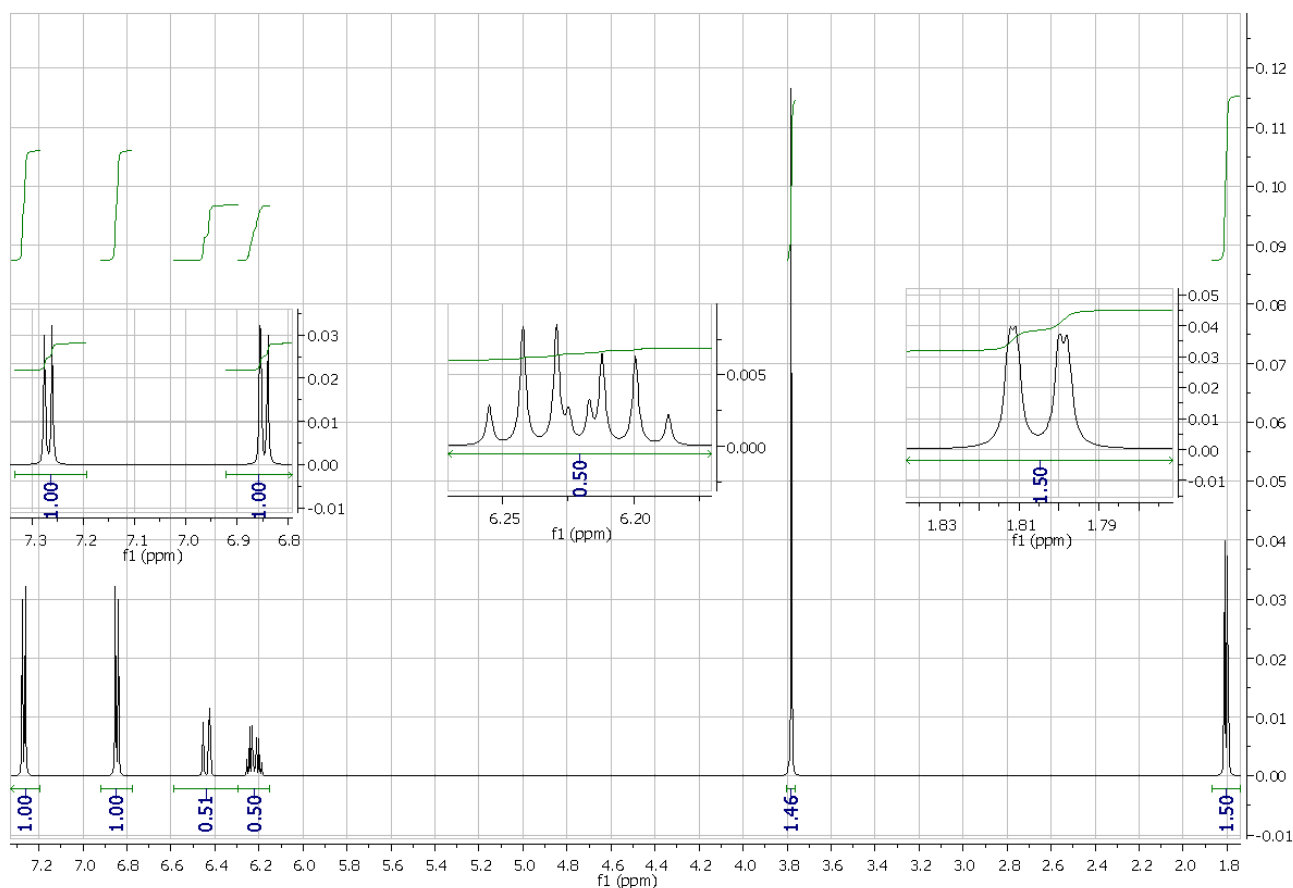
b) Propose an alternative synthesis of *p*-anisaldehyde (compound **2**). Use *p*-cresol (4-methylphenol) as a starting material.

c) Name a purification procedure that could be used to separate products **1** and **2**.

d) Identify compounds **1–10** and **12** and draw their structures.

DMT can be metabolized in at least two different ways in one's mouth. One pathway is governed by a monoamine oxidase and aldehyde dehydrogenase enzyme activity (MAO-ADH). Other products are obtained through other modifications. Two products are given below.
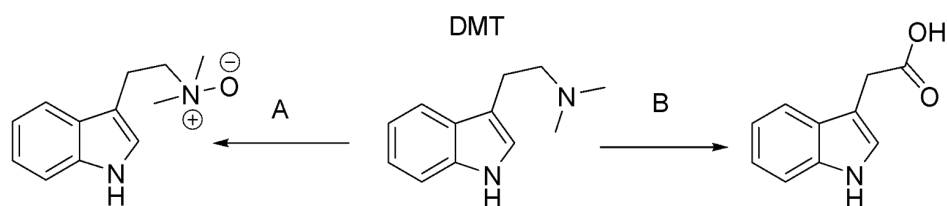
e) MAO-ADH enzyme is hidden under the letter: **A**; **B**; Both; None.