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ROUND 1 2013

Focus on analytical and inorganic chemistry

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Basic rules:

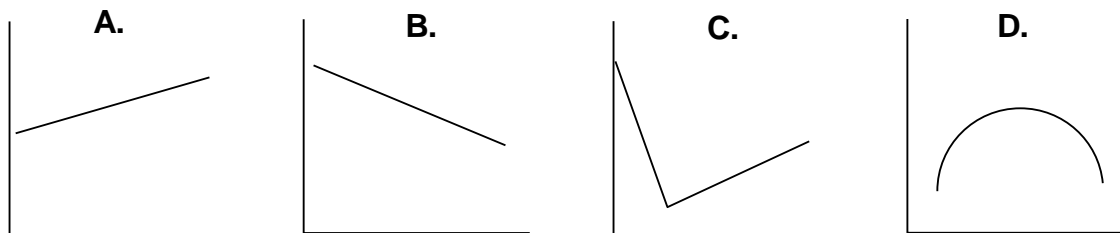
- any school student can participate in Baltic Chemistry Competition (BCC), copy of valid school student card may be required;
- participants cannot be University students till the end of February 2013;
- participants register for participation by sending answers in one of first two rounds;
- all answers and parts of solutions **must** be written in specially designed answer sheets according to directions (grading will be done automatically by analyzing answer sheet file);
- students must submit their own work; completely identical solutions will be graded with 0 points;
- **working language is English** (problems are in English and students are expected to answer them in English);
- **deadline for submission of answers is 10th January 2013;**
- if you have more questions or you would like to submit answers, you have to write to bchem@inbox.lv

Organizers and problem authors wish you success and enjoy competition!!

Problem 1 Choose one! (50 points)

This problem contains 50 multiple choice questions. Choose one correct (or the most correct) answer for each question. Each correct answer gives you 1 point, each incorrect answer -0,5 points. Each unanswered question is valued with zero points. You cannot receive less than zero points in total for this problem.

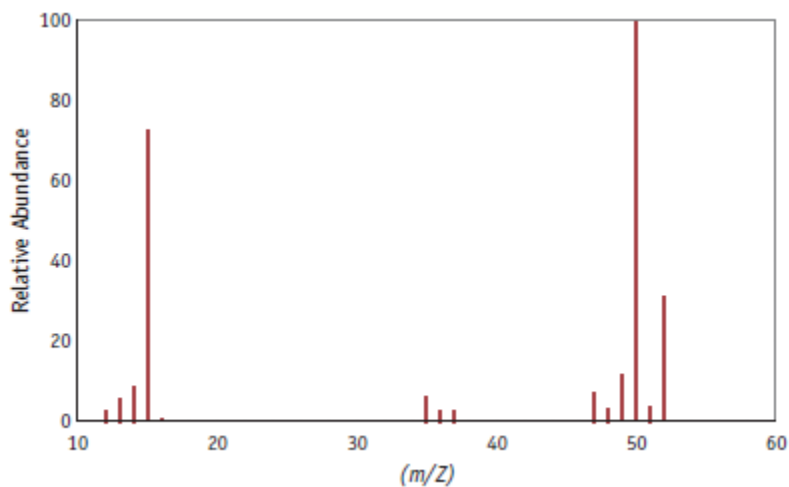
- Periodic rule was discovered in 1869 by:
 - Boris Elcin
 - Dmitri Mendeleev
 - Lothar Meyer
 - Svante Arrhenius
 - Albert Einstein
- A solution forms gas bubbles without characteristic smell, when it is treated with potassium hydrogensulphate solution. This solution might contain:
 - potassium cyanide
 - potassium hydroxide
 - potassium sulphite
 - potassium carbonate
 - none of above
- Which graph shows changes of electrical conductivity, when barium hydroxide is added to solution of sodium sulphate.



- A
 - B
 - C
 - D
 - none of above
- Number of sigma and pi bonds in nitrogen(I) oxide is respectively:
 - 2, 2
 - 2, 3
 - 3, 1
 - 1, 3
 - none of above
 - Little John walked on beach of Baltic Sea near Liepaja, Latvia. He found a small stone, similar to amber which is common in this region, and placed it into pocket. After some time his pocket burst into flames and a white powder was formed from the stone. What was possible composition of this sample?
 - Iron(II) iodide
 - Phosphorous
 - Sodium peroxide
 - Potassium ozonide
 - none of above
 - Which statement about aragonite, vaterite and calcite is true.
 - They all are soluble in concentrated boric acid
 - They all are polymorphic forms of calcium carbonate
 - They all react with diluted acetic acid and forms gas with characteristic smell of roasted eggs

- d. They all have cubic face centered unit cell
 - e. None of above
7. About two hundred years ago Benjamin Franklin discovered that 1 teaspoon of oil would cover 2000 m^2 of water. If there is approximately 5 mL of oil in a teaspoon, what is the thickness of the layer of oil?
- a. $1,5 \text{ \AA}$
 - b. $2,5 \times 10^{-9} \text{ m}$
 - c. $2,5 \text{ pm}$
 - d. $2 \text{ }\mu\text{m}$
 - e. none of above
8. The coordination number for dichlorobisethylenediaminecobalt(III) chloride is:
- a. 2
 - b. 4
 - c. 6
 - d. 8
 - e. none of above
9. Shape of complex ion $[\text{Ni}(\text{CN})_5]^{3-}$ is:
- a. octahedral
 - b. tetrahedral
 - c. tetragonal pyramidal
 - d. trigonal pyramidal
 - e. none of above
10. Homolytic bond fission of Cl-Cl bond results in formation of:
- a. Cl^+ and Cl^- ions
 - b. two Cl atoms
 - c. two Cl radicals
 - d. one hydrated electron
 - e. none of above
11. Chlorine ions Cl^+ exist in:
- a. liquid NaCl
 - b. NaCl solution
 - c. mass spectrometer
 - d. such particles does not exist
 - e. none of above
12. Little Peter mixed cold tap water (0°C), ice and solid deuterium oxide and mixed it. What will be at the bottom of the container?
- a. deuterium oxide
 - b. ice
 - c. water
 - d. it is homogenous mixture
 - e. none of above
13. Accurately weighing the solute, solutions of precise concentration can be made from:
- a. potassium dichromate
 - b. sodium hydroxide
 - c. ammonia
 - d. potassium permanganate
 - e. none of above

14. Spectrum of compound X is given in figure below (from book “Chemistry and Chemical reactivity”)



Molar mass of compound X is (all numbers in g/mol):

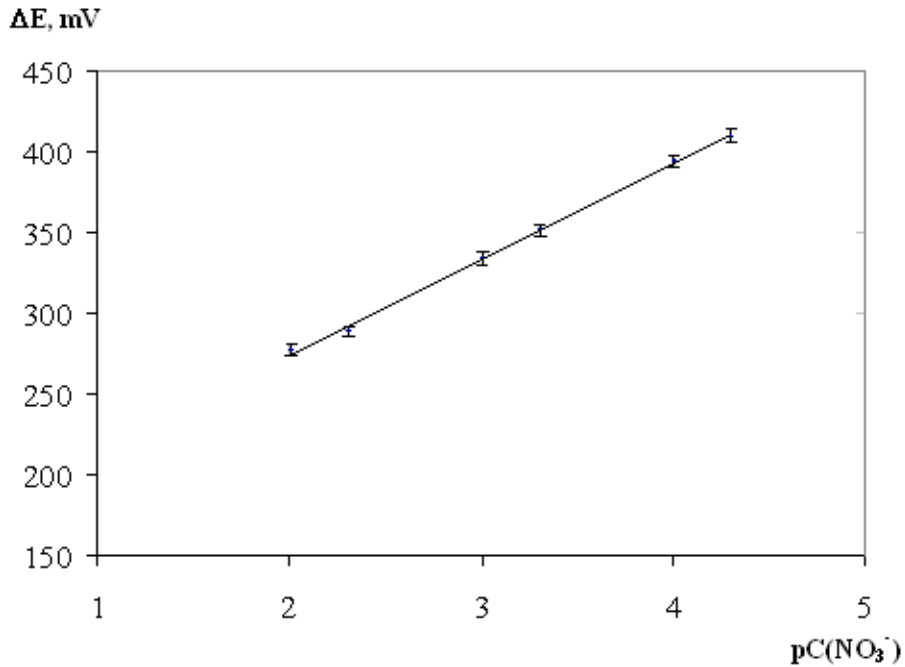
- 50
 - 15
 - 52
 - it is impossible to determine molar mass
 - none of previous answers
15. Compound A (same which was investigated in previous question) contains:

I. C II. Cl III. O IV. H V. Br

- I, II, III
 - only I and H
 - I, III, IV
 - I, II, IV
 - none of above
16. Three equal almost empty balloons were tightened at the top of three Erlenmeyer flasks. The first and second flasks contained concentrated sulfuric acid, but the third one contained concentrated hydrochloric acid. 5 grams of iron, 5 grams of copper and again 5 grams of copper were placed in the flasks (one metal in one flask). Which balloon will be the largest after five minutes:
- 1st
 - 2nd
 - 3rd
 - all will be equal
 - none of previous answers
17. Sodium sulfite solution was mixed with potassium hydroxide solution and then potassium permanganate(VII) solution was added. What is final color of this solution?
- blue
 - colorless
 - brown
 - green
 - none of above

18. The calibration graph for ionometric determination of nitrate ions in solution is given below, where

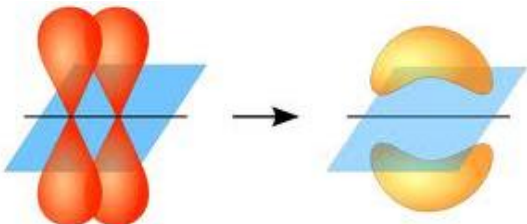
$x = -\log(C(\text{NO}_3^-))$ and $y = \Delta E$.



(No.17 continued) Slope equal to:

- a. 60
 - b. 155
 - c. -80
 - d. +80
 - e. none of above
19. A solution of nitric acid (HNO_3) was mixed with zinc. Oxidizing agent (element) in this reaction is:
- a. N
 - b. O
 - c. H
 - d. Zn
 - e. none of above
20. Which of these processes (in industry) requires most energy per 1 ton of product?
- a. production of sulfuric acid
 - b. production of nitric acid
 - c. production of aluminium
 - d. production of zinc blende
 - e. production of nitrogen(I) oxide
21. If 5 grams of sulfur were mixed with 5 grams of iron, what is the mass of iron(II) sulfide which was obtained in this reaction if the yield is 85%?
- a. 10 g
 - b. 5 g
 - c. 7,85 g
 - d. 6,68 g
 - e. none of above

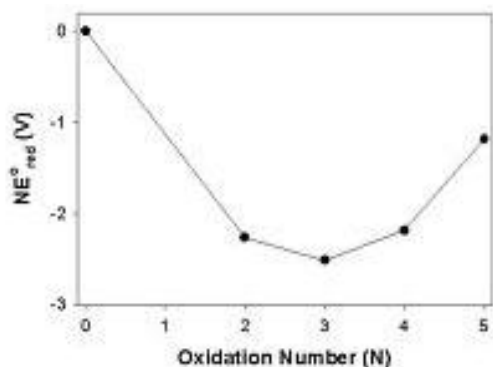
22. The pK_a for unknown acid HA is $5 \cdot 10^{-4}$ M. What is pH for 0,01 M solution of this acid?
- 3,0
 - 2,7
 - 1,9
 - 5,4
 - 3,3
 - none of above
23. (continues from previous question) Which particle has the highest concentration in previous solution?
- H_3O^+
 - H^+
 - OH^-
 - A^-
 - HA
24. Figure below corresponds to:



- formation of classic Italian pizza
 - formation of pi bond
 - formation of sigma bond
 - formation of delta bond
 - formation of hydrogen bond
 - none of above
25. Compounds which have giant covalent structures also have:
- high melting points;
 - They conduct electricity when turned into liquid state;
 - Low sublimation enthalpies;
 - Low melting points and low hardness;
 - Compounds are very hard.
- Correct statement(-s) is(are):
- only III
 - III and IV
 - only I
 - I and IV
 - I, II, IV
 - II, III, IV
 - none of above answers
26. Electron formula $1s^2 2s^2 2p^6$ corresponds to:
- Cl^+ ion
 - O_2^{2-} ion
 - CH_4 molecule
 - Ar
 - none of above

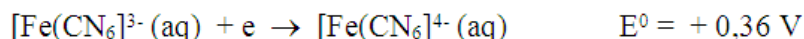
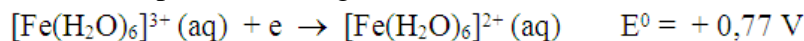
27. Which molecule is paramagnetic?
- O₂
 - N₂
 - CO
 - H₂
 - none of above
28. Which of particles O₂²⁺, O₂⁺, O₂, O₂⁻ is the most stable?
- O₂²⁺
 - O₂⁺
 - O₂
 - O₂⁻
 - all have equal stability
29. Which of particles O₂²⁺, O₂⁺, O₂, O₂⁻ is the most stable?
- O₂²⁺
 - O₂⁺
 - O₂
 - O₂⁻
 - all have equal stability

30. The figure below shows the Frost diagram of unknown chemical element. The most stable oxidation number of this element is:



- 0
 - +1
 - +2
 - +3
 - +4
31. “The strongest known oxidizing agent in real life” is:
- fluorine gas
 - hydrogen peroxide
 - potassium permanganate
 - chlorine gas
 - electrical current
32. If standard reduction potentials for Ce⁴⁺(aq) → Ce³⁺(aq) and for Au³⁺(aq) → Au(s) is 1,72 V and 1,50 V respectively, it means:
- cerium(IV) can oxidize metallic gold to Au³⁺
 - cerium(IV) can oxidize metallic gold to Au³⁺ only in acidic medium
 - gold(III) can oxidize Ce³⁺ to Ce⁴⁺
 - gold(III) can oxidize Ce³⁺ to Ce⁴⁺ only in acidic medium

33. Reduction standard potentials are given below:



Which statement is true?

- $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is the strongest reducing agent among the four ions
 - $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is the strongest reducing agent among the four ions
 - $[\text{Fe}(\text{CN})_6]^{3-}$ is more stable than $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
 - $[\text{Fe}(\text{CN})_6]^{3-}$ is strongest oxidizing agent among the four ions
 - none of answers above is correct
34. We have following table about dipole moments of molecules. Elements A, B and C are in one group.

Molecule	Dipole moment, D
H-A	1,82
H-B	1,08
H-C	0,82

Which statement is true?

- molecule HC forms hydrogen bonds, while HB does not
 - relative electronegativity for element B is higher than for element A
 - relative electronegativity for element B is higher than for element C
 - molecule H-C have better solubility in 40% ethanol/water solution than H-B
 - H-C has the highest melting point
35. Which of given ions will undergo reduction reaction most vigorously?
- perchlorate
 - chlorate
 - chlorite
 - hypochlorite
 - chloride
36. If John will mix $\text{Ag}^{2+}(\text{aq})$ solution with metallic silver which of processes mentioned will occur?
- annihilation
 - explosion
 - disproportionation
 - addition reaction
 - isomerisation
37. Which of these compounds can be optically active?
- $\text{K}_3[\text{Cr}(\text{oxalate})_3]$
 - H_2O_2
 - Copper(II) acetate
 - trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
 - cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
38. When sodium hydroxide solution is added to metallic beryllium:
- no reaction occurs
 - white precipitate of $\text{Be}(\text{OH})_2$ is formed
 - gas with molar mass $> 18 \text{ g/mol}$ is formed
 - $\text{Na}_2[\text{Be}(\text{OH})_4]$ is formed
 - Be polymer is formed

39. Valence of O (underlined) in beryllium oxoacetate $[\text{Be}_4\text{O}(\text{OOCCH}_3)_6]$ is:
- II
 - +2
 - 2
 - IV
 - none of above
40. Which of these answers contain solutions in increasing order of pH value? Concentration for all solutions is equal.
- $\text{K}_2\text{CO}_3, \text{KOH}, \text{KHCO}_3, \text{K}_2\text{SO}_4$
 - $\text{HI}, \text{H}_2\text{CO}_3, \text{NaCl}, \text{NaHCO}_3$
 - $\text{Na}_2\text{SO}_3, \text{Na}_2\text{S}, \text{NaBr}, \text{NaOH}$
 - $\text{Zn}(\text{CH}_3\text{COO})_2, \text{ZnCl}_2, \text{Zn}(\text{OH})_2, \text{KCl}$
 - none of above
41. When crystals of water are formed, which process occurs first?
- adsorption
 - nucleation
 - crystal growth
 - diffusion
 - absorption
42. A student investigated a solution of a weakly soluble electrolyte with the general formula G_2F , where G^+ is cation and F^{2-} anion. pK_s of this electrolyte is 5,00. Equal volumes of G^+ solution and F^{2-} solution were mixed, concentrations in each case are given below.
- 0,10 M G^+ + 0,10 M F^{2-}
 - 0,001 M G^+ + 0,001 M F^{2-}
 - 0,01 M G^+ + 0,01 M F^{2-}
 - 0,05 M G^+ + 0,1 M F^{2-}
- In which case was precipitation observed.
- only I
 - II, III and IV
 - all cases
 - I and II
 - none of above
43. Mixture of 2-amino-4-(methylthio)butanic acid and 2-aminopropanoic acid can be separated by:
- electrophoresis
 - paper chromatography
 - NMR
 - IR spectroscopy
 - mass spectrometry
 - potentiometric titration
- only method II
 - methods I and II
 - methods III and IV
 - methods I, II, III and IV
 - all mentioned methods
 - none of above is correct

44. Buffer solution with $\text{pH} = 7,0$ can be prepared from solution of:
- sodium hydroxide and water
 - hydrochloric acid and water
 - sodium hydroxide and hydrochloric acid
 - potassium permanganate and hydrogen bromide
 - sodium hydroxide and phosphoric acid
45. Which of these indicators are(is) suitable for titration of acid ($\text{pK}_a = 6,25$) with potassium hydroxide?
- methyl orange
 - methyl red
 - phenolphthalein
 - all mentioned
 - none of above
46. Compound vapor has relative density against helium $D(\text{He}) = 5$. Compound does not completely dissociate into ions and it sinks in water if it is in solid state, but mixes with water if it is in liquid state. This compound contains element:
- oxygen
 - boron
 - carbon
 - fluorine
 - none of above
47. Little John weighed a piece of copper several times. If his random error is greater than systematic error then he should:
- get scales which are more precise
 - ensure that temperature in laboratory remains the same
 - increase mass of copper sample
 - increase number of measurements
 - burn copper and analyze copper(II) oxide
48. Dependence of light absorption from mass concentration is a... relationship.
- parabolic
 - exponential
 - polynomial
 - linear
 - there is no relationship between these two
49. Solution of chloride of element A is colorless. Element A can be found in group ... of periodic table.
- VIII A
 - VII A
 - VIII B
 - VII B
 - III B

50. Chromatogram of sample A is shown in picture below. Which of these statements are true?

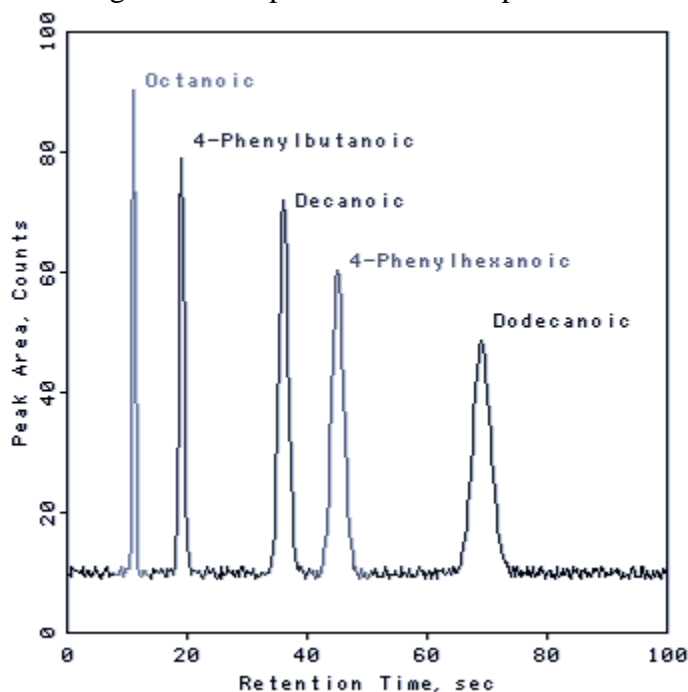


Figure from: statisticaldesigns.com

- sample does not contain aspirin
- sample contains exactly five compounds
- sample contains less than five compounds
- sample contains at least five compounds
- none of above is correct

Problem 2 Let's dissolve! (20 points)

Silver chloride has very low solubility in water. However its solubility significantly increases in ammonia or sodium thiosulfate solution due to the formation of complex ions.



- Calculate how many grams of silver chloride can be dissolved in 1 L of water!
- Write silver complex ion formation reactions with ammonia and thiosulfate ions!
- Calculate how many grams of silver chloride can be dissolved in 100 mL 1.0 M ammonia solution and 100 mL 1.0 M sodium thiosulfate solution!

Formation of complex ions also affects the redox potential.

- Calculate standard reduction potential of Ag^+/Ag in saturated silver chloride (dissolved in 1.0 M ammonia) solution!
- Is it possible to reduce Ag^+ ions in saturated silver chloride (dissolved in 1.0 M ammonia) solution with H_2 gas (with pressure 1.0 atm) bubbled into the solution? If yes, then calculate the pH, which is necessary for the reaction!

Problem 3 Hard rock café! (20 points)

We know the following about an oxide mineral:

- its oxygen content is 31.64 m/m%;
- it contains two metallic elements in a 1:1 mole ratio in addition to oxygen;
- the difference in the atomic number of the metals is 4.

1. Determine the empirical formula of the mineral from calculations and find its name.

When the oxide is reacted with carbon and chlorine gas at high temperatures, the products are carbon monoxide and two metal chlorides. One of the chlorides is colorless; the other one is dark yellow.

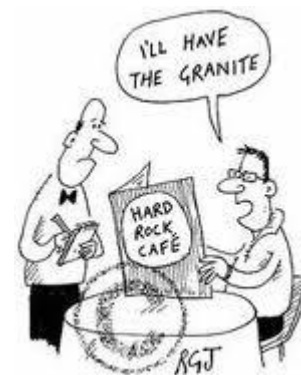
2. Give the balanced equation of the reaction!

3. One of the chlorides has an unusual state of matter. What is the reason for this? How can you explain that the fluoride of the same metal has the highest melting point from all among its halogenides, although it has the lowest molar mass?

The previous reaction is the first step of the preparation of the metal.

4. How does the preparation continue? Give the method and equations.

-* picture from mineral.eng.usm.my



Problem 4 Bad smell! (24 points)

Aqueous hydrogen sulfide is a common reagent, but it has an unpleasant smell. Its first acidic dissociation constant is generally accepted to be $K_{a1} = 10^{-6.9}$. The second dissociation constant is at least three orders of magnitude smaller. The solubility of hydrogen sulfide in water is 4 g/dm³.

1. What is the pH of a saturated H₂S solution? When increasing the pH of the saturated solution, what will be the pH when 99% of the hydrogen sulfide is in HS⁻ form?

The second dissociation constant has a much more contested value. Older textbooks contain $K_{a2} = 10^{-13}$ - 10^{-14} .

2. Using 10^{-14} as the constant, what percentage of the hydrogen sulfide would be in sulfide ion form in solutions containing 5 mol/dm³ OH⁻?

Practical considerations show that these constant values are probably inaccurate. Spectroscopical measurements showed that while making H₂S solutions more basic, the HS⁻-ion concentration does not significantly decrease until a 5 mol/dm³ OH⁻ concentration is reached. (Oxygen was carefully removed from the samples.)

3. Supposing that a 1% concentration decrease could be detected, give an estimate for the second dissociation constant based on this experiment.



Strongly basic solutions are not really practical for dissociation constant determinations.

4. *Why?*

The precipitation of metal sulfides is a phenomenon that can be more helpful in the estimation. Qualitative analysis says that a sulfide precipitate forms on adding saturated H_2S solution to tin(II) solution acidified with a few drops of reagent acid, but no precipitation is observed with zinc solutions.

5. *Estimate the second dissociation constant supposing that*

i) *the metal concentration in the original solution is 0.01 mol/dm^3*

ii) *acidification is carried out with nitric acid giving $c(\text{HNO}_3) = 0.2 \text{ mol/dm}^3$ in the original metal soln*

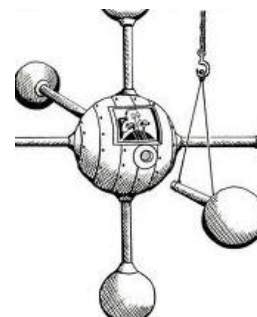
iii) *identical volumes are mixed from the original metal and the H_2S solution*

iv) $pL(\text{ZnS}) = 22,9$ $pL(\text{SnS}) = 26,0$.

It is interesting that without acidification ZnS precipitates in the same experiment.

6. *What will be the pH of the resulting solution?*

Problem 5 Complex compound (28 points)



Organometallic compounds act as catalysts in many important industrial processes. In this task you will determine the identity of one such compound, using various spectroscopic data, and then investigate its derivative, which is thought to be even better suited for industrial applications, due to its thermal stability.

Metal **M** makes an organometallic complex **A**, which, when added to a popular organic solvent **B** gives a yellow solution.

When a well known compound **C** is dissolved in the solvent **B**, it gives a purple solution. This solution of **C** is added to compound **A**, to produce an emerald green solution of **D**, which has **C** as one of its ligands. A neutral molecule **E** is also produced in this reaction.

- Metal **M** was examined using X-ray diffraction. The first diffraction peak at is due to a $\{111\}$ reflection at $2\theta = 41.11^\circ$. The X-ray wavelength is 1.542 \AA .
 - Write down the Bragg's law and calculate the $\{111\}$ plane spacing. Based on your result, calculate the lattice parameter.
 - Given that **M** has an fcc structure and a density of 12.43 g cm^{-3} , identify the metal.
- ^{13}C -NMR spectra were obtained for compounds **C** and **B**. The following peaks were obtained for **B**: 137.8; 129.2; 128.4; 125.5; 21.4 ppm.

The spectrum of **C** only showed one signal at 143.5 ppm.

 - Given that **C** contains one element only, deduce **C**'s identity.
 - Give the structure of the common organic solvent **B** and assign as many signals as you can. What is the trivial name for **B**?
- Compound **A** was examined using ^1H NMR. The following signals were obtained:
- 9.50 ppm (minus 9.50) (quartet, $^2J(\text{P-H}, 14 \text{ Hz})$, 1H); three signals from 7.08 to 7.88 ppm (multiplets, total 45H).

An IR spectrum of **A** has a sharp absorption at 1920 cm^{-1} .

 - Using the information provided, deduce the structure of **A**, and explain your reasoning.

- b. Hence deduce the structure of **D** and **E**.
c. Given that both the complexes are coloured, propose a method for determining concentrations of their solutions. What additional information do you need for that?

Problem 6 Cigarette smoke (21 point)

Cigarette smoke is a complex aerosol containing more than 4400 chemicals. Among these chemicals are many volatile organic compounds (VOCs), e.g., benzene, toluene, ethylbenzene, and styrene (see Figure 1).

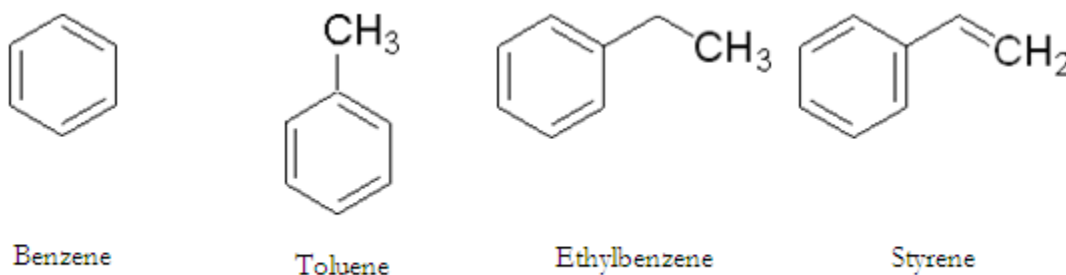


Figure 1: Chemical structures benzene, toluene, ethylbenzene, and styrene

The concentrations of VOCs in cigarette smoke can be measured by several different analytical instruments. Gas chromatography with flame ionisation detection (GC-FID) and gas chromatography with mass spectrometric detection (GC-MS) are, however, the most commonly used analytical techniques for analysis of VOCs.

1. Discuss why gas chromatography (GC) and not high resolution liquid chromatography (HPLC) is the most commonly used analytical technique for separation of mixtures of VOCs.

A new method for sampling, sample preparation and analysis of the 4 selected VOCs (see Figure 1) in cigarette smoke has recently been developed and validated. In this study, only the vapour-phase portion of cigarette smoke was analyzed using an Agilent 6890 GC-FID.

VOCs were desorbed from a SPME (solid-phase membrane extractor) at 260°C in a heated inlet and focused onto an Agilent DB-624 capillary column (30.0 m × 0.320 mm inner diameter × 1.80 μm film thickness), which is an intermediate-polarity column specifically designed for the analysis of VOCs. The GC oven, equipped with cryo cooling, was programmed to start at -20 °C, hold for 2 min, and ramped to 200 °C at 8 °C/min, for a total run time of 29.50 min. Nitrogen was used as carrier gas. A section of a GC-FID chromatogram of the vapor-phase for ‘Marlboro ultralight’ is shown in Figure 2. The four compounds quantified in this study are labeled A-D in the plot.

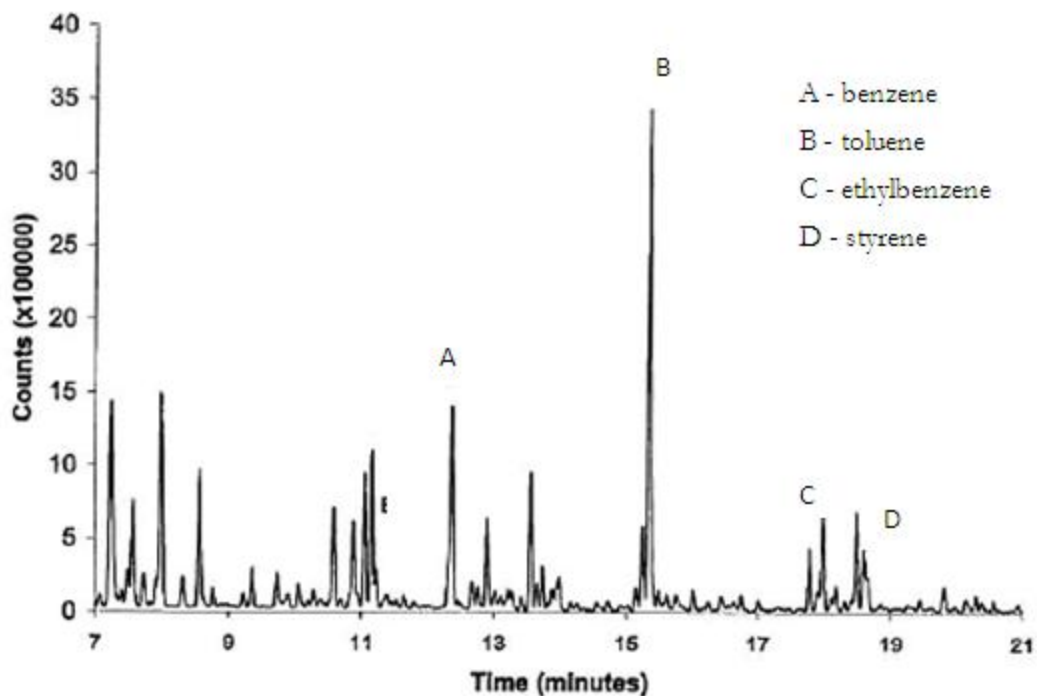


Figure 2: GC-FID chromatogram of the vapour-phase for 'Marlboro ultralight'

- 2. Many peaks coelute in the GC-FID chromatograms of VOCs (e.g., ethylbenzene and styrene coelutes with other VOCs). The presence of interfering compounds is undesirable and lead to biases (inaccurate measurements) and low precision of the peak quantification. Describe four ways to improve the selectivity of the VOC analysis.**

A quantification stock solution of benzene, toluene, ethylbenzene and styrene (**Solution A**) was prepared by weighing 10.0 mg of benzene (of 95.0% purity), 20.0 mg of toluene (of 97.5% purity), 10.0 mg of ethylbenzene (of 99% purity) and 5 mg of styrene (of 98% purity) in a 100 mL volumetric flask and adjusting to 100 mL with methanol. A 10 times dilution of the quantification stock solution (**Solution A**) was prepared by adding 1000 μL of **Solution A** to a 10 mL volumetric flask and adjusting to the mark with methanol. This new quantification standard solution is named **Solution B**.

Five standard solutions were prepared in 25 mL volumetric flasks by adding varying amounts of **Solution A** or **Solution B**. After adding the quantification standards the volumes of the volumetric flasks were adjusted to 25 mL with methanol. The preparation of the standards is described in Table 1a and 1b together with the peak areas of two VOCs (benzene and toluene) calculated from the GC-FID chromatograms of the five standard solutions.

- 3. Fill in the missing values in Table 1a and 1b for preparation of five standard solutions. The five standard solutions should be prepared in 25 mL volumetric flasks. Show examples of calculations. Then draw calibration curves for benzene and toluene (use the chart on the next page) based on the external standard method. Remember to label the x- and y-axes.**

Table 1a: Concentrations of benzene, toluene, ethylbenzene and styrene in the two quantification stock solutions

	Benzene	Toluene	Ethylbenzene	Styrene
Concentrations of the four VOCs in the quantification stock solution (Solution A)				
Concentrations of the four VOCs in the dilution of the quantification stock solution (Solution B)				

Table 1b: Detailed scheme for preparation of five standard solutions from **Solution A** and **Solution B**, and the peak areas calculated from the GC-FID chromatograms of the five standard solutions

	Std 1	Std 2	Std 3	Std 4	Std 5
Added volume (in μL) of Solution A containing both benzene and toluene	----- ---				
Added volume (in μL) of Solution B containing both benzene and toluene		----- ---	----- ---	----- ---	----- ---
Benzene concentration in $\mu\text{g/mL}$	0.19	0.38	0.95	1.90	3.80
Peak area of benzene	9150	15800	35750	69000	135500
Toluene concentration in $\mu\text{g/mL}$	0.39	0.78	1.95	3.90	7.80
Peak area of toluene	7995	15990	39975	79950	159900
Total volume of standards	25 mL	25 mL	25 mL	25 mL	25 mL

Method validation and quality control.

In another study, an optimized and validated analytical method, which provided high selectivity and sensitivity, was used to analyse VOCs in U.S. cigarette brands ranging from full flavoured to ultralight brands. These samples were analysed in seven analytical batches. Each batch of samples (that were analysed at seven consecutive days) contained cigarette smoke samples, one field blank and one reference solution. The results obtained for benzene for the replicate field blanks and the replicate reference solutions are shown in Table 2. The response factor (RF) for benzene using this method was estimated to 47000 using single-point calibration ($RF_{\text{benzene}} = 47000 \text{ mL}/\mu\text{g}$). The certified value for benzene in the reference solution is $0.74 \mu\text{g/mL}$.

Table 2: Peak areas of benzene in replicate analyses of seven field blanks and reference materials.

	Field blank (peak area)	Reference solution (peak area)
Batch 1	742	35602
Batch 2	712	36709
Batch 3	890	34802
Batch 4	690	35692
Batch 5	943	34729
Batch 6	910	36482
Batch 7	1052	37800

- 4. Estimate the concentration detection limit (LOD), the lower limit of quantification (LOQ), the precision (coefficient of variation) and accuracy for the method. Finally prepare a control chart with warning and action limits and state whether observations meet the criteria for stability of a control chart.**