Link: http://www.kdc.lu.lv/skoleniem/konkurss/baltija/

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 end of February 2013;
- participants registry for participation by sending answers in one of first two rounds;
- all answers, parts of solutions **must** be written in specially designed answer sheets according to directions (grading will be done automatically by analyzing answer sheet file);
- each student must submit each 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);
- 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.

1. Periodic rule was discovered in 1869 by:
   a. Boris Elcin

b. Dmitri Mendeleev
c. Lothar Miller
d. Svante Arrheniuss
e. Albert Einstein
2. Solution forms gas bubbles without characteristic smell, when it is treated with potassium hydrogensulphate solution. This solution might contain:
    a. potassium cyanide
    b. potassium hydroxide
    c. potassium sulphite
    d. potassium carbonate
    e. none of above
3. Which graph shows changes of electrical conductivity, when barium hydroxide is added to solution of sodium sulphate.
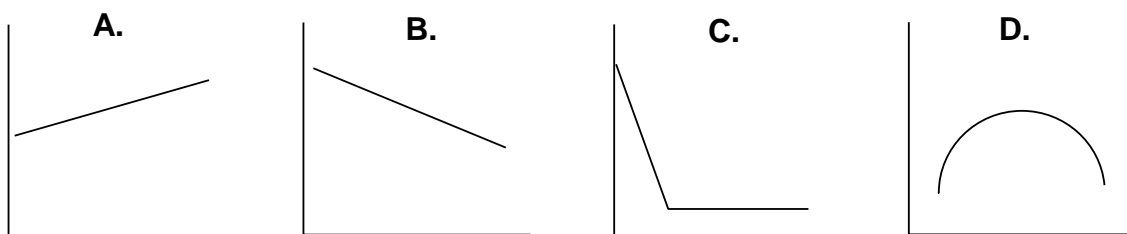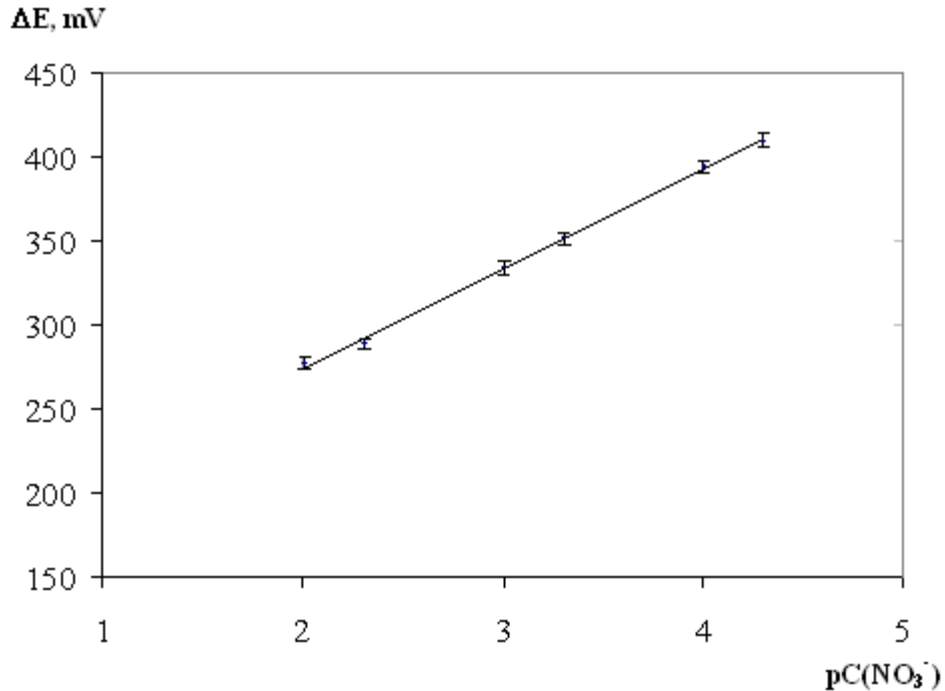

    a. A
    b. B
    c. C
    d. D
    e. none of above
       Correct graph would be V shape, as conductivity decreases due to formation of insoluble $BaSO_4$, then increases due to increase of ions in solution.
4. Number of sigma and pi bonds in nitrogen(I) oxide is respectively:
    a. 2, 2
    b. 2, 3
    c. 3, 1
    d. 1, 3
    e. none of above
5. Little John walked on beach of Baltic Sea near Liepaja, Latvia. He found small stone, similar to amber which is common in this region, and placed it into pocket. After some time pocket went into flames and white powder formed. What is possible composition of this sample?
    a. Iron(II) iodide
    b. Phosphorous
    c. Sodium peroxide
    d. Potassium ozonide
    e. none of above
6. Which statement about aragonite, vaterite and calcite is true.
    a. They all are soluble in concentrated boric acid
    b. They all are polymorphic forms of calcium carbonate
    c. 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 Franclin discovered thar 1 teaspoon of oil would cover 2000 m^2 of water and there are approximately 5 mL of oil in teaspoon, what is the thickness of the layer of oil?
    a. 1,5 Å
    b. $2,5*10^{-9}$ m
    c. 2,5 pm
    d. 2 μm
    e. none of above

8. Coordinaion number for dichlorobisethylenediaminecobalt(III) chloride is:
    a. 2
    b. 4
    c. 6
    d. 8
    e. none of above

9. Shape of complex ion $[Ni(CN)_5]^{3-}$ 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 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. Which phase forms lowest layer?
    a. deuterium oxide
    b. ice
    c. water
    d. it is homogenous mixture
    e. none of above

13. Spectrum of compound X is given in figure below (from book "Chemistry and Chemical reactivity")
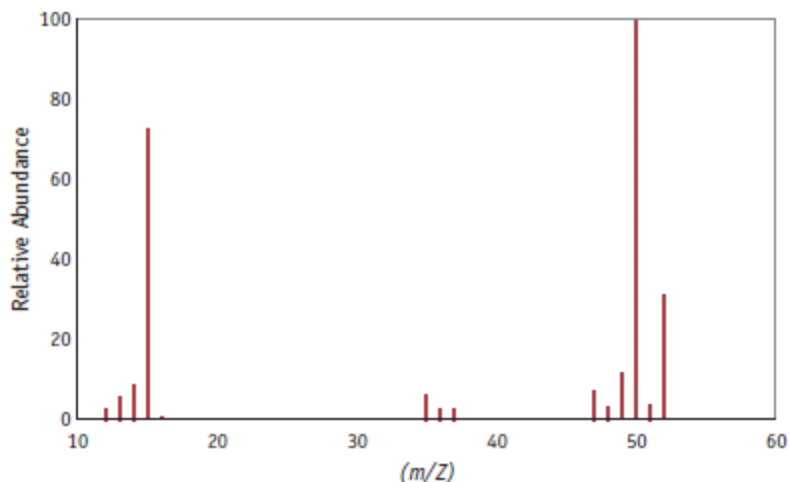
Molar mass of compound X is (all numbers in g/mol):

a. 50
b. 15
c. 52
d. it is impossible to determine molar mass /molecular ion may not be observed /
e. none of previous answers (also accepted as true; you ccould identify CH_3Cl and then give its' molar mass, M = 50.5 g/mol)

14. Compound A (same which was investigated in previous question) contains:

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

a. I, II, III
b. only I and H
c. I, III, IV
d. I, II, IV
e. none of above

15. By weighting solute solution of precise concentration can be made from:

a. potassium dichromate
b. sodium hydroxide
c. ammonia
d. potassium permanganate
e. none of above

16. Three equal almost empty balloons were tighten at the top of three Erlenmeyer flask. First and second flask contained concentrated sulfuric acid, but third one contained concentrated hydrochloric acid. 5 grams of iron, 5 grams of copper and again 5 grams of copper were placed in flask (one metal in one flask), Which balloon will be the largest after five minutes:

a. 1st
b. 2nd
c. 3rd
d. all will be equal
e. none of previous answers

17. Calbration graph for ionometric determination of nitrate ions in solution is given below, where

$x = -\log(C(NO_3^-))$ and $y = \Delta E$.

Figure axes: y-axis labeled ΔE, mV (values 150, 200, 250, 300, 350, 400, 450); x-axis labeled $pC(NO_3^-)$ (values 1, 2, 3, 4, 5).

(No.17 continued) Slope equal to:
- a. 60
- b. 155
- c. -80
- d. +80
- e. none of above

18. Sodium sulfite solution was mixed with potassium hydroxide solution and then potassium permanganate(VII) solution was added. What is final color of this solution?
- a. blue
- b. colorless
- c. brown
- d. green
- e. none of above

19. Solution of nitric acid (HNO_3) were 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? [not exactly correct question, as amount of product is not given, but c is the most reasonable answer]
- 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 mass of iron(II) sulfide which was obtained in this reaction if yield is 85%?
    a. 10 g
    b. 5 g
    c. 7,85 g
    d. 6,68 g
    e. none of above
22. K_a for unknown acid HA is $5*10^{-4}$M. What is pH for 0,01 M solution of this acid?
    a. 3,0
    b. 2,7
    c. 1,9
    d. 5,4
    e. 3,3
    f. none of above
23. (continues from previous question) Which particle has the highest concentration in previous solution?
    a. H_3O^+
    b. H^+
    c. OH^-
    d. A^-
    e. HA
24. Figure below corresponds to:
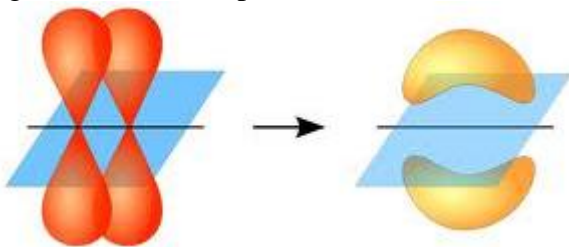
    a. formation of classic Italian pizza
    b. formation of pi bond
    c. formation of sigma bond
    d. formation of delta bond
    e. formation of hydrogen bond
    f. formation of hydrogen bond
    g. none of above
25. Compounds which have giant covalent structures also have:
        I. high melting points;
        II. They conduct electricity when turned into liquid state;
        III. Low sublimation enthalpies;
        IV. Low melting points and low hardness;
        V. Compounds are very hard.
    Correct statement(-s) is(are):
    a. only III
    b. III and IV
    c. only I
    d. I and IV

    e. I, II, IV

    f. II, III, IV

    g. <mark>none of above answers (correct are I and V, if typical examples of giant covalent structures are diamond and graphite)</mark>

26. Electron formula $1s^2 2s^2 2p^6$ corresponds to:

    a. Cl^+ ion

    b. O_2^{2-} ion

    c. CH_4 molecule

    d. Ar

    e. <mark>none of above</mark>

27. Which molecule is paramagnetic?

   a. <mark>O_2</mark>

    b. N_2

    c. CO

    d. H_2

    e. none of above

28. Which of particles O_2^{2+}, O_2^+, O_2, O_2^- is the most stable?

    a. <mark>O_2^{2+} (as it has triple bond)</mark>

    b. O_2^+

    c. O_2

    d. O_2^-

    e. all have equal stability

29. Which of particles O_2^{2+}, O_2^+, O_2, O^{2-} is the most stable?

    a. O_2^{2+}

    b. O_2^+

    c. O_2

    d. <mark>O_2^- [deleted question as here should be O^{2-} oxide ion]</mark>

    e. all have equal stability

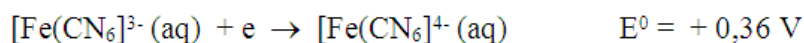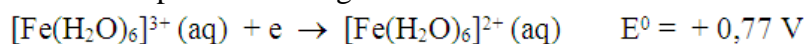30. Figure below shows Frost diagram of unknown chemical element. The most stable oxidation number of this element is:
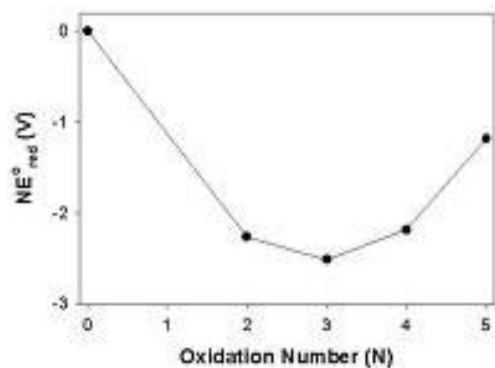
    a. 0

    b. +1

    c. +2

    d. <mark>+3</mark>

    e. +4

31. "The strongest known oxidizing agent in real life" is:

a. fluorine gas
    b. hydrogen peroxide
    c. potassium permanganate
    d. chlorine gas
    e. electrical current
32. If standard reduction potentials for $Ce^{4+}(aq) \rightarrow Ce^{3+}(aq)$ and for $Au^{3+}(aq) \rightarrow Au(s)$ is 1,72 V and 1,50 V respectively, it means:
    a. cerium(IV) can oxidize metallic gold to Au^{3+}
    b. cerium(IV) can oxidize metallic gold to Au^{3+} only in acidic medium
    c. gold(III) can oxidize Ce^{3+} to Ce^{4+}
    d. gold(III) can oxidize Ce^{3+} to Ce^{4+} only in acidic medium
    e. none of above is correct
33. Reduction standard potentials are given below:

$$[Fe(H_2O)_6]^{3+} (aq) + e \rightarrow [Fe(H_2O)_6]^{2+} (aq) \qquad E^0 = +0,77\ V$$

$$[Fe(CN_6]^{3-} (aq) + e \rightarrow [Fe(CN_6]^{4-} (aq) \qquad E^0 = +0,36\ V$$

Which statement is true?
    a. $[Fe(H_2O)_6]^{3+}$ is the strongest reducing agent
    b. $[Fe(H_2O)_6]^{2+}$ is the strongest reducing agent
    c. $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(H_2O)_6]^{3+}$
    d. $[Fe(CN)_6]^{3-}$ is strongest oxidizing agent
    e. 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?
    a. molecule HC forms hydrogen bonds, while HB not
    b. relative electronegativity for element B is higher than for element A
    c. relative electronegativity for element B is higher than for element C
    d. molecule H-C have better solubility in 40% etanol/water solution than H-B
    e. H-C has the highest melting point
35. Which of given ions will undergo reduction reaction most vigorously?
    a. perchlorate
    b. chlorate
    c. chlorite
    d. hypochlorite
    e. chloride
36. If John will mix $Ag^{2+}(aq)$ solution with metallic silver which of processes mentioned will occur?
    a. annihilation
    b. explosion
    c. disproportionation
    d. addition reaction

e. isomerisation
<mark>[deleted question answer should be synproportion, opposite reaction of disproportion]</mark>

37. Which of these compounds is optically active?
    a. <mark>$K_3[Cr(oxlate)_3]$</mark>
    b. H_2O_2
    c. Copper(II) acetate
    d. trans-$[Pt(NH_3)_2Cl_2]$
    e. cis-$[Pt(NH_3)_2Cl_2]$

38. When sodium hydroxide solution is added to metallic beryllium:
    a. no reaction occurs
    b. white precipitate of $Be(OH)_2$ is formed
    c. gas with molar mass > 18 g/mol is formed
    d. <mark>$Na_2[Be(OH)_4]$ is formed</mark>
    e. Be polymer is formed

39. Valence of O (underlined) in beryllium oxoacetate $[Be_4\underline{O}(OOCCH_3)_6]$ is:
    a. II
    b. +2
    c. -2
    d. <mark>IV</mark>
    e. none of above

40. Which of these answers contain solutions in increasing order of pH value? Concentration for all solutions is equal.
    a. K_2CO_3, KOH, $KHCO_3$, K_2SO_4
    b. <mark>HI, H_2CO_3, NaCl, $NaHCO_3$</mark>
    c. Na_2SO_3, Na_2S, NaBr, NaOH
    d. $Zn(CH_3COO)_2$, $ZnCl_2$, $Zn(OH)_2$, KCl
    e. none of above

41. When crystals of water are formed, which process occurs first?
    a. adsorption
    b. <mark>nucleation</mark>
    c. crystal growth
    d. diffusion
    e. absorption

42. Student investigated solution of weakly soluble electrolyte with 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, cocentraions in each case are given below.
    I. 0,10 M G + 0,10 M F
    II. 0,001 M G + 0,001 M F
    III. 0,01 M G + 0,01 M F
    IV. 0,05 M G + 0,1 M F
    In which case precipitation was observed.
    a. <mark>only I</mark>
    b. II, III and IV
    c. all cases
    d. I and II
    e. none of above

43. Mixture of 2-amino-4-(methylthio)butanic acid and 2-aminopropanoic acid can be separated by:
   I. electrophoresis
   II. paper chromatography
   III. NMR
   IV. IR spectroscopy
   V. masspectrometry
   VI. potentiometric titration
   a. only method II
   b. methods I and II
   c. methods III and IV
   d. methods I, II, III and IV
   e. all mentioned methods
   f. none of above is correct
44. Buffer solution with pH = 7,0 can be prepared from solution of:
   a. sodium hydroxide and water
   b. hydrochloric acid and water
   c. sodium hydroxide and hydrochloric acid
   d. potassium permanganate and hydrogen bromide
   e. sodium hydroxide and phosphoric acid
45. Which of these indicators are(is) suitable for titration of acid (pK_a = 6,25) with potassium hydroxide?
   a. methyl orange
   b. methyl red
   c. phenolphthalein
   d. all mentioned
   e. none of above
46. Compound vapor has relative density against helium D(He) = 5. Compound does not 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:
   a. oxygen
   b. boron
   c. carbon
   d. fluorine
   e. none of above
47. Little John weighted piece of copper several times. If his random error is greater than systematical error then he should:
   a. take scales which are more precise
   b. ensure that temperature in laboratory remains the same
   c. increase mass of copper sample
   d. increase number of measurements
   e. burn copper and analyze copper(II) oxide
48. Dependence of light absorption from mass concentration is … relationship.
   a. parabolic
   b. exponential
   c. polynomial

d. linear
e. 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.
    a. VIII A
    b. VII A
    c. VIII B
    d. VII B
    e. III B
50. Chromatogram of sample A is shown in picture below. Which these statements are true?
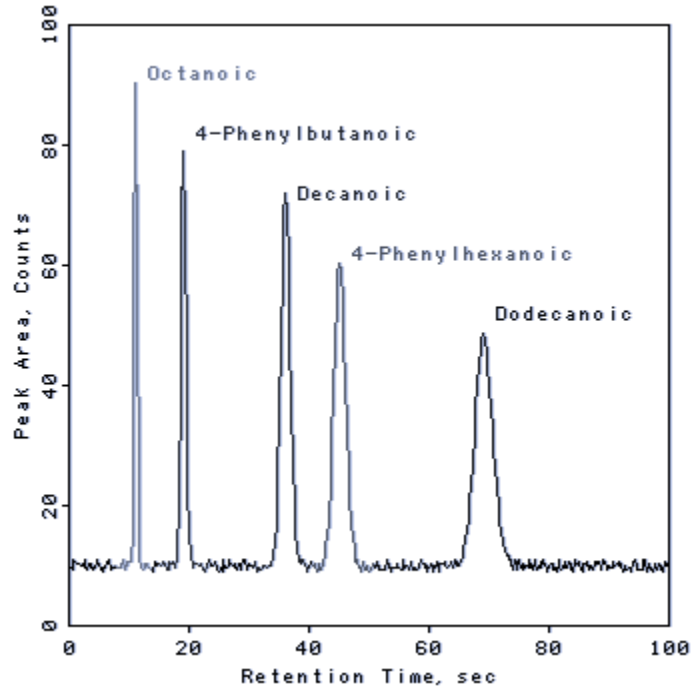

Figure from: statisticaldesigns.com

    a. sample does not contain aspirin
    b. sample contains exactly five compounds
    c. sample contains less than five compounds
    d. sample contains at least five compounds
    e. none of above is correct

Problem 2   Let's dissolve! (20 points)

1.

$[Ag^+][Cl^-] = 10^{-9.74}$

$[Ag^+] = [Cl^-] = s$

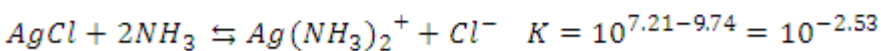$s^2 = 10^{-9.74}$

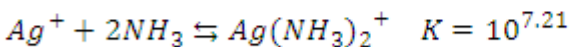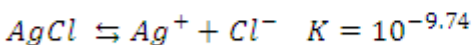$s = 1.35 \cdot 10^{-5}$ mol/L

2.

$Ag^+ + 2S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-}$
$Ag^+ + 2NH_3 \rightarrow Ag(NH_3)_2^+$

3.

for NH_3

$$AgCl \leftrightarrows Ag^+ + Cl^- \quad K = 10^{-9.74}$$

$$Ag^+ + 2NH_3 \leftrightarrows Ag(NH_3)_2^+ \quad K = 10^{7.21}$$
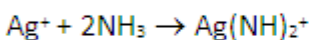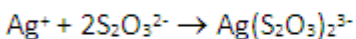
$$AgCl + 2NH_3 \leftrightarrows Ag(NH_3)_2^+ + Cl^- \quad K = 10^{7.21-9.74} = 10^{-2.53}$$

$$\frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = 10^{-2.53}$$
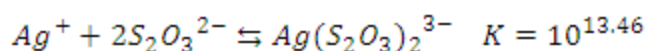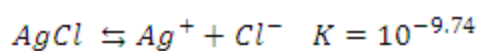
$$\left[Ag(NH_3)_2{}^+\right] = [Cl^-] = x$$

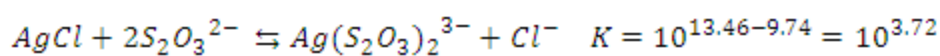$$[NH_3] = 1 - 2x$$

$$\frac{x^2}{(1-2x)^2} = 10^{-2.53}$$

x = 0.0490 mol/L

$$m = xVM = 0.0490 \cdot 0.1 \cdot 143.5 = 0.703 \text{ g}$$

for $Na_2S_2O_3$

$$AgCl \leftrightarrows Ag^+ + Cl^- \quad K = 10^{-9.74}$$

$$Ag^+ + 2S_2O_3{}^{2-} \leftrightarrows Ag(S_2O_3)_2{}^{3-} \quad K = 10^{13.46}$$

--|

$$AgCl + 2S_2O_3{}^{2-} \leftrightarrows Ag(S_2O_3)_2{}^{3-} + Cl^- \quad K = 10^{13.46-9.74} = 10^{3.72}$$

$$\frac{\left[Ag(S_2O_3)_2{}^{3-}\right][Cl^-]}{[S_2O_3{}^{2-}]^2} = 10^{3.72}$$

$$\left[Ag(S_2O_3)_2{}^{3-}\right] = [Cl^-] = x$$

$$[S_2O_3{}^{2-}] = 1 - 2x$$

$$\frac{x^2}{(1-2x)^2} = 10^{3.72}$$

x = 0.497 mol/L

$$m = xVM = 0.497 \cdot 0.1 \cdot 143.5 = 7.13 \text{ g}$$

4.

$$x(Ag^+) = \frac{1}{K \cdot [NH_3]^2} = \frac{1}{10^{7.21} \cdot (1 - 2 \cdot 0.0490)^2} = 7.58 \cdot 10^{-8}$$

$$[Ag^+] = x(Ag^+) \cdot C = 7.58 \cdot 10^{-8} \cdot 0.0490 = 3.71 \cdot 10^{-9} \text{ M}$$

$$E = E^o + 0.059 \lg[Ag^+] = 0.80 - 0.50 = 0.30 \text{ V}$$

5.

$$E = E^o + 0.059 \lg[H^+]^2 = -0.30 \text{ V}$$

$$0.059 \lg[H^+]^2 = -0.30 \text{ V}$$

$$[H^+] = 0.00287 \text{ M}$$

$$pH = -\lg 0.00287 = 2.54$$

Problem 3   Hard rock café! (20 points)

1. There are many ways to arrive at a solution, we accepted any correct reasoning not just the one presented here.

In 100 g of the compound: $m(O) = 31.64$ g, so $m(Me) = 68.36$ g.
In this sample $n(O) = m/M = 1.9775$ mol. We know that the mole ratio of the metals is 1:1. Let us take $n(Me_1) = n(Me_2) = x$ mol. This has to give a chemically reasonable ratio with the amount of oxygen.

The first two metals with an atomic number difference of 4 is K–V. We can write the following equation: $39.10x + 50.94x = 68.36$, so $x = 0.7592$ mol. Related to the amount of oxygen, this is not a good solution: $1.9775:0.7592 = 2.6047:1$. The last pair in this period is Co–Ga: $58.93x + 69.72x = 68.36$, so $x = 0.5314$ mol, the oxygen metal ratio is $3.7216:1$. The integer 3:1 ratio is in between the two. Checking the other metals in the period, Ti and Fe give a reasonable fit: $47.87x + 55.85x = 68.36$, so $x = 0.6591$ mol and the ratio is $3.000:1$.

The compound in question has the empirical formula $FeTiO_3$. The mineral with this composition is named *ilmenite*.

2. $2\ FeTiO_3 + 7\ Cl_2 + 6\ C \rightarrow 2\ FeCl_3 + 2\ TiCl_4 + 6\ CO$
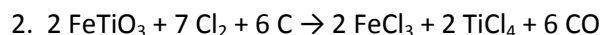
3. Titanium tetrachloride is exceptional in being a liquid at room temperature. It contains apolar molecules that form a lattice held together with weak van der Waals interaction only at low temperatures.

Titanium tetrafluoride, however, has a polymeric structure with octahedral $\{TiF_6\}$ fragments held together with strong chemical bonds.

4. Titanium can be reduced from the chloride with different agents. A typical reagent is magnesium.

$TiCl_4 + 2\ Mg \rightarrow Ti + 2\ MgCl_2$
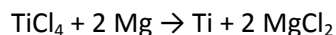
Problem 4   Bad smell! (24 points)

1. The sulfur containing species have a total concentration of 0.117 mol/dm^3. Hydrogen ions coming from the second dissociation step can be neglected. The first dissociation of a weak acid in this concentration gives pH $= 3.92$. (3 points)

The same first dissociation step gives pH $= 8.90$ as the answer for the second question. (2 points)

2. Using the second dissociation constant given, the ratio $[HS^-]/[S^{2-}] = 5$ results. This means that 83% of hydrogen sulfide would be in sulfide ion form in this solution. (2 points)
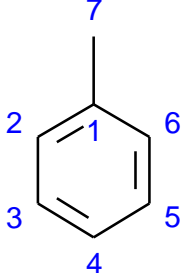
3. In moderately basic solutions HS^- ion will be the dominant species, present in 100%. The detectable 1% decrease in 5 mol/dm^3 hydroxide ion solutions will mean 99% of hydrogen sulfide as HS^- ion. So $[HS^-]/[S^{2-}] > 99$, and $K_2 < 2 \cdot 10^{-17}$. (3 points)
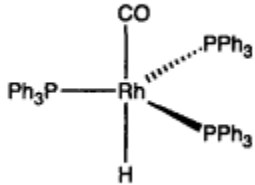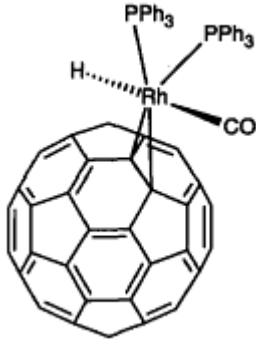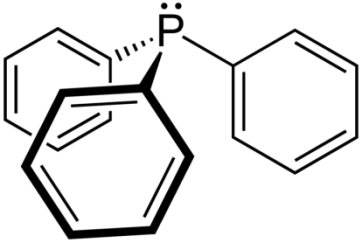
4. In concentrated solutions activity coefficients can significantly deviate from unity. (2 points)

5. From the concentrations and the appearances of the precipitates two limits can be estimated: based on no ZnS precipitate: $K_2 < 3.41 \cdot 10^{-15}$, based on SnS: $K_2 > 2.71 \cdot 10^{-18}$. (4+4 points)

f) If we take the precipitation of ZnS complete, then the pH of the solution is determined by the hydrogen ions formed in the $Zn^{2+} + H_2S \rightarrow \underline{ZnS} + 2\,H^+$ process, as the hydrogen sulfide dissociation is suppressed. Final pH = 2 in this case. However the complete precipitation is not obvious and depends on the true value of the second dissociation constant. If $K_2 = 10^{-17}$ then pH = 2.39 and only 40% of the zinc is precipitated. (2+2 points)

Problem 5   Complex compound (28 points)

1 a	Important note! Points are taken for an incorrect number of significant figures in numerical calculations.
	$\lambda = 2d \sin \Theta$ $$d = \frac{\lambda}{2 \sin \Theta} = \frac{1.542}{2 \sin \frac{41.11°}{2}} = 2.196 \text{Å} \; [2]$$ $$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$ $$\therefore \; a^2 = 2.196\sqrt{3} \approx 3.803 \text{ Å} \equiv 3.803 \times 10^{-8} \; cm \; [3]$$
1 b	In an fcc structure there are four formula units (here – atoms) per unit cell. Given the density and the lattice parameter, calculated above, the atomic mass of **M** can be derived: $$\rho = \frac{m}{V} = \frac{4M}{N_A a^3} \; \therefore \; M = \frac{N_A \rho a^3}{4} = 102.9 \; g \; mol^{-1} \; [2]$$ **M** = Rh (rhodium)
2 a	Since **C** contains one element only and gives a signal in ^{13}C-NMR, it must be some allotrope of carbon. In addition, it must contain carbon in sp^2 hybridization state. Given the colour of the toluene solution, **C** can only be the buckminsterfullerene **C$_{60}$**, which is aromatic and highly symmetric, as seen from the spectrum. **C** = C$_{60}$
2 b	

Table for 2 b:

Signal (ppm)	Carbon number
21.4	7
123.1	
125.4	2-6
128.3	
137.8	1

Note: no points should be taken for incorrect assignment of signals at 123.1, 125.4, 128.3 ppm.
B = C$_7$H$_8$, toluene

3 a	The signal at – 9.50 ppm is most probably due to a hydrogen, directly attached to the metal. It shows coupling over two bonds (as hinted in the problem) to phosphorus, which has a spin of ½, just like ^{1}H. This means, that if the hydrogen signal is split into a quartet there must be three phosphorus atoms two bonds away from it (i.e. attached directly to the metal). The other signals in the NMR spectrum must be due to the hydrogens of the other ligands. The signals are characteristic to aromatic compounds, and bearing in mind the presence of phosphorus, we can predict, that there are going to be **three triphenylphosphine** ligands attached to rhodium in this complex (this correlates nicely with the chemical shifts and the total intensity: 5*3*3 = 45) From the IR spectrum we can infer, that there is also one or two C≡O ligands attached to the rhodium atom. RhH(CO)(PPh$_3$)$_3$, a yellow solid, fits the description very well. **A** = RhH(CO)(PPh$_3$)$_3$
3 b	**D** = RhH(CO)(PPh$_3$)$_2$C$_{60}$ (a dark green solid) **E** = PPh$_3$ (triphenylphosphine)
3 c	Since both the complexes are coloured, they absorb in the near UV/ visible light region of the electromagnetic spectrum. Thus, UV-Vis spectroscopy can be used. To carry out the spectroscopic analysis the maximum absorption wavelengths for both compounds are required, as well as the molar extinction coefficient at the desired wavelengths. A = εlC – Lambert-Beer law, where A is the absorption, ε is the extinction coefficient, l is the sample thickness and C is the concentration
Notes	The material for this task was taken from the following paper: *Claridge, J.B., Douthwaite, R.E., Green, M.L.H., Lago, R.M., Tsang, S.C., York, A.P.E. 1993. Studies on a new catalyst for the hydroformylation of alkenes using C$_{60}$ as a ligands. Journal of Molecular Catalysis 89:113–120* Molecular structure for the coordination complex compounds were taken from *Hirsch, A 1994. The Chemistry of the Fullerenes. New York: Thieme*

Problem 6   Cigarette smoke (28 points)

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).
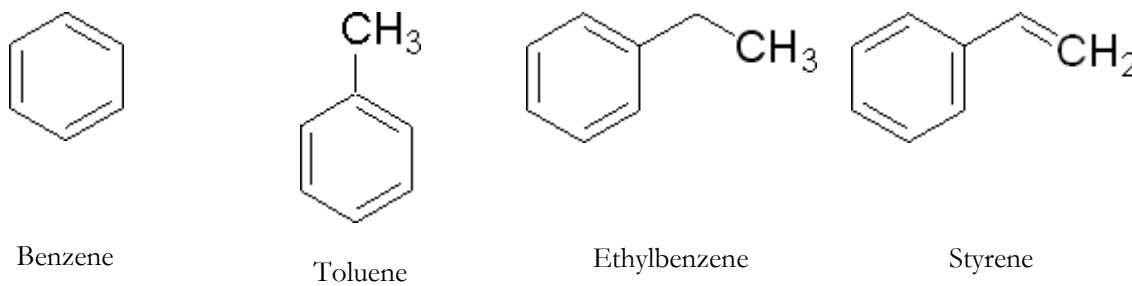

Benzene   Toluene   Ethylbenzene   Styrene

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. (12% - 3.36 points)

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 (use approximately 2 – 3 lines for the argumentation).

- *because the VOCs are often injection as a gas by either head-space/desorption, which is well fitted to GC. HPLC cannot handle gas injections.*
- *because VOCs have low boiling points can they all easily be separated on GC*
- *(EI/CI can easily ionize all VOCs, while ESI which is the typical interface to HPLC cannot ionize all VOCs (e.g., benzene, toluene, ethylbenzene etc) in neither modes).*

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 analysed 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 vapour-phase for 'Marlboro ultralight' is shown in Figure 2. The four compounds quantified in this study are labelled A-D in the plot.
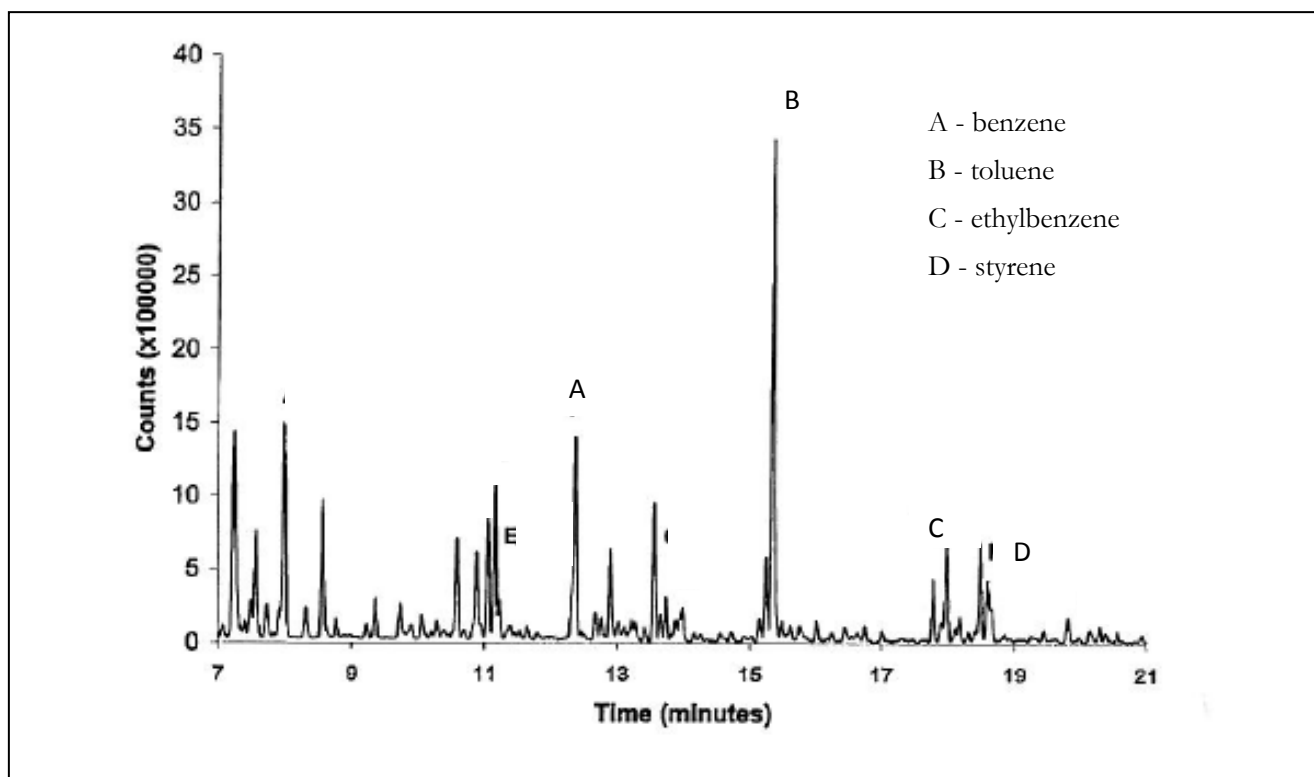

Figure 2: GC-FID chromatogram (retention time between 7 and 21 min) of the vapour-phase for 'Marlboro ultralight'

2. (22% - 6,16 points)

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. **Discuss at least four ways to improve the selectivity of the VOC analysis (use approximately 10 – 15 lines for the argumentation).**

1) *Use a more selective detector than FID. A mass selective detector in SCAN (or preferably SIM) mode will greatly improve the selectivity and the latter also the sensitivity of the analysis.*
2a) *Change the temperature program (decrease the gradient from 8 °C/min to e.g., 4 °C/min)*

2b) *Increase the number of theoretical plates (N = L/H)*

    a. *Increase the column length (e.g., an increase of the column length from 30 to 60 m will theoretically lead to an increase in N with $\sqrt{2}$*
    b. *Decrease the plate height: (1) decrease the column diameter, decrease the film thickness, change the flow rate (most likely not so important), change carrier gas to Helium or Hydrogen (the latter only for GC-FID)*
3) *Perform a more extensive (and selective) sample preparation (normal phase)*
4) *Change the column stationary phase. This will most likely not lead to an improvement as the DB-624 capillary column is of intermediate-polarity and is specifically designed for the analysis of volatile priority pollutants.*

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 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 2a and 2b together with the peak areas of the four VOCs calculated from the GC-FID chromatograms of the five standard solutions.

3. (33% - 9.24 points)

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**)	*0.095 mg/mL*	*0.195 mg/mL*	*0.099 mg/mL*	*0.049 mg/mL*
Concentrations of the four VOCs in the dilution of the quantification stock solution (**Solution B**)	*9.5 μg/mL*	*19.5 μg/mL*	*9.9 μg/mL*	*4.9 μg/mL*

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		*100*	*250*	*500*	*1000*
Added volume (in μL) of **Solution B** containing both benzene and toluene	*500*	----------------	----------------	----------------	----------------
Benzene concentration in μg/mL	0.19	0.38	0.95	1.90	3.80
Peak area of benzene	9150	15800	35750	69000	135500
Toluene concentration in μg/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
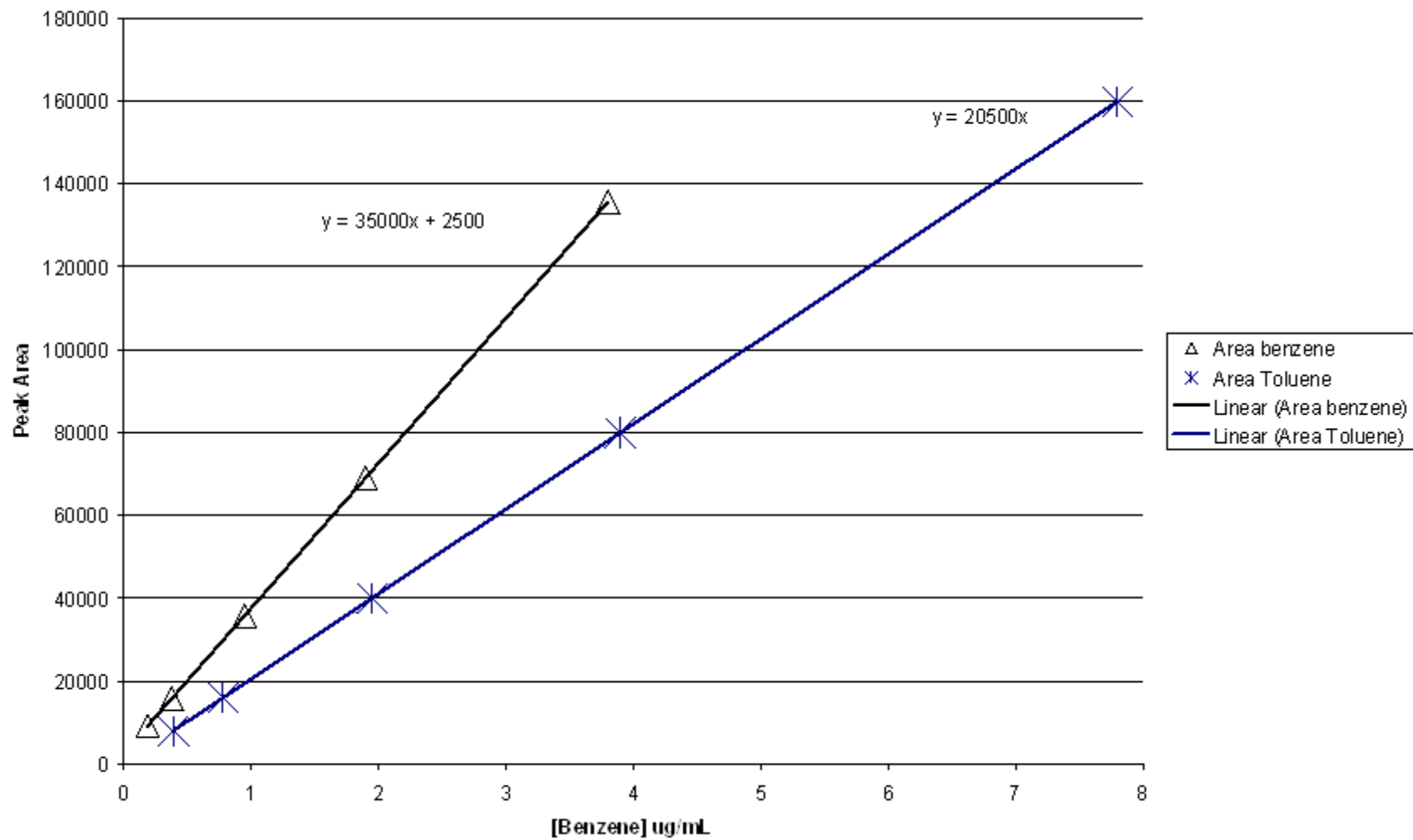
Method validation and quality control.

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 ($RF_{benzene}$ = 47000 mL/µg). The certified value for benzene in the reference solution is µg/mL 0.74 µg/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. (33% - 9.24 points)

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 (Show the calculations; remember to label the x- and y-axes).

Estimation of LOD and LOQ:

$s_{blank} = 135.9802$ (peak area)

$\bar{x} = 848.4286$ (peak area)

$LOD \cong (3 \cdot 135.9802 + 848.4286)/47000 = 0.026731 \ \mu g/mL = \underline{\underline{2.7 \cdot 10^{-2} \ \mu g/mL}}$

$LOQ \cong (10 \cdot 135.9802 + 848.4286)/47000 = 0.046984 \ \mu g/mL = \underline{\underline{4.7 \cdot 10^{-2} \ \mu g/mL}}$

Precision and accuracy:

$\bar{x}_{control} = 35973.71/47000 = 0.765398176 \ \mu g/mL$

$CV_{control} = 1101.066/47000/\bar{x}_{control} = 3.06075\% \ \underline{\underline{= 3.1\%}}$

$(\mu - \bar{x}_{control}) = (0.74 \ \mu g/mL - 0.765398176 \ \mu g/mL)/0.74 * 100\% = -3.43219\% \ \underline{\underline{= -3.4\%}}$

Quality control scheme