Problem 1 (author M.K. Beklemishev)

1. Reaction of titration: $3C_6H_8O_6 + KIO_3 = KI + 3C_6H_6O_6 + 3H_2O$ (1 point). Starch coloring appears with an excess of iodate as a result of liberation of iodine: $KIO_3 + 5KI + 6HCl = 3I_2 + 6KCl + 3H_2O$ (0.5 points). If 9.5 mL of iodate has been spent, the amount of ascorbic acid in the sample equals $9.5 \cdot 0.100 \cdot 3 = 2.85$ mmol (1 point, 2.5 points in total).

2. Transformations of dehydroascorbic acid (DHA) (1 point each, 2 points in total):

 $C_6H_6O_6$ (DHA) + $H_2O = C_5H_8O_5$ (xylosone) + CO_2 (slowly), and then rapidly:

 $C_5H_8O_5$ (xylosone) + $C_6H_8O_6$ (AA) = $C_5H_{10}O_5$ (xylose) + $C_6H_6O_6$ (DHA).

The scheme explains the autocatalytic decomposition of ascorbic acid.

3. As the titration had been already started, a certain amount of DHA was formed in solution. When the solution was being stored, DHA was gradually transforming into xylosone that rapidly reacted with xylose (that in turn partially passed into furfural but the degree of this transition it is not important for the solution of the problem, as the authors helpfully provided us with the *total* concentration of the two products). We may note that the reaction of xylose formation requires an equivalent amount of the initial AA; for this reason, the amount of AA decomposed equals the amount of xylose and furfural formed, i.e. 0.55 mmol. (The initial amount of DHA is insignificant, as it regenerates itself. After the whole amount of AA had been spent, the transformation of DHA stopped at the stage of xylosone.) Thus, the analyst undertitrated 0.55 mmol of AA, i.e. titrated 1 - 0.55 = 0.45 mmol AA (1 point), which needed 0.45 mmol / (0.100 M \cdot 3) = 1.5 mL of 0.100 M iodate solution (1 point).

4. Beside xylose and furfural (0.55 mmol) in solution, there was 0.45 mmol of DHA that was constantly regenerating while xylose was being formed. When all the AA was used up, the DHA had to slowly pass into xylosone, the final product-to-be in the absence of AA. Thus, under the conditions of equilibrium in solution, there were 0.55 mmol of (xylose + furfural) and 0.45 mmol of xylosone (1 point).

5. For example, the oxidation with atmospheric oxygen (to yield DHA or other products) (0.5 points).

6. As 3 mmol of AA reacts with 7 mmol of iodate, and iodate accepts 6 electrons in the reduction to iodide, then an AA molecule loses 14 electrons (0.5 points):

- $3 \mid C_6H_8O_6 14e^- \rightarrow \dots$
- 7 | $IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$

The formal oxidation state of carbon in $C_6H_8O_6$ equals $(6 \cdot 2 - 8) / 6 = +2/3$. If a molecule loses 14 electrons, i.e. 14/6 = 7/3 electrons per carbon atom, then the average oxidation state

must rise to 2/3 + 7/3 = 9/3 = +3. Among the oxygen-containing compounds, such a high oxidation state of carbon is achieved only for oxalic acid H₂C₂O₄ and its salts. The equation of the reaction of titration: $3C_6H_8O_6 + 7KIO_3 = 9H_2C_2O_4 + 7KI + 3H_2O$ (1 point for the composition of H₂C₂O₄, 0.5 points for its structure, 1.5 points in total).

Problem 2 (author S.S. Fedotov)

1. The easiest way to start solving the problem is to consider the compound G. Its formula as a nitride may be regarded as M_3N_x where x – is the valence of M.

$$3: x = \frac{w(M)}{M(M)}: \frac{w(N)}{M(N)} = \frac{100 - w(N)}{M(M)}: \frac{w(N)}{M(N)} = \frac{59.80}{M(M)}: \frac{40.20}{14} = \frac{20.826}{M(M)}$$

Simple searching (x = 1, M = 6.94 g/mol) give the appropriate answer that M is Li (lithium). Hence, L is lithium hydride, LiH, obtained by the reduction of G. Indeed, LiH and its analogs (LiBH₄, LiAlH₄ etc.) are broadly applied in preparatory chemistry as strong reduction agents. Thus, F is hydrogen, H₂. For E presents in minerals like olivine, Mg₂SiO₄, dolomite, $(Mg,Ca)CO_3$ and carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O_3$, it can be concluded, that E is magnesium and Z is magnesium hydride, MgH_2 . Now let us turn to the compound D. The reaction can be written as following: $xCH_3I + 2H = HI_x + H(CH_3)_x$, where **D** is $H(CH_3)_x$. $M(H) = M(D) - xM(CH_3)$. At x = 2 we obtain D molar mass 65.4 g/mol, which is equal to atomic mass of zinc. Therefore, H - Zn, $D - Zn(CH_3)_2$, $C - ZnI_2$, $Y - ZnH_2$. Zn is neighbored by Cu (on left) and Ga (on right) in the Periodic table. It is clear that a huge part of copper salts form blue solutions mostly, while almost all gallium salts are colorless. Now we have K – copper, A – copper sulfate $CuSO_4$ ·5H₂O and X corresponds to copper (I) hydride, CuH (what is confirmed by the heavy element mass fraction w(Cu) = $\frac{w(Cu)}{M(CuH)} = \frac{63.5}{64.5} = 0.9845$). So, the interaction between A and B is an ox/red process, such that B demonstrates its strong reducing properties. In this context the only candidate for **B** is hypophosphoric acid, H_3PO_2 . $J - H[CuCl_2]$ (0.2 points for K and H, 0.25 points for the other compounds, 0.6 points for calculations, 4 points in total).

2. Reactions (each reaction is 0.3 points, 3 points in total):

$$\begin{aligned} 2\text{CuSO}_4 + 3\text{H}_3\text{PO}_2 + 3\text{H}_2\text{O} &= 2\text{CuH}\downarrow + 3\text{H}_3\text{PO}_3 + 2\text{H}_2\text{SO}_4 \\ 2\text{LiH} + \text{ZnI}_2 &= \text{ZnH}_2 + 2\text{LiI} \\ \text{Mg} + \text{H}_2 &= \text{MgH}_2 \\ \text{ZnH}_2 &= \text{Zn} + 3\text{H}_2 &= 3\text{LiH} + \text{NH}_3 \\ \text{ZnH}_2 &= \text{Zn} + \text{H}_2\uparrow \\ \text{MgH}_2 + \text{H}[\text{CuCl}_2] &= \text{MgCl}_2 + \text{CuH}\downarrow + \text{H}_2\uparrow \\ \end{aligned}$$

3. In water both CuH and ZnH_2 are being covered with a thin film of insoluble oxides and hydroxides and thus being passivated. Magnesium hydride forms a slightly soluble hydroxide on the surface hindering a violent reaction to proceed. Nonetheless, the decomposition of MgH₂ occurs in water significantly. On the contrary lithium hydroxide is readily soluble that is why LiH reacts with water immediately with considerable release of heat (1 point in total).

4. MgH_2 was supposed to serve as a storage system for the safe transportation of hydrogen with its subsequent extraction (reaction with water). Moreover, recently MgH_2 has been proposed as advanced anode material for lithium ion batteries (1 point).

5. H_3PO_2 possesses one OH-group that is able to participate in the dissociation process in water (0.5 points for each structure and explanation, 1 point in total).

Problem 3 (authors R.V. Panin, E.B. Deeva)

1. The equations for the autoionization of N_2O_4 and N_2O_5 should be presented as follows (0.5 points for each equation, 1 point in total):

$$N_2O_4 \neq NO^+ + NO_3^-$$

 $N_2O_5 \neq NO_2^+ + NO_3^-$

2. On the basis of the properties given one can easily determine **X** to be NO (colourless and readily reacts with air to form a brown NO₂). The blue color of the solution formed is a strong evidence for copper (II) nitrate formation, so $\mathbf{A} = \text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, then $\mathbf{D} = \text{Cu}(\text{NO}_3)_2$.

According to the elemental analysis data for **B**, $v(Cu) : v(N) = \frac{52.9}{63.5} : \frac{5.8}{14} = 0.83 : 0.41 = 2 : 1$. Assuming nitrogen to be in the form of nitrate group, one may propose the formula of **B** as $Cu_2NO_3(OH)_k$. Since copper is hardly removed by gas products, 1 mole $Cu_2NO_3(OH)_k$ should arise from 2 moles of $Cu(NO_3)_2 \cdot 2.5H_2O$, then the molar mass of **B** equals to $2 \cdot 232.5 \cdot 0.516 = 240$ g/mol, where $k = \frac{240 - 127 - 62}{17} = 3$, i.e. $B = Cu_2NO_3(OH)_3$.

For **C** one can calculate $v(Cu) : v(O) = \frac{79.9}{63.5} : \frac{20.1}{16} = 1.26 : 1.26 = 1 : 1$, i.e. **C** = CuO.

Note: one may achieve the same result taking into account the stability of a copper oxidation state during the whole process.

Considering the NO₂ dissociation equation one should await **Y** to built up from NO⁺ and NO₃. Thus CuN₄O₁₀ may be represented by only unique way as Cu⁺² + NO⁺ + $3NO_3^-$ or NO⁺[Cu(NO₃)₃]⁻. According to the elemental analysis data for Z: $v(Zr) : v(N) = \frac{20.4}{91.2} : \frac{18.8}{14} = 0.22 : 1.34 = 1 : 6$. Taking into consideration the structural analogy of Y and Z, one may assume only one zirconium atom to exist per one Z formula unit, thus the molar mass of Z equals to 91.2 / 0.204 = 447.06 g/mole. Consequently the Z formula could be presented as ZrN_6O_m , where $m = \frac{447.06 - 91.2 - 84}{16} = 17$, i.e. $Z = ZrN_6O_{17}$ or $Zr^{+4} + NO_2^+ + 5NO_3^-$ what equals to $NO_2^+[Zr(NO_3)_5]^-$. Finally E is evidently to be $Zr(NO_3)_4$ (0.5 points for each compound A - E, X, Z, 0.25 points for each ion, 4.5 points in total).

3. The equations of the reactions given should be written as follows (0.5 points for each equation, 3.5 points in total):

$$6Cu + 16HNO_3 (30\%) + 7H_2O = 6Cu(NO_3)_2 \cdot 2.5H_2O + 4NO^{\uparrow}$$

Scheme I

I.
$$8Cu(NO_3)_2 \cdot 2.5H_2O \xrightarrow{t \circ C} 4Cu_2NO_3(OH)_3 + 12NO_2\uparrow + 3O_2\uparrow + 14H_2O\uparrow$$
$$4Cu_2NO_3(OH)_3 \xrightarrow{t \circ C} 8CuO + 4NO_2\uparrow + O_2\uparrow + 6H_2O\uparrow$$

Scheme II.

$$Cu + 3N_2O_4 \xrightarrow{CH_3CN} NO[Cu(NO_3)_3] + 2NO^{\uparrow}$$

$$NO[Cu(NO_3)_3] \xrightarrow{t \circ C} Cu(NO_3)_2 + 2NO_2^{\uparrow}$$

Scheme III.

$$\operatorname{ZrCl}_{4} + 5\operatorname{N}_{2}\operatorname{O}_{5} \xrightarrow{\operatorname{HNO}_{3}} \operatorname{NO}_{2}[\operatorname{Zr}(\operatorname{NO}_{3})_{5}] + 4\operatorname{NO}_{2}\operatorname{Cl}^{\uparrow}$$
$$2\operatorname{NO}_{2}[\operatorname{Zr}(\operatorname{NO}_{3})_{5}] \xrightarrow{\operatorname{t}^{\circ}\operatorname{C}} 2\operatorname{Zr}(\operatorname{NO}_{3})_{4} + 4\operatorname{NO}_{2}^{\uparrow} + \operatorname{O}_{2}$$

4. One should consider the N–N bond and the maximal nitrogen valence equals to 4 in the N_2O_4 structure (1 point for the graphic formula).

$$\begin{array}{cccc} 0 & 0 & 0 \\ N-N & 0 & 0 \\ 0 & 0 & 0 \end{array}$$

Problem 4 (author D.V. Kandaskalov)

1. Thiophene is more electron-enriched compound than benzene. Therefore, it is more reactive against electrophiles (1 point).

2. Thiophenes provide predominantly α -position for reactions with electrophiles. Indeed, the slow step of electrophilic substitutions is the formation of σ -complex. Electrophile attack onto α -position produces σ -complex which is more stable than that formed as a result of attack onto β -position as the first σ -complex has three mesomeric forms but the second one has only two mesomeric forms. In other words, the positive charge is more delocalized when eloectrophile attacks onto α -position Therefore, the major product is 2-nitrothiophene (1 point).

$$\stackrel{H}{\underset{E}{\longrightarrow}} S \oplus \longrightarrow \stackrel{H}{\underset{E}{\longrightarrow}} S \xrightarrow{E^{+}} S \xrightarrow{E^{+}} S \xrightarrow{E^{+}} S \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow}} E \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow}} S \oplus \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow}} F \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow}} S \oplus \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow} S \oplus \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow}} S \oplus \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow} S \oplus \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow}} S \oplus \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow}} S \oplus \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow}} S \oplus \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow} S \oplus \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow}} S \oplus \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow}} S \oplus \xrightarrow{H} \stackrel{H}{\underset{H}{\longrightarrow} \stackrel$$

3. The comparison of molecular formulae of compounds **G** ($C_{22}H_{18}N_2O_4S_3$) and **F** ($C_{12}O_6S_3$) allows for concluding that 2 equivalents of RNH₂ participate in the reaction. So, molecular formula of RNH₂ is $C_5H_{11}N$. Accounting for fact that this molecule has 3 types of carbon atoms, we can conclude that it is cyclopentlyamine (1 point).

4. The reaction between thiophene and bromine can produce both monobromide and polybrominated products. The next step is bromine/lithium exchange followed by reaction of product with oxalic acid derivative (ethyl oxalyl chloride). From molecular formula of **B** ($C_{12}H_{12}O_6S$) we can conclude that 2 equivalents of acyl chloride participate in this reaction. Therefore, **A** is 2,5-dibromothiophene,

$$\overset{S}{\longrightarrow} \overset{Br_2}{\longrightarrow} \overset{Br}{\longrightarrow} \overset{S}{\longrightarrow} \overset{Br}{\xrightarrow} \overset{A}{\xrightarrow} \overset{1. \text{ BuLi, Cul}}_{A} \overset{O}{\xrightarrow} {\xrightarrow} {\to} \overset{O}{\xrightarrow} {}}{\xrightarrow} \overset{O}{\xrightarrow} {}}{\xrightarrow} \overset{O}{\xrightarrow} \overset{O}{\xrightarrow}$$

Then compound **B** was again brominated; product was treated with ethyl thioglycolate. Molecular formula of **D** ($C_{20}H_{20}O_8S_3$) allows for concluding that two molecules of ethyl thioglycolate participated in the second step. Thus, **C** is dibromo derivative of **B**. Only β -positions of thiophene ring are suitable for bromination in molecule of **B**. The comparison of molecular formulae of **C** ($C_{12}H_{10}Br_2O_6S$) and **D** shows that transformation of **C** into **D** consists of not only substitution of bromine atom with *S*-nucleophile but also elimination of two water molecules. It is known that **D** has four types of hydrogen atoms (4 + 4 + 6 + 6). Compound **C** contains two symmetric ethyl groups (4 + 6). Compound **D** is formed with participation of two equivalents of ethyl thioglycolate. So, two more types of hydrogen atoms (4 + 6) belong to ethyl groups from these fragments which are, evidently, symmetric too. Therefore, **D** is product of nucleophilic substitution followed by double condensation producing two novel thiophene rings:



Next step is esters hydrolysis affording tetracarboxylic acid **E** dehydration of which furnishes double anhydride $F(C_{12}O_6S_3)$:



Synthesis was accomplished by transformation of anhydride moieties into imides:



(7 structural formulae, 1 point for each, 7 points in total)

Problem 5 (author A.Ya. Borschevsky)

1. Denote for short m/z = a. Let the charge number of a protonated ion be z. As mass spectrometer measures the mass-to-charge ratio, an ion will be registered on the mass scale with the value $a = \frac{M + zm_p}{z}$, where m_p – the mass of proton H⁺. Let's choose two ions (1 and 2) with the charges, differing by k (whole number). The peak of ion 2 with smaller charge z is situated on the right side of the spectrum. Then the charge of ion 1 equals z + k. We then have the following set of equations (2 points for the equations):

$$\frac{M + zm_p}{z} = a_2, \qquad \qquad \frac{M + (z + k)m_p}{z + k} = a_1, \text{ from where}$$
$$z = \frac{a_1 - m_p}{a_2 - a_1}k, \qquad \qquad M = z(a_2 - m_p).$$

Let there be, for example, $a_1 = 939.2$, $a_2 = 1372.5$, k = 6, then (2 points for the results):

$$z = \frac{939.2 - 1.0073}{1372.5 - 939.2} \cdot 6 = 12.99 \approx 13, M = 13 \cdot (1372.5 - 1.0073) = 17829.4 \approx 17829 \text{ Da}$$

2. As the charges of the neighboring ions in the mass spectrum differ by 1, sequential addition of the unit to z = 13, or subtraction from z = 13, gives the charges for all the series (from left to right): 20, 19, 18, 17, 16, 15, 14, 13, 12 (0.5 points).

3. A liquid droplet is stable with respect to dividing into two parts, when $U_{el} + U_{surf}$ is lower than the total energy of the two droplets of smaller size. A droplet of the volume V/2 has radius $r/\sqrt[3]{2}$, thereby, taking into account that $S = 4\pi r^2$, we obtain (4 points):

$$\frac{q^{2}}{8\pi\varepsilon_{0}r} + 4\pi\sigma r^{2} < 2 \cdot \left[\frac{(q/2)^{2}}{8\pi\varepsilon_{0}(r/\sqrt[3]{2})} + 4\pi\sigma(r/\sqrt[3]{2})^{2} \right], \text{ from where}$$

$$q^{2} < \frac{2^{1/3} - 1}{2 - 2^{1/3}} \cdot 64\pi^{2}\varepsilon_{0}\sigma r^{3} = 0.35 \cdot 64\pi^{2}\varepsilon_{0}\sigma r^{3}$$
(1)

4. Replacing the inequality in (1) by equality, we get (0.75 points):

$$q_{\text{max}} = \sqrt{0.35 \cdot 64\pi^2 \varepsilon_0 \sigma r^3} = 8\pi (0.35 \cdot 8.854 \cdot 10^{-12} \text{ J}^{-1} \text{C}^2 \text{m}^{-1} \cdot 7.28 \cdot 10^{-2} \text{ J} \cdot \text{m}^{-2} \cdot (10^{-7} \text{ m})^3)^{\frac{1}{2}}$$
$$q_{\text{max}} = 3.775 \cdot 10^{-16} \text{ C} = 2356e$$

5. *a*) The peak with the lowest mass 720 Da corresponds to the ion C_N^+ , totally stripped of functional groups, then N = 720 / 12 = 60, that is fullerene – C_{60} (0.25 points). *b*) All the intervals between peaks equal 69 Da, and correspond to sequential detachment of CX₃-groups from carbon cage. Molecular mass of X equals (69 - 12) / 3 = 19, thereby element X – fluorine (0.25 points). *c*) The mass spectrum contains 13 peaks with 12 intervals hence the number of functional groups equals 12. Thus one deals with trifluoromethylated fullerene $C_{60}(CF_3)_{12}$ (0.25 points, 0.75 points in total).

Problem 6 (author S.G. Bakhtin)

1. 2-Isopropyl-5-methylheptanedicarboxylic acid (1 point)



2. 2-Isopropyl-5-methylcyclohexanone. A molecule of I has two asymmetric C carbons. Therefore, it has $2^2 = 4$ stereoisomers (IUPAC name – 1 point, 4 structural formulae, 0.5 points for each; 3 points in total)



3. Let us denote molar fraction of (-)-I as χ . Then, $-30\chi + 92(1 - \chi) = -3$. $\chi = 0.78$. So, equilibrium content of $\chi((-)$ -I) is 78%, content of $\chi((+)$ -*iso*I) is 22%. K = 22/78 = 0.28.

Epimers differ by configuration of a single asymmetric center. In the acidic conditions, two diastereomers of chiral ketone can interconvert through enol **X** (broad band in IR spectrum demonstrates clearly the presence of OH group) (enol structure – 1 point, if stereocenter in enol is wrong or absent – 0.5 points; calculation of contents of isomers 2 points, calculation of equilibrium constant 1 point; 4 points in total):



4. The possible chair conformations for (2R,5R)- and (2S,5R)-menthones are:



For (2R,5R)-isomer one alkyl group has axial disposition, another one is in equatorial position in every conformation. For (2S,5R)-isomer there is the most stable conformation wherein both alkyl groups are located in equatorial positions. We can conclude that this compound is thermodynamically more stable. Compound predominates in the equilibrium mixture. So, (2S,5R)-isomer is (-)-I. Therefore, (2R,5R)-isomer is (+)-*iso*I (two structural formulae, 1 point for each; 2 points in total).

Problem 7 (author D.V. Kandaskalov)

1. a) ${}^{147}_{62}\text{Sm} \rightarrow {}^{143}_{60}\text{Nd} + {}^{4}_{2}\text{He}$ (0.5 points);

b)
$$k = \frac{\ln 2}{\tau_{\frac{1}{2}}} = \frac{\ln 2}{1.06 \cdot 10^{11}} = 6.52 \cdot 10^{-12} \text{ years}^{-1}$$
 (1.5 points, 2 points in total).

2. The total quantity of ¹⁴³Nd is the sum of initial quantity $n_0(^{143}Nd)$ and the quantity $n_t(^{143}Nd)$, which is formed during ¹⁴⁷Sm decay:

$$n(^{143}\text{Nd}) = n_0(^{143}\text{Nd}) + n_t(^{143}\text{Nd}).$$

We can find n_t ⁽¹⁴³Nd) from decay equation (1st order reaction):

$$\ln \frac{n_0 ({}^{147}\text{Sm})}{n_t ({}^{147}\text{Sm})} = \ln \frac{n_t ({}^{147}\text{Sm}) + n_t ({}^{143}\text{Nd})}{n_t ({}^{147}\text{Sm})} = kt \quad \Rightarrow \quad n_t ({}^{143}\text{Nd}) = n_t ({}^{147}\text{Sm}) \cdot (e^{kt} - 1)$$

Thereby, we obtain

$$n(^{143}\text{Nd}) = n_0(^{143}\text{Nd}) + n_t(^{147}\text{Sm}) \cdot (e^{kt} - 1)$$

Let us divide now this equation by the quantity of ¹⁴⁴Nd:

$$\frac{n({}^{143}\text{Nd})}{n({}^{144}\text{Nd})} = \frac{n_0({}^{143}\text{Nd})}{n({}^{144}\text{Nd})} + \frac{n_t({}^{147}\text{Sm})}{n({}^{144}\text{Nd})}(e^{kt} - 1) \equiv y = b + ax$$

The equation describes a line. From *x* and *y* values for two points, we can find *a* and *b*. Coefficient *b* is right the ratio $n_0(^{143}\text{Nd}) / n_0(^{144}\text{Nd})$:

$$\begin{cases} 0.510 = b + a \cdot 0.111\\ 0.515 = b + a \cdot 0.280 \end{cases} = \begin{cases} a = 0.0297\\ b = 0.5061 \end{cases}$$

Thereby, $n_0(^{143}\text{Nd}) / n_0(^{144}\text{Nd}) = 0.5061$ (4 points).

3. In the previous item we found that a = 0.0297. Now we can determine the meteorite age (2 points):

$$a = e^{kt} - 1 \Rightarrow e^{kt} = a + 1 \Rightarrow t = \frac{\ln(a+1)}{k} = \frac{\ln(1.0297)}{6.52 \cdot 10^{-12}} = 4.49 \cdot 10^9 \text{ years}$$

4. As the samarium-147 half-life time is about one hundred billion years, it is not possible to determine precisely an age of a rock with the age 10000 years: the number of decayed atoms is negligibly small.

For example let's take t = 10000 years:

$$\frac{n({}^{143}\text{Nd})}{n({}^{144}\text{Nd})} = \frac{n_0({}^{143}\text{Nd})}{n({}^{144}\text{Nd})} + \frac{n_t({}^{147}\text{Sm})}{n({}^{144}\text{Nd})}(e^{kt} - 1) = \frac{n_0({}^{143}\text{Nd})}{n({}^{144}\text{Nd})} + \frac{n_t({}^{147}\text{Sm})}{n({}^{144}\text{Nd})}(e^{6.52 \cdot 10^{-12} \cdot 10^4} - 1) \approx \frac{n_0({}^{143}\text{Nd})}{n({}^{144}\text{Nd})}(e^{kt} - 1) = \frac{n_0({}^{143}\text{Nd})}{n({}^{144}\text{Nd})}(e^{6.52 \cdot 10^{-12} \cdot 10^4} - 1) \approx \frac{n_0({}^{143}\text{Nd})}{n({}^{144}\text{Nd})}(e^{kt} - 1) = \frac{n_0({}^{144}\text{Nd})}{n({}^{144}\text{Nd})}(e^{k$$

The final ratio 143 Nd / 144 Nd is very close to initial one (2 points).

Problem 8 (authors Yu.S. Golovko, B.N. Garifullin) 1. 226 Ra $\rightarrow ^{222}$ Rn + 4 He (0.5 points)

The same number of atoms of both samples undergoes the radioactive decay per time 2. unit. Thus: $\lambda \binom{226}{86} \text{Ra} N\binom{226}{86} \text{Ra} = \lambda(\mathbf{X}) N(\mathbf{X})$, where N is the number of atoms of respective isotope in the sample. Then the formula for M(X) calculation would be:

$$M(\mathbf{X}) = \frac{m(\mathbf{X}) \cdot T_{\frac{1}{2}} \binom{226}{86} \text{Ra} \cdot M\binom{226}{86} \text{Ra}}{T_{\frac{1}{2}}(\mathbf{X}) \cdot m\binom{226}{86} \text{Ra}} = \frac{0.001 \text{ g} \cdot 1601 \cdot 365.25 \text{ days} \cdot 226 \text{ g/mol}}{138.4 \text{ days} \cdot 4.55 \text{ g}} = 210 \text{ g/mol}$$

The calculated molar mass can be attributed to many nuclides of different elements. It is impossible to unambiguously decide about the isotope (1.5 point).

 α -Activity is an additive value summarized of activities of individual isotopes. α -3. Radioactivity observed in norm (natural radioactive families) is constant. The tissue analysis is reasonable if X isotope activity is not less than 0.3 - 0.2 = 0.1 Bq/kg.

From the equation $\ln \frac{A}{A_0} = -\lambda(\mathbf{X})T$ (where $\lambda(\mathbf{X}) = 5.80 \cdot 10^{-8} \text{ sec}^{-1}$) one gets the formula for calculating the time elapsed since the poison was applied:

$$T = -\frac{1}{\lambda} \ln \frac{M(\mathbf{X})A}{\lambda m(\mathbf{X})N_{A}} = -\frac{1}{5.80 \cdot 10^{-8} \text{ sec}^{-1}} \ln \frac{210 \text{ g/mol} \cdot 0.1 \text{ kg}^{-1} \text{sec}^{-1} \cdot 70 \text{ kg}}{5.80 \cdot 10^{-8} \text{ sec}^{-1} \cdot 1 \cdot 10^{-6} \text{ g} \cdot 6.02 \cdot 10^{23}} = 2.93 \cdot 10^{8} \text{ sec},$$

or about nine years and three months. The suddenness of the politician death allows concluding that the dates of poisoning and fatality coincide. Exhumation of Y. Arafat's body would have become meaningless at the end of 2014 (2 points).

From mass number of the nuclide (210) and neutrons to protons ratio (1.5) one gets: 4. $2.50 \cdot Z = 210$. Then the atomic number of the element is 84 – polonium. The most widespread isotope ²¹⁰Po is considered in the task (1 point).

5. (1 point for each reaction, 2 points in total)

$${}^{209}_{83}\text{Bi} + {}^{1}_{0}n \rightarrow {}^{210}_{84}\text{Po} + {}^{0}_{-1}n \qquad {}^{209}_{83}\text{Bi} + {}^{1}_{1}p \rightarrow {}^{210}_{84}\text{Po}$$

The sample of X has the mass of 9.2 g (9.2 g/cm³ \cdot 1 cm³) and contains ²¹⁰Po atoms in 6. the amount of $N = \frac{m(\mathbf{X})}{M(\mathbf{X})} N_{\rm A} = \frac{9.2 \text{ g}}{210 \text{ g/mol}} \cdot 6.0 \cdot 10^{23} = 2.6 \cdot 10^{22}$. From these, $N(\text{dec.}) = \lambda(\mathbf{X})N =$ $5.8 \cdot 10^{-8} \cdot 2.6 \cdot 10^{22} = 1.5 \cdot 10^{15}$ atoms undergo the decay every second, and the same number of α -particles with the total initial kinetic energy of 1210 J is formed. Recalculation to one particle finally gives (3 points):

$$E_k = \frac{1210 \text{ J}}{1.5 \cdot 10^{15} \cdot 1.6 \cdot 10^{-19} \text{ J}} = 5.0 \cdot 10^6 \text{ eV} = 5.0 \text{ MeV}$$