SUMMARY OF THE MAIN RESULTS AND SCIENTIFIC CONTRIBUTIONS

of Chief Asisstant Professor Dr. Eng. Maria Atanasova Petrova
on a competition to occupy an academic position "Associate Professor"
4.2. Chemical Sciences (Inorganic chemistry)

In the presented scientific publications, the synergistic extraction of the metals from the lanthanoids group (excluding radioactive Pm) was investigated with mixtures of chelating extracants (4-benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-one (HP), thenoyltrifluoroacetone (HTTA), 8-hydroxyquinoline (HQ), 5,7-dibromo-8-hydroxyquinoline, 4-benzoyl-3-phenyl-5-isoxazolone (HPBI)) and various synergistic additives (quaternary ammonium salt (methyltrialkyl (C_8-C_{10}) ammonium chloride − Aliquat 336 in chloride (QCl) and perchlorate form ($QClO_4$) , tridodecylamine, N, N-dioctyl methylamine, 1-(2-pyridilazo)-2-naphthol, 4-(2-pyridilazo)-resorcinol, dibenzo-18-crown-6, 18-crown-6, dibenzo-24-crown-8, benzo-18-crown-6, 3,5-dichlorophenol, diphenylsulfoxide, 1,10- phenanthroline, 2,2 '-bipyridyl and different phosphine oxides). The term synergism is used in extraction chemistry to mark the greater effectiveness of a mixture of two or more extractants during the extraction process of metals compared to their extraction with each reagent separately.

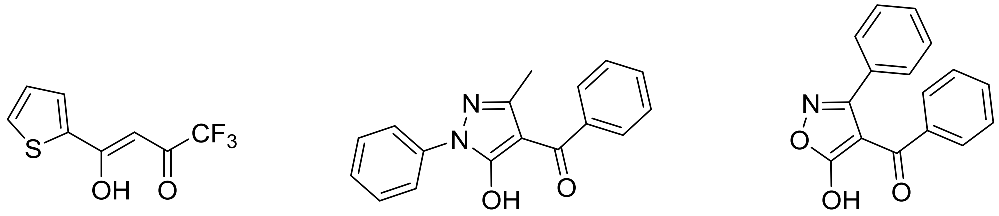


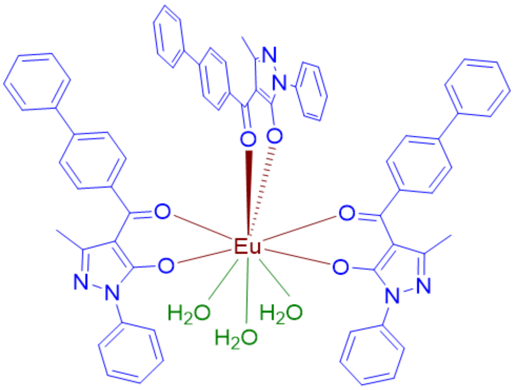
Figure 1. Chemical structures of HTTA, HP and HPBI.

The lanthanoid family (4f-elements) includes the elements numbered 58-71 in the periodic table. In the nomenclature of IUPAC in Inorganic Chemistry from 2005, the group name lanthanoids also includes lantanum, although "lanthanoid" means "similar to lantanum" and therefore the lanthanum should not be included in this group. Besides, he doesn't own the f-electrons. The same recommendations indicate that the name "lanthanoids" is preferred to "lanthanides", since the "id" ending is usually used to denote a negative ion in binary compounds. The group name "rare earth metals" includes Sc, Y and lantanoids, and is derived from the fact that, before the simple substances of the elements were obtained, their oxides were obtained (substances very difficult to melting, poorly soluble in H_2O) i.e. they had the same properties as Al_2O_3, MgO, which in the 18-19 century were called lands. Due to the extremely nearby chemical properties of the lanthanoids, separating them from each other is an extremely difficult task for chemists and this is one of the most complex divisions in inorganic chemistry. Some methods of subsequent selectivity of ions from each other contain up to 1000 steps (manipulations). The liquid-liquid extraction is the only industrial technology for the internal group separation of 4f-elements. The synergistic effect can be expressed and assessed by the synergistic coefficients: $SC = \log (D_{1,2}/D_1 + D_2)$, where: D_1, D_2 and $D_{1,2}$ are the distribution ratios of the metal between the organic and aqueous phases, with each reagent separately and with mixtures of the two extractants. Synergism is observed when $SC > 0$ and antagonism – when $SC < 0$. Distribution ratio is a ratio of the total (analytical) concentration of the substance in the organic phase to its analytical concentration in the aqueous phase: $D = \frac{[M]_{(o),eq}}{[M]_{(aq),eq}} x \frac{V_{aq}}{V_o}$.

Over the years, this phenomenon in extraction chemistry has been analysed with different combinations of molecules two or more, but mainly mixtures involving acidic and neutral extractants have shown a significant effect. The following four conditions are necessary to establish the existence of a synergism in the extraction of metal ion: (i) one of the ligands must be capable of neutralizing the charge of the extracted metal, preferably with the formation of a metallic chelate complex; (ii) the second ligand added in the role of synergist must be able to displace from the chelating complex a number of coordinated water molecules, which makes the complex less hydrophilic:

$$M^{n+} + nHL + xS \rightleftharpoons ML_n{\cdot}S_x + nH^+;$$

iii) the second extractant is less coordinated than the first one and is usually unable to displace it and (iv) the maximum coordination number and the ligands geometry must be conducive to the formation of a mixed complex with suitable architecture. These conditions, defined in 1960, are valid to this day, practically unchanged, for the predominant number of extraction systems including chelate and neutral extractants.



In some cases it is possible that, as a result of the use of ligands mixtures, the extraction of the metal is less effective than the aditive extraction provided by the self-use of the two extractants. This effect is called antagonistic or antisynergistic. The destruction of synergism also occurs when, as a result of interaction between the two ligand, their active concentration decreases.

The main scientific tasks are:

1. To determine the conditions under which the metal extraction of the 4f-series is carried out using new, not described in the literature systems. The mechanism of the extraction process should be clarified and the composition of the extracted metal complexes in the organic phase should be determined as well.
2. To calculate the equilibrium extraction constants and to analyse the factors influencing the equilibrium (ion radius of the metals, the nature of the chelating agent and the synergist, etc.).
3. The influence of the inert organic diluents on the process of synergistic extraction separation of lanthanoids should be investigated.
4. To calculate the synergistic coefficients and the coefficients of separation of the investigated lanthanoids on the basis of the experimental results obtained and to analyse the factors influencing these parameters.
5. To study the behavior of metals from the entire 4f-series and describing the patterns obtained.
6. To analyze the possibilities for application of ionic liquids as an innovative organic environment in the extraction of lanthanoids: advantages and disadvantages. To determine the effect of the mutual solubility between water and ionic liquids on the extraction mechanism and the factors influencing this intense ion exchange (inorganic ions in the aqueous phase and the presence of organic molecules in the organic ion phase).

The great interest in synergistic extraction is driven by the fact that extraction and ion exchange methods play an important role both in obtaining and splitting lanthanoids. The correct selection of a combination of extractants in some cases leads to an increase in the extraction of metals up to 10^6 times, and in some cases to better separation too. Therefore, the right choice of extractants is an important step for an effective extraction process. The timeliness of research is due to the opportunities offered by extraction methods for extracting metals from primary mineral sources, waste recycling and nuclear waste disposal. The pre-extraction of lanthanoids is a prerequisite for resolving this important technological and environmental problem.

The scientific value and timeliness of the research is confirmed by the fact that they (albeit published recently) have been spotted and cited by a number of well-known researchers (more than 500 citations) working in one of the largest scientific laboratories over the issues in chemistry of extraction processes of metals and spent nuclear fuel.

Scientific results and contribution:

1. One of the most important advantages and significant scientific input in the research of Dr. Atanasova is that she has studied the metals and behavior of the entire 4f series, while most of the studies in the field of other scientists are limited to the representatives of these metals. Similar studies covering the full group of lanthanoids up to 2013 years were extremely rare, ≤ 10. It is known that the chemical properties of lanthanoids are very similar, so detailed profound knowledge of their insignificant differences is important for their extraction and separation.
2. In the extraction of lanthanoids with chelating agent e.g. tenoyltrifluoroacetone (HTTA), 5,7-dibromo-8-hydroxyquinoline or 8-hydroxyquinoline (HQ) in the organic phase chelate complexes of the type LnL_3 are extracted/formed (Russ. J. Inorg. Chem., 2007; J. Serb. Chem. Soc. 2008; Balkan Conference of Young Scientists, Plovdiv, 2005; Ecology, 2005).
3. In the extraction of lanthanoids with 4-benzoyl-3-methyl-1-phenyl-pyrazol-5-one (HP), the presence of autosynergism has been established, resulting in the formation of adducts of the type $LnP_3 \cdot HP$ (Annual Proceedings of Technical University in Varna, 2004).
4. All mixed systems tested in the published scientific research studies indicate a significant synergistic effect, which can reach up to 10^6, but in most cases exceeds 10^3.
5. When lanthanoids are extracted with mixtures of chelating extractants (HTTA, HP, HPBI) and the quaternary ammonium salt Aliquat 336 extraction of anionic-type of complexes was established $Q^+[Ln(TTA)_4]^-$, $Q^+[LnP_4]^-$ and $Q^+[Ln(PBI)_4]^-$. The synergistic extraction of Ln (III) with a mixture of 4- benzoyl-5-isoxazolone and tridodecylamine or N, N-dioctylamine is described by the equation:

$$Ln^{3+}{}_{(aq)} + 4HBPI_{(o)} + AmHClO_{4(o)} \rightarrow (AmH)^+[Ln(BPI)_4]^-{}_{(o)} + 4H^+{}_{(aq)} + ClO_4^-{}_{(aq)}$$

where $AmH^+ = MDOAH^+$ or $TDDAH^+$.

- ✓ A significant influence of the anion of the synergistic agent (quaternary ammonium salt) on the extraction process was found. A theoretical explanation of the process with the chloride and perchlorate anion of salt is given. When changing the anion of salt (Cl^- with ClO_4^-), the extraction constants decrease by 3-4 order.
- ✓ The obtained data for the extraction of the investigated lanthanoids with the specified chloride and perchloronic form of salt allow to be concluded that in the formation of the complexes takes part quaternary ammonium salt rather than an ion pair $Q^+ \cdot P^-$ (or $Q^+ \cdot TTA^-$) obtained in the interaction of both ligands, (Sep. Purif. Technol., 2004, 171-176; Solvent Extr. Ion Exch., 27, 2009, 159-171; Sep. Purif. Technol., 2010, 300-304).
- ✓ The data show that the values of $\log K_I$ are higher (up to 8 times) than those obtained for the extraction of the metals of the 4f-series with thenoyltrifluoroacetone (HTTA) as well as approximately 4 times higher as compared with 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (HP) used as a chelating extractant. It can be concluded that the equilibrium constant values increase as the pK_a value decreases, (Solvent Extr. Ion Exch., 27, 2009, 159-171). It is seen that the separation factors decrease in the order HTTA > HP > HPBI, while the lanthanoid extraction increases in the order HTTA < HP < HPBI. It is interesting to note that HTTA, which is a much poorer extractant for lanthanoids than HPBI, exhibits a separation for the pairs Lu/La, Eu/La, and Lu/Eu, which is 8.9, 13.8, and 1.77 times higher than those obtained when HPBI is used as the extractants. As a whole, the synergistic solvent extraction and separation decrease in the order $HPBI–QClO_4 > HP–QClO_4 > HTTA–QClO_4$.

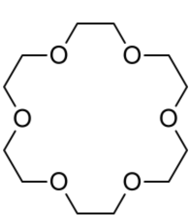
6. The interaction between the ligands HTTA-QCl ($QClO_4$), HP-QCl ($QClO_4$) in the organic phase has been investigated. The values of concentrations of ionic pairs $Q^+ \cdot L^-$ derived from the use of quaternary ammonium salt in its perchlorate form are more than two orders of magnitude lower than those obtained in the interaction of the chelant extractant with QCl.

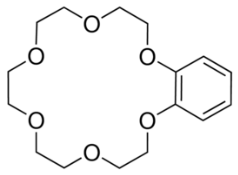
$$HTTA(HP)_{(o)} + QA_{(o)} \leftrightarrow Q^+ \cdot TTA^-(Q^+ \cdot P^-)_{(o)} + H^+{}_{(aq)} + A^-{}_{(o)},$$

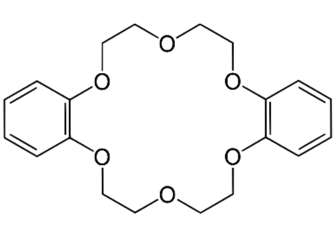
where $A^- = Cl^-$ or ClO_4^-.

It was established that the equilibrium constant values describing the ion pair formation decrease in the order: cyclohexane-tertachloromethane-benzene-chloroform for all combinations of extractants, (Proceedings of the Jubilee Conference with International Participation, UCTM, 2003, J. UCTM, 2003).

7. In the case of synergistic extraction of Pr with mixtures of extractants HTTA− QCl ($QClO_4$) and HP − QCl ($QClO_4$) in C_6H_6 with preliminary receiving/obtaining of ion pair, it is established that the ionic pair $Q^+ \cdot L^-$ does not exert a noticeable influence on the extraction process after that, (Annual Proceeding of Technical University of Varna, 2004, 181-191).
8. It was found that in the extraction of lanthanoids with a mixture of two β-diketons, complexes of the type $LnP_3 \cdot HTTA$ (where P^- is the anion of the chelating agent 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one) are extracted. So, β-diketon with a lesser value of pK_a i.e. HTTA participates as a neutral molecule in the formation of a complex of mixed type, (Ecology, 2005, 99-104).
9. Synergistic extraction of lanthanoids with a mixture of three ligands: 4-benzoyl-3-methyl-1-phenyl-2-pyazoline-5-one (HP), thenoltrifluoroacetone (HTTA) and the quaternary ammonium salt – Aliquat 336 (QCl) in C_6H_6, has been investigated. Based on the slope analysis method, the formation of a complex $Q[LnP_3(TTA)]$ in the organic phase was established. The equilibrium constants values are calculated for the metals La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+}. While for metals Eu^{3+} and Gd^{3+} and other members of the 4f series it was established an antagonism, (Scientific conference 60 years department of Inorganic chemistry, 11 November, 2005; J. UCTM, 2006, 75-80).
10. The inert organic diluents used have been found to have a significant effect on the metal distribution ratios of the lanthanoid series. This influence is explained by the solvative interactions of diluents with extractants (Sep. Purif. Technol. 2004; J. UCTM, 2004). For a given metal, the values of $\log K_{P,Q}$ for both HP−QCl and HP−$QClO_4$ mixtures are increased in the order $CHCl_3 < CCl_4 < C_6H_{12}$ and therefore it can be concluded that the increase in the solvent's diluent capacity hinders the extraction process.
11. It was found that, in a number of cases, during the extraction of lanthanoids with mixtures of chelating extractants and various synergists, there was not only an increase in extraction process, but also of the selectivity between lanthanoids. Part of the presented scientific studies (8 scientific reports) are on the extraction processes of lanthanoids with the use of crown-ethers as synergistic additives. In the course of these studies, a number of conclusions were drawn concerning their role in the extraction process, as well as the impact of the synergists on the mechanism and selectivity. In the use of crown ethers, the coefficients of separation of heavy lanthanoids (which are generally difficult to divide) are significantly higher than those obtained using individual ligands and certain other mixed systems. The main conclusion is that crown-ethers are effective synergists with particularly well-expressed selective properties, (Sep. Sci. Technol. 2005, 1104-1113; Plovdiv, 2005; Acta Chim. Slovenika, 2006; Russ. J. Inorg. Chem., 2007; Chem. Papers, 2008; J. Serb. Chem. Soc., 2008; Bul. Chem. Ind., 2005; J. UCTM, 2006, 81-84).
    - ✓ It was found that the SC values for HP − 18C6 (B18C6, DB18C6) − C_6H_6 systems increased in the following order: 18C6 < B18C6 < DB18C6. For the three extraction systems the formation of $LnP_3 \cdot S$ complex was established in the organic phase. For a given crown-ether, the SC values increase with the expansion of the lanthanoid atomic number. It is interesting to note also that SC is much higher when using diluent C_6H_6 than that obtained for the system HP−DB18C6−1,2-dichloroethane, (Acta Chim. Slovenika, 2006).







    - ✓ The composition of the extracted complexes LnQ_3 with 8-hydroxyquinoline (HQ) and $LnQ_3 \cdot S$ with mixtures HQ−DB18C6 (DB24C8) − 1, 2-dichloroethane (J. Serb. Chem. Soc., 2008) was defined. The formation of trivalent lantanoid complexes follows the order: DB18C6 >

DB24C8. It can be concluded that the DB24C8 molecule is too large (4.5 ÷ 5.6 Å) to form a relatively stable complex with HQ and the reduction of complexing ability may be due to increased steric effects. The synergistic enhancement factors as well as separation factors between the adjacent metal ions are large when DB18C6 is used as synergistic agent in combination with HQ. The equilibrium constants of the synergistic species were found to increase monotonically with decrease in ionic radii of the metal ions. With increasing atomic number, ionic radii decrease at constant charge, and consequently the charge densities increase and formation of extractable complexes is favored. Thus, an increase of the extraction efficiency is observed from La to Lu.

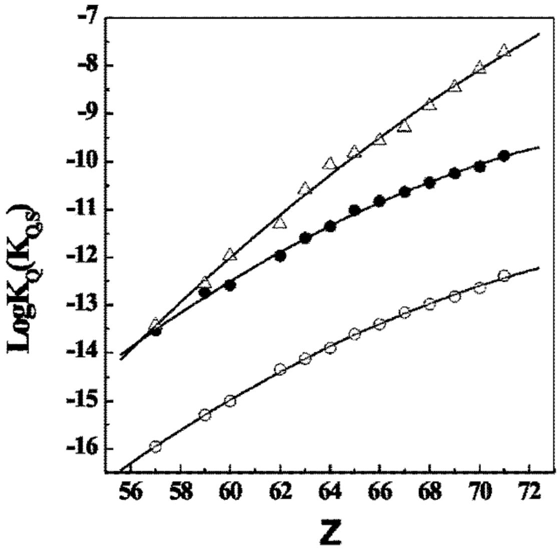
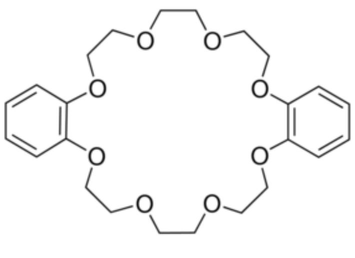
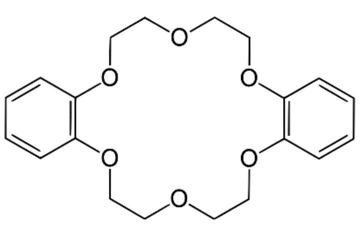


Figure 2. Log $K_Q(K_{Q,S})$ vs. Z (open circles: HQ (8-hydroxiquinoline); solid circles: HQ−DB24C8; triangle: HQ−DB18C6).

✓ The composition of the extracted complexes LnQ_3 with 8-hydroxyquinoline (HQ) and $LnQ_3 \cdot S$ with mixtures HQ−18C6(B18C6)−1,2-dichloroethane (Russ. J. Inorg. Chem., 2007). A difference in the values of the extraction constants for a lanthanoid was observed in the use of mixtures HQ–18C6 and HQ–B18C6 decreasing from La to Lu. The introduction of a synergistic agent leads to an increase in extraction in the following sequence 18C6 > B18C6. The obtained data show very high values for separation of neighboring pairs of metals when using the system HQ –18C6. A reduced selectivity is observed in the order HQ–18C6 > HQ –B18C6, and in the same time reduced extraction capacity in the exact order. An interesting fact is that the presence of the crown-ether 18C6 in the mixed system causes the selectivity of higher lanthanoids twice as high as the calculated value when the B18C6 is a synergist.

✓ The introduction of a second ligand, crown-ether, resulted in increased extraction efficiency of the 4f-ions in the order DB24C8 > DB18C6 in the presence of the chelating reagent HTTA also dissolved in 1.2-dichloroethane: Ln $(TTA)_3 \cdot S$, (Sep. Sci. Technol., 2005). It has been established a greater stability for the formed mixed complexes in coordinating the DB24C8 molecule. The calculated separation factors show a fairly uniform selectivity for the three HTTA, HTTA − DB24C8 or HTTA − DB18C6 systems. For example, the Sm/Nd metal ion pair is 2.40, 2.23 and 2.51, respectively.

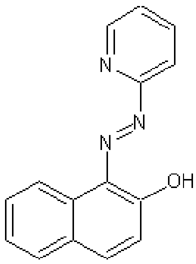


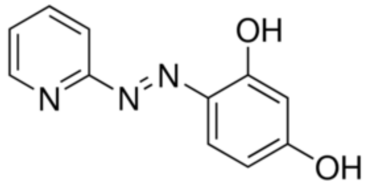


✓ The separation factors of Lu/La and Lu/Eu couples obtained using the HP−DB18C6 (DB24C8)−$C_2H_4Cl_2$ systems were 1.61, 1.42 and 2.77, 1.82 times higher than those calculated for the reagent HP used alone. Therefore, the introduction of additives enhances both the extraction of metals and the selectivity between them.

Scientific input: The main contribution is that crown-ethers are effective synergists with particularly well-expressed selective properties for 4f-elements. There are many obtained regularities summarized and the observed trends analized when replacing the chelating extractant, changing the size of the crown ether and the diluent used.

12. The use of the synergistic systems HTTA and HP in combination with 1-(2-pyridilazo)-2-naphthol and 4-(2-pyridilazo)-resorcinol described in a few publications (Sep. Purif. Technol. 49, 2006, 101-105; Proceedings Est. Ac. Sci., 55, 2006, 202-211; J. UCTM. 2004, 465-472) is not a random target of a scientific attention from a large number of researchers (a total of 44 citations). It was found that in the presence of 4-(2-pyridylazo)-resorcin the lanthanoids have been extracted as Ln(TTA)$_3$•S and LnP$_3$•S. The separation of the lanthanoids with synergistic mixtures was higher than those obtained with HTTA or HP alone. In the most cases, an enhancement of the metal ions separation was observed upon the change of the chelating extractant HP with HTTA. The resulting synergistic coefficients and metal separation factors demonstrate the difference in behaviour between light and heavy lanthanoids. The established synergism in the second half of the 4f-series, Gd÷Lu, is significantly better expressed. The resulting selectivity is extremely high.





Scientific contribution: New synergistic, atypical, extraction systems are proposed successfully for extractions and separation of lanthanoids.

13. A systematic study of the metal extraction of the 4f-series using the synergistic agent diphenylsulfoxide containing S=O group with a strong coordination ability demonstrates the extraction of mixed adducts into the organic phase not only with significantly improved extraction and clear synergism, but also improved selectivity compared to the systems using only the chelating agent HTTA or HP. The different mechanism when receiving the adducts was observed and discussed in both synergistic systems HTTA(HP)−DPSO, (J. Solution Chem. 2009):

$$\mathrm{Ln}^{3+}_{(aq)} + 3\mathrm{HTTA}_{(o)} + \mathrm{S}_{(o)} \overset{K_{T,S}}{\rightleftharpoons} \mathrm{Ln(TTA)_3}\bullet\mathrm{S}_{(o)} + 3\mathrm{H}^{+}_{(aq)}$$

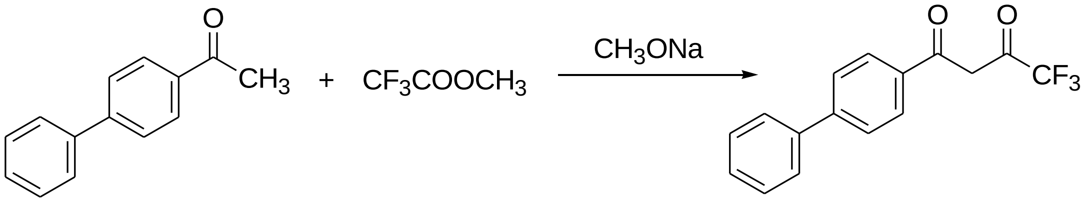
$$\mathrm{Ln}^{3+}_{(aq)} + 3\mathrm{HP}_{(o)} + \mathrm{S}_{(o)} \overset{K_{P,S}}{\rightleftharpoons} \mathrm{LnP_3}\bullet\mathrm{S}_{(o)} + 3\mathrm{H}^{+}_{(aq)}$$

In most cases, the values of log$K_{P,S}$ are 3 times higher than those obtained for log$K_{T,S}$. The change of the main extractant HTTA with HP in combination with the same synergist leads to significantly increased extraction of metals. This is explained by the fact that HTTA is a weaker acid (pK_a = 6.2 compared to HP (pK_a = 3.95).

Scientific input: New synergistic extraction systems are proposed for extraction and separation of lanthanoids.

14. In the study (Acta Chim. Slovenika, 2010) it has been shown that the type of oxo-donor (TOPO, TPPO, TBPO) has a major influence on both the type of the adducts formed and the values of the equilibrium

constants in the use of the reagent 4,4,4-trifluoro-1-(biphenyl-4-yl) butane-1.3- dion, HL, synthesized in order to study its complexing properties in solution (C_6H_6) and its use as the main extragent for lanthanoids. The composition of the extracted complexes is defined LnL_3 in the use of HL independently and $LnL_3 \cdot 2S$ in the presence of synergistic agent TOPO and TBPO or $LnL_3 \cdot S$ with a mixture of HL-TPPO. About 28 values of the equilibrium constants were calculated in the study. The change of the second ligand oxo-donor leads to an increase in the values of $K_{L,S}$ in the following order TBPO < TPPO < TOPO.



Scientific contribution: The β-diketone was synthesized and its complexing abilities are analysed independently and in combination with three phosphorus-containing oxo-donors. It was found that the addition of a second ligand increased the extraction efficiency with an estimated high synergism (10^3-10^4). The coefficients of separation of neighboring metals are quite high for the four systems tested.

15. A high synergistic effect is established from 10^2 to 10^6 during the extraction of Ln(III) ions with chelating extractants HTTA or HPBI in the presence of a second ligand 1,10-phenanthroline or 2,2 '-bipyridyl. The following metal complexes have been extracted in the organic phase, $CHCl_3$: $Ln(TTA)_3 \cdot S$ and $Ln(PBI)_3 \cdot S$. Changing the chelating extractant from HPBI to HTTA, in combination with the same synergistic agent, results in a significant decrease of the lanthanoid's extraction. This fact can be explained by taking into account that HTTA is a weaker acid (pK_a=6.2) than HPBI (pK_a=1.23). 1,10-Phenanthroline has been observed to be of a more pronounced extraction capacity used as a synergistic agent than the reagent 2,2'-bipyridyl. The obtained values of equilibrium constants and synergistic coefficients are two orders of magnitude lower when using the last synergistic agent. Synergism changes approximately from 10^2 to 10^6. So, the combination of two bidentate ligands, the acidic chelating agent and the Lewis base phenanthroline or bipyridyl, produces a very strong synergic effect in solvent extraction of lanthanoids. In the synergistic systems the selectivity among the lanthanoids has been increased upon the change of the chelating extractant HPBI with HTTA.

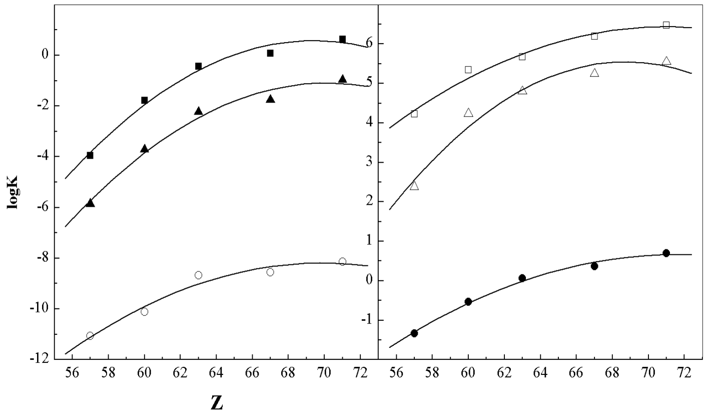


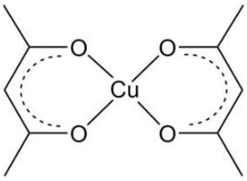
Figure 3. LogK_L($K_{L,S}$) vs Z. (○: HTTA, ▲: HTTA–bipy, ■:HTTA–phen; ●:HPBI ; △: HPBI–bipy; □: HPBI–phen).

It was demonstrated based on the obtained data and previous studies that the type of chelating agent is of paramount importance for the selectivity of the metals of the lantanoid series. The main conclusion is that effective extraction leads to a small separation of metals. In most cases, synergistic systems, using which the extraction constants are the largest, provide less selectivity (smaller separation options) for lanthanoids (J. Chem. Eng. Data, 2010).

Scientific input: New extraction systems have been compiled and tested to extract and separate trivalent lanthanoids as the obtained results and established regularities are extremely valuable.

16. The solvent extraction of trivalent lanthanoids (La, Nd, Eu, Ho and Lu) with mixtures of chelating extractant 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (thenoyltrifluoroacetone, HTTA) or 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-on (HP) and 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (S) in $C_2H_4Cl_2$ as a diluent from aqueous chloride medium at constant ionic strength μ=0.1 is investigated, (Bul. Chem. Commun., 2007). It was found that in the presence of 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one the lanthanoids have been extracted as $Ln(TTA)_3{}^{\bullet}S$ and $LnP_3\bullet S$. On the basis of the experimental data, the values of the equilibrium constants have been calculated. The parameters of the extraction process were determined and the synergistic effect as well as the separation factors between two adjacent lanthanoids(III) were calculated. The addition of a synergist to the chelating extractant improves the extraction efficiency of the lanthanoid ions and produces rather large synergistic effects, especially for HTTA−S system. As a whole, for particular metal ion the change of the chelating extractant (HP with HTTA) does not cause a significant difference in the separation factors but as a whole the obtained S. F. values for the both systems(HP−S and HTTA – S) are extremely high.

17. The possibility of adsorption of the solid chelate complexes $Cu(acac)_2$ and $Cr(phen)_3$ in the bentonite interlayer area was investigated (J. of UCTM, 35, 2000, 73-80; J. of UCTM 39, 2004, 199-208). The resulting hybrid materials are tested with IR, X-ray, TG-DTA, TEM and atomic absorption. The influence of the ions Na^+, K^+, Ba^{2+} and Fe^{3+} on the insertion of the complexes of the d-Metals in the interlayer space of the clay is considered. It was found that the activated bentonite adsorbing 4.9×10^{-4} mol from the chelate $Cu(acac)_2$ in contrast to the not activated clay, which adsorbing 1.6×10^{-5} mol. The nature and type of ions used to modify the clay have a significant impact on adsorptive abilities.



Scientific contribution: A method has been tested to extract d-elements in the form of chelated compounds from aqueous solutions in order to possible elimination of similar products from water and soil contamination due to their potential harm to humans and ecosystems. Heavy metals are one of the main pollutants in the environment with extremely toxic effects on living organisms.

18. Aqueous−ionic liquid (A−IL) biphasic systems have been examined in terms of water and acid solubilities in the IL−rich phase at ambient temperature. First, the biphasic mixtures were composed of acids of various concentrations (H^+; Cl^-, H^+; NO_3^-, H^+; ClO_4^- from $1x10^{-2}$ to $1x10^{-4}$ mol dm^{-3} mainly) and four ionic liquids of the imidazolium family $[C_1C_nim][Tf_2N]$, (n = 4, 6, 8 and 10). The effect of ionic strength (μ = 0.1 mol dm^{-3}, by use of Na^+; Cl^-, Na^+; NO_3^- or Na^+; ClO_4^-, according to the acid investigated), the nature of the IL cation as well as the nature of the acid on the mutual solubilities of (H_2O, H^+, $[C_1C_nim]^+$ and $[Tf_2N]^-$) entities were determined. Then, three chelating compounds (HL), which belong to the β-diketone family (thenoyltrifluoroacetone (HTTA), 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP) and 4-benzoyl-3-phenyl-5-isoxazolone (HPBI)), were added to $[C_1C_4im][Tf_2N]$, and subsequent determination of the H^+ distribution between the two phases allowed the determination of their dissociation constants (pK_{aIL}) in the water-saturated ionic liquid phase. A very strong effect of the IL cation onto the HTTA pK_{aIL} value was observed from n = 4 to n = 10. The influence of this phenomenon on lanthanide extraction process is discussed, (J. Solution Chem., 2015, 606-620).

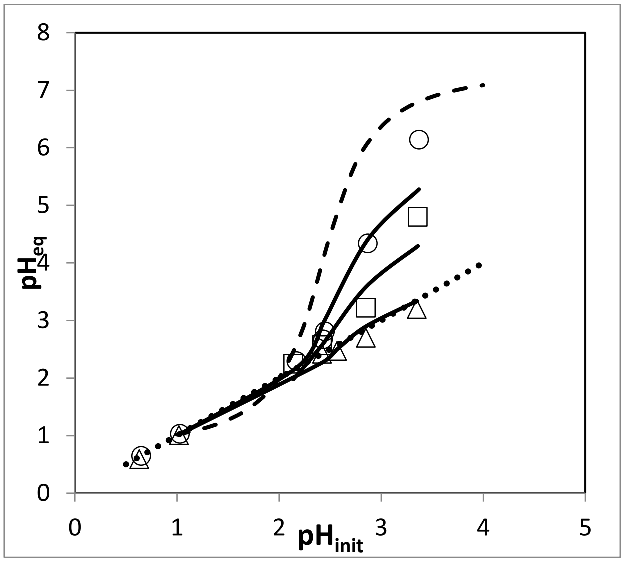


Figure 4. Effect of increasing concentrations of HTTA dissolved in [C_1C_4im][Tf_2N] on the H^+ concentration at equilibrium, in the pH range 0.5 – 3.5. ○: [HTTA] = 7x10^{-3} mol dm^{-3}; □: [HTTA] = 1.5x10^{-2} mol dm^{-3}; Δ: [HTTA] = 3x10^{-2} mol dm^{-3}. Dotted line: y = x. Dashed line: in the absence of ligand. Solid lines: fits (see text).

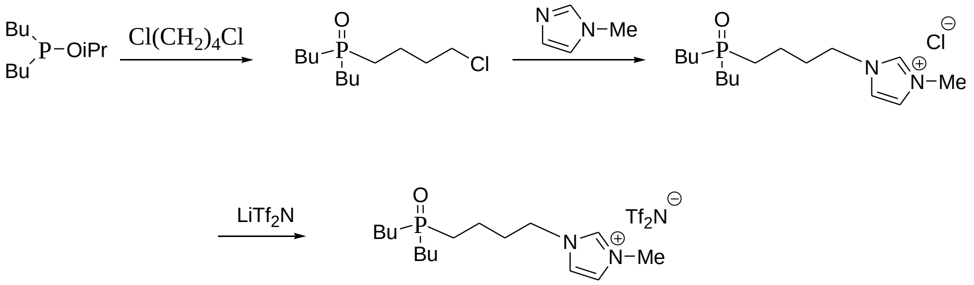
The obtained results give insights into the mutual solubilities in aqueous/IL biphasic systems in terms of water, H^+, [C_1C_nim]$^+$ and [Tf_2N]$^-$ equilibria between the two phases. For the chemical conditions of our work, the main factor influencing these subtle equilibria is the alkyl chain length on the imidazolium cation. We have also developed a new, simple, analytical method aiming at determining the pK_{aIL} values of acidic ligands dissolved in water-saturated IL phases and we have evidenced a strong effect of the IL's cation chemical structure onto the pK_{aIL} values. Owing to the observed similarities in pK_{aIL} values for HTTA, HP and HPBI in [C_1C_4im][Tf_2N], we would suspect that HTTA, HPBI and HP would extract lanthanoid ions more or less similarly (i. e. with comparable efficiencies, all other chemical condition being equal) if dissolved in [C_1C_4im][Tf_2N], by contrast to the large differences evidenced in molecular solvent extraction systems for these three ligands. This rather deceiving prediction may be modulated by the IL nature and we also estimate that in [C_1C_{10}im$^+$][Tf_2N^-] the extraction peculiarities of HTTA, HPBI and HP would be observed again, owing to their negligible deprotonation in this IL phase. Should these assumptions reveal true, this would offer an additional way of tuning extraction of metal ions using ILs' phenomenology, drawbacks and even shortcomings.

Scientific input: A highly innovative study is presented with quantitative analytical information of particular importance in the application of ionic liquids as diluents in the extraction processes due to the exceptional exchange of ions in both directions: aqueous ↔ organic phase.

19. A detailed NMR study on the possible interactions between a series of imidazolium based ionic liquids (1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, RmimTf_2N, n=4, 6, 8, 10) and commonly applied in solvent extraction and separation science of 4f and 5f-ions acidic chelating and neutral extractants is presented, (J. Solution Chem., 2015, 2416). Analytical techniques applied are ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra and NOESY experiments. Investigation of the types and strengths of the solvent-solute interactions is necessary for a knowledge-based features concerning chemical solubility, reactivity and selectivity as ILs have a strong influence on the solvent extraction mechanism of metallic species in comparison with traditional molecular solvents used. The goal of the scientific research is to gain insight on the role of ILs as a perspective efficient "green" medium in the solvent extraction processes with more pro-ecological aspect. The experimental results show that no IL/E interactions occurred in chloroform solution independently on the length of the imidazolium alkyl chain and on the structure and acidity of the ligand.

Scientific input: The purpose of research is to obtain data on the role of the ILs as a promising effective "green" organic environment in extraction processes. The experimental results show unequivocally that no interactions have occurred, no interaction between the ILs/E, regardless of the length of the alkyl chain of the cation of the Ils, as well as the structure and acidity of the ligands. So, ILs can be used as pure, inert diluents in liquid-liquid extraction processes of lanthanoid ions.

20. The $C_1C_4im^+$ and Tf_2N^- solubilities in nitric aqueous phases have been measured for several ligand types and concentrations (0.04 M tributylphosphine oxide -TBPO, 0.05 M *N*,*N'*-dimethyl-*N*,*N'*-dibutylmalonamide -DMDBMA, 0.10 M 1-methyl-3-[4-(dibutylphosphinoyl)butyl]-3*H*-imidazol-1-ium bis-trifluoromethylsulphonylimidate -[$C_1imC_4P(O)Bu_2$][Tf_2N] and 1.1 M N,N-dihexyloctanamide –DHOA), (J. Phys. Chem. B, 2016). The data evidence a significant difference between the IL's cation and anion solubilities, as a consequence of several ion exchange and/or ion pairing mechanisms involving all ions present in the system but also the protonation/nitric extraction ability of the ligand.



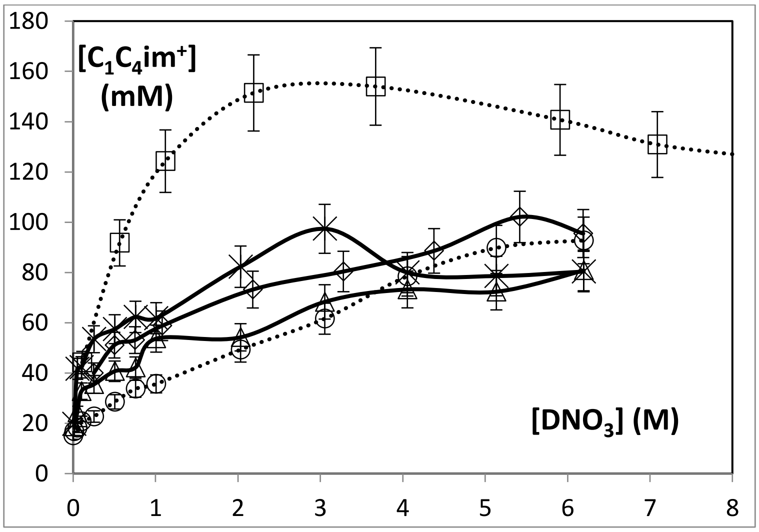


Figure 5. $C_1C_4im^+$ concentration variations as a function of initial DNO_3 concentration in the aqueous phase. □: TBP 1.1 M ; ✳ : [$C_1imC_4P(O)Bu_2$][Tf_2N], 0.1 M ; ◊ : DMDBMA 0.05 M ; Δ : TBPO 0.04 M ; ○ : no ligand added. Dotted and solid lines are guide for the eye only.

New data on the $C_1C_4im^+$ and Tf_2N^- aqueous solubilities as a function of nature and concentration of ligands have been obtained. They evidence the great complexity of systems composed of acidic aqueous phases in contact with (ligand+IL) phases. In particular, a comprehensive understanding of the difference in the IL's cation and anion solubilities would impose a minute analytical examination of phase composition at equilibrium but this is rather difficult, if not impossible. Our data emphasize the difficulty in determining the ecological toxicity of ILs. One should also take into account the differences in cation and anion solubilities, depending on the nature of the aqueous phases in which they are prone to dissolve. On an applied perspective, these results raise additional concerns about the use of ILs. We would like to stress, however, that this is not a definitive condemnation of ILs for two main reasons. First, a quantitative limit to what is considered as "acceptable" and "unacceptable" solubilities should be defined and is certainly dependent on the chemical structure of anions and cations. This difficult balance between advantages and disadvantages should not only consider toxicity arguments. ILs are known to be very efficient extracting phases, after all, so they also provide benefits in terms of environmental safety, not talking of economic concerns. On a more fundamental point of view, many metallic extraction mechanisms towards ILs obey an ion exchange process, therefore involving aqueous phase pollution. It has been proposed that a way to fight such undesirable consequence of efficient metallic ion extraction would be to look for ion-pairing as the dominant extraction process. However, this cannot solve the general question of ILs' ion solubilities, at least for the very low metal concentrations (in the range of traces up to ca. 10^{-4} M) that are used in fundamental works. This is because, for the range of ligand concentration commonly used (from 1 M TBP to tens of mM DMDBMA, for instance), the "natural" (i.e. in the absence of metal) solubilities as evidenced in our work are at least ca. two orders of magnitude above that possibly avoided by the ion-paring mechanism.

Scientific input: Extremely inovative scientific investigation imposed by the implementation of the IL in extraction processes in recent years and environmental issues that raise this new organic ionic environment. The main contribution is to obtain analytical data on the transfer of ions, components of the IL, in the aqueous phase and their impact on the extraction mechanism of metals.

Scientific publications with pedagogical focus:

A) The method of electronic balance is applied for balancing of complex oxidation-reduction reactions (Chemistry, 15(3), 2006, 192-197):

$$Na_3[Co(NO_2)_6] + HCl \rightarrow CoCl_2 + NO + NO_2 + NaCl + H_2O$$

$$Li + HN_3 \rightarrow LiN_3 + NH_3 + N_2,$$

$$Na_2S_3 + KMnO_4 + H_2SO_4 \rightarrow Na_2SO_4 + K_2SO_4 + MnSO_4 + S + H_2O,$$

$$(NH_4)_2S_5 + HNO_3 \rightarrow (NH_4)_2SO_4 + H_2SO_4 + NO + H_2O,$$

$$Na_2S_3O_3 + Cl_2 \rightarrow NaCl + Na_2SO_4 + SO_2 + S,$$

$$KMnO_4 + H_2O_2 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + O_2 + H_2O.$$

An alternative method for oxidation-reduction equation balancing permitting easier and without formal admittances determination of stoichiometric coefficents is proposed, (Chemistry, 18(4), 2009, 280-285):

$$NH_4Cl + C \rightarrow CO + Cl_2 + N_2 + H_2O,$$

$$FeAsS + HNO_3 \rightarrow Fe(NO_3)_3 + H_3AsO_4 + H_2SO_4 + NO_2 + H_2O,$$

$$MoSi_2 + HF + HNO_3 \rightarrow MoF_6 + SiF_4 + NO + H_2O,$$

$$K_4[Fe(CN)_6] + O_2 \rightarrow Fe_2O_3 + K_2CO_3 + CO_2 + N_2.$$

The technique of material balance method or algebraic method was used for balancing of a complex redox equation depending of five degrees of freedom:

$$NH_4ClO_4 + HNO_3 + HCl + H_2O \rightarrow HClO_4{\cdot}2H_2O + N_2O + NO + NO_2 + Cl_2$$

In paper published in J. Chem. Education entitled „Unbalanced Chemical Equations“, it has been noted that the equation summarizes the experimentally observed facts for production of perchloric acid is „an excellent example of the usefulness of the technique of the material balance“. The published method makes it possible to successfully align complex redox equations, (Chemistry, 19 (2), 2010, 141-144) as the equalizing of chemical reactions is inherently a solution of linear homogeneous systems algebraic equations. The stoichiometric coefficients can be considered unknown, and the elements of the matrix of coefficients in front of them represent the number of atoms of each element in each chemical compound. The resulting matrix possesses as many rows as the chemical elements involved in the reaction. The number of columns is determined by the amount of chemical compounds. The elements of the matrix are positive if the relevant chemical elements are involved in the composition of the reactic substances and have a negative sign if they enter in the chemical composition of the reaction products. The object of attention is obviously only the positive values of the coordinates of the solution of the system, which in turn depends on at least one parameter. Typically, the quantity of parameters equals the difference in the number of compounds and the number of chemical elements (i.e. degrees of freedom). Finding a solution with positive coordinates of this system is complicated because the decision depends on five parameters on which additional restrictive conditions apply due to the requirement of positive stoichiometric coefficients. Although that there are some criticisms that the method is founded on „mathematics, not chemistry" and that when several elements are involved in an equation the balancing is laborious, sometimes the material balance method is the unique possibility for successful balancing of such complex redox equations.

A modified form of the material balance method for redox equalizing equations possessing two degrees of freedom, with different sets of disproportionate stoichiometric coefficients, is also proposed. This proposed approach makes it possible to significantly reduce the number of equations giving the balance of atoms to each element in the left and right parts of the chemical equation and allowing the sets of stoichiometric coefficients to be determined easily and quickly, (Chemistry, 20(1), 2011, 67-75):

$$Li + HN_3 \rightarrow LiN_3 + NH_3 + N_2,$$

$$K_2Cr_2O_7 + H_2S + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + S + H_2O,$$

$$Na_2S_3 + KMnO_4 + H_2SO_4 \rightarrow Na_2SO_4 + K_2SO_4 + MnSO_4 + S + H_2O$$

The modified method is based on the assimilation of the number of atoms of the chemical elements on both sides of the reaction, resulting in a homogeneous system with unknown stoichiometric coefficients. The number of equations drawn is equal to the number of different chemical elements that have taken part in the chemical interaction. For each equation of the system, the coefficients before the unknown coincide with the number of atoms of the chemical elements involved in the reaction. Obtaining a permissible set of stoichiometric coefficients (satisfying the reaction) in practice means solving the described system with positive targets coordinates. In the illustrated examples, the decision of this system depends on two parameters. Finding different sets of permissible stoichiometric coefficients in the first example allows clarification of the possibility of another mechanism of reaction. This type of analysis cannot be realized in the classical method of electronic balance, which is a significant scientific contribution. The advantages of the proposed method to the popular method of electronic balance are indicated, which in most cases (if not known the reaction mechanism) allows finding only one set of coefficients and avoiding attribution of non-characteristic oxidation levels of some chemical elements as in the compound FeAsS, as well as other formal assumptions.

A comparative study of the material balance method and the method of electronic balance for balancing to complex redox equations was conducted, (Chem. Educator, 16, 2011, 267-271):

$$Na_3[Co(NO_2)_6] + HCl \rightarrow CoCl_2 + NO + NO_2 + NaCl + H_2O$$

$$C_6H_{12}O_6 + KMnO_4 + H_2SO_4 \rightarrow CO_2 + MnSO_4 + K_2SO_4 + H_2O$$

$$FeAsS + HNO_3 \rightarrow Fe(NO_3)_3 + H_3AsO_4 + H_2SO_4 + NO_2 + H_2O$$

$$KMnO_4 + H_2S \rightarrow K_2SO_4 + K_2S_2O_3 + MnS + S + H_2O$$

$$Li + HN_3 \rightarrow LiN_3 + NH_3 + N_2$$

The material balance method based on the Basic Law on mass preservation, in its altered form, makes it possible to catch up more easily and quickly a wide variety of complex redox equations. It is very useful in balancing the redox equations with two degrees of freedom, which can be leveled with endless sets of stoichiometric coefficients. If the reaction mechanism is unknown, the popular method of oxidation, for example, allows only one set of stoichiometric coefficients to be obtained.

The possibilities for equalization of oxidation-reduction reactions, possessing two degrees of freedom (two parameters) were investigated. Similar reactions can be leveled with an unlimited number of mutually simple stochyometric coefficients, (Chemistry, 22 (2), 2013, 254-264). It is shown which coefficients may be independent parameters and, for the example under consideration:

$$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + NO + H_2O$$

the areas where each pair of independent parameters can receive values are found so that the stoihiometric coefficients are positive numbers. The parameters by which the positive coefficients are obtained are called eligible, and the set of all permissible parameters form a permissible multiplicity. The detailed description of the topography of this permissible multitude is precisely the main scientific contribution of the published research study. The main objective is to find possible combinations (the permissible multiple) of the two independent parameters, as well as to create an algorithm for the determination of this permissible multitude. It is worth stressing that in many cases the determination of the permissible multitude is a relatively complex task.

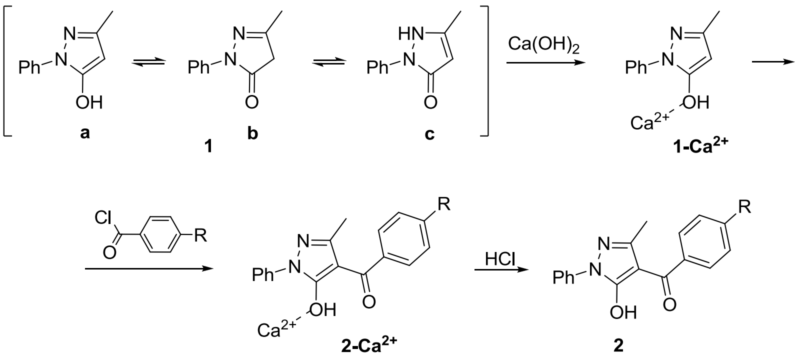
An algorithm and a program product are proposed, allowing equalizing of redox reactions with any number of degrees of freedom to determine positive values of the coefficients of the linear combination of independent parameters, which allows them to find the remaining stoichiometric coefficients (Chemistry, 22 (6), 2013, 864-874). This allows you to find an unlimited number of mutually simple positive stoichiometric coefficients. This work investigates the case when the independent (positive) parameters coincide with part of the stoihiometric coefficients. If the test is narrow to two parameters only, we can claim that part of the stoihiometric coefficients are the coordinates of random points from the first quadrant. The algorithm was successfully used in the equalization of two redox reactions, possessing two degrees of freedom:

$$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + NO + H_2O,$$

$$(NH_4)_2S_5 + HNO_3 \rightarrow (NH_4)_2SO_4 + H_2SO_4 + NO + H_2O.$$

The proposed algorithm and program should only be applied in cases of equalization of redox reactions with a large number of degrees of freedom due to the more complex mathematical apparatus used. In all other cases, it is appropriate to use traditional methods of electronic balance or the method of semi-reactions.

B) In a laboratory experiment, eight students have synthesized 3-methyl-4-(4-methylbenzoyl)-1-phenyl-pyrazol-5-one by selectively C-acylation of 3-methyl-1-phenyl-1-N-pyrazol-5-on, (J. Chem. Education, 92, 2015, 382-384). Calcium hydroxide is used to push the tautomeric equilibrium toward the enol form, to protect the hydroxyl functionality as a complex, to trap the liberated hydrogen chloride, and to keep the reaction media basic.



The product is obtained in excellent yield and recrystallized from various solvents and solvent systems. The chromatographic and physical parameters are determined and the results are analyzed. The signals in the NMR spectra of acyl pyrazolone are assigned and then compared with those of three previously synthesized acyl pyrazolones and two corresponding O-acylated products.

Studentsacquiredtheoreticalandexperimentalknowledgeinthe following tasks: (1) what precautions to take during the laboratory exercises depending on the reagents and solvents hazards, (2) how to perform efficiently a three step sequence for selective C-acylation of pyrazolone, (3) how to carry out TLC and analyze the results, (4) how to accomplish the recrystallization from a single solvent and from a solvent system, (5) how to analyze 1D and 2D NMR spectra. All eight second-year undergraduate students acquired sufficient experimental technique and knowledge in NMR spectra interpretation and application in structure determination.

C) The publication (Chemistry, 19 (5), 2010, 336-349) included the most important recommendations of IUPAC concerning the nomenclature of the coordination compounds from 2005 years. The promotion of the proposed new rules for the construction of formulas and names is important since the last revision of the inorganic nomenclature also made important changes in the area of coordination compounds. Numerous examples illustrate the proposed rules and are given in the paper with pedagogical aims.

A very interesting link of the Avogadro constant with the unit of quantity of substance in SI (mol) is considered in one paper. The new proposals of the International Committee on measures and weights for the re-definition of 4 base units (kilogram, ampere, Kelvin and mol) are commented. The proposals for the new definitions of mole and kilogram include the Avogadro constant. There are some methods by which the constant can be calculated, as well as the change in value and the improvement of experimental methods today (Chemistry 20 (3), 2011, 183-190).

The chronology of the discovery of chemical elements over the centuries from antiquity to the present day has been critically addressed from a chemical and political point of view in a publication (Chemistry 23 (2), 2014, 275-290), where special attention is paid to the French chemists and the work of Marie Curie. In (Chemistry 24 (1), 2015, 125-144) a summary review of the origin of the names and symbols of all chemical elements found so far, together with the reasons for the offer of these exact names and the rules introduced by the IUPAC, is presented.

D) 2011 year − International Year of Chemistry: 100 years since the award of Marie Curie with the Nobel Prize in Chemistry (Nauka (Science), 1 (21), 2011, 7-9). It is not accidental that the choice falls on Marie Curie because she is the only scientist in the world with Nobel awards in physics and chemistry. Her entire creative path is exceptional and as the biographer of the Steele is presented «The woman who changed the course of science». According to the testament of the inventor of the dynamite Alfred Nobel, made in 1895, the Chemistry Prize is awarded "to the person who made the most important discovery or improvement in chemistry". In 1911, M. Curie received the Nobel Prize in Chemistry for "merit and advancement of chemistry through the discovery of the elements radium and polonium, isolation of radium and the study of nature and composition of this remarkable element". For scientific input of this shortable paper we cannot speak, but the impact of this short and powerful reading among the scientists in Bulgaria is indisputable.

The 100 anniversary of the International Union of Pure and Applied Chemistry (IUPAC) was celebrated in 2019 by chemists around the world, which as a global organization has an important role to play in accepting and validating concepts, names and symbols, (Chemistry, 28 (2), 2019, 398-413). The fact that this tribute is celebrated only once in time, the published message reveals briefly how this organization works, its role, structure and competence. The main objective is to summarise briefly the overall mission of this so much recognized international union historically in a century under the key idea of creating a common language in the field of chemistry and its long-lasting impact and unstoppable development.

The global breakfast for ladies is an international event, organized by IUPAC in connection with its 100 anniversary (https://iupac.org/100/global-breakfast/), designed to encourage and support women working in chemistry, to expand their professional contacts at local, national and world level, (Nauka (Science), 1 (29), 2019, 9-16). Although a cup of coffee or tea may not change the world, it can change to some extent the trajectory of women by sharing the experience with ladies who have made themselves known in chemistry. Women are increasingly confident about activities in science, culture, politics and business, which only 150 years ago were considered exclusively male priorities. Quite interesting material is the served of the readers, scientists in Bulgaria, describing historical facts in science chemistry, the participation of women in the discovery of chemical elements, as well as some of the significant scientific achievements of the Bulgarian women in chemistry.

The International Year of the periodic table of chemical elements, 2019, will provide an opportunity to show how they are essential for linking the cultural, economic and political aspects of the world society through a single common language, such as at the same time is celebrated the genesis and the development of the periodic table in the last 150 years, launched in 1869 by the Russian chemist Prof. Dmitry Mendeleev (Chemistry, 28 (6), 2019, 807-816). A short biography, a story about the life of this extraordinary talent and its contributions not only in chemistry, but also in science in general are extremely interesting presented with unpopular facts and events in (Nauka (Science), 6 (29), 2019, 10-16) 185 years of the birth of Dmitry Ivanovich Mendeleev (1834-1907) – exceptional talent with a strange behaviour. On March 1st, 1869, Mendeleev first printed out the so famous table, and on March 13 he sent around 200 (150 in Russian and 50 in French lanaguage) copies of the scientists chemists from different countries in Europe not only in Russia this printed page, modestly titled "Attempting to systematizing based on their atomic weight and chemical similarities ". Despite a number of shortcomings in this first variant, it was clear to Mendeleev that the mathematical regularities in the modification of the atomic weights in the vertical and the horizontal plan probably reflected some law, and immediately used these regularities for unexpected and quite brave predictions.

Scientific contributions: In the presented publications the main contribution is the creation and development of new models for balancing complex oxidation-reduction reactions. A summary scientific study of the history of detection and naming of chemical elements has been made. The latest proposals and recommendations of IUPAC have been reported in order to disseminate and enforce innovations among the chemical community in Bulgaria and to be realized in school chemistry courses and among university students, in particular for students and also for students and chemistry teachers in secondary schools. Chemical education should follow and keep everything good from traditions and comply with the requirements and international practice in order to keep up with the world level of science and education and to make historical trips in the past without forgetting it, because the firstwalkers in ancient Egypt and the pioneers after them as Robert Boyle and Antoine Lavoisier are not left without followers today, who have their own universal language of chemistry and international alphabet today.

Sofia, January 2020

Assistant Professor, Dr. Eng. Maria Atanassova