



Gaziosmanpaşa University

Graduate School of  
Natural and Applied Sciences**Journal of New Results in Science**

Received: 31.01.2014

Accepted: 19.03.2014

Editors-in-Chief: Naim Çağman

Area Editor: Yakup Budak

**Effect of Some Electron Donor and Electron Acceptor Groups on Stability of Complexes According to the Principle of HSAB**

Savaş Kaya<sup>a,1</sup> ([savaskaya@cumhuriyet.edu.tr](mailto:savaskaya@cumhuriyet.edu.tr))  
Sultan Erkan Kariper<sup>a</sup> ([sultanerkan58@gmail.com](mailto:sultanerkan58@gmail.com))  
Ayhan Ungördü<sup>a</sup> ([aungordu@cumhuriyet.edu.tr](mailto:aungordu@cumhuriyet.edu.tr))  
Cemal Kaya<sup>a</sup> ([kaya@cumhuriyet.edu.tr](mailto:kaya@cumhuriyet.edu.tr))

<sup>a</sup>Chemistry Department, Faculty of Science, Cumhuriyet University, 58100, Sivas, TURKEY

**Abstract** – Chemical hardness is an important feature of substances. Lewis acids and bases have been classified to considering the chemical hardness concept and HSAB (Hard and Soft Acid- base) Principle has been demonstrated by Pearson. HSAB principle is an extremely useful qualitative theory that enables predictions of what adducts will form in a complex mixture of potential Lewis acids and bases. Furthermore, chemical hardness is associated with chemical reactivity of molecules. In this study, effect of the chemical hardness in complexes formation was investigated. For this purpose, complexes with  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$  ions of pyrithione (PT) ligand and its derivatives were studied. All calculations were made using the Gaussian 09, Revision B.01 program. The obtained geometries were further optimized at the b3lyp/ 6-31g (d,p) level using Gaussian package. In complex formation reactions, reaction energy ( $\Delta E$ ) has been calculated.

**Keywords** – HSAB, Pyrithione, DFT, Chemical hardness, Coordination complexes

**1. Introduction**

Chemical hardness fundamentally signifies the resistance toward the deformation or polarization of electron cloud of the atoms, ions, or molecules [1]. Chemical hardness is one of extremely useful conceptual constructs of chemistry and physics. Based on this concept, Lewis acids and bases are classified as hard and soft and HSAB Principle [2], [3] was put forward by Pearson. According to HSAB Principle, "hard acids prefer to coordinate to hard bases and soft acids prefer to coordinate soft bases." Low polarizability chemical species are expressed with hard concept while high polarizability chemical species are expressed with

---

<sup>1</sup>Corresponding Author

soft concept. The interaction between hard acids and hard bases is electrostatic interaction and the interaction between soft acids and soft bases is covalent interaction. Both electrostatic interaction and covalent interaction are strong interactions.

Hard and soft acids and bases were originally defined only in general terms [4]:

Soft base-donor atom is of high polarizability, low electronegativity, easily oxidized and associated with empty, low-lying orbitals.

Hard base donor atom is of low polarizability, high electronegativity, hard to reduce, and associated with empty orbitals of high energy and hence inaccessible.

Soft acid the acceptor atom is of low positive charge, large size, and has several easily excited outer electrons, polarizable.

Hard acid acceptor atom is of high positive charge, small size, and does not have easily excited outer electrons, not polarizable.

Some hard/ soft acids and bases are given in Table 1 and Table 2.

**Table 1.** Some Hard and Soft Acids [2]

Hard Acids	Soft Acids
H <sup>+</sup> , Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup>	Cu <sup>+</sup> , Ag <sup>+</sup> , Au <sup>+</sup> , Tl <sup>+</sup> , Hg <sup>+</sup> , Cs <sup>+</sup>
Be <sup>2+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> , Sn <sup>2+</sup>	Pd <sup>2+</sup> , Cd <sup>2+</sup> , Pt <sup>2+</sup> , Hg <sup>2+</sup>
Al <sup>3+</sup> , Se <sup>3+</sup> , Ga <sup>3+</sup> , In <sup>3+</sup> , La <sup>3+</sup>	CH <sub>3</sub> Hg <sup>+</sup>
Cr <sup>3+</sup> , Co <sup>3+</sup> , Fe <sup>3+</sup> , As <sup>3+</sup> , Ir <sup>3+</sup>	Tl <sup>3+</sup> , Tl(CH <sub>3</sub> ) <sub>3</sub> , RH <sub>3</sub>
Si <sup>4+</sup> , Ti <sup>4+</sup> , Zr <sup>4+</sup> , Th <sup>4+</sup> , Pu <sup>4+</sup> , VO <sub>2</sub> <sup>+</sup>	RS <sup>+</sup> , RSe <sup>+</sup> , RTe <sup>+</sup>
UO <sub>2</sub> <sup>+</sup> , (CH <sub>3</sub> ) <sub>2</sub> Sn <sup>2+</sup>	I <sup>+</sup> , Br <sup>+</sup> , HO <sup>+</sup> , RO <sup>+</sup>
BF <sub>3</sub> , BCl <sub>3</sub> , B(OR) <sub>3</sub>	I <sub>2</sub> , Br <sub>2</sub>
Al(CH <sub>3</sub> ) <sub>3</sub> , Ga(CH <sub>3</sub> ) <sub>3</sub> , In(CH <sub>3</sub> ) <sub>3</sub>	Heavy metals
RPO <sup>+</sup> , ROPO <sup>+</sup>	
RSO <sup>+</sup> , ROSO <sup>+</sup> , SO <sub>3</sub>	
I <sup>7+</sup> , I <sup>5+</sup> , Cl <sup>7+</sup>	
R <sub>3</sub> C <sup>+</sup> , RCO <sup>+</sup> , CO <sub>2</sub> , NC <sup>+</sup>	

**Table 2.** Some Hard and Soft Bases

Hard Bases	Soft Bases
H <sub>2</sub> O, OH <sup>-</sup> , F <sup>-</sup>	R <sub>2</sub> S, RSH, RS <sup>-</sup>
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , SO <sub>4</sub> <sup>2-</sup>	I <sup>-</sup> , SCN <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>
Cl <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , ClO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>	R <sub>3</sub> P, R <sub>3</sub> As, (RO) <sub>3</sub> P
ROH, RO <sup>-</sup> , R <sub>2</sub> O	CN <sup>-</sup> , RCN, CO
NH <sub>3</sub> , RNH <sub>2</sub> , N <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub> , C <sub>6</sub> H <sub>6</sub> , H <sup>-</sup> , R <sup>-</sup>

In density functional theory, some chemical properties are identified as response functions of the electronic energy ( $E$ ) with respect to number of electrons [5],[6]. Chemical hardness is

defined as second derivative of the energy  $E$  with respect to the number  $N$  of the electron at a constant external potential ( $v$ ).

$$\eta = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_v \quad (1)$$

Softness ( $\sigma$ ) is the inverse of hardness and is given as follows,

$$\sigma = \frac{1}{\eta} \quad (2)$$

Chemical hardness and electronegativity can be calculated directly from the calculated ionization potential and electron affinity as [7],

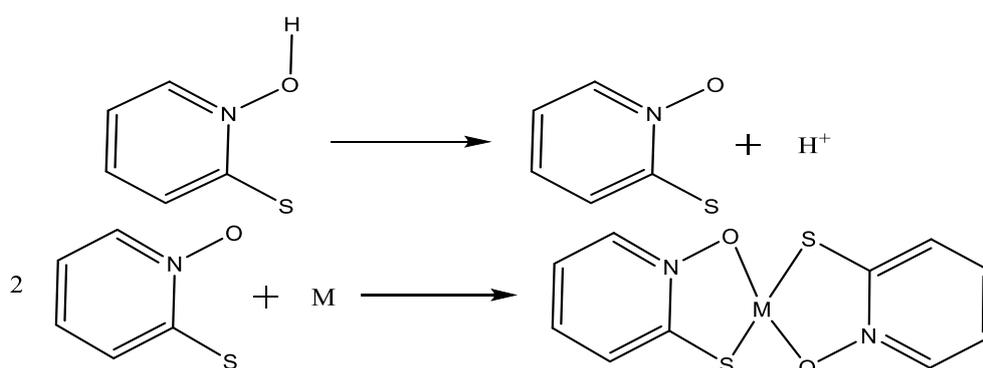
$$\eta = \left( \frac{I - A}{2} \right) \quad (3)$$

where  $I$  and  $A$  are the ionization potential and electron affinity of any chemical system (atom, ion, molecule, or radical). As a result of Koopmans theorem [8], the energies of the HOMO and the LUMO orbitals of the molecule have been associated the ionization potential and the electron affinity. According to Koopmans theorem, the frontier orbital energies are given as,

$$E_{HOMO} = -I$$

$$E_{LUMO} = -A$$

Hard molecules have a large HOMO-LUMO gap, and soft molecules have a small HOMO-LUMO gap. A small energy gap leads to high polarizability, and a large gap means low polarizability. If polarizability of acid and bases increases, covalent interaction among them increases. As a result of this, acid-base complex will be more stable.



**Figure 1** Schematic presentation of the binding with metal of PT ligand

1-Hydroxypyridine-2(1H)-thione (pyrithione) has been widely studied due mostly to its useful antimicrobial activity. Pyrithiones are commonly used to prevent bio deterioration in aqueous functional fluids including adhesives, latex paints and cosmetics [9],[10],[11], [12]. Formation reaction of the PT ligand is as Figure 1.

## 2. Method

All calculations were made using the Gaussian 09, Revision B.01 [13]. The initial molecular modeling of pyriothione and its derivatives were optimized by B3LYP methods. The obtained geometries were further optimized at b3lyp/ 6-31g(d,p) level and calculated with ab initio methods. Atomic charge values were determined to describe the reactivity of the molecules and calculated according to scheme of Mulliken.  $\Delta E$  values calculated by the following equation,

$$\Delta E = E_{Complex} - (E_{Metal} + 2E_{Ligand})$$

Here  $\Delta E$  is complex stability energy,  $E_{Complex}$  is electronic energy of complex,  $E_{Metal}$  is electronic energy of metal,  $E_{Ligand}$  is electronic energy of ligand.

## 3. Result and Discussion

In this study, pyriothione (PT) and its derivatives which 3-metil-pyriothione (S-MPT), 6-metil-pyriothione (O-MPT), 3-amino-pyriothione(S-NPT), 6-amino-pyriothione (O-NPT), 3-nitro-pyriothione (S-NiPT), 6-nitro-pyriothione (O-NiPT) have been analyzed.

According to Lewis acid-base theory[14], a base is defined as an electron pair donor and an acid as an electron pair acceptor . HSAB theory is an theory that related with Lewis acid-bases. In this study, electron donor  $\text{NH}_2$ ,  $\text{CH}_3$  and electron acceptor  $\text{NO}_2$  groups were connected where neighboring atoms of electron donating atom of PT ligand. Thus, hardnesses of electron donor atoms of ligand were chanced. This change in chemical hardness of electron donor atoms of PT and its derivatives affected the stability of complexes.

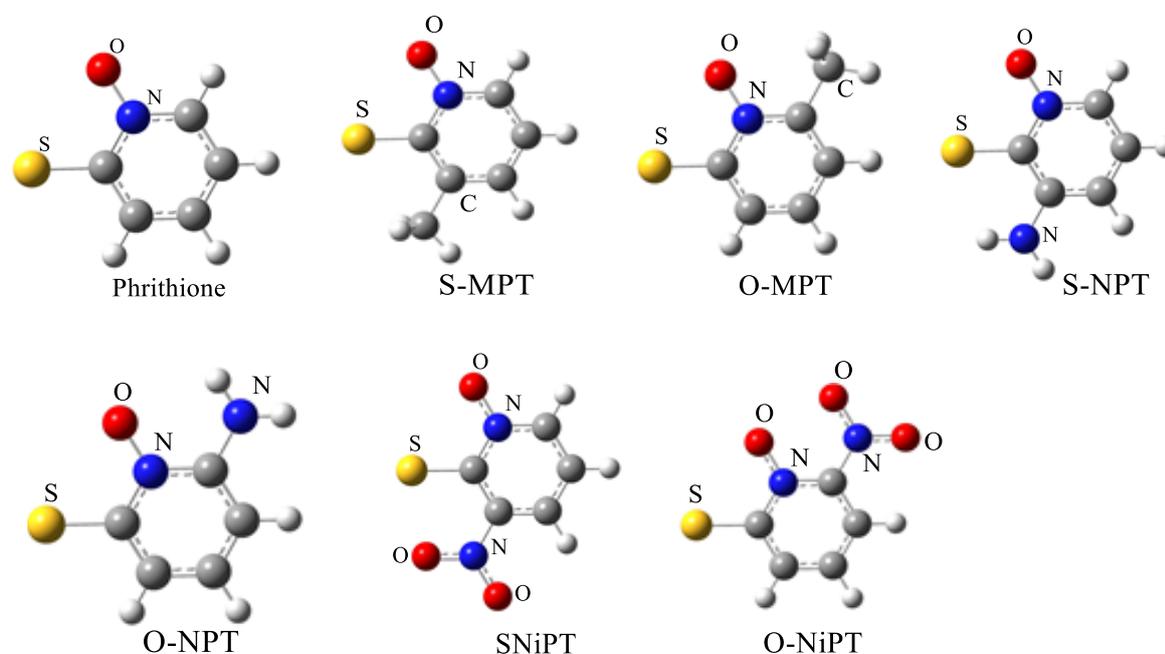
Electronic energy values of formed complexes with  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Cu}^{2+}$  cation of said ligands complexes. According to obtained results, softnesses of O and S atoms of PT ligand increased when  $\text{NH}_2$  and  $\text{CH}_3$  connected to neighboring atoms of electron donating atom of PT ligand because  $\text{NH}_2$  and  $\text{CH}_3$  are electron donor groups. Moreover, electron density and Mulliken charges of S and O atoms in ligand increased due to electron donor groups. At the same time, observed that HOMO value increased of ligand when connected electron donor groups. As a result of increase in HOMO energy value, electron density, Mulliken charges, the reactivity of the ligand increases and ligand gives easily electron to metal. Therefore more stable complexes occurred. Hardnesses of O and S atoms of PT ligand increased when  $\text{NO}_2$  connected to neighboring atoms of electron donating atom of PT ligand because  $\text{NO}_2$  is electron acceptor group. Besides, electron density and Mulliken charges of S and O atoms in ligand decreased due to electron acceptor  $\text{NO}_2$  group. As a result of this, reactivity of ligand decreases and ligand gives difficultly electron to metal. Therefore more unstable complexes occurred.

Glembotskii [15] suggested that power of a ligand is directly proportional to the electron density of the reactive center of the molecule. Electronic charges of S and O atoms and HOMO and LUMO energy values of ligands are given in Table 3.

**Table 3.** The calculated frontier orbital energy values and selected Mulliken atomic charges for pyrrithione and its derivatives (au).

	HOMO	LUMO	S	O
<b>PT</b>	-0.27429	-0.16684	-0.509459	-0.546449
<b>O-MPT</b>	-0.27430	-0.16565	-0.510111	-0.546075
<b>S-MPT</b>	-0.27434	-0.16415	-0.495657	-0.546532
<b>O-NPT</b>	-0.27322	0.16307	-0.506467	-0.569554
<b>S-NPT</b>	-0.26968	-0.15971	-0.497079	-0.552674
<b>O-NiPT</b>	-0.27380	-0.18297	-0.449709	-0.463441
<b>S-NiPT</b>	-0.27493	-0.18529	-0.344079	-0.512715

The higher HOMO energy level means that the molecule easily releases the electrons to the unoccupied orbitals of the metal atom. So, reactivity of ligand increases. According to HOMO values was followed in this order: S-NiPT < S-MPT < O-MPT < PT < O-NiPT < O-NPT < S-NPT. Structures of pyrrithione and its derivatives are given below,

**Figure 2.** PT ligand and its derivatives

Complexes with  $Mg^{2+}$ ,  $Cu^{2+}$ ,  $Ca^{2+}$  and  $Zn^{2+}$  metal ions of ligands in Figure 2 were examined and the following results were obtained.

**Table 4.** Calculated  $\Delta E$  values of PT ligand complexes

PT	$E_{Metal}$	$E_{Ligand}$	$E_{Complex}$	$\Delta E$
<b><math>Mg^{2+}</math></b>	-199.227344	-721.093946	-1642.384281	-608.085225
<b><math>Cu^{2+}</math></b>	-1639.213089	-721.093946	-3082.513256	-697.963198
<b><math>Ca^{2+}</math></b>	-676.866860	-721.093946	-2119.853845	-501.438179
<b><math>Zn^{2+}</math></b>	-1778.107414	-721.093946	-3221.372386	-676.129513

**Table 5.** Calculated  $\Delta E$  values of O-MPT ligand complexes

O-MPT	E Metal	E Ligand	E Complex	$\Delta E$
Mg <sup>2+</sup>	-199.227344	-760.418760	-1721.040638	-612.307523
Cu <sup>2+</sup>	-1639.213089	-760.418760	-3161.164642	-699.066642
Ca <sup>2+</sup>	-676.866860	-760.418760	-2198.503256	-501.302229
Zn <sup>2+</sup>	-1778.107414	-760.418760	-3300.023420	-677.011107

**Table 6.** Calculated  $\Delta E$  values of S-MPT ligand complexes

S-MPT	E Metal	E Ligand	E Complex	$\Delta E$
Mg <sup>2+</sup>	-199.227344	-760.414808	-1721.033926	-613.054937
Cu <sup>2+</sup>	-1639.213089	-760.414808	-3161.158360	-700.083954
Ca <sup>2+</sup>	-676.866860	-760.414808	-2198.494903	-501.020088
Zn <sup>2+</sup>	-1778.107414	-760.414808	-3300.016877	-677.864665

**Table 7.** Calculated  $\Delta E$  values of O-NPT ligand complexes

O-NPT	E Metal	E Ligand	E Complex	$\Delta E$
Mg <sup>2+</sup>	-199.227344	-776.459891	-1753.125453	-613.908633
Cu <sup>2+</sup>	-1639.213089	-776.459891	-3193.249635	-700.779623
Ca <sup>2+</sup>	-676.866860	-776.459891	-2230.587833	-502.754330
Zn <sup>2+</sup>	-1778.107014	-776.459891	-3332.108653	-678.875160

**Table 8.** Calculated  $\Delta E$  values of S-NPT ligand complexes

S-NPT	E Metal	E Ligand	E Complex	$\Delta E$
Mg <sup>2+</sup>	-199.227344	-776.456783	-1753.109791	-607.981467
Cu <sup>2+</sup>	-1639.213089	-776.456783	-3193.237730	-694.159325
Ca <sup>2+</sup>	-676.866860	-776.456783	-2230.578273	-501.961722
Zn <sup>2+</sup>	-1778.107014	-776.456783	-3332.097720	-675.915181

**Table 9.** Calculated  $\Delta E$  values of O-NiPT ligand complexes

O-NiPT	E Metal	E Ligand	E Complex	$\Delta E$
Mg <sup>2+</sup>	-199.227344	-925.593620	-2051.339109	-580.982797
Cu <sup>2+</sup>	-1639.213089	-925.593620	-3491.462633	-666.605048
Ca <sup>2+</sup>	-676.866860	-925.593620	-2528.808758	-473.554085
Zn <sup>2+</sup>	-1778.107014	-925.593620	-3630.321873	-644.840026

**Table 10.** Calculated  $\Delta E$  values of S-NiPT ligand complexes

S-NiPT	E Metal	E Ligand	E Complex	$\Delta E$
Mg <sup>2+</sup>	-199.227344	-925.597958	-2051.352893	-583.352710
Cu <sup>2+</sup>	-1639.213089	-925.597958	-3491.479504	-671.747947
Ca <sup>2+</sup>	-676.866860	-925.597958	-2528.816354	-472.876513
Zn <sup>2+</sup>	-1778.107014	-925.597958	-3630.336284	-648.438818

Unit of E Metal, E Complex, E Ligand is Hartree and unit of  $\Delta E$  kcal mol<sup>-1</sup>

As shown values in Tables 4-10 that chemical hardness is an important concept in terms of chemical stability of the complexes. For to obtain more stable ligand-metal complexes, hard electron donor atom of the ligand must be softened. So chemical hardness mustn't be ignored in complex synthesis

## Acknowledge

This research was made possible by TUBITAK ULAKBİM, high performance and Grid Computing Center (*TR-Grid Research e-Infrastructure*)

## 5. References

- [1] C.G. Dulal, I. Nazmul, *Inter. Journal of Quantum Chemistry*. 111(2011) 40-51.
- [2] Pearson, R.G. *Chemical Hardness: Applications from Molecules to Solids*; Wiley-VCH: Weinheim, Germany, 1997
- [3] Pearson, R.G. Hard and Soft Acids and Bases. *J. Am. Chem. Soc.* **1963**, 85, 3533-3539.
- [4] R.G. Pearson, Recent advances in the concept of hard and soft acids and bases, *Journal of Chem. Edu.* 64(1987)561-567.
- [5] Pearson, R. G. Maximum Chemical and Physical Hardness. *J. Chem. Edu.* **1999**, 76, 267-275.
- [6] Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press, Oxford, U,K, 1989.
- [7] D.J. Tozer, F.D. Proft, Computation of the hardness and the problem of negative electron affinities in density functional theory, *J. Phys. Chem.* 2005, 109, 8923-8929.
- [8] T. Koopmans, Ordering of Wave Functions and Eigenenergies to the Individual Electrons of an Atom, *Physica*. 1(1933)104-113.
- [9] W. Paulus, *Microbicides for the Protection of Materials* London.(1993).
- [10] M. A. Robinson et al., *J. Inorg. Nucl. Chem.* 26(1964)1277-1281.
- [11] B.L. Barnett, H.C. Kretschmar, F.A Hartman, Structural characterization of bis(Noxopyridine-2-thionato)zinc(II), *Inorg. Chem.*, 16(1977)1834-1838
- [12] A.D. Bond, W. Jones, Structure prediction as a tool for solution of the crystal structures of metallo-organic complexes using powder X-ray diffraction data, *Acta Cryst.* 58(2002) 233- 243
- [13] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

- [14] G.N Lewis., Valence and Structure of atoms and molecules, Chemical Catalog Company, Incorporated, 1923.
- [15] A.V. Glembotskii, Theoretical principles of forecasting and modifying collector properties, *Tsvet. Metal.*, 50 (1977) 61-65.