New Materials, Compounds and Applications
Vol.3, No.3, 2019, pp.187-192

STUDY OF EXTRACTION OF SOME IONS OF METALS WITH ACETYLACETONE

F.S. Aliyeva, F.O. Mamedova, Y.E. Yusifov, F.M. Chyragov*

Department of Chemistry, Baku State University, Baku, Azerbaijan

Abstract. Reagents were synthesized on the basis of acetyl acetone which consist of –C =N- and –N=N- group. Extraction possibilities of some metals with synthesized reagents were studied. It was found that all reagents with respect to the studied elements behave similarly. Based on the extraction abilities elements can be positioned in a row of iron> copper> Ni> Co> zinc>Mn> cadmium. In all cases, the best element to be extracted is iron.

Keywords: *Extraction of chelating compounds by new derivatives of acetyl acetone, β-diketones.*

Corresponding Author: *Prof. F.M. Chyragov, Department of Chemistry, Baku State University, Z.Khalilov str.23, Baku, Azerbaijan, AZ1148, e-mail: ciraqov@mail.ru*

Received: *19 May 2019;* ***Accepted:*** *18 November 2019;* ***Published:*** *15 December 2019.*

1. Introduction

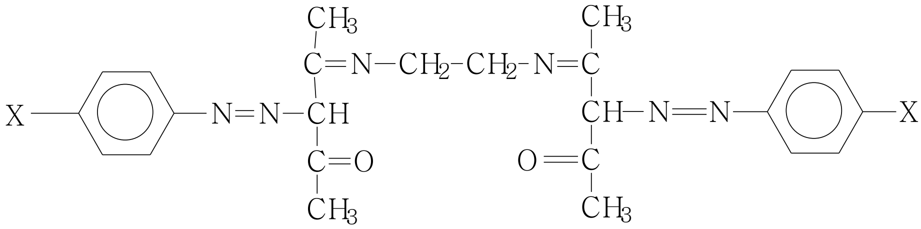
Extraction of chelate compounds as a very reliable method of separation of elements has long been known (Uysal Akku *et al*., 2015; Payehghadr *et al*., 2013; Zolotov & Kuzmin, 1971; Ramesh & Rao, 1987). Chelating agents are used to extract heavy metals from contaminated water, soil (Tandy *et al.*, Al-Qahtani, 2017; Lim *et al.*, 2004). These reagents form colored complex compounds with certain metal ions. Therefore, they are used for extraction-photometric determination of metals (Chyragov *et al.*, 1992; Alieva *et al.*, 2005). However, many metals form unpainted extractable complexes with chelating agents (Zolotov & Kuzmin, 1971).

In the literature, the extraction ability of alkyl and Schiff derivatives of β-diketones with respect to metal ions is known (Abdullayev *et al.*, 1998; Chyragov *et al.*, 1995). It was found that all reagents, in relation to the elements under study, behave similarly. In all cases, iron is extracted best of all elements.

As a continuation of these studies, the extraction ability of a number of metals with new acetylacetone derivatives was studied in this work.

2. Experimental part

The reagents were synthesized by the method of (Busev, 1972; Alieva *et al.*, 2004). The composition and structure of the synthesized compounds were established by X-ray analysis, IR and PMR spectroscopy (Alieva *et al.*,2015; Maharramov *et al.*, 2015).



X = -H (R_1); -F (R_2); -Cl (R_3); -Br (R_4); -J (R_5).

For creation of the required pH, HCl (pH 1-2) and ammonium acetate solution (pH 3-11) were used. The value of pH was controlled by an ionomer-130 supplied with glass electrode. The metal concentration was measured by photometric mehod (photocolorimeter CK-2, l = 1 cm) and Atomic Absorption Spectrometry (AAS spectrophotometer 1 N). The initial solutions of metal salts of $FeCl \cdot 6H_2O$, $CuSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $ZnSO_4 \cdot 7H_2O$, $MnCl_2 \cdot 4H_2O$ are used. For extraction of composites as organic solvents carbon tetrachloride, benzene, chloroform, isobutyl alcohol was used. It was found that the distribution of the complex compounds according to the nature of the solvent are changed in the following patterns: CCl_4> C_6H_6> $CHCl_3$>isobutanol i.e. with a decrease in the percentage of the dielectric constant of the solvent extraction of v complexes increases.

That is why for further extraction of compositions non-polar solvent CCl_4 was used. That means that our synthesized reagents form uncharged complexes, the analytical value of which are known to be highest.

We have developed a method of determining the metal extraction experiment by constructing calibration curve. Three series of measurements depending on the distribution coefficients of elements on pH were studied. The experiments were carried out as follows: 10 flasks with a capacity of 25 ml were taken, 1 ml of a 10^{-3} M reagent solution was added to each flask and each flask was diluted to the mark with a corresponding buffer solution, poured into a separatory funnel, 5 ml CCl_4 was added, shaken for 5 minutes and waited before separation of the organic phase. The organic phase was separated and the metal concentration was determined. The determination of the metal concentration in the respective flasks was carried out in a similar manner. All measurements are in good deal with each other. Based on the data obtained, graphs of the dependence of the distribution coefficient of elements on the concentration of hydrogen ions are constructed. In all cases, the logarithm of the distribution coefficient on pH describe the bell curve. The ascending branch of the curve associated with an increase in the dissociation of reagents with increasing pH, the downward- with hydrolysis of elements in the alkaline range.

All reagents with respect to the studied elements behave similarly. In all cases, the best element to be extracted is iron. It was found that the extraction of metal ions decreases in the order: iron> copper> nickel> cobalt> zinc> manganese> cadmium.

From Fig. 1 it can be seen that in case of the reagent R_5 iron maximally extracted at pH3, log distribution ratio of iron at pH 3 is equal to 2 and remains unchanged until pH8, after raising the pH its value increases and reaches a maximum pH6, log of nickel coefficient with PH3 is 0.25 and peaks at pH 7.0, log of cobalt distribution coefficient at pH 4 is 0.17, and its maximum value is observed at pH 9, log distribution coefficient at PH3 is equal to 0.10.

The maximum value observed of log D for zinc is observed at pH8. Log coefficient of distribution of manganese at PH3 is equal to 0.12; and its maximum value is observed at pH 9. Such elements as Cd (II), Pb (II) at pH 3 are not removed and the values of their distribution coefficients under any pH are never more than one.

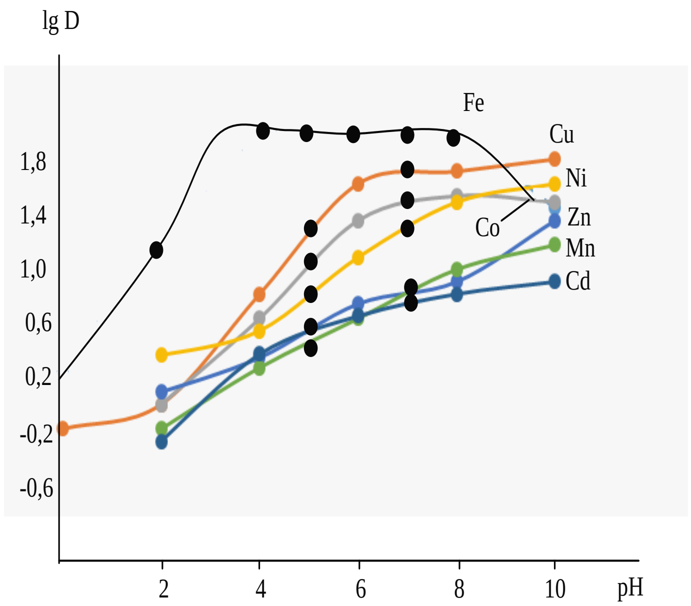


Figure 1. The dependence of the distribution coefficients of the elements on the concentration of hydrogen ions for the reagent R_2

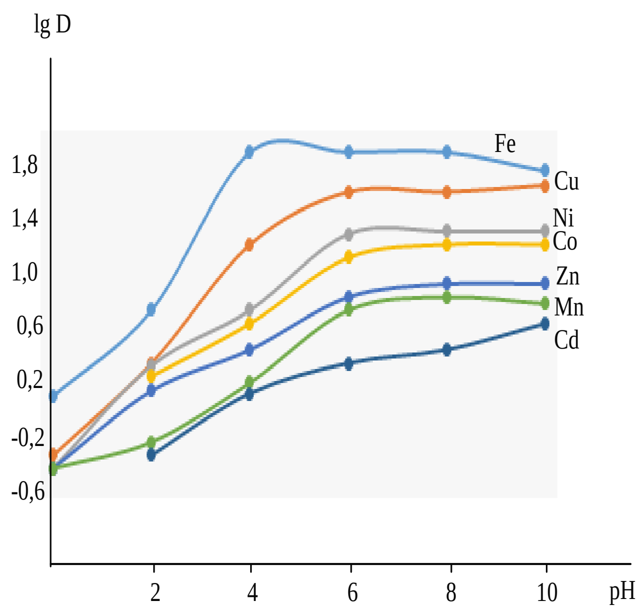


Figure 2. The dependence of the distribution coefficients of the elements on the concentration of hydrogen ions for the reagent $R_5(1)$, $R_4(2)$, $R_3(3)$, $R_2(4)$, $R_1(5)$

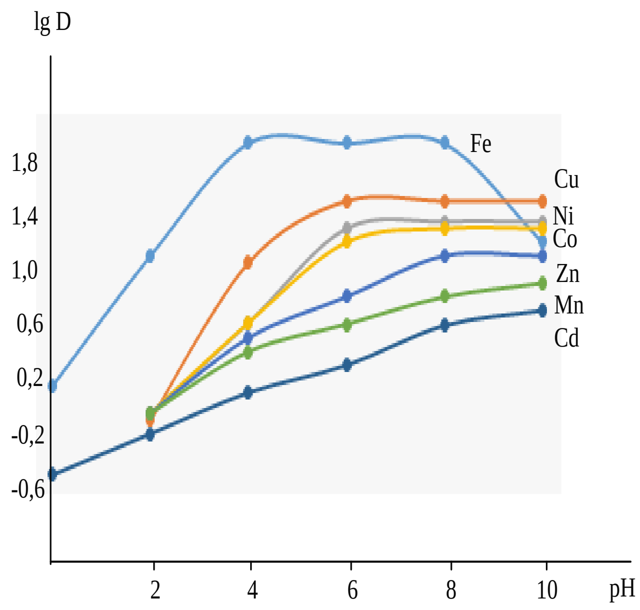


Figure 3. The dependence of the distribution coefficients of the elements on the concentration of hydrogen ions for the reagent R_5(1), R_4(2), R_3(3), R_2(4), R_1(5)

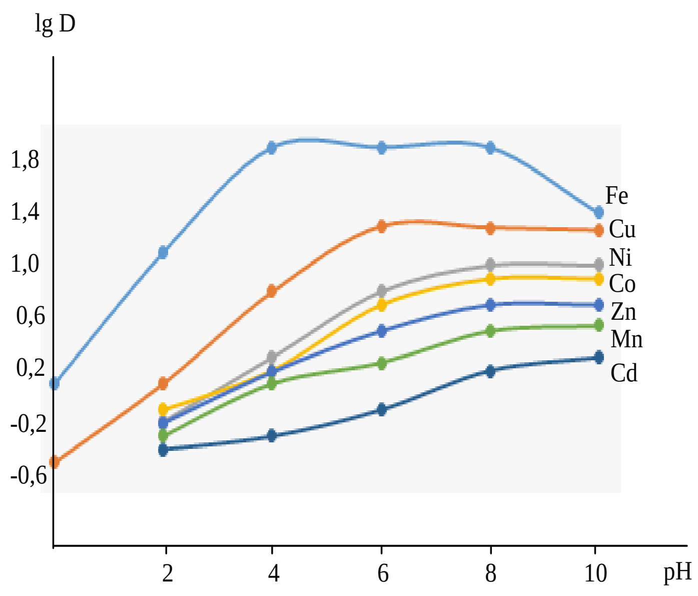


Figure 4. The dependence of the distribution coefficients of the elements on the concentration of hydrogen ions for the reagent R_5(1), R_4(2), R_3(3), R_2(4), R_1(5)

Now analysis of the value of the degree of extraction of elements with a reagent R_5 will be processed. When the degree of extraction of iron (III) with PH3 is 100, copper is extracted by 20%, nickel 90%, cobalt 60%, zinc 40%, 3% manganese.

From all of the above mentioned elements colored compounds with R, except iron (III), form only Cu ions only at high pH values.

A similar pattern is observed in the case of other reagents, but with worse results (Fig. 2-5). Thus, in the case of R_3 reagent at pH4 iron is extracted by 96.4%, copper 9%, nickel 52%, cobalt 4%, zinc 3.8 %.

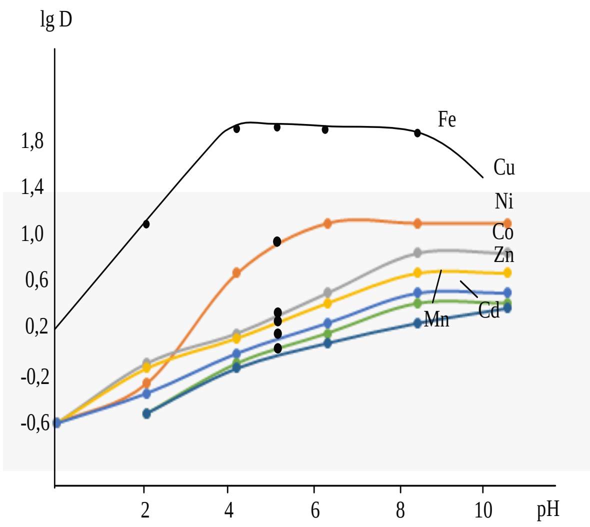


Figure5. The dependence of the distribution coefficients of the elements on the concentration of hydrogen ions for the reagent R_5

In the case of the reagent R_3 at pH5 iron is maximally extracted but the values is equal to 97.2%. Under these conditions, copper is recovered by 50%, nickel 30% Cobalt 21%, zinc 14%, manganese 12%, cadmium 0.9%.

The data obtained will assess the concentration extraction constant, convenient for comparing extraction ability of a number of reagents and a number of metals.

Table 1. The logarithms of the apparent (concentration) extraction constants of elements of the synthesized compounds

Reagent / **Element**	**R_5**	**R_4**	**R_3**	**R_2**	**R_1**
Fe	0	0	0	0	0
Cu	0,18	2,3	2,5	2,5	2,5
Ni	3,4	3,5	3,6	3,8	3,9
Co	3,4	4,6	3,7	4,0	4,1
Zn	4,4	4,8	4,9	5,2	5,2
Mn	6,1	6,2	6,1	6,4	5,3
Cd	6,29	6,85	6,3	6,6	6,3

Calculation of extraction constants was performed according to the equation $\log C_{ext} = \log D - npH - H\log[HA]$.

Stoichiometry of complexes were determined based on the slope of the straight sections of the logarithm of the distribution coefficients from the acidity of the solution.

The evaluation of the results of logarithms of extraction constants are shown in Table. From this table it can be seen that intrusion of substituents in the methylene bridge of benzoyl acetone enhances extraction of reagents extraction ability of fluorine-containing reactants than other reactants.

Comparison of extraction constants for a number of elements examined visually identify a particular behavior of iron. Extraction constant of iron is higher than for the next best extracted element by 4% in the order of magnitude, for R_5 by 3.8 order of magnitude than for the R_4.

Extraction constants of the remaining elements are much less than one, so it is difficult to expect that the substituted acetyl acetone will find use as reagents for the extraction of elements other than iron.

References

Abdullayev, R., Chiragov, F.M., Gambarov, D.G. & Chidinov, E. (1998). Extraction of metals derived from acetyl acetone. Math.BSU, 3.

Alieva, R.A., Chyragov, F.M., Mahmudov, K.T. (2005). Azo-derivatives 2-tenoilthriphtoracetylacetone as a reagent for the photometric determination of copper (II). *Analytical Chemistry Journal*, *60*(2), 157-161.

Aliyeva R.A., Chyraqov F.M. & Mahmudov K.T. (2004). Dissociation constans for sulfoariazodirivatives of acetilasetone and stability constans for their complexec. *Russ. J. Inorg. Chem.*, *49*, 1111-1113.

Aliyeva, R.A., Mammadova, F.M. & Bahmanova F.N. (2015). Investigation of complex compounds formed by new polydaneous reagents based on acetylacetone. *Int. Conf. On Actual Problems of Modern Biology and Chemistry*, 88-89.

Al-Qahtani K.M.A. (2017). Extraction Heavy Metals from Contaminated, Water using Chelating Agents, *Oriental Journal of Chemistry*, *33*(4), 1698-1704.

Busev A.I. (1972). *Synthesis of new organic reagents for inorganic analysis*, Moscow, Moscow State University, 245.

Chyragov F.M., Gambarov D.G., Hasanov N.Ya., Granovskaya P.B. (1992). Extraction-photometric determination of iron(III) using methyl-/2-hydroxypropyl/-N-/p-fluorophenyl/ azomethine. *Journal of Analytical Chemistry*, *47*(7), 1241-1244 (In Russian).

Chyragov F.M., Hasanov N.Ya., Gambarov D.G. (1995). Extraction of metals by Schiff derivatives of β-diketones. *Collected papers of young scientists*, Baku, 61-63 (In Russian).

Lim, T.T., Tay, J.H. & Wang, J.Y. (2004). Chelating-agent-enhanced heavy metal extraction from a contaminated acidic soil. *Journal of Environmental Engineering*, *130*(1), 59-66.

Maharramov, A.M., Aliyeva, R. & Mammadova, F.O. et al. (2015). Study of crystalline structures of new organic reagents synthesized on acetylacetone. *VI Scientific Conference on Chemistry of Coordination Compounds, 9.*

Payehghadr, M., Shahbala, K. & Shafikhani, H. (2013). Spectrophotometric complexation studies of some transition and heavy metals with a new pyridine derivative ligand and application of It for solid phase extraction of ultratrace copper and determination by flame atomic absorption spectrometry. *American Journal of Anal. Chem.*, *4*(01), 1.

Ramesh, V. & Rao, G.N. (1987). Metal extraction industry by β – diketonextragent. *Indian J. Technol*., *25*(9), 418-420.

Tandy, S., Bossart, K., Mueller, R., Ritschel, J., Hauser, L., Schulin, R. & Nowack, B. (2004). Extraction of heavy metals from soils using biodegradable chelating agents. *Environmental Science & Technology*, *38*(3), 937-944.

Uysal Akku¸ G., Al, E. & Korcan, S.E. (2015). Selective extraction of toxic heavy metals and biological activity studies using pyrimidylthioamide functionalised calix [4] arene. *Supramolecular Chemistry*, *27*(7-8), 522-526.

Zolotov, Y.A. & Kuzmin, N.M. (1971). *Extraction and Concentration*. Moscow, Chemistry, 372.