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EXTRACTION-PHOTOMETRIC DETERMINATION OF MANGANESE (II) WITH 2,4-DIHYDROXYTHIOPHENOL AND AMINOPHENOLS

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The interaction of manganese (II) ions with 2,4-dihydroxythiophenol in the presence of aminophenols was studied. The action of aminophenols on hydroxy halogen thiophenolate of manganese (II) (pH 2.3–8.1) forms a yellow compound, which is extracted well by halogen-containing solvents. The extraction of the above compounds into the organic phase is 97.3–99.1%. The chloroform extract of hydroxythiophenolate complex of manganese (II) by aminophenols has absorption maximum at 400–420 nm ($\epsilon = (2.14–2.70) \cdot 10^4$).

Keywords: manganese (II), 2,4-dihydroxythiophenol, aminophenols, mixed ligand complexes (MLC), light absorption

Derivatives of thiophenol (L) are used for determining a number of elements: V, Mo [1], W [1, 2], Nb, Ta [3], Ti [4], Ni [5], Cu [6] and others. The purpose of this work is to develop high selective methods extraction spectrophotometric determination of Mn (II) by using mixed ligand complexes (MLC) with 2,4-dihydroxythiophenol and 2-(N,N-diethylaminomethylthio)-4-methoxyphenol (**AP₁**), 2-(N,N-dibutylaminomethylthio)-4-methoxyphenol (**AP₂**), 2,6-bis-(N,N-dimethylaminomethyl)-4-methylphenol (**AP₃**), 2,6-bis-(N,N-dimethylaminomethyl)-4-chlorophenol (**AP₄**), 2-(N,N-dimethylaminomethyl)-4-methylphenol (**AP₅**), 2-(N,N-diethylaminomethyl)-4-bromophenol (**AP₆**) and 4-chloro-2-(N,N-dimethylaminomethyl)-6-thiophenylmethylphenol (**AP₇**).

Experimental part

Reagents and solutions. We used 0.01 M solutions L and AP in chloroform. Initial solution of 0.1 mg/ml Mn (II) was prepared as described in [7]. The concentration of the manganese solution was adjusted gravimetrically. To create the necessary pH range was used ammonium-acetate buffer solution pH (3–11) and HCl (pH 0–2). The ionic force of the solutions was kept constant ($\mu = 0.1$) by introducing calculated amount of KCl.

L and AP were synthesized by methods [9] and [10] respectively.

Instruments. The absorbance of the extracts was measured using a KFK-2 photocolori-

meter and a SF-26 spectrophotometer, equipped with 5 and 10 mm path-length cells. pH controlled at potentiometer I-120.2. The volume of organic phase in every cases was 5ml.

Method. Into the separatory funnel was inserted 0.1–1.0 ml of initial solution Mn (II) with an interval 0.1 ml 2.0–2.3 ml of 0.01 M solution of L 2.0–2.5 ml 0.01 M AP. The volume of organic phase was adjusted to 5ml with chloroform and in the aqueous phase to 20 ml with distilled water. The required pH was adjusted by adding 0.1 M HCl solution. After 5–8 minutes the organic layer was separated and its optical density was measured at room temperature at KFK-2 at 400nm.

Determining sign of the charge homogeneous ligand complexes (HLC). Experiments on the electromigration in the U shaped tube and ion exchange on the anion exchanger EDE-10P was shown anionic character of yellow painted HLC Mn(II)-L. While inserting in system Mn (II)-L AP was observed extraction of this compounds in the organic phase like MLC (mixed ligand complexes).

Results and discussion

Choosing of extractant. Manganese (II) can be extracted some of solutions with organic solvents such as CCl₄, C₆H₆, C₂Cl₄, C₆H₅-CH₃, CHCl₃, C₆H₅Br, C₆H₅Cl, C₂H₄Cl₂. Extraction ability of Mn increases by increasing dielectric constant of solution.

Table 1

Chemical-analytical characteristics of methods determining Mn (II) DLC with L и AP

AP	pH ₀₆	pH _{det}	$\lambda_{\max}$, nm	$\Delta\lambda$, nm	$\varepsilon \cdot 10^{-4}$	$\lg \beta$	$\lg K_{\text{equl}}$	$\lg K_{\text{ex}}$	R, %	D	Linear range mkq/ml
AP ₁	3.5-7.9	5.5-6.7	415	134	2.43	11.3	7.52	10.21	98.5	262.7	1.0-125
AP ₂	2.8-7.9	5.8-6.9	420	139	2.70	10.9	7.14	10.38	98.6	281.7	1.1-120
AP ₃	3.0-8.1	5.2-6.4	410	129	2.35	11.5	8.43	11.22	98.8	329.3	1.0-125
AP ₄	2.3-7.6	5.6-6.8	420	139	2.65	10.8	8.08	12.39	99.1	440.4	1.3-125
AP ₅	3.2-8.0	5.0-6.1	410	129	2.30	11.6	7.67	9.08	97.3	144.1	1.0-110
AP ₆	3.4-7.5	5.3-6.3	400	119	2.18	11.9	6.36	10.84	98.3	231.3	1.3-125
AP ₇	3.2-8.1	5.6-6.7	400	119	2.14	11.9	7.23	12.67	98.4	246.0	1.1-125

This is in accordance with the nature of ion associated compounds. All further investigations were carried out with chloroform. The content of manganese after reextraction in the organic phase was determined photometrically with the antranilic acid [11], but in aqueous phase with different ways. Extraction ability of complexes evaluated dispensation coefficient (D) and extraction percent (R%). While single step extraction with chloroform extraction percent of manganese is 97.3-99.1 % like MLC (table 1).

Effect of pH of the aqueous phase.

The dependence of optical density of extracts MLC Mn (II)-L-AP- in chloroform from the pH of the aqueous phase was presented in fig.1. As follows from figure 1 and table 1 MLCs were formed at 2.3-8.1 pH range and output of complexes are maximum at 5.0-6.8 pH range.

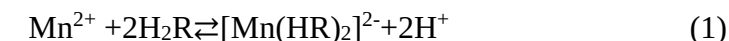
Electronic spectra of complexes. The adsorption spectra of the complexes were shown in fig.2. The chloroform extracts of MLCs of Mn (II)-L-AP have maximum light absorbance at 400 - 420 nm. Coefficient of mo-

lar absorption is $(2.14- 2.70) \cdot 10^4$.

Effects of concentration of ligands and time. For a complete forming MLCs of Mn (II)-L-AP requires 31-32 and 25-26 fold excess of L and AP, respectively. MLCs of Mn (II)-L-AP forms almost in a trice, stable in aqueous and organic solvents and do not decompose within three days and after extraction-more month.

Compound of complexes and equation of complex formation. The molar ratio of Mn(II):L:AP was established by Staric-Barbanel, Asmus and Shifting equilibrium methods [12]. In all cases, the ratio of Mn(II):L:AP is 1:2:2 (in case of AP₃ and AP₄ is 1:2:1). In experience [11] were described complexes of Mn(II) at pH range 4-6 in the solution where dominate Mn (II) ions.

Based on the determination of the molar ratios of the reactants and the account of the ionic state can be assumed that reaction of Mn (II) with L(H₂R) and AP flows in follows:



The equation 2' corresponds to the interaction of $[\text{Mn}(\text{HR})_2]^{2-}$ with the cation HAP_1^+ (AP₁, AP₂, AP₅, AP₆ и AP₇), and equation 2'' with $\text{H}_2\text{AP}_3^{2+}$ (AP₃ и AP₄).

The constants of equilibrium were calculated according to the equation:

$$\lg K_{\text{eq}} = \lg D - 2 \lg [\text{HAP}_1^+] \quad (3')$$

and in case with AP₃ and AP₄ (equation 2'')

$$\lg K_{\text{eq}} = \lg D - \lg [\text{H}_2\text{AP}_3^{2+}] \quad (3'')$$

The extraction constants were calculated according to equation.

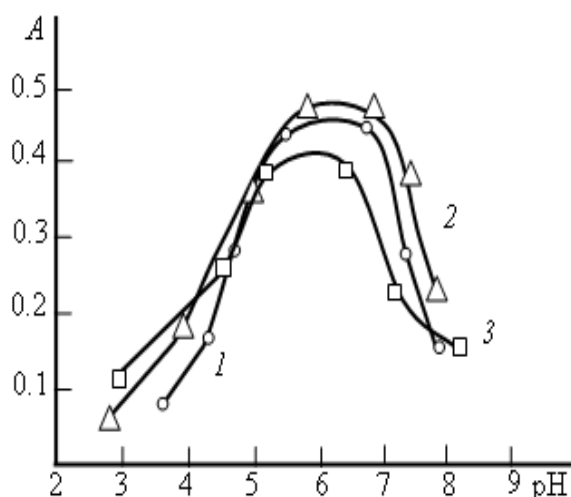


Fig. 1. Effect of pH on aqueous phase and optic density MLC Mn(II) with L and AP

1. Mn(II)-L-AP₁; 2. Mn(II)-L-AP₂; 3. Mn(II)-L-AP₃. $C_{Mn(II)} = 3.65 \cdot 10^{-5}$ mol/l, $C_L = (1.12 - 1.16) \cdot 10^{-3}$ M, $C_{AP} = (0.92-0.96) \cdot 10^{-3}$ M; KFK-2, $\lambda = 400$ nm, $\ell = 0.5$ cm

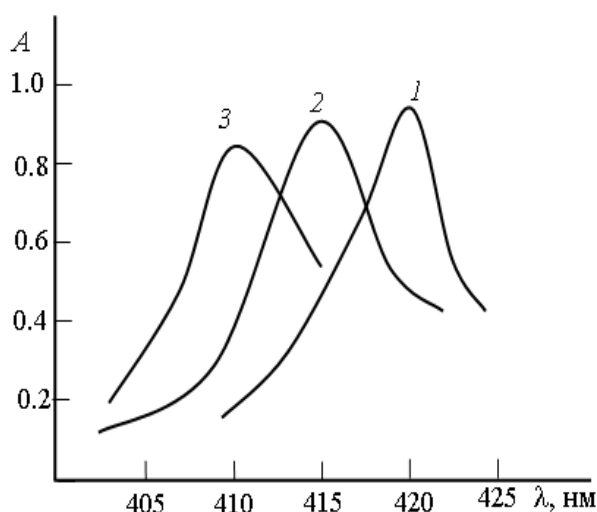


Fig. 2. The absorption spectra of MLC Mn(II) with L and AP

1. Mn(II)-L-AP₁; 2. Mn(II)-L-AP₂; 3. Mn(II)-L-AP₃; $C_{Mn(II)} = 3.65 \cdot 10^{-5}$ mol/l, $C_L = (1.12 - 1.16) \cdot 10^{-3}$ M, $C_{AP} = (0.92-0.96) \cdot 10^{-3}$ M; SP-26, $\ell = 1.0$ cm

$$\lg K_{ex} = \lg D - 2\lg [HR^{2-}] - 2\lg [HAP_1^+] \quad (4')$$

$$\lg K_{ex} = \lg D - 2\lg [HR^{2-}] - \lg [H_2AP_3^{2+}] \quad (4'')$$

The peaks of $\lg K_{eq}$ и $\lg K_{ex}$, calculated by formulas (3',3'',4',4'') for the complexes Mn(II)-L-AF shown in table 1 below.

Calibration curves are linear at concentration range 0.25-25 mkq/ml of Mn(II). Photometric detection limit of Mn(II) as MLC was calculated by the equation [12]. The detection limit of Mn(II) at $P = 0.95$ is 0.014-0.023 g / ml.

The stability constants ($\lg \beta$) of MLC was calculated with the method intersection of curves is 10.8-11.9 [12].

Effect of extraneous ions. Number of extraneous ions, in determining of allowable manganese (II) like MLCs Mn(II)-HDTP-AP₁, evaluated with the factor of selectivity. The maximum permissible ratio of ion: manganese (by weight) in which determination error does not exceed ± 3.5 %. Determination of manganese (II) in the form of MLC Mn(II)-HDTP-AP₁ does not interfere fold amounts of the following elements: Li, Na, K (3000); Cl⁻, NO₃⁻ (1000); Ca, Ba, Sr (550); In(II), Cd(II), Mg(II) (200); Hg(II), Zn(II) (120); Co(II), Ni(II), Fe(II), Fe(III), U(VI) (100); Cu(II), Pb(II), Cr(III) (80); Al(III), Ga(III), In(III), Bi(III), Sb(III), Zr(IV), Hf(IV) (110); Ti(IV), Nb(V), Ta(V) (80); V(V), Mo(VI), W(VI) (70).

Comparative characteristics of determination methods of the manganese (II). In the table 2 were given data that allows compare the analytical characteristics of determination methods of manganese (II) with [8, 13-15] techniques. It is obvious that H₂R has advantages than other reagents: The absorption maxima was shifted to longer oblast of the spectra, the molar coefficient of absorption is higher than the molar absorbance coefficient of other complexes, the pH of the reaction shift to more acidic region, which increased selectivity. The developed techniques were used for the determination of manganese in different industrial and natural objects.

Table 2

The data which allows compare analytical characteristics of determining Mn(II) with given reagents

Reagent(s)	pH _{opt}	$\lambda_{\max}$, nm	$\Delta\lambda$, nm	$\varepsilon \cdot 10^{-4}$	lg β	R, %	D	An interval of subor- dination to Ber law, mkq/ml	Ref.
L + AP ₁	5.5-6.7	415	134	2.43	11.3	98.5	262.7	1.0-125	Data base
L + AP ₂	5.8-6.9	420	139	2.70	10.9	98.6	281.7	1.1-120	
L + AP ₃	5.2-6.4	410	129	2.35	11.5	98.8	329.3	1.0-125	
L + AP ₄	5.6-6.8	420	139	2.65	10.8	99.1	440.4	1.3-125	
L + AP ₅	5.0-6.1	410	129	2.30	11.6	97.3	144.1	1.0-110	
BPhen+ AlY*	6.7	370	20	1.45	8.2	98.9	192.0	-	13
BPhen+ AlPC	8.3	390	20	2.27	7.2	99.0	199.0	5-112.5	13
Phen+ AlY	10	370	20	1.12	9.17	98.8	161.0	-	13
Phen+ AlPC	9.1	390	20	1.95	8.01	98.8	162.0	2.5-100	14
Dip+ AlY	11	360	10	1.01	6.7	98.4	125.0	-	15
Dip+ AlPC	8.8	380	20	1.15	5.3	-	-	-	15
Ox	7.2-12.5	395	-	0.85	-	-	-	-	7
mOx	6.0-6.5	413	-	0.70	-	-	-	-	7

Notes: BPhen-4,7-diphenylphenantroline; Phen- 1,10-phenantroline; Dip-2,2'-Dipyridil; AlY – alizarin yellow P; AlP- alizarin yellow PC; Ox - 8-hydroxyquinoline; mOx- 8-mercaptohydroxyquinoline

Determination of standard samples manganese alloys. Weight alloy of sample is 0.1-0.5 g [A-195-3 - (11.3 Si; 0.3 Mn; 0.6 Fe; 0.23 Zn; 0.14 Cu; 0.08 Ti; 0.17 % Mg; ost.Al), A-195-4 - (12.3 Si; 0.13 Mn; 0.9 Fe; 0.3 Zn; 0.11 Cu; 0.2 Ti; 0.12 % Mg; rest of Al), A-195-5 - (13.2 Si; 0.08 Mn; 1.1 Fe; 0.38 Zn; 0.04 Cu; 0.4 Ti; 0.09 % Mg; ost. Al),] was dissolved in 10 ml of an aqueous dissolution of 5 ml HCl (1: 1) + 1-2 ml of HNO₃ (1: 1) at 50 ° C, added to a flask with 50 ml and diluted with water to the mark.

An aliquot part was placed into a separatory funnel and the manganese was determined by using the developed techniques ($S_r = 0.031$).

Determination of manganese in the soil (depth of cut of 10-20 cm, $n=3$, $p=0.95$).

A portion of the soil (0.5 g) is a light brown color, was taken from the caspian zone, calcined in a muffle furnace for 3 h. After cooling, a sample of treated and dissolved in the graphite dish at 50-60 ° C with a mixture of 16 ml of conc. HF, 5 ml of conc. HNO₃ and 15 ml of conc. HCl.

For the purpose of removing excess hydrogen fluoride was added 3 times in a solution of 8 ml of conc. HNO₃ and evaporated each time to 5-6 ml. The solution was transferred into a flask which volume is 100 ml, and the

volume is adjusted to the mark with distilled water. In an aliquot parts of the solution of manganese determined with developed techniques. The results of the analysis of this methods ($X_{cp} = (2.3-2.7) \cdot 10^{-3}$ ($S_r = 0.012-0.031$)) are compliance with the obtained results with methods 8-hydroxyquinoline and 8-mercaptohydroxyquinoline: $X_{cp} = (2.3-2.7) \cdot 10^{-3}$ ($S_r = 0.014-0.033$).

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MANQANIN (II) 2,4-DİHİDROKSİTİOFENOL VƏ AMİNOFENOLLARLA EKSTRAKSİYALI-FOTOMETRİK TƏYİNİ

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Manqanın(II) 2,4-dihidroksitiofenol və aminofenollarla kompleksmələğətməsi spektrofotometrik tədqiq edilmişdir. Müəyyən edilmişdir ki, müxtəlifliqandlı kompleks pH 2.3-8.1-də əmələ gəlir. Onların üzvi fazaya ekstraksiyası 97.3-99.1% təşkil edir. Maksimum işıqudma $\lambda = 400-420$ nm dalğa uzunluğunda baş verir $((2.14-2.70) \cdot 10^4)$.

Açar sözlər: manqan(II), 2,4-dihidroksitiofenol, aminofenollar, müxtəlifliqandlı komplekslər, işıqudma

ЭКСТРАКЦИОННО-ФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МАРГАНЦА (II) 2,4 – ДИГИДРОКСИТИОФЕНОЛОМ И АМИНОФЕНОЛАМИ

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Спектрофотометрическим методом исследовано комплексообразование Mn(II) с 2,4-дигидрокситиофенолом в присутствии аминоксенолов. Установлено, что разнолигандные комплексы образуются при pH 2.3–8.1. Полнота извлечения их в органическую фазу составляет 97.3–99.1%. Максимумы в спектрах светопоглощения наблюдаются при $\lambda = 400-420$ нм $((2.14-2.70) \cdot 10^4)$.

Ключевые слова: марганец (II), 2,4- гидрокситиофенол, аминоксенолы, разнолигандные комплексы, светопоглощения