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Sorption of Copper (II) from Aqueous Solutions on Complexing Ion Exchangers and Determination of Copper by Diffuse Reflectance Spectroscopy

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The present paper is devoted to sorption concentration of copper (II) from different solutions on a number of complexing ion exchangers and subsequent determination of Cu (II) in a phase of amphoteric ion exchanger AMF-2T of macroreticular structure by diffuse reflectance spectroscopy. The sorption properties of the sorbents were investigated. The apparent stability constants for copper complexes in ion exchanger phase were calculated. The sorption-spectroscopic method is proposed for Cu (II) determination in aqueous solutions. The calibration curve is linear at concentration range 0.05 – 3.0 mg/L (sample volume is 25.0 mL) and the detection limit is 0.03 µg/mL. The presence of Ni (II), Co (II), Cr (III), Fe (II,III), Zn (II) as well as C₂O₄²⁻ and PO₄³⁻ (100-fold excesses) does not hinder the determination of Cu (II).

Key words: copper, ion exchange, sorption, diffuse reflectance spectroscopy.

Introduction

The production technologies applied in chemical industries often suppose the formation of wash water and waste water with different contents of heavy non-ferrous metals and various salt compositions [1]. For example, the hydrometallurgical production of chemical power sources from manganese ores and concentrates is based on complete purification of manganese salts from impurities of non-ferrous metals (Cu²⁺, Co²⁺, Ni²⁺, Zn²⁺), as their contents should not exceed 10⁻⁶ % [2-4]. The purification of such water from metal impurities can be carried out

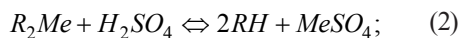
by precipitation, electrochemical or ion exchange and adsorption methods [5-9].

It is known that heavy metal ions act harmfully on vital processes of men and animals, coming into living organism together with natural water. In view of that, the standards for water quality are getting higher, and the contents of heavy metal ions in waste and fresh water are under a strict control [10,11]. The sorption purification of water [12,13] is considered one of the most effective methods for water purification, as it allows water recycling after the recovery of non-ferrous metal ions (Me²⁺) by

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ion exchange. The process runs in accordance with the following scheme:



It can be seen from this scheme that the process provides the opportunity to purify the water by means of ecologically pure technology, as well as to isolate the valuable compounds.

It should be noted that the determination of copper in this media is a matter of practical interest, as copper is present in this water in multiple forms [14,15]. This analytical problem can be resolved by means of the high-selective complexing ion exchangers. Such kind of resins is capable to recover the copper ions from solutions completely, and to achieve high purification grade. It is also advantageous that after that the subsequent analytical determination of copper can be carried out directly in the ion exchanger phase using diffuse reflectance spectroscopy.

Basically, the solid phase determination of non-ferrous and noble metals is appealing for investigators as it has high sensitivity, provides the opportunity to obtain analytical signal directly in the sorbent phase by means of diffuse reflectance spectroscopy [16,17], is relatively cheap and easy to use even under field conditions [18-23]. That is why the present paper is devoted to investigation of copper (II) ions recovery from solutions with different composition on complexing ion exchangers with macroporous structure as well as to subsequent determination of Cu (II) in the resin phase by diffuse reflectance spectroscopy.

Experimental

For the investigation carboxylic cation exchanger KB-2T as well as aminocarboxylic amphoteric ion exchanger AMF-2T with long-chained cross-linking agent – tetravinyl-ester of

pentaerythrite (TVEPE) were taken. To make a comparison of sorption properties of these resins, we also chose carboxylic cation exchanger KB-4 as well as amphoteric exchangers ANKB-35 and AMF-2S, where cross-linking agents were divinylbenzene (DVB) and divinylsulfide (DVS), respectively. All the ion exchangers investigated are manufactured by “TOKEM” company (Kemerovo, Russia).

The ion exchangers were preliminary prepared according to standard procedures and loaded with 2 M HCl. The ion exchange capacity as well as the acid-base properties of these sorbents was determined by potentiometric titration method with the indicator glass electrode using a potentiometer (model EV-74, Russia). The physical-chemical characteristics of the resins investigated are shown in Table 1.

The sorption of copper (II) ions was carried out under batch experiment conditions. The initial stock solutions of copper (II) chloride, sulfate or nitrate with concentrations 0.5 mol/L were prepared from accurately weighed samples of $CuCl_2 \cdot 2H_2O$; $CuSO_4 \cdot 5H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$. The working solutions with concentrations 0.1 – 0.8 mmol/L were prepared from stock solutions. The necessary pH value of these solutions was achieved by adding the appropriate mineral acids (0.5 M solutions of HCl , H_2SO_4 or HNO_3), whereas the constant ionic strength (0.5) was maintained by adding of appropriate sodium salt (0.5 M $NaCl$ and $NaNO_3$, as well as 0.2 M Na_2SO_4). By choosing copper (II) concentrations as well as pH and ionic strength values we attempted to make our experiment closer to real industrial conditions [1,2,4-7,9-13]. All the reagents used in the present work were of analytical purification grade.

The resin quantities (0.2 g) were preswollen for 4 h in salt solutions (without Cu^{2+}) with necessary pH values and after that they were stirred with the copper (II) solutions (20.0 mL)

Table 1. Physical-chemical and sorption properties of ion exchangers investigated

Trade name ^a	Functional groups	Cross-linking agent	Specific swelling volume, cm ³ /g in H ⁺ -form	Static exchange capacity, mmol/g in Na ⁺ -form		\overline{pK}_a
				pH = 1.5	pH = 9.0	
KB-2T	$\left[\begin{array}{c} \text{---CH}_2\text{---CH---CH}_2\text{---} \\ \diagup \quad \diagdown \\ \text{COOH} \quad \text{COOH} \end{array} \right]_n$	TVEPE	2.9	-	7.4	2.00
KB-4	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{---CH}_2\text{---C---} \\ \\ \text{COOH} \end{array} \right]_n$	DVB	2.4	-	4.5	2.25
ANKB-35	$\left[\begin{array}{c} \text{---CH---CH}_2\text{---} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{CH}_2\text{---N---} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{COOH} \quad \text{CH}_2\text{COOH} \end{array} \right]_n$	DVB	3.1	1.5	4.3	2.05
AMF-2T	$\left[\begin{array}{c} \text{---CH---CH}_2\text{---} \\ \\ \text{C=O} \\ \\ \text{NH} \\ \\ \text{C}_2\text{H}_4 \\ \\ \text{N---} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{COOH} \quad \text{CH}_2\text{COOH} \end{array} \right]_n$	TVEPE	3.2	1.3	5.5	1.87
AMF-2S	$\left[\begin{array}{c} \text{---CH---CH}_2\text{---} \\ \\ \text{C=O} \\ \\ \text{NH} \\ \\ \text{C}_2\text{H}_4 \\ \\ \text{N---} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{COOH} \quad \text{CH}_2\text{COOH} \end{array} \right]_n$	DVS	2.6	1.1	5.5	1.93

^a TVEPE – tetra vinyl-ester of pentaerythritol; DVB – divinylbenzene; DVS - divinylsulfide

in thermostat at $(20 \pm 1)^\circ \text{C}$. The equilibrium time was 24 h.

After sorption, the resins and solutions were separated and then solid and liquid phases were analyzed. The concentration of copper (II) ions in initial and equilibrium solutions was determined by spectrophotometrical method with 4-(2-pyridylazo)-resorcin (PAR) [24] at $\lambda = 395 \text{ nm}$ or $\lambda = 415 \text{ nm}$ (in solutions with $\text{pH} \leq 3.0$ and $\text{pH} = 4.0 - 5.0$, respectively) using a spectrophotometer (model Specol 1300, Germany). The solid-phase analysis was carried out from diffuse reflectance spectra using the colorimeter Spectroton (Russia). This colorimeter embodies the principle of concurrent measurements of diffuse reflectance using 24 fixed wavelengths (visible spectrum) during light exposure of solid sample by pulse xenon lamp ISK-25 with the subsequent mathematical processing of results. The wet resin samples were placed into a cell and the spectra were recorded at a wavelength of 380 – 720 nm. A cell is a fluoroplastic disk (10 mm height, 80 mm diameter) with a cylindrical hole of 5 mm depth and 16 mm diameter. The preparation procedure of samples is briefly presented below.

The effectiveness of sorption recovery of copper (II) was estimated from distribution ratio (D , L/g) and separation factor (S):

$$D = \frac{\overline{[Cu^{2+}]}}{[Cu^{2+}]}; \quad (4)$$

$$S = \frac{\frac{\overline{[Cu^{2+}]}}{[Cu^{2+}]} / \frac{\overline{[H^+]}}{[H^+]}}{\frac{\overline{[Cu^{2+}]}}{[Cu^{2+}]} / \frac{\overline{[H^+]}}{[H^+]}}}, \quad (5)$$

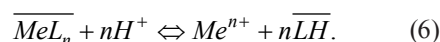
where $\overline{[Cu^{2+}]}$ and $\overline{[H^+]}$ are the equilibrium concentrations of Cu^{2+} and H^+ in the resin phase, respectively; $[Cu^{2+}]$ and $[H^+]$ are the equilibrium concentrations of these ions in solution.

Based on potentiometric titration data, we have calculated apparent ionization constants [23] of functional groups of the ion exchangers represented in Table 1 and apparent stability

constants of copper complexes in the resin phase. The calculation procedure is described below.

All the results were statistically processed by standard methods [15,25]: the average from 5 parallel tests was measured, then the variance, standard deviation and confidence intervals were calculated using Student's t at the confidence level of 0.95. The standard deviation of the total analytical procedure was less than 6%.

Calculation of apparent stability constants of copper complexes in the sorbent phase by decomposition of resin complexes [26]. The copper complex in the resin phase was decomposed by acid solution and after the equilibrium (24 h) was established, the equilibrium concentrations of $[Cu^{2+}]$ and $[H^+]$ were determined in solution. Based on these data, the equilibrium concentrations of metal complex in the resin phase $\overline{[MeL_n]}$ and of protonated functional groups of the resin $\overline{[LH]}$ were calculated. In general, the reaction of decomposition of the resin complexes can be presented as follows:



The equilibrium constant ($\overline{K_{eq}}$) of this reaction is:

$$\overline{K_{eq}} = \frac{[Me^{n+}][\overline{LH}]^n}{\overline{[MeL_n]}[H^+]^n}; \quad (7)$$

After the mathematical transformation, the following equation is taken:

$$\lg \frac{[Me^{n+}]}{\overline{[MeL_n]}} = \lg \overline{K_{eq}} + n \lg \frac{[H^+]}{\overline{[LH]}}; \quad (8)$$

It is obvious that the expression (8) is linear equation in the coordinates $\lg \frac{[Me^{n+}]}{\overline{[MeL_n]}} - \lg \frac{[H^+]}{\overline{[LH]}}$.

Therefore, the point of intersection of this straight line with the ordinate axis defines $\lg \overline{K_{eq}}$ and the slope tangent is equal to n .

Then using the potentiometric titration data, the ionization constants of the resin functional groups ($\overline{pK_a}$) were calculated [23]. After that, the stability constants of resin complexes ($\overline{K_{St}}$) were calculated from:

$$\lg \overline{K_{St}} = np\overline{K_a} - \lg \overline{K_{eq}} \quad (9)$$

Preparation of samples for diffuse reflectance spectroscopy. The solid-phase spectroscopy method is based on formation of colored compounds on a surface of sorbents and includes measurements of diffuse reflectance coefficients [16-23]. To obtain the analytical signal in the resin phase, the sorbent quantities (0.2 g) in the H^+ -form (preswollen at the necessary pH value) were placed into graduated flasks and 10.0 mL of 0.05 % aqueous PAR solution were added drop by drop to the resin samples. The suspensions were stirred over a period of 10 min. Afterwards the resins were filtered and 25.0 mL of the copper (II) solution with the necessary pH value were added. The suspension were stirred again over a period of 15 min. Then the ion exchangers were filtered and the diffuse reflectance coefficients were measured.

In the solid-phase spectroscopy method, the change of Gurevich-Kubelka-Munk function $\Delta F(R)$ is used as an analytical signal [16,17]:

$$\Delta F(R) = [(1-R)^2 / 2R] - [(1-R_0)^2 / 2R_0]; \quad (10)$$

where R and R_0 are diffusion reflectance coefficients (quantities of dimension 1) of copper compound in the resin phase and of the ion exchanger in the H^+ -form, respectively.

Procedures for plotting the calibration curve. The quantities of preswollen ion exchangers (0.2 g) in the H^+ -form were mixed with 10.0 mL of PAR (0.05 % aqueous solution) and suspensions were stirred over a period of 10 min. Then the resins were filtered and 25.0 mL of copper solutions (at the necessary pH

values) with concentrations 0.01; 0.05; 0.10; 0.25; 0.50; 1.0; 2.0 and 3.0 mg/L were added to the samples saturated with PAR. Afterwards the suspensions were stirred again over a period of 15 min. After that, the resins were filtered and the diffusion reflectance coefficients were measured at 500 nm. The calibration curve was plotted as a function of the concentration of copper (II).

Results and Discussion

Sorption concentration of copper (II) on ion exchangers investigated. It is known [26] that the sorption of transition metal ions on complexing ion exchangers occurs as a result of both ion exchange and coordination interaction between these ions and sorbent's functional groups. Moreover, these interactions depend on pH value of contacting solution: with the increase in pH of external solution, the concentration of coordination- active (non-protonated) functional groups of the complexing resins is growing. This phenomenon leads to the increase in recovery degree of transition metal ions, in particular, of copper (II). Table 2 contains the distribution ratios of copper (II) in dependence on pH of contacting solution. The values from Table 2 support this statement.

Therefore, the acid-base equilibrium on iminodiacetate ion exchangers depends on acidity of contacting solution. With the increase in pH up to 7 and more, the gradual transition of the sorbent into non-protonated state takes place. The complex-forming ability of ion exchangers grows in this case [26].

Thus at pH = 3 – 5, two carboxylic resin groups take part in complex-forming reaction with copper (II) ions. That is why the distribution ratios increase (Table 2). The obtained data leads us to the conclusion that the optimal pH values for Cu (II) recovery under our experimental conditions are 4.5 – 5.0 (when pH > 5.0, the

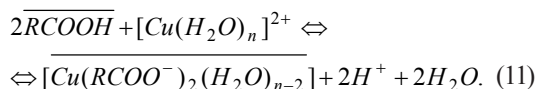
Table 2. Sorption of copper (II) on complexing ion exchangers in dependence on pH values of contacting solutions

Trade name	pH of contacting solution	Distribution ratios of Cu (II) in solution ^a		
		sulfate	nitrate	chloride
KB-2T	1.0	4	4	11
	2.0	30	30	42
	3.0	65	74	99
	4.0	84	97	132
	5.0	97	124	183
KB-4	1.0	-	-	11
	2.0	1	4	24
	3.0	4	11	36
	4.0	7	15	42
	5.0	11	20	42
AMF-2T	1.0	30	42	42
	2.0	172	205	310
	3.0	192	310	374
	4.0	205	347	412
	5.0	211	359	438
AMF-2S	1.0	20	20	42
	2.0	146	190	217
	3.0	172	245	262
	4.0	183	262	300
	5.0	192	279	320
ANKB-35	1.0	20	4	30
	2.0	109	56	132
	3.0	103	74	172
	4.0	172	97	192
	5.0	183	124	217

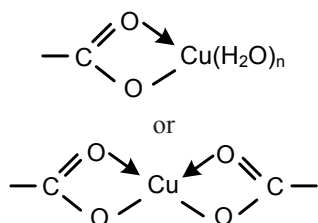
^a Initial Cu (II) concentration in solution is 0.8 mmol/L

copper hydroxocomplexes are formed because of hydrolysis).

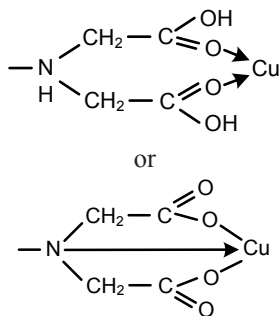
Therefore, the sorption of copper (II) on carboxylic ion exchangers at pH = 3 – 5 can be presented in general as follows:



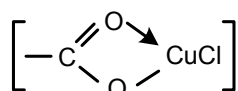
Depending on sorption conditions, the following coordination centers can be formed on carboxylic resins [27]:



Besides these coordination centers, the following ones can be formed on amphoteric ion exchangers with iminodiacetate groups [28]:

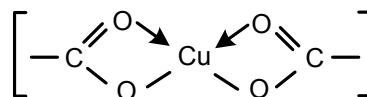


It can be seen from Table 2 that the highest recovery of Cu^{2+} is observed in chloride solutions. It is probable that monochloride copper (II) complexes are formed in solution in this case [27], and thus the following complexes with composition $[Me] : [R] = 1 : 1$ are formed in the resin phase:



During copper (II) sorption from sulfate or nitrate solutions, the ion exchanger complexes

with composition $[Me] : [R] = 1 : 2$ are formed [27]:



The investigated ion exchangers exhibit different affinity with copper (II) ions: sorption on amphoteric exchangers is characterized by greater values of distribution ratios in comparison with cation exchangers (Table 2). This fact is also supported by the form of isotherms of copper (II) sorption (Fig. 1 and 2). It can be seen from these Figures, that the amphoteric macroreticular ion exchanger AMF-2T possesses the highest selectivity (convex curve), whereas cation exchanger KB-4 has the least selectivity (concave curve). The similar dependencies are obtained from calculation of separation factors, as well as equilibrium and stability constants of resin complexes of copper (II) (Table 3). It can be seen from this Table that the resin AMF-2T reveals the highest selectivity to Cu^{2+} and that the stability of copper complexes on this sorbent is maximal. With the increase in copper concentration in the contacting solution from 0.1 to 0.8 mmol/L at the optimal pH value (5.0), the selectivity of ion exchangers to copper (II) remains practically on the same level. As the changes in separation factors and constants are insignificant, we provide their average values for each sorbent in Table 3.

It should be noted that the ion exchangers with macroreticular structure (KB-2T and AMF-2T) reveal higher sorption ability to $Cu(II)$ in comparison with the other sorbents of their type (KB-4 for cation exchangers and AMF-2S, ANKB-35 for amphoteric resins). The increase in length of the cross-linking agent TVEPE compared to DVB improves the flexibility of polymer net, maintains higher ionic permeability of the resins and makes their functional groups available for sorption of copper (II) [29].

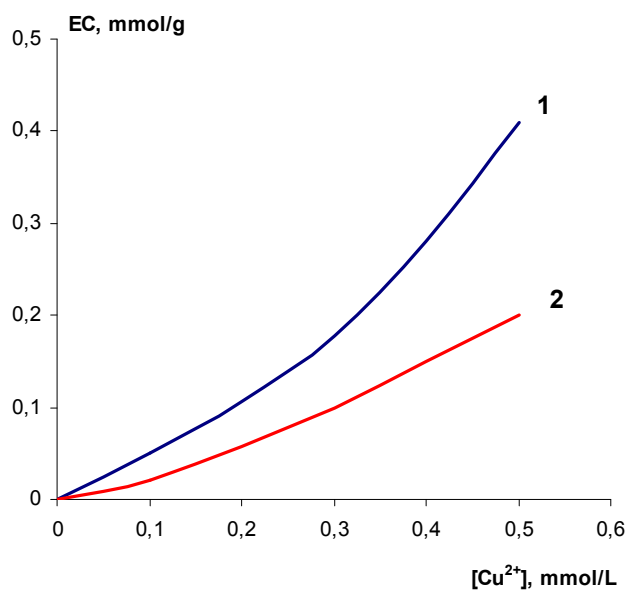


Fig. 1. Isotherms of sorption of copper (II) from sulfate solutions on carboxylic cation exchangers KB-2T (1) and KB-4 (2)

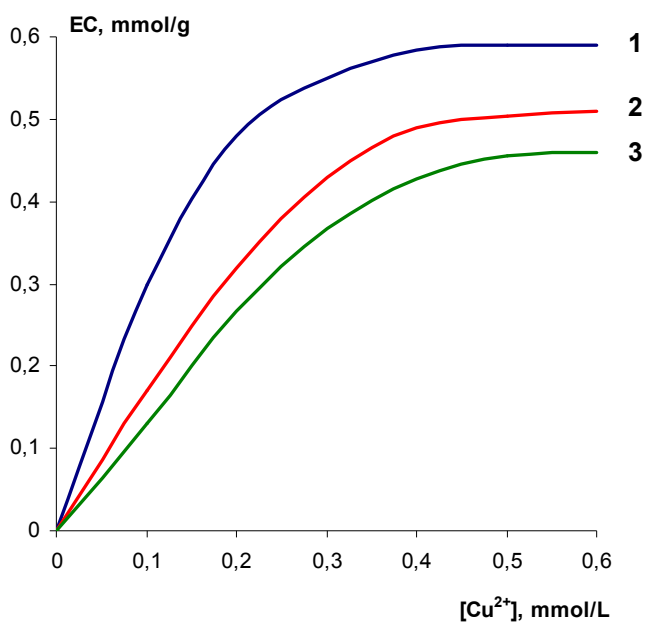


Fig. 2. Isotherms of sorption of copper (II) from sulfate solutions on aminocarboxylic amphoteric ion exchangers AMF-2T (1), AMF-2S (2) and ANKB -35 (3)

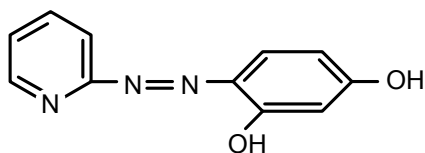
The lesser selectivity of cation exchangers to *Cu(II)* in comparison with amphoteric sorbents can be probably explained by their monofunctional chemical structure. Among the amphoteric resins with non-macroeconomic physical structure, AMF-2S reveals higher selectivity to Cu^{2+} than ANKB-35. It can be unambiguously accounted to the structure of its functional groups: absence of benzene ring in comparison with ANKB-35 (Table 1). Moreover, the nature and concentration of solution components produce an effect on energy of coordination bond *L – Me* as well as on energy consumption of the system during complex formation. In turn, it also affects the stability constants of resin complexes and equilibrium constants [30].

Therefore, the iminodiacetate amphoteric ion exchanger with macroreticular structure AMF-2T and the other amphoteric resins (AMF-2S and ANKB-35) can be recommended for recovery of copper (II) from natural and waste water as well as from aqueous solutions with different salt composition.

Development of copper (II) determination method by means of diffuse reflectance spectroscopy. For this purpose, we took the amphoteric resin AMF-2T with macroreticular structure, as its sorption ability was maximal among the other sorbents investigated.

To obtain the analytical signal, we chose PAR as a reagent, since it is widely used for spectrophotometrical determination of transition metal ions. This reagent forms stable complexes with these metals in a wide pH range (0 – 14). The color of the solutions obtained is stable over a long time period (up to several hours) and the solutions of PAR are stable during several months. Moreover, these systems follow Beer's law over a wide range of concentrations of determined ions, and there is no interfering effect of solution components [24].

The structural formula of PAR is as follows:



Depending on pH of solution, PAR can exist in six different forms [24,31]. For instance, the protonated forms H_5R^{3+} ; H_4R^{2+} and H_3R^+ exist at $pH \leq 2$, having absorption maxima at wavelengths of 433, 390 and 395 nm, respectively. At $pH = 2.1 - 4.2$, the presence of neutral PAR molecules is observed ($\lambda_{max} = 385$ nm). The ionic form of the reagent HR^- is present in solutions with $pH = 4.2 - 7.0$; its absorption maximum is at $\lambda = 415$ nm. In basic solutions at $pH = 10.5 - 13.2$, the both hydroxyl groups of PAR are subjected to dissociation and R^{2-} ions have the absorption maximum at 490 nm [31].

PAR forms the colored complexes in solutions with transition metal ions, with ratios *Me* : PAR = 1 : 1 or 1:2. The spectrophotometrical copper (II) determination is usually carried out in acidic solutions ($pH = 1 - 6$) [24,31].

Since we have revealed in our study that $pH=5.0$ is optimal for sorption concentration of copper (II), we assume that ionic form of PAR - HR^- is present in the resin phase.

It is known [17] that the colored surface compound can be obtained, from the one hand, by a preceding copper sorption on a resin, followed by treatment of the concentrate with a definite amount of PAR. From the other hand, it can be obtained by a preceding sorption of PAR on a resin with the subsequent sorption of copper on the modified sorbent. The preliminary experimental tests have shown that the analytical signal of the second method is much higher than the signal of the first method. That is why we started from the preliminary modification of the sorbent with PAR. It should be noted that sorption

Table 3. Separation factors (S), equilibrium constants ($\overline{K_{eq}}$) and stability constants ($\overline{K_{St}}$) of copper complexes in the phase of ion exchangers

Trade name	Solution type ^a	S	$\overline{K_{eq}}$	$\lg \overline{K_{St}}$
KB-2T	A	0.67	1.49	4.39
	B	0.67	1.49	4.41
	C	0.73	1.38	4.41
KB-4	A	0.37	2.66	4.37
	B	0.44	2.25	4.18
	C	0.44	2.25	4.15
AMF-2T	A	1.76	0.51	5.14
	B	1.83	0.54	5.02
	C	2.25	0.44	5.15
AMF-2S	A	1.17	0.85	4.39
	B	1.17	0.85	4.75
	C	1.49	0.67	4.09
ANKB-35	A	1.49	0.67	4.64
	B	1.17	0.85	4.55
	C	1.83	0.54	4.79

^a Type of initial solution:

A - $CuSO_4 - H_2SO_4 - Na_2SO_4 - H_2O$;

B - $Cu(NO_3)_2 - HNO_3 - NaNO_3 - H_2O$;

C - $CuCl_2 - HCl - NaCl - H_2O$

Initial Cu (II) concentration in solution is 0.1 - 0.8 mmol/L; pH = 5.0

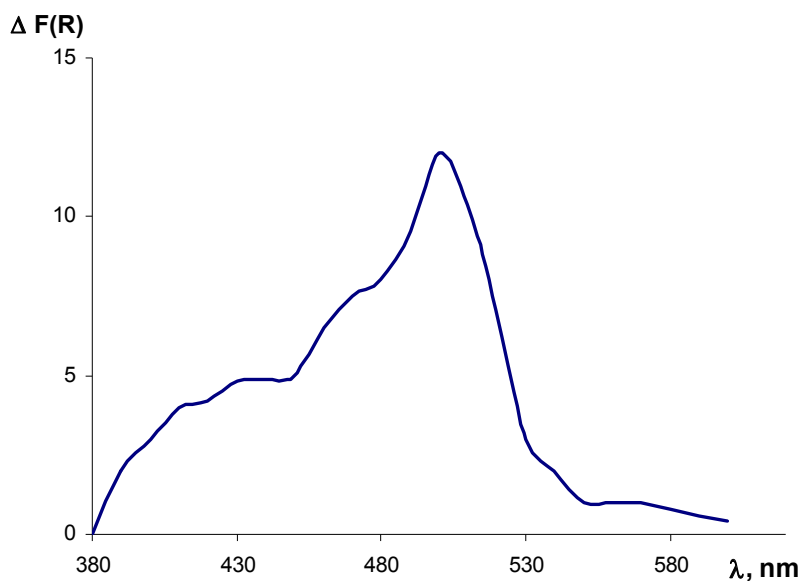


Fig. 3. Diffuse reflectance spectrum of copper (II) compound with PAR in the phase of ion exchanger AMF-2T. Initial concentration of copper (II) is 0.8 mmol/L; PAR – 0.002 mol/L; pH = 5.0

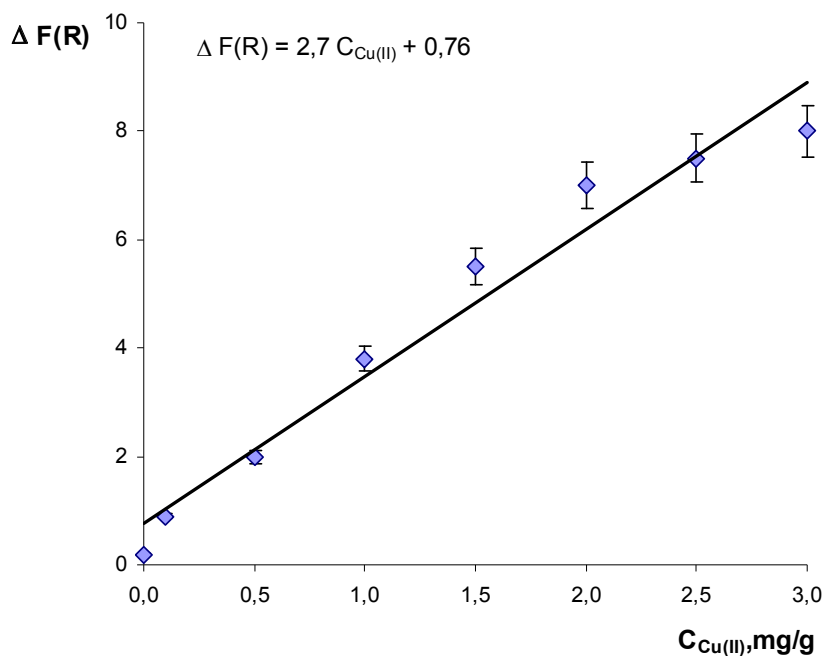


Fig. 4. Calibration curve for the system $\overline{RH} - \text{PAR} - \text{Cu(II)}$. Initial concentration of PAR is 0.002 mol/L; pH = 5.0

Table 4. Sorption-spectroscopic determination of copper (II) in aqueous solutions

Object of analysis ^a	Copper content, mg/L		Standard deviation, S	Relative standard deviation, S _r
	Added	Found		
MS 1	0.25	0.27 ± 0.03	0.02	0.07
MS 2	1.5	1.4 ± 0.08	0.09	0.06
MS 3	2.5	2.6 ± 0.11	0.09	0.03

^a MS – model solution; n = 5; P = 0.95

Table 5. Inhibitory effect of some foreign ions on sorption-spectroscopic copper determination

Foreign ion ^a	Ratio of foreign ion to copper (II)	Found copper (II), mg/L	Relative error, ε (%)
<i>Ni(II)</i>	10 : 1	1.40	- 7
	100 : 1	1.47	- 2
	500 : 1	1.68	12
<i>Co(II)</i>	10 : 1	1.43	- 5
	100 : 1	1.49	- 1
	500 : 1	1.67	11
<i>Cr(III)</i>	10 : 1	1.40	- 7
	100 : 1	1.49	- 1
	500 : 1	1.68	12
<i>Fe(II, III)</i>	10 : 1	1.38	- 8
	100 : 1	1.51	1
	500 : 1	1.62	8
<i>Zn(II)</i>	10 : 1	1.41	- 6
	100 : 1	1.49	-1
	500 : 1	1.61	7
<i>C₂O₄²⁻</i>	10 : 1	1.44	- 4
	100 : 1	1.53	2
	500 : 1	1.79	19
<i>PO₄³⁻</i>	10 : 1	1.43	- 5
	100 : 1	1.49	- 1
	500 : 1	1.64	9

^a Initial concentration of copper (II) is 1.5 mg/L

Table 6. Sorption-spectroscopic determination of copper (II) in manganese (II) solutions obtained after leaching of manganese ores

Object of analysis ^a	Cu (II) found, mg/L	
	by sorption-spectroscopic method	by flame AAS method
IS 1	0.51 ± 0.02	0.49 ± 0.04
IS 2	0.57 ± 0.03	0.56 ± 0.04
IS 3	0.60 ± 0.03	0.59 ± 0.05

^a IS – industrial solution; n = 5; P = 0.95

of PAR can be carried out either immediately before the sorption-spectroscopic analysis, or in advance, keeping the PAR-modified sorbent in air-dry state over a long time period. In the latter case the analysis time is substantially shortened.

We have determined that the maximal analytical signal in the system $\overline{RH} - PAR - Cu(II)$ is observed at PAR concentration of 0.05 % (0.002 mol/L) over a period of 5–10 min. The maximum in diffuse reflectance spectrum is located at 500 nm (Fig. 3). Under the found optimal conditions, we plotted the calibration curve of $\Delta F(R)$ as a function of copper concentration (Fig. 4). This calibration curve is linear in copper concentrations range of 0.01 – 3.0 mg/L (0.0004 – 0.05 mmol/L). The standard deviation for each experimental point of the calibration curve is also presented in Fig. 4. The average uncertainty of the analytical procedure is $\pm 4.7\%$. The calibration curve follows the equation:

$$\Delta F(R) = 2.7C_{Cu(II)} + 0.76; \quad (12)$$

where $C_{Cu(II)}$ is the concentration of copper (II).

It is obvious that expression (12) is linear equation.

The relative detection limit determined by 3σ method is 0.03 $\mu\text{g/mL}$.

The reproducibility of the developed method was tested on a number of sorption-spectroscopic

copper determination cases in model solutions (Table 4).

The inhibitory effect of some accompanying ions on sorption-spectroscopic determination of copper is presented in Table 5. The metal ions presented in this Table can form complexes with PAR [24,31], whereas oxalate and phosphate can form complexes with copper (II) [32].

It can be seen from Table 5 that the presence of nickel (II), cobalt (II), iron (II,III), chrome (III), zinc (II) as well as oxalate and phosphate ions (100-fold excesses) do not hinder the solid-phase spectroscopy determination of copper (II).

Using the obtained calibration curve, we have carried out the sorption-spectroscopic determination of copper (II) in manganese (II) solutions obtained after processing of manganese ores of Siberian region of Russia. The results are presented in Table 6. Since PAR forms stable complexes with manganese (II) at pH = 9 [24,31], the reciprocal influence of $Cu(II)$ and $Mn(II)$ can be excluded.

The results obtained allow us to recommend the complexing ion exchanger AMF-2T with macroreticular structure for the selective concentration of copper (II) and its subsequent determination in the phase of this resin using diffuse reflectance spectroscopy.

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Сорбция меди (II) из водных растворов на комплексообразующих ионитах и определение меди спектроскопией диффузного отражения

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Данная работа посвящена сорбционному концентрированию меди (II) из различных растворов на ряде комплексообразующих ионитов и последующему определению Си (II) в фазе амфотерного ионита АМФ-2Т макросетчатой структуры спектроскопией диффузного отражения. Исследованы сорбционные свойства ионитов и рассчитаны кажущиеся константы устойчивости комплексов меди в фазе ионообменников. Предложен сорбционно-спектроскопический метод определения Си (II) в водных растворах. Градуировочный график линеен в интервале концентраций 0.05 – 3.0 мг/л (объем пробы 25.0 мл), предел обнаружения составляет 0.03 мкг/мл. Присутствие Ni (II), Co (II), Cr (III), Fe (II,III), Zn (II), а также ионов $C_2O_4^{2-}$ и PO_4^{3-} (100-кратные избытки) не мешает определению Си (II).

Ключевые слова: медь, ионный обмен, сорбция, спектроскопия диффузного отражения.
