Sorption of Thiocyanate Silver Complexes and Determination of Silver by Diffuse Reflectance Spectroscopy

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The present paper is focused on sorption concentration of silver (I) on some complex-forming ion exchangers in the initial thiocyanate form and subsequent determination of Ag(I) in the phase of anion exchanger AN-25 by diffuse reflectance spectroscopy. The sorption and kinetic characteristics of the sorbents were investigated. The apparent stability constants of thiocyanate silver complexes in the ion exchanger phase were calculated. The sorption-spectroscopic method is proposed for Ag(I) determination in aqueous solutions. The calibration curve is linear in the concentration range of 10-200 mg/L (sample volume is 10.0 mL) and the detection limit is 2 μg/mL. The presence of Na^+, K^+, Mg^{2+} (macrocomponents) as well as of Ni (II), Co (II), Cu (II) do not hinder the determination of silver (I).

Key Words : Silver, Ion exchange, Thiocyanate complexes, Diffuse reflectance spectroscopy

Introduction

The consumption of noble metals is substantially increasing over time. It should be noted that their native reserves are getting more and more exhausted and such raw materials as arsenopyrite minerals are already engaged in processing. Up to 80% of gold and silver are mixed in these minerals with quartz-coaly-sericitic schists.[1-3] That is why the improvement of production technologies is required for the recovery of gold and silver. The sorption methods together with leaching of noble metals from ores by non-cyanide reagents (*e.g.* potassium thiocyanate) allow to obtain the solutions with high metal contents. The recovery efficiency of these methods comes from the high exchange capacity and selectivity of organic ion exchangers.[4-6]

It is worth to note that the application of thiocyanates for gold and silver leaching from refractory ores is becoming more appealing for researches. The reason comes from the cheapness of this reagent and the possibility to use it in acidic media, which is good for hydrometallurgical schemes.[1,2,4-6] However, the formation of gold and silver complexes in the thiocyanate systems, as well as the sorption equilibria in such systems still remain insufficiently studied. Moreover, the analytical chemistry of thiocyanate media remains almost unexplored, although the application of thiocyanate technology for recovery of gold and silver unavoidably entails the problem of analytical control. That is why our investigations in the last 5 years were focused on sorption recovery of gold and silver by thiocyanate reagents as well as on the development of analytical control methods for such systems.

Our previous work[7] was devoted to sorption and separation of thiocyanate complexes of gold and silver on some high-selective complex-forming anion exchangers in the initial chloride form. Our attention was concentrated on recovery of gold and its determination in the anion exchanger phase. The present paper is focused on further research of the problem and is devoted to the sorption concentration of silver on complex-forming resins in the initial sulfate and thiocyanate forms. The latter form is of particular scientific value, since the thiocyanate silver complexes possess high stability (*e.g.* log β_4 = 4.75-9.75 in solutions[4]). That is why the high recovery degree of silver on such sorbents can be hypothesized and, therefore, the possibility of its subsequent direct determination in the resin phase using diffuse reflectance spectroscopy.

It should be noted that, from the one hand, the solid-phase determination of noble metals is less developed, especially using the organic resins, though these sorbents possess high exchange capacity and complex-forming ability during recovery of noble metal ions.[8,9] From the other hand, these methods are rather attractive for determination of these metals due to their high sensitivity and possibility to estimate the analytical signal directly in the sorbent phase using the diffuse reflectance spectroscopy.[10,11] Moreover, this method is cheap, easy to use even under field conditions.[12-16]

Therefore, the present paper is devoted to selective recovery of silver (I) in the form of thiocyanate complexes and its subsequent determination in the resin phase by diffuse reflectance spectroscopy.

Experimental Section

Strong basic anion exchanger AV-16 GS, weak basic anion exchangers AN-25, AP-100, AP-2-10 P as well as ampho-teric ion exchanger ANKF-5 were chosen for investigation. These resins have different physical structure. Their physical-chemical characteristics are presented in Table 1.

The ion exchangers were preliminary prepared according to standard procedures and loaded with 2 M H_2SO_4 and 2 M

Table 1. Physical-chemical characteristics of ion exchangers investigated

Trade name [a]	Copolymer	Physical structure	Functional groups	Specific swelling volume, cm³/g in Cl⁻-form	Total pore volume, cm³/g	Static exchange capacity, mmol/g in Cl⁻-form
AN-25	VP	MP	—N(CH₃)₂	3.9	0.59	5.0
AV-16 GS	PEPA	MP	—CH₂—N—(CH₂)₂—N—(CH₂)₂—NH ... CH₂ CHOH CH₂ —CH₂—N— / CH₂ CHOH CH₂ N Cl⁻	4.6	0.57	8.2
AP-100	St-DVB	P	—N(CH₃)₃ —N(CH₃)₂	3.6	1.2	3.8
AP-2-10 P	St-DVB	P	—N(CH₃)₂	3.9	3.7	2.6
ANKF-5	VP	P	—CH—CH—P(=O)(ONa)(ONa) —CH₂—N(CH₃)₂	2.3	3.5	3.8 (2.6 for Na⁺-form)

[a] VP-vinylpyridine; PEPA-polyethylene polyamine; St-styrene; DVB-divinylbenzene; MP-macroporous; P-porous

KSCN, respectively for sulfate or thiocyanate forms.

The choice of these sorbents was stipulated by their good sorption characteristics found in our previous investigations[5-9] for recovery of gold and silver ions from different solutions.

The initial stock solution with concentration 0.05 mol/L was prepared from an accurately weighed sample of AgNO₃ (analytical pure grade). The sorption concentration of silver (I) was carried out from AgNO₃ solutions with concentrations 10-200 mg/L (0.09-1.85 mmol/L) and pH values of contacting solutions were 1.5-6.0. These concentrations were chosen aiming to make our experiment close to real industrial conditions.[4,17]

The sorption of silver was carried out under batch experiment conditions. The resin quantities were 0.2 g (dry substance) and the contacting solution volume was 20.0 mL. The ion exchangers were preswollen for 4 h in distilled water and after that they were stirred with the solutions in thermostat at (20 ± 1) °C. The stirring time intervals varied from 10 min to 24 h (for several extended experiments, the stirring time was up to 48 h). After sorption, the resins and solutions were separated and then solid and liquid phases were analyzed. The concentration of silver ions in initial and equilibrium solutions was determined by potentiometric titration method[18] with the silver indicator electrode and silver-silver chloride reference electrode using a potentiometer (model EV-74, Russia). The solid-phase analysis was carried out from diffuse reflectance spectra using the transportable colorimeter (model Spectroton, Russia). The colorimeter Spectroton embodies the principle of concurrent measurements of diffuse reflectance using 24 fixed wave-

lengths (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 (0.2 g) 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 silver (I) was estimated from recovery degree (R_D, %) and distribution ratio (D, L/g):

$$R_D = [(C_0 - C_{eq}) \cdot 100]/C_0; \tag{1}$$

$$D = EC/C_{eq}; \tag{2}$$

where C_0 and C_{eq} are the initial and equilibrium molar concentrations of silver (I) ions, respectively; EC is the exchange capacity of the ion exchangers for silver in mmol/g (or mg/g).

The acid-base properties of the sorbents investigated were studied by a potentiometric titration method with the glass electrode. On the basis of our experimental data, the average apparent ionization constants of functional groups of the ion exchangers as well as the apparent stability constants of silver complexes in the resin phase were calculated. The calculation procedures are described below.

The kinetics of sorption of silver (I) ions on the ion exchangers investigated was studied by the "limited bath" method[19-22] and the diffusion coefficients of Ag (I) (D_S, cm²/s) were calculated. The kinetic experiment procedure is also described below.

All the results were statistically processed by standard methods[18-23]: the average from 3-4 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 constants of acid-base ionization of ion exchangers[24]. The constants values are calculated using the potentiometric titration data. For each point of the titration curve, the functional groups content is determined and the apparent ionization degree (α) of the sorbent can be calculated:

$$\alpha = [\overline{H^+}]/C_0; \qquad (3)$$

where $[\overline{H^+}]$ is the equilibrium concentration of H^+ ions in the ion exchanger phase, mmol/mL; C_0 is the initial concentration of the titrant solution (0.1 M HCl).

Then a curve is plotted on the coordinates $pH = f(\lg\alpha/(1-\alpha))$ and at $\alpha = 0.5$, the apparent acid-base ionization constants of functional groups of the ion exchangers ($p\overline{K_a}$) can be calculated from Henderson's equation:

$$p\overline{K_a} = pH - m\lg\left(\frac{\alpha}{1-\alpha}\right); \qquad (4)$$

where m is the slope angle tangent of the curve.

Calculation of apparent stability constants of complexes in the sorbent phase according to the equilibrium constant[24]. This is calculated using the potentiometric titration data of the ion exchangers.

In general, the process of formation of complex between the metal ions (M^{m+}) and the ion exchanger functional groups ($\overline{L}$) can be represented as follows:

$$M^{m+} + n\overline{L} \Leftrightarrow \overline{ML_n}, \qquad (5)$$
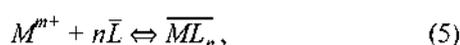
where line denotes the resin phase.

Therefore,

$$\overline{K_{eq}} = \frac{[\overline{ML_n}]}{M^{m+}[\overline{L}]^n} = \overline{K_{st}}, \qquad (6)$$

where $\overline{K_{eq}}$ is the equilibrium constant of the reaction (5) and $\overline{K_{st}}$ is the stability constant of the complex in the ion exchanger phase.

The concentrations $[\overline{ML_n}]$ and $[M^{m-}]$ can be obtained in the system investigated at the equilibrium state, whereas the concentration $[\overline{L}]$ can be calculated from the constant $p\overline{K_a}$:

$$\lg[\overline{L}] = \lg[\overline{LH}] + \frac{pH - p\overline{K_a}}{m}; \qquad (7)$$

where $[\overline{LH}] = C_0 - [\overline{H^-}]. \qquad (8)$

The number of ligand groups of ion exchanger ($\bar{n}$) per ion of metal can be taken from the following equation:

$$\bar{n} = [\overline{L_c}]/[\overline{M_c}], \qquad (9)$$

where $[\overline{L_c}]$ and $[\overline{M_c}]$ are the equilibrium concentrations of ligand and metal ions in the resin phase, respectively, mmol/mL.

"Limited bath" method for sorption kinetics of silver (I). The quantities of preswollen ion exchanger (0.1 g) in the SCN⁻- form were stirred with 25.0 mL of AgNO₃ solution (0.25 mmol/L) at (20 ± 1) °C over a period from 30 s to 24 h. The suspensions were intensively stirred (more than 800 revolutions/min) to avoid the film diffusion.[19-21] After a certain time period, the resins and solutions were quickly separated and the concentration of Ag^+ ions was determined in the solutions. Then the exchange degree (F) was calculated by the following equation:

$$F = Q_t/Q_\infty; \qquad (10)$$

where Q_t and Q_∞ are the amount of silver sorbed to time t and the equilibrium amount, respectively, mmol.

According to the Boyd's method,[25] the kinetic coefficient B was calculated from

$$B = \frac{(1.08)^2 \cdot F^2}{t}. \qquad (11)$$

The obtained data were plotted as a function $Bt = f(t)$. For a process limited by gel diffusion,[19-22,25] this function should be linear. After that, the diffusion coefficients ($\overline{D_S}$) were calculated according to the equation:

$$\overline{D_S} = \frac{Br^2}{\pi^2}; \qquad (12)$$

where r is the radius of the resin grain, cm.

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.[10-16] To obtain the analytical signal in the resin phase, the sorbent quantities (0.2 g) in the SCN⁻-form were preliminary saturated with Ag(I) ions with concentrations of 0.02-2.0 mmol/L during 24 h. After that, the resins were filtered, dried and stored in glass bottles with stoppers. These air-dried resins can be prepared in advance because they are very stable over a long time period (more than 6 months). In this case they should be swollen before use.

Then 10.0 mL of dithizone solution in ethanol with concentration of (0.98-2.93)·10⁻⁴ mmol/L were added drop by drop to the swollen resin samples. The suspensions were stirred over a period of 20 min. Afterwards the ion exchangers were filtered and the diffusion 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[10,11]:

$$\Delta F(R) = [(1-R)^2/2R] - [(1-R_0)^2/2R_0]; \qquad (13)$$

where R and R_0 are diffusion reflectance coefficients (quantities of the dimension 1) of silver compound with reagent in the resin phase and of the ion exchanger in the SCN⁻- form, respectively.

Procedure for plotting the calibration curve. The quantities of preswollen anion exchanger AN-25 in the SCN^--form (0.2 g) were mixed with 20.0 mL of $AgNO_3$ solutions with concentrations 10.0; 20.0; 50.0; 75.0; 100.0; 150.0 and 200.0 mg/L. The suspensions were stirred over a period of 30 min. Then the resins were filtered and 10.0 mL of 0.1M EDTA as well as 10.0 mL of dithizone solution in ethanol ($2.93 \cdot 10^{-4}$ mmol/L) were added drop by drop to the samples. The suspensions were stirred again over a period of 20 min. After that, the resins were filtered and the diffusion reflectance coefficients were measured at 670 nm. The calibration curve was plotted as a function of the concentration of silver (I).

Results and Discussion

Sorption concentration of silver (I) on ion exchangers investigated. The structure of ion exchangers chosen for our investigation specifies their selective properties to noble metal ions. These properties are determined not only by character and location of functional groups, but also by character of sorbent matrix and its porosity.[24] Since the thiocyanate silver complexes are rather stable,[4] the ion exchangers' transformation to initial thiocyanate form improves their complex-forming abilities.

During a contact of silver (I) ions with the ion exchangers investigated the following interactions can take place:
- formation of silver (I) complexes with functional groups of the sorbents;
- formation of sulfate or thiocyanate complexes of silver (I) directly in the sorbent phase;
- anion exchange of sulfate or thiocyanate ions to nitrate ions present in the solution;
- formation of silver (I) complexes in solution with SO_4^{2-} and SCN^- ions (as a result of anion exchange with NO_3^- ions and subsequent sorption of these complexes).

The relative dominance of this or that process depends on particular experimental conditions of sorption equilibrium.

Before the sorption of silver (I), we have carried out the potentiometric titration of the ion exchangers investigated. These results were necessary to obtain the exchange capacity values in dependence on pH of the contacting solutions. Then we computed the apparent constants of acid-base ionization of the sorbents, summarized in Table 2. Despite the fact that with the increase in pH of the contacting solutions from 1.5 to 6.0, the exchange capacity of the sorbents is growing, it is still high even in the strong acidic medium. It makes these ion exchangers promising for application under the industrial conditions, where the sorption of noble metals is carried out in strong acidic media.[1]

The results of the sorption concentration of silver (I) on ion exchangers in thiocyanate and sulfate initial forms are represented in Table 3. It can be seen from these data that the ion exchangers in the initial thiocyanate form possess substantially greater sorption ability than that ones in the sulfate form. It may be grounded by a greater stability of

Table 2. Exchange capacity of ion exchangers investigated and apparent constants of their acid-base ionization

Trade name	EC^a, mmol/g in Cl^--form	$p\overline{K}_a$
AN-25	2.60	2.21
AV-16-GS	6.45	1.61
AP-100	4.06	1.88
AP-2-10P	3.35	2.15
ANKF-5 (anion exchange part)	3.75	2.01
ANKF-5 (cation exchange part)	–	$p\overline{K}_b = 11.83$

^{a}pH of the contacting solutions is 1.5

Table 3. Sorption concentration of silver (I) on ion exchangers investigated

Trade name^a	SO_4^{2-}-form				SCN^--form			
	D		R_D		D		R_D	
	1	2	1	2	1	2	1	2
AN-25	1200	3150	92	97	261	6400	72	98
AV-16-GS	51	55	34	35	6400	6400	98	98
AP-100	23	25	18	20	1200	6400	92	98
AP-2-10P	35	35	26	26	829	6400	89	98
ANKF-5	25	27	20	22	6400	6400	98	98

^{a}Initial concentration of silver (I) is 65 mg/L; pH = 1.5. Sorption time: 1-24 h, 2-48 h.

Table 4. Apparent ion exchange stability constants for silver (I) complexes

Trade name^a	$\log \overline{K}_{st}$	
	SO_4^{2-}-form	SCN^--form
AN-25	1.13	0.46
AV-16-GS	1.39	1.44
AP-100	2.42	3.03
AP-2-10P	1.58	2.50
ANKF-5	–0.52	0.76

^{a}Initial concentration of silver (I) is 65 mg/L

thiocyanate silver complexes. We have calculated the apparent stability constants of the ion exchangers investigated for the both forms (Table 4). The obtained values are in agreement with our expectations concerning the stability of complexes.

It can be seen from Table 3 that ion exchangers in SCN^--form recover Ag (I) almost completely within 48 h (89-98% recovered within first 24 h). Perhaps the stable thiocyanate silver complexes formation in the resin phase dominates in this case. At the same time, the ion exchangers in SO_4^{2-}-form (excluding AN-25) recover silver (I) ions only up to 35% over a period of 48 h. In this case it seems like the anion exchange process predominates over the formation of silver complexes:

$$\overline{R_2SO_4} + NO_3^- \leftrightarrow \overline{2RNO_3} + SO_4^{2-} \qquad (14)$$
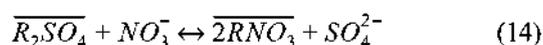
The especially high selectivity of anion exchanger AN-25 can be probably explained either by its chemical and
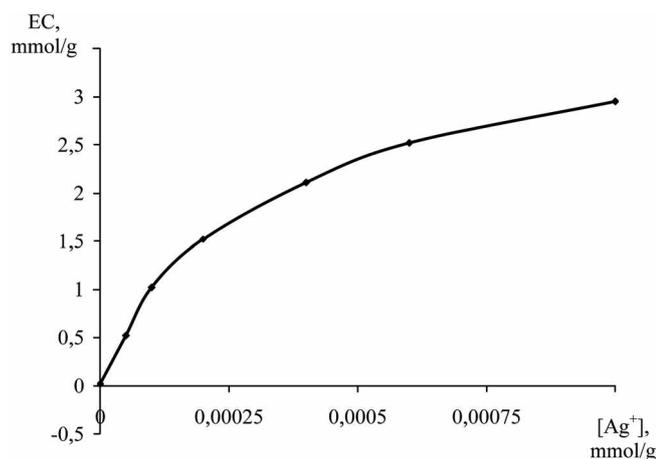
Figure 1. Isotherm of sorption of silver (I) ions on anion exchanger AN-25 in SCN^--form.
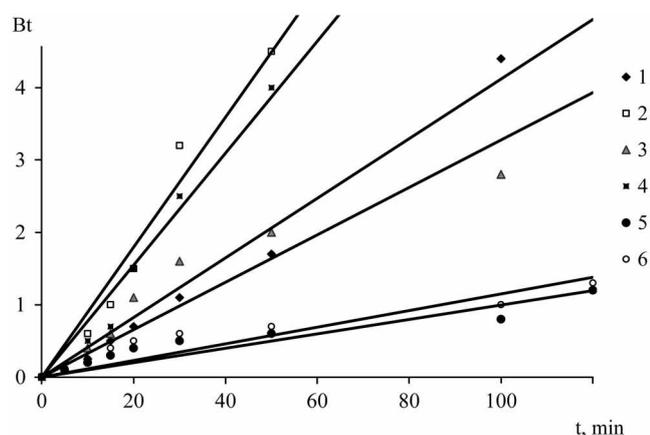
Figure 2. Kinetic dependences of Bt function on sorption time at different diameters of resin grains: AV-16-GS (1, 2); AP-100 (3, 4); AN-25 (5, 6). Grain diameter: 1 – (0.07 ± 0.01); 2 – (0.04 ± 0.01); 3, 5 – (0.09 ± 0.01); 4, 6 – (0.06 ± 0.01).

physical structure or by formation of stable sulfate silver complexes in the phase of this sorbent (Table 4).

Since the purpose of our work was to study the sorption of thiocyanate silver complexes, our further investigations were connected with anion exchangers in SCN^--form.

Since the isotherms of silver (I) sorption on these ion exchangers are convex, this process is highly selective. For instance, Figure 1 demonstrates such an isotherm for AN-25.

Having studied the statics, the kinetic investigations were carried out for anion exchangers AN-25, AP-100 and AV-16 GS in SCN^--form. Figure 2 shows the dependences of *Bt* function on sorption time at different diameters of the resin grains. It can be seen from this Figure that kinetic curves are linear, *i.e.* the sorption process is limited by gel diffusion.[19-22,23] Using these data, we have calculated the kinetic sorption parameters of silver (I) - time of half-exchange ($t_{0.5}$) and diffusion coefficients (Table 5). It shows that the kinetic parameters of these anion exchangers allow recommending them for recovery of silver (I) ions. These kinetic properties create a good condition for subsequent

Table 5. Kinetic parameters of sorption of silver (I) on anion exchanger in SCN^--form

Trade name[a]	Grain diameter, cm	$t_{0.5}, s$	$\bar{D}_i \times 10^{-8}$, cm^2/s
AV-16-GS	0.07	478	6.79
	0.04	237	4.45
AP-100	0.09	325	15.8
	0.06	135	15.0
AN-25	0.09	2940	1.75
	0.06	1565	1.29

[a]Initial concentration of silver (I) is 65 mg/L; pH = 1.5

analytical determination of Ag(I) in the resin phase.

Development of silver (I) determination method by means of diffuse reflectance spectroscopy. For this purpose, we have chosen the anion exchanger AN-25 in SCN^--form because of its practical applicability for recovery of noble metal ions.[1-5] By the way, our previous work[7] was also carried out with this resin.

For obtaining of the analytical signal, we have chosen diphenyldithiocarbazone (dithizone) as a reagent, since it is widely used for spectrophotometrical determination of silver ions in solutions.[18,26] It is known that silver forms dithizonates with this reagent in solutions[27]:

one-substituted

or
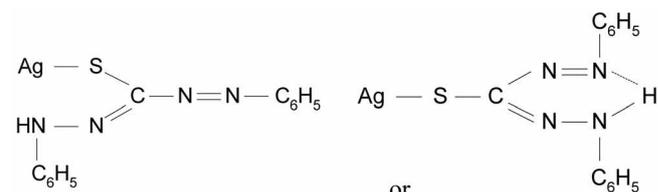
and two-substituted
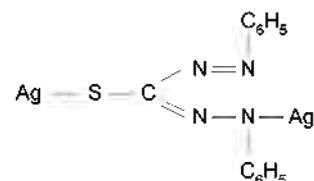
It is known from References[27-29] that in acidic medium the chelate one-substituted goldish-yellow dithizonate of silver (I) is formed during extraction with dithizone solution in tetrachloride carbon. The absorption maximum of this compound is located at 462 nm.[26-29] It can be assumed that the same complex of silver and dithizone might be formed in the ion exchanger phase, since such complex is more stable than thiocyanate one[28,29] and pH of contacting solution is equal to 1.5.

To obtain the analytical signal in the phase of anion exchanger AN-25, we have carried out the sorption pre-concentration of silver (I) ions on this resin in SCN^--form. The Ag(I) concentration varied from 0.02 to 2.0 mmol/L. It should be noted that sorption of silver can be either carried out just before the sorption-spectroscopic analysis, or made

ΔF(R)
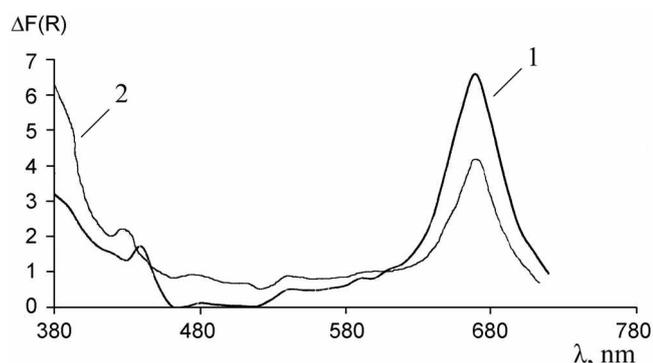
Figure 3. Diffuse reflectance spectrum of silver (I) compound with dithizone in the phase of anion exchanger AN-25 (1). initial concentration of silver (I)–0.09 mmol/L; dithizone – 2.93 × 10⁻⁴ mmol/L; pH = 1.5; initial concentration of silver (I)–0.04 mmol/L; dithizone – 0.98 × 10⁻⁴ mmol/L; pH = 1.5 (2).

in advance, keeping the sorbent in the form of thiocyanate silver complexes in air-dried state over a long time period (see sample preparation procedure). In the latter case the analysis time is substantially shortened.

We have determined that the maximum analytical signal in the system $\overline{RSCN}$-Ag(I)-dithizone is observed at the concentration of dithizone in ethanol of 2.93×10^{-4} mmol/L over a period of 5-10 min. The maximum in diffuse reflectance spectrum is located at 670 nm (Figure 3). Under the chosen optimal conditions, the calibration curve of $\Delta F(R)$ was plotted as a function of silver concentration (Figure 4). It can be seen that this curve is linear in the silver concentrations range of 10-200 mg/L (0.09-1.85 mmol/L). The standard deviation for each experimental point of the calibration curve is also represented at Figure 4. The average total uncertainty of the analytical procedure is ± 4.4%. The calibration curve follows the equation:

$$\Delta F(R) = 0.041 C_{Ag(I)} + 2.31 , \qquad (15)$$

where $C_{Ag(I)}$ is the concentration of silver (I).

It is obvious that expression (15) is linear equation.

The relative detection limit determined by 3σ method is 2 μg/mL. By the definition, the detection limit (DL) of an
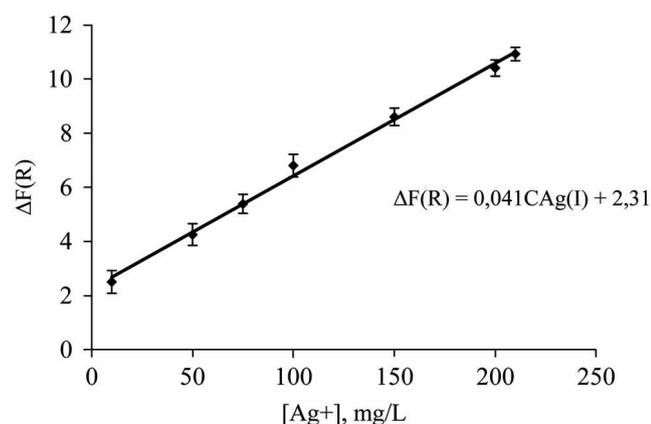
Figure 4. Calibration curve for the system $\overline{RSCN}$-Ag(I)-dithizone. Initial concentration of dithizone is 2.93×10^{-4} mmol/L; pH = 1.5.

analytical method is the minimal substance concentration that can be reported with 98% confidence to be greater than the blank experiment.[18] In our investigation, the DL was determined through the minimal analytical signal $\Delta F(R)_{min}$ that was confidently distinguishable from the background signal $\Delta F(R)_b$. To calculate the DL values, the following equation was used:

$$DL = \frac{3\sigma_b - 2.31}{0.041} \qquad (16)$$

where σ_b is the population standard deviation of $\Delta F(R)_b$.

The σ_b value was determined in the system $\overline{RSCN}$-Ag(I)-dithizone under the same conditions as when the calibration curve was made up, $C_{Ag(I)} = 0$, $n = 10$ and P = 98% (n is the number of replicate blank samples and P is the confidence level).

The reproducibility of the developed method was tested at sorption-spectroscopic silver determination in model solutions (Table 6). It can be seen from these data that the relative standard deviation does not exceed 0.02.

The inhibitory effect of some accompanying ions on sorption-spectroscopic determination of silver is represented in Table 7. It is known from[26-28] that the presence of Ni^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, Au(I, III) and platinum group metals produces the inhibitory effect on spectrophotometrical determination of silver (I) with dithizone. To make our experiment close to real industrial conditions for thiocyanate silver leaching from ores,[2,7] we have selected some of these foreign ions. Since the platinum group metals and Fe(II) are absent in these ores, their inhibitory effect was not studied. Gold (I, III) is separated after the sorption concentration,[7] thus it does not hinder the silver determination. The inhibitory effect of Pb (II) is also absent, since it takes place

Table 6. Sorption-spectroscopic determination of silver (I) in aqueous solutions

Analysis object	Silver content, mg/L		Standard deviation, S	Relative standard deviation, S_r
	Added	Found		
MS 1 [a]	50.0	49.4 ± 1.0	1.0	0.02
MS 2	75.0	74.7 ± 1.4	1.2	0.02
MS 3	100.0	99.6 ± 1.6	1.3	0.01

[a]MS-model solution

Table 7. Inhibitory effect of some foreign ions on sorption-spectroscopic silver determination

Foreign ion [a]	Ratio of foreign ion to Ag (I)	Found Ag (I), mg/L	Relative error, ε (%)
Na⁻	1000	99.7 ± 1.6	–0.3
K⁺	1000	98.9 ± 2.2	–1.1
Mg²⁺	1000	99.0 ± 2.1	–1.0
Ni (II)	1	94.5 ± 2.1	–5.5
Co (II)	1	92.2 ± 1.6	–7.8
Cu (II)	1	89.2 ± 1.5	–10.8

[a]$N_{Ag(I)}$ = 100 mg/L

only in basic media (pH~8-11).[26,29] That is why we have studied the effect of macrocomponent ions, which are always present in water (Na^+, K^+, Mg^{2+}), as well as of non-ferrous metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}). It can be seen from Table 7 that macrocomponent ions do not hinder the sorption-spectroscopic determination of silver (I) even in the 1000-fold excesses. However, the presence of non-ferrous metal ions (more than 1-fold excesses) has substantial hindering effect on this determination. That is why it is important to mask these ions by EDTA.

The results obtained allow us to recommend the complex-forming anion exchanger AN-25 in the initial thiocyanate form for the selective concentration of silver (I) and its subsequent determination with dithizone in the phase of this resin using diffuse reflectance spectroscopy.

Conclusions

1. The sorption concentration of silver (I) on some complex-forming ion exchangers in the initial sulfate and thiocyanate forms has been investigated. The apparent constants of acid-base ionization of the resins and stability constants of ion exchanger's complexes as well as kinetic parameters were calculated. These characteristics prove the high sorption ability and good kinetic properties of the resins in the initial thiocyanate form.

2. The method for determination of silver with dithizone in the phase of anion exchanger AN-25 by diffuse reflectance spectroscopy has been proposed. The calibration curve is linear in the concentrations range of 10-200 mg/L and the detection limit is 2 μg/mL. The presence of Ni (II), Co (II), Cu (II) (one-fold excesses) as well as of Na (I), K (I), Mg (II) (1000-fold excesses) does not hinder the determination of silver (I).

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