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

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The present paper is focused on simultaneous sorption concentration of gold (III) and silver (I) from thiocyanate solutions using high-selective anion exchanger AN-25 and subsequent separation of these ions at various concentrations of thiocarbamide (eluent). As a result, silver (I) ions are completely eluted from AN-25 and gold (III) ions remain in the resin phase and can be determined directly in the solid phase by diffuse reflection spectroscopy. It is proposed to use the sorption-spectroscopic method for Au(III) determination in aqueous solutions. The calibration curve is linear in the concentration range of 1-19 mg/L (sample volume is 10.0 mL) and the detection limit is 0.05 μg/mL. The presence of Cu(II), Co(II), Fe(II) do not hinder this determination. Au(III) was determined in industrial solutions.

Key Words : Gold, Silver, Anion exchanger, Sorption, Separation

Introduction

The demand for noble metals is constantly increasing, while alluvial deposits and native reserves of gold and silver are getting more and more exhausted. The raw materials with complex composition are already engaged in processing, for instance, arsenopyrite minerals, in which gold is combined with sulfides in the form of fine and emulsive formations, and up to 80% of the mineral ores composition is presented with quartz-coaly-sericitic schists.[1,2] That is why the novel, improved technologies are required for the recovery of noble metals.

It is known[3] that the cyanidation is now considered as the basic method for recovery of gold and silver from ores, combined with subsequent precipitation of noble metals from solutions by zinc dust or by electrolysis. The main restrictions imposed by this method are the use of high-toxic reagents and incompleteness of washing of dissolved noble metals, *i.e.* their losses.[1,3] That is why the active search for alternative reagents to cyanide as well as the possible ways to intensify the recovery of noble metals from ores is carried out. Such reagents are thiocyanate, thiosulfate and thiocarbamide solutions.[4-8] The application of sorption methods together with leaching allows to obtain solutions with high contents of noble metals.[4,9-12] However, because of high selectivity of sorbents to gold and silver ions, the separation of these ions after sorption and their subsequent analytical determination are rather hindered.

It is known[13-15] that spectrophotometrical methods are widely used for determination of noble metal ions in solutions. Usually these methods are compatible with separation and concentration methods.[13-15] However, the gold determination in solutions with complex composition usually requires extraction or masking because of inhibitory effect of different non-ferrous and noble metal ions.[15,16] That is why the sorption-spectroscopic methods are of great importance in this case, since they allow to estimate the analytical signal directly in the sorbent phase using the diffuse reflectance spectroscopy.[17,18] The determination of different metal ions in the sorbent phase is based on fast-proceeding solid-phase colored reactions. Apart from increasing in sensitivity of determination, the method itself is easy to use, cheap and applicable under field conditions.[19-25]

It should be noted that the solid-phase determination of noble metals is developed to a lesser extent. It is usually done with polymeric supporters or chemically modified silica.[23,26] The information about application of ion exchangers for this purpose is absent, though selective organic resins possess high exchange capacity and complex-forming ability during recovery of noble metal ions.[4,10-12]

That is why the present paper is devoted to simultaneous sorption concentration of gold (III) and silver (I) ions from thiocyanate solutions and their subsequent separation by elution as well as to gold determination in the resin phase by diffuse reflectance spectroscopy.

Experimental Section

Weak and strong basic anion exchangers with different physical structure were taken for investigation. Their physical-chemical characteristics are presented in Table 1.

The ion exchangers were preliminary prepared according to standard procedures and loaded with sodium chloride. The choice of these sorbents was due to their promising characteristics for recovery of gold or silver ions from different solutions in our previous investigations.[4,10-12]

The initial stock solutions were prepared from an accurately weighed samples of $HAuCl_4$ and $AgNO_3$ (analyt-

Table 1. Physical-chemical characteristics of anion exchangers investigated

Trade name[a]	Copolymer	Physical structure	Functional groups	Specific swelling volume, cm^3/g in Cl^--form	Static exchange capacity, mmol/g in Cl^--form	Manufacturer
AN-25	VP-DVB	MP	$-N(CH_3)_2$	3.9	5.0	TOKEM, Kemerovo (Russia)
AP-100	St-DVB	P	$-N^+(CH_3)_3$ $-N(CH_3)_2$	3.6	3.9	Purolite (U.K.)
AV-17-8	St-DVB	G	$-N^+(CH_3)_3$	3.5	3.4	TOKEM, Kemerovo (Russia)
AV-17-10P	St-DVB	P	$-N^+(CH_3)_3$	3.7	3.7	TOKEM, Kemerovo (Russia)

[a]VP - vinylpyridine; DVB - divinylbenzene; St - styrene; MP - macroporous; P - porous; G - gel

ical pure grade). Their concentrations were 0.03 mol/L and 0.05 mol/L, respectively. 0.25 M KSCN solution (analytical pure grade) was used for synthesis of thiocyanate complexes of noble metals.

The sorption concentration of gold and silver was carried out from model solutions of their thiocyanate complexes. The concentrations of these solutions were varied from 5-50 mg/L (0.025-0.25 mmol/L) and 10-100 mg/L (0.09-0.9 mmol/L) for gold and silver, respectively. The concentration of thiocyanate ions was 0.25 mol/L and pH values of contacting solutions were 2-6. These concentrations were chosen aiming to make our experiment close to real industrial conditions.[7,9] Moreover, we have used the industrial gold-containing solution with the following composition: Au(III)- 8.1-8.6 mg/L; Fe(III)- 120-130 mg/L; SCN^-- 0.6 mol/L; Cu^{2+}, Ni^{2+}, Co^{2+}- on a level about of one tenth and hundredth of mg/L. The industrial solution was obtained after leaching of gold-containing concentrate in thiocyanate medium (pH~2). This concentrate was obtained by oxidation of ore and contained ~19.5 g Au/t.

The sorption of gold and silver was carried out under batch experiment conditions. The anion exchanger quantities were 0.2 g (dry substance) and the contacting solution volume was 20.0 mL. The resins 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. After sorption, the resins and solutions were separated and then solid and liquid phases were analyzed. The concentration of thiocyanate gold and silver complexes in initial and equilibrium solutions was determined by flame atomic absorption spectroscopy using an atomic absorption spectrophotometer (model Saturn-2, Russia). The concentration of thiocyanate ions was determined by Volhard titration.[27] The solid phase analysis was carried out from diffuse reflectance spectra using the transportable colorimeter (model Spectroton, Russia). The operation principles of this colorimeter were discussed in our previous works.[25,28] The preparation procedure of samples is described below.

The effectiveness of sorption recovery of thiocyanate gold and silver complexes was estimated from recovery degree (R_D, %) and distribution ratio (D, L/g):

$$R_D = \lfloor (C_0 - C_{eq}) \cdot 100 \rfloor / C_0 ; \qquad (1)$$

$$D = EC/C_{eq}; \qquad (2)$$

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

The separation coefficients (K_S) of gold and silver were calculated from:

$$K_S = D_1/D_2, \qquad (3)$$

where D_1 and D_2 are distribution ratios of gold and silver, respectively.

The desorption of gold and silver was carried out by thiocarbamide solutions (10-100 g/L) in 0.3 M H_2SO_4. This desorption agent was chosen because the thiocarbamide forms the stable cationic complexes $[Au(NH_2-CS-NH_2)_2]^+$ and $[Ag(NH_2-CS-NH_2)_3]^+$ with gold and silver in the sulfuric acidic medium. The complexes are easily eluted from anion exchangers. Moreover, the elemental gold or silver can be obtained from these complexes by electrodeposition.[1,2,4]

All results were statistically processed by standard methods[27,29]: the average for 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 then 6%.

Preparation of samples for diffuse reflectance spectroscopy. The solid-phase spectroscopy method deals with the formation of colored compounds on a surface of sorbents and includes measurement of diffusion reflectance coefficients.[17-25] To obtain the analytical signal in the resin phase, the anion exchanger quantities (0.2 g) were saturated with solutions of thiocyanate gold (III) complexes with concentrations of 0.00025-0.25 mmol/L during 24 h. After that, the resins were filtered and 2.0 mL of 10% $SnCl_2 \cdot 2H_2O$ (pH=2) were added drop by drop to the samples. The suspensions were stirred over a period of 20 min. Afterwards the anion exchangers were filtered again and the diffusion reflectance coefficients were measured.

Moreover, the analytical signal in the resin phase was

obtained by simultaneous sorption recovery of gold and silver and their subsequent separation. For this purpose, the anion exchanger quantities (0.2 g) were saturated during 24 h by thiocyanate solutions of gold (III) and silver (I) complexes with concentrations of 0.00025-0.25 mmol/L and 0.0009-0.9 mmol/L for Au and Ag, respectively. After that, the resins were filtered and elution of silver (I) ions was carried out by 50 mL of thiocarbamide solution (40 g/L) in 0.3 M H_2SO_4. The analytical control of silver ions was carried out by flame atomic absorption method. Then the resins were washed by distilled water (in order to remove the excess of thiocarbamide) and 2.0 mL of 10% $SnCl_2 \cdot 2H_2O$ (pH=2) were added drop by drop to the samples. The suspensions were stirred over a period of 20 min. Afterwards the resins were filtered again 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:[17,18]

$$\Delta F(R) = \left\lfloor (1-R)^2/2R \right\rfloor - \left\lfloor (1-R_0)^2/2R_0 \right\rfloor, \qquad (4)$$

where R and R_0 are diffusion reflectance coefficients (quantities of the dimension 1) of gold (III) compound with reagent in the anion exchanger phase and of the anion exchanger, respectively.

Procedure for plotting the calibration curve. The resin quantities (0.2 g) were mixed with 10.0 mL of thiocyanate gold (III) complexes solutions with concentrations of 0.05; 0.1; 0.5; 0.7; 1.0; 2.0; 3.0; 5.0; 7.0; 10.0; 15.0 and 20.0 mg/L. The suspensions were stirred over a period of 30 min. Then the resins were filtered and 10.0 mL of 0.1 M EDTA as well as 2.0 mL of 10% $SnCl_2 \cdot 2H_2O$ (pH=2) were added drop by drop to the samples. The suspensions were stirred again over a period of 20 min. After that, the anion exchangers were filtered and the diffusion reflectance coefficients were measured at 630 nm. The calibration curve was plotted as a function of the concentration of gold.

Results and Discussion

Sorption concentration of gold and silver and their separation. The behavior of noble metals in thiocyanate solutions is a problem that has not drawn much attention of researches yet. It is known[30] that two mesomeric electron structures exist for thiocyanate ions, namely -S-C≡N and S=C=N-. Therefore, the formation of thiocyanates (S-thiocyanates) and isothiocyanates (N-thiocyanates) can be expected. It is known from the work[7] that at 0.01-0.5 mol/L concentration of thiocyanate ions (these concentrations are used for leaching in practice), the complexes $[Au(SCN)_2]^-$ and $[Au(SCN)_4]^-$ as well as $[Ag(SCN)_2]^-$ are characteristic for gold and silver, respectively. Moreover, the equilibrium $Au(I) \Leftrightarrow Au(III)$ occurs in solutions[31] and at the concentration of thiocyanate ions below 0.14 mol/L, AgNCS precipitate is formed.[7] That is why the Ag(I)-Au(I,III)-KSCN-H_2O system investigated in the present paper is very complex (from a standpoint of its ionic state) and probably requires a special study, which is beyond the scope of our present investigation.

The physical and chemical structure of the anion exchangers investigated explains their selective properties to noble metal ions, since the functional groups of these sorbents can realize the coordination coupling with gold and silver ions, besides the usual ion exchange.[32,33] Furthermore, porous and macroporous structure of ion exchanger matrix facilitates the sorption of large complex ions.

Table 2 contains the data on simultaneous recovery of thiocyanate gold and silver complexes by anion exchangers investigated in dependence on pH value of contacting solution. It should be noted that in our previous works,[4,11,12] where sorption was carried out from individual solutions of gold and silver thiocyanate complexes, the average recovery degrees were on the level of 82-92% and 89-93% for silver and gold, respectively. It can be seen from Table 2 that the recovery degrees decrease for both noble metals during their

Table 2. Sorption properties of anion exchangers investigated during simultaneous recovery of thiocyanate gold (III) and silver (I) complexes

Trade name[a]	pH of contacting solution	Sorption of thiocyanate complexes of						K_S
		Gold (III)			Silver (I)			
		EC to Au, mg/g	D	R_D	EC to Ag, mg/g	D	R_D	
AN-25	2	3.6	105	64	3.2	40	40	2.6
	4	3.6	105	64	3.1	37	35	2.8
	6	3.5	96	62	2.9	30	33	3.2
AP-100	2	3.5	94	60	3.1	38	35	2.7
	4	3.5	94	60	3.1	38	35	2.5
	6	3.4	90	58	3.0	35	33	2.6
AV-17-10P	2	3.1	74	55	2.5	35	32	2.1
	4	3.2	81	57	2.5	35	32	2.3
	6	3.4	88	60	2.4	34	30	2.6
AV-17-8	2	2.9	32	36	1.8	9	13	3.5
	4	2.9	32	36	1.8	10	15	3.2
	6	2.8	31	35	1.8	10	15	3.1

[a]Initial concentrations are 0.08 mmol/L and 0.16 mmol/L for Au(III) and Ag(I), respectively; C_{KSCN} = 0.25 mol/L

simultaneous presence. It can be probably explained by the competing effect of these complexes. Moreover, the change in pH values from 2 to 6 has almost no effect on sorption properties of the anion exchangers investigated. Since the acidic solutions are the most important for industrial application, the further study was carried out at pH=2.

The anion exchangers investigated can be disposed in the following row according to their sorption ability:

AN-25 > AP-100 > AV-17-10P > AV-17-8.

As it was expected, the gel anion exchanger AV-17-8 possesses the lowest selectivity to sorbed thiocyanate complexes of gold and silver. Under these conditions, the macroporous anion exchanger AN-25 has the largest selectivity, and thus it was chosen for further investigation.

The isotherms of sorption of thiocyanate gold and silver complexes on AN-25 are represented in Figure 1. It can be seen that these curves are convex, *i.e.* this anion exchanger possesses the sufficient selectivity in the systems investigat-
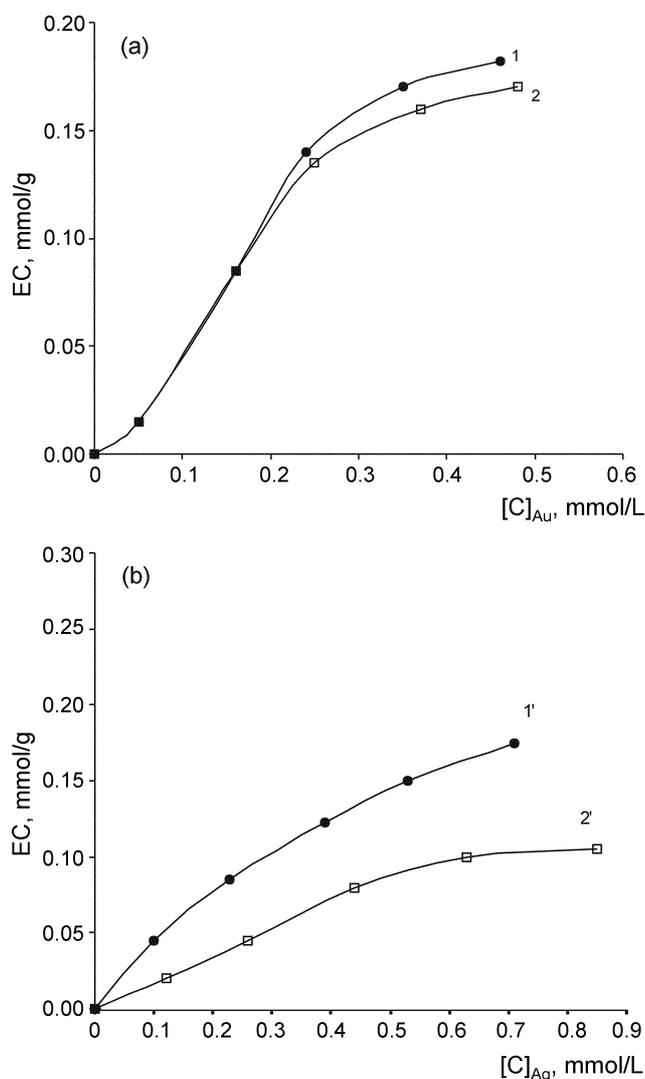
ed.

The effect of initial concentrations of thiocyanate gold and silver complexes on sorption properties of anion exchanger AN-25 is presented in Table 3. It can be seen from these data that AN-25 recovers thiocyanate gold complexes to a greater extent than the silver ones. This fact can be probably explained by higher affinity of this sorbent to the gold complex.

The results on desorption of thiocyanate gold and silver complexes from the anion exchanger AN-25 are represented in Figure 2. The data obtained show that 30-40 g/L concentration of thiocarbamide is enough to elute more than 90% of the sorbed silver, while about 100 g/L of the thiocarbamide concentration is required for desorption of the same amount of gold. These results allow to carry out the separation of gold and silver ions and show perspectives for their analytical control.

Development of gold(III) determination method by means of diffuse reflectance spectroscopy. Since the silver ions are almost completely eluted from anion exchanger AN-25 by sulfuric acidic thiocarbamide solution, and gold

Table 3. Sorption of thiocyanate gold (III) and silver (I) complexes on anion exchanger AN-25

Initial concentration[a], mmol/L		Distribution ratio		K_S
Au	Ag	Au	Ag	
0.08	0.16	105	40	2.6
0.10	0.21	300	167	1.8
0.33	0.35	531	173	3.1
0.52	0.60	583	182	3.2
0.69	0.83	432	159	2.7
0.82	1.06	354	124	2.9

[a]$C_{KSCN} = 0.25$ mol/L; pH=2

Figure 1. Isotherms of sorption of thiocyanate gold (a) and silver (b) complexes on anion exchanger AN-25 at pH = 2. 1,1' individual complexes, 2,2' simultaneous presence of gold and silver complexes.
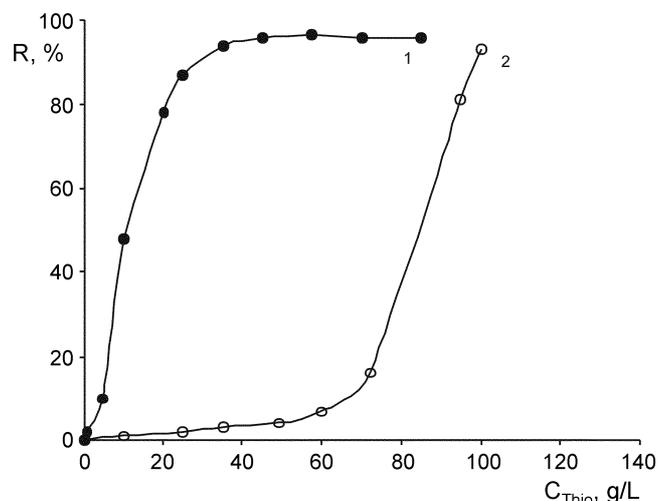
Figure 2. Desorption of silver (1) and gold (2) from anion exchanger AN-25 in dependence on thiocarbamide concentration in 0.3 M H_2SO_4. The initial concentrations during sorption are 0.33 mmol/L and 0.35 mmol/L for gold and silver, respectively.

ions remain in the resin phase, it is advisable to carry out the analytical control directly in the sorbent phase using diffuse reflectance spectroscopy. That is why we have selected the sorption analytical system on the basis of anion exchanger AN-25 for solid-phase determination of gold.

It is known[13,15,16] that hydrated tin (II) oxide and metal gold are formed in solution during gold (III) reduction by tin (II) chloride. They form a mixed colloid, the color of which depends on medium acidity and changes with its increase from yellow to red-brown. The absorption maximum in gold chloride solutions is located at 500 nm.[13,15,16] It should be noted that thiocyanate gold complexes are slightly investigated. That is why the mechanism of color development during the interaction between these complexes and $SnCl_2$ demands a special study. Probably this mechanism can be explained by reduction of $[Au(SCN)_4]^-$ species to $[Au(SCN)_2]^-$. The absorption spectra of these complexes in solution are shown in Figure 3.

We have used tin (II) chloride as a reagent to obtain the analytical signal in the phase of anion exchanger AN-25. The maximum in diffuse reflectance spectrum is observed at 630 nm (Figure 4). We have determined that the maximum of analytical signal in the system AN-25-Au(III)-KSCN-$SnCl_2$ is achieved over a period of 20 min. Under the chosen optimal conditions, the calibration curve of $\Delta F(R)$ was plotted as a function of gold concentration. This curve is linear in the gold concentration range of 1-19 mg/L. The relative detection limit determined by 3σ method is 0.05 μg/mL. The calibration curve follows the equation:

$$\Delta F(R) = 0.017C_{Au} + 1.31, \tag{5}$$

where C_{Au} is the concentration of thiocyanate gold complexes.

It is obvious that expression (5) is linear equation.

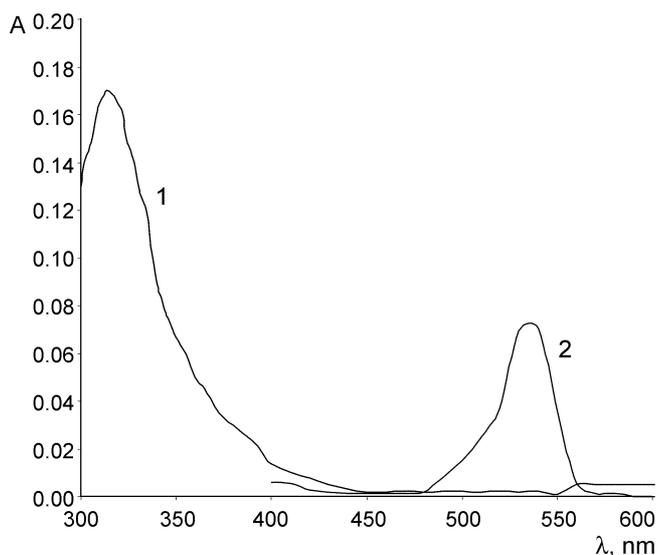The reproducibility of the developed method was tested at

Figure 3. Absorption spectra of thiocyanate gold (III) complexes (1) and of gold (III) compound with $SnCl_2$ (2) in solution. The initial concentration of thiocyanate gold (III) complexes is 0.08 mmol/; pH = 2.
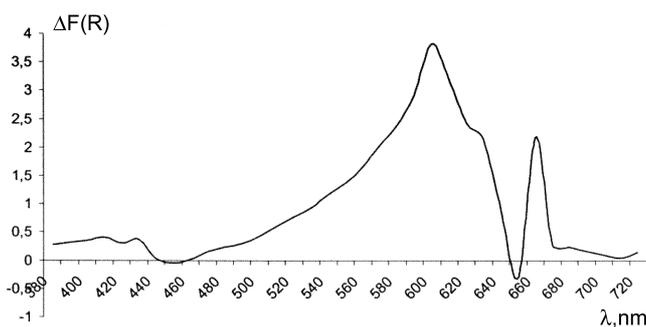

Figure 4. Diffuse reflection spectrum of gold (III) compound with tin (II) chloride in the phase of anion exchanger AN-25. The initial concentration of thiocyanate gold (III) complexes is 0.08 mmol/; pH = 2.

Table 4. Sorption-spectroscopic gold determination in model solutions

Analysis object	Gold content, mg/L		Standard deviation S	Relative standard deviation S_r
	Added	Found		
MS 1[a]	0.1	0.3 ± 0.001	0.008	0.02
MS 2	0.5	0.6 ± 0.04	0.02	0.04
MS 3	3.0	3.0 ± 0.04	0.02	0.04
MS 4	7.0	7.0 ± 0.02	0.01	0.02

[a]MS model solution

sorption-spectroscopic gold determination in model solutions (Table 4). It can be seen from these data that the relative standard deviation does not exceed 0.04.

The inhibitory effect of some accompanying elements on sorption-spectroscopic gold determination was also studied and the results are presented in Table 5. These data show that gold determination with tin (II) chloride can be carried out in the presence of copper (II) (5-fold excess), iron (II) and cobalt (II) (10- and 20-fold excesses). Silver (I), zinc (II) and aluminum (III) ions hinder the determination of gold (III) in any amounts. That is why these ions as well as greater amounts of copper (II) should be masked by EDTA. However, since silver (I) ions were already separated from gold (III) ions, they have no inhibitory effect on gold (III) determination by diffuse reflectance spectroscopy.

Using the calibration curve obtained, we have determined the content of gold in industrial solutions. Before the sorption-spectroscopic determination, Fe(III) ions were removed by precipitation with 2 M NaOH. Then the solution was filtered and filtrate was treated by 2 M HCl up to pH=2.

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

Foreign ion[a]	Ratio of foreign ion to Au(III)	Found Au(III), mg/L	Relative error ε,%
Co(II)	20	1.8	-17
Cu(II)	5	1.4	+7
Fe(II)	10	1.6	-6

[a]C_{Au} = 1.5 mg/L

Table 6. Sorption-spectroscopic determination of gold in industrial solutions

Analysis object	Au(III) found, mg/L	
	by sorption-spectroscopic method	by flame AAS method
IS 1[a]	6.1 ± 0.62	8.1 ± 1.4
IS 2	6.3 ± 0.63	8.4 ± 1.3
IS 3	6.8 ± 0.58	8.6 ± 1.3

[a]IS - industrial solution

The results are presented in Table 6.

The results obtained allow us to recommend the complex-forming anion exchanger AN-25 for the selective recovery of thiocyanate gold (III) and silver (I) complexes, their separation and subsequent determination of gold (III) in the phase of this sorbent using diffuse reflectance spectroscopy.

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