

## Ion Exchange Recovery of Rhenium and Its Determination in Aqueous Solutions by Diffuse Reflection Spectroscopy

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The existing technological schemes for processing rhenium-containing raw materials involve the recovery of Re from solutions, which can be effectively achieved by anion exchange method. The application of anion exchange also allows to study rhenium state in aqueous solutions and to develop analytical control methods. The present work is focused on investigation of ion exchange equilibrium in the analytical system Re(VII)-HCl-SnCl<sub>2</sub>-KSCN-anion exchanger by means of sorption-desorption method as well as by electron, IR- and diffuse reflection spectroscopy. It was shown that rhenium can be quantitatively recovered from this system. It is proposed to use the sorption-spectroscopic method for Re(VII) determination in aqueous solutions. The calibration curve is linear in the concentration range of 0.5-20.0 mg/L (sample volume is 25.0 mL) and the detection limit is 0.05 mg/L. The presence of Mo(VI), Cu(II), Fe(II, III), Ni(II), Zn(II) as well as K<sup>+</sup>, Na<sup>+</sup> do not hinder the solid-phase determination of rhenium. Rhenium (VII) determination by diffuse reflection spectroscopy was carried out in model solutions as well as in samples of river-derived water and in solutions obtained after the dissolution of spent catalysts.

**Key Words :** Rhenium, Anion exchanger, Sorption, Diffuse reflection spectroscopy

### Introduction

The unique physical-chemical properties possessed by pure rhenium as well as its alloys and compounds, make possible to apply them widely in various fields of modern industry. For instance, rhenium compounds are used as catalysts in production of chemicals. Such a demand for rhenium and its compounds resulted in development of analytical chemistry of rhenium.<sup>1</sup>

The existing technological schemes for processing rhenium-containing raw materials involve the production of Re solutions with the subsequent recovery of rhenium. For this purpose, it is common to use sorption processes. Namely, the leading method for separation of rhenium from cations of accompanying elements is anion exchange.<sup>2,3</sup> The ion exchange methods are very effective for investigation of rhenium state in aqueous solutions as well as for development of analytical control methods.<sup>4</sup>

The ion exchange recovery of rhenium is usually carried out from hydrochloric acid solutions in the form of rhenium (VII) compounds.<sup>5</sup> The reduction of rhenium in the concentrated hydrochloric acid by means of such reducing agents as Sn(II) or HI leads to sequential formation of Re(V) and Re(IV) compounds: [ReOCl<sub>5</sub>]<sup>2-</sup>, [ReCl<sub>6</sub>]<sup>2-</sup>, etc.<sup>6</sup>

The analytical determination of rhenium in solution is usually carried out by photometric or spectrophotometric methods by reducing the perrhenate-ions in hydrochloric acid medium in the presence of thiocyanate ions.<sup>1,7</sup> If rhenium is reduced by SnCl<sub>2</sub>, then the complex thiocyanate

compound is formed, and its composition depends on Re : SCN<sup>-</sup> and Re : Sn(II) ratios. For example, if Re : SCN<sup>-</sup> = 1 : 2, the complex [ReO<sub>2</sub>(SCN)<sub>2</sub>]<sup>2-</sup> is expected to be formed, whereas if Re(VII) : Sn(II) = 1 : 1, the compound has the formula [ReO<sub>2</sub>(SCN)<sub>4</sub>]<sup>3-</sup>.<sup>8-10</sup>

It is noted in the works<sup>11,12</sup> that the following step-by-step complex formation of rhenium with thiocyanate ions takes place:



Therefore, due to the complexity of this analytical system, the low content of rhenium in many materials as well as the inhibitory effect of many solution components, it is required to make the above-mentioned reaction more sensitive and more selective. That is why an effective scheme of rhenium analytical control should include the determination of rhenium in the sorbent phase as the final stage. For this purpose, we have used the diffuse reflection spectroscopy method, which is easy to use, cheap and applicable under field conditions.<sup>13-17</sup>

Earlier we have studied the recovery of rhenium from industrial products.<sup>18</sup> It was shown that the highest concentration degrees of perrhenate ions were characteristic for anion exchangers AV-17-10P and AN-105-10P. The aim of the present work is to investigate ion exchange equilibrium in the analytical system Re(VII)-AV-17-10P (AN-105-10P)-HCl-SnCl<sub>2</sub>-KSCN and to develop rhenium determination method by diffuse reflection spectroscopy.

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### Experimental Section

For our investigation, we have chosen the strong basic anion exchanger AV-17-10P and weak basic one AN-105-10P porous sorbents on the basis of styrene-divinylbenzene copolymers. Their physical-chemical characteristics are given in Table 1.

The resins were preliminary prepared according to standard procedures and loaded with sodium chloride. The ion exchange equilibrium was investigated under batch experiment conditions. The exchanger quantities were 0.2 g (dry substance) and the contacting solution volume was 25.0 mL. The resins were preswollen for 4 h in distilled water and after that they were stirred with the solution investigated.

The sodium perrhenate stock solution (0.005 mol/L) was prepared from an accurately weighed sample of pure supplier (analytical grade). The operating rhenium (VII) solutions were prepared by diluting the stock solution. Different series of rhenium (VII) solutions were prepared, in which the hydrochloric acid concentration was from 0.50 to 5.5 mol/L. Moreover,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (1 mol/L) and KSCN (2 mol/L) were added in these solution. The volumetric ratio of Re,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and KSCN was 1 : 2 : 2.

Apart from these model solutions, the river-derived water (from the Yenisey river) as well as dissolved rhenium-containing spent catalysts were taken for investigation. The latter had the following composition, mol/L: Mo(VI)~0.1; Re(VII)~0.02;  $\text{Al}_2(\text{SO}_4)_3$ ~0.25;  $\text{H}_2\text{SO}_4$ ~0.5. This solution was diluted up to 100 times.

The resin samples were stirred with the solution in thermostat at  $(20 \pm 1)^\circ\text{C}$ . 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. Rhenium concentration in solutions was determined by a spectrophotometrical method<sup>7</sup> in the form of thiocyanate complexes ( $\lambda = 432 \text{ nm}$ ,  $l = 1 \text{ cm}$ ) using an automatic spectrophotometer (model Specord UV Vis, Germany) or by flame atomic absorption spectroscopy using an atomic absorption spectrophotometer (model Saturn-2, Russia). The resin samples were washed with distilled water and dried. Then their IR-spectra were registered using an IR-spectrometer (Model Specord M 80, Germany). Moreover, the special control samples of anion exchangers were prepared for IR-spectrometry according to the procedure described below.

The diffuse reflection spectra of the sorbents investigated

were registered by means of the transportable colorimeter (model Spectroton, Russia). This colorimeter embodies the principle of concurrent measurement of diffuse reflection 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 (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 procedure for samples preparation is given below.

From the data obtained, the recovery degree of rhenium (R, %) as well as static exchange capacity (amount of the Re(VII) sorbed in mmol/g of the resin) and distribution ratio D were calculated:

$$D = \text{mmol Re(VII) sorbed per g resin} / \text{mmol Re(VII) per mL of solution.} \quad (1)$$

$$R(\%) = [(C_0 - C_{\text{eq}}) \cdot 100] / C_0. \quad (2)$$

All results were statistically processed by standard methods<sup>19</sup>: 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 than 6%.

**Preparation of samples for IR-spectrometry.** The resin quantities (1.0 g) were mixed with 150 mL sodium perrhenate solutions (0.005 mol/L) at  $\text{pH} > 1$ . After 24 h, the resins were separated from solutions and rhenium (VII) concentration was determined in the filtrates. Then the resins were washed with distilled water, slightly dried and after that they were treated with the following solutions series:

HCl (4 M);  
HCl (4 M)- $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (1 M);  
HCl (4 M)- $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (1 M)-KSCN (2 M).

All the solutions were added drop by drop to the volume of 25.0 mL. The treated resin samples were left for 24 h (equilibrium time). After that they were dried and ground in a vibration mill. Then their IR-spectra were registered by means of resins tableting with KBr (0.3 g of the resin to 200 mg of KBr).

**Preparation of samples for diffuse reflection spectroscopy.** The solid-phase spectroscopy method includes the formation

**Table 1.** Physical-chemical characteristics of anion exchangers investigated

Trade name <sup>a</sup>	Physical structure	Copolymer	Porogene	Aminating agent	Functional groups	Specific swelling volume, $\text{cm}^3/\text{g}$ in Cl <sup>-</sup> -form	Static exchange capacity, mmol/g, in Cl <sup>-</sup> -form	Manufacturer
AN-105-10P	P	St + DVB	HD	CHA	$  \begin{array}{c}  \text{CH}_2-\text{CH}_2 \\    \quad \quad   \\  -\text{CH}_2-\text{N}-\text{CH} \\    \quad \quad   \\  \text{H} \quad \quad \text{CH}_2-\text{CH}_2  \end{array}  $	2.7	3.2	TOKEM, Kemerovo (Russia)
AV-17-10P	P	St + DVB	HD	QAB	$-\text{CH}_2-\overset{+}{\text{N}}(\text{CH}_3)_3$	3.8	3.7	TOKEM, Kemerovo (Russia)

<sup>a</sup>P-porous; St-styrene; DVB-divinylbenzene; HD-hexadecane; CHA-cyclohexylamine; QAB-quaternary ammonia base.

of colored compounds on a surface of sorbent and measurement of diffusion reflection coefficients.<sup>20-22</sup> The desired analyte compound was obtained on the resin surface according to the following procedures:

**Formation of thiocyanate complex in the anion exchanger phase:** 20.0 mL of Re(VII) solution with rhenium content of 0.8-3.0  $\mu\text{mol}$  were placed into graduated flasks ( $V = 50.0$  mL). Then 15.0 mL of 4 M HCl and 2.0 mL of 1 M  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  were added and the solutions were brought up to a flask's mark with distilled water.

The resin quantities (0.2 g) were mixed with 25.0 mL of the above-mentioned solutions. After 24 h (equilibrium time), the resins were filtered and 2.0 mL of 2 M KSCN were added drop by drop to the samples. The treated resins were left again for 24 h. After that, the diffusion reflection coefficients were measured.

**Sorption of rhenium thiocyanate complexes from solutions:** 20.0 mL of Re(VII) solution with rhenium content of 0.8-3.0  $\mu\text{mol}$  were placed into graduated flasks ( $V = 50.0$  mL). Then 15.0 mL of 4 M HCl, 2.0 mL of 1 M  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and 2.0 mL of 2 M KSCN were added and these solutions were brought up to a flask's mark with distilled water.

The resin quantities (0.2 g) were mixed with these solutions (25.0 mL). After 24 h, the resins were filtered and then the diffusion reflection coefficients were measured.

After the equilibrium attainment, the anion exchanger samples gain orange or red-orange color. These samples can be stored dry for approximately a year.

In the solid-phase spectroscopy method, the change of Gurevich-Kubelka-Munk function  $\Delta F(R)$  is used as an analytical signal<sup>20-22</sup>:

$$\Delta F(R) = [(1 - R)^2/2R] - [(1 - R_0)^2/2R_0], \quad (3)$$

where  $R$  and  $R_0$  are diffusion reflection coefficients (quantities of the dimension 1) of rhenium complex in the exchanger phase and of the anion exchanger, respectively.

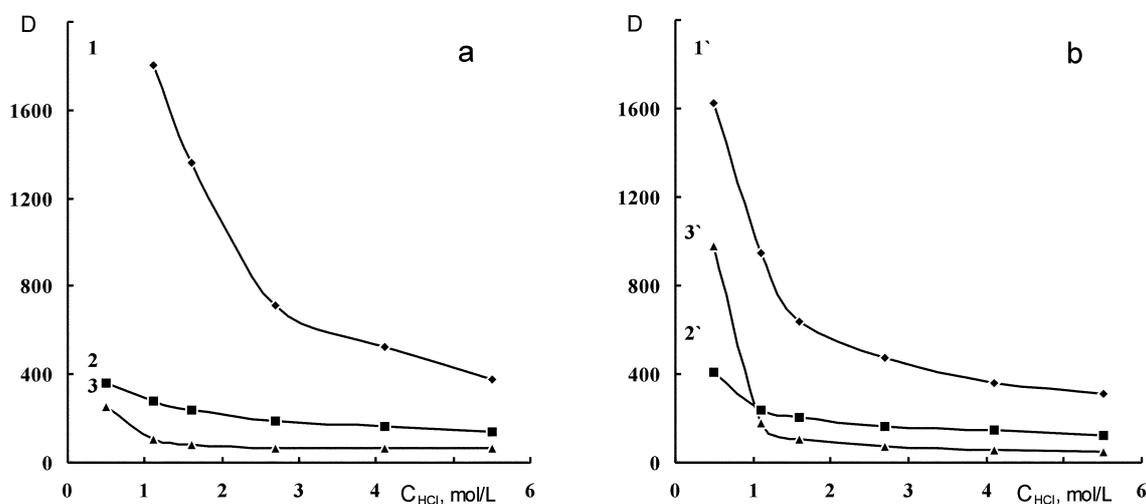
#### Procedures for plotting the calibration curves.

**Formation of thiocyanate complex in the anion exchanger phase:** 0.25; 0.5; 1.0; 2.0; 3.0; 5.0; 7.0 and 9.0 mL of Re(VII) solution (50 mg/L) were placed into graduated flasks ( $V = 25.0$  mL) and 7.5 mL of concentrated HCl as well as 1.0 mL of 1 M  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  were added. The solutions were brought up to a flask's mark with distilled water. Then 0.2 g of resin were mixed with these solutions and stirred over a period of 30 min. After that the resins were filtered and 2.0 mL of 2 M KSCN solution were added drop by drop to the exchangers. Afterwards the ion exchangers were filtered once again and the diffusion reflection coefficients were measured at 470 nm. The calibration curve of  $\Delta F(R)$  was plotted as a function of the rhenium concentration.

**Sorption of thiocyanate complex from solution:** 0.25; 0.5; 1.0; 2.0; 3.0; 5.0; 7.0 and 9.0 mL of Re(VII) solution (50 mg/L) were placed into graduated flasks ( $V = 25.0$  mL). Then 7.5 mL of concentrated HCl, 1.0 mL of 1 M  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  as well as 1.0 mL of 2 M KSCN were added and the solutions were brought up to a flask's mark with distilled water. Then 0.2 g of resin were mixed with these solutions and stirred over a period of 30 min. After that the resins were filtered and the diffusion reflection coefficients were measured at 470 nm. The calibration curve of  $\Delta F(R)$  was plotted as a function of the rhenium concentration.

## Results and Discussion

**Study of ion exchange equilibrium in rhenium-containing analytical systems.** Ion exchange equilibria of perrhenate ions in hydrochloric acid solutions are now investigated only for weak acidic media because in practice it is required to carry out the selective extraction of rhenium from molybdenum-containing solutions. Since the strong acidic solutions (1-4 M HCl) are also used in analytical practice for rhenium determination,<sup>7</sup> we have investigated the sorption recovery of rhenium (VII) from 0.50-5.5 M HCl



**Figure 1.** Dependence of rhenium distribution ratios on hydrochloric acid concentration for anion exchangers AN-105-10P (a) and AV-17-10P (b): 1, 1'- $\text{ReO}_4^-$ -HCl; 2, 2'- $\text{ReO}_4^-$ -HCl- $\text{SnCl}_2$  (1 M); 3, 3'- $\text{ReO}_4^-$ -HCl- $\text{SnCl}_2$  (1 M)-KSCN (2 M). The initial rhenium (VII) concentration is 0.005 mol/L.

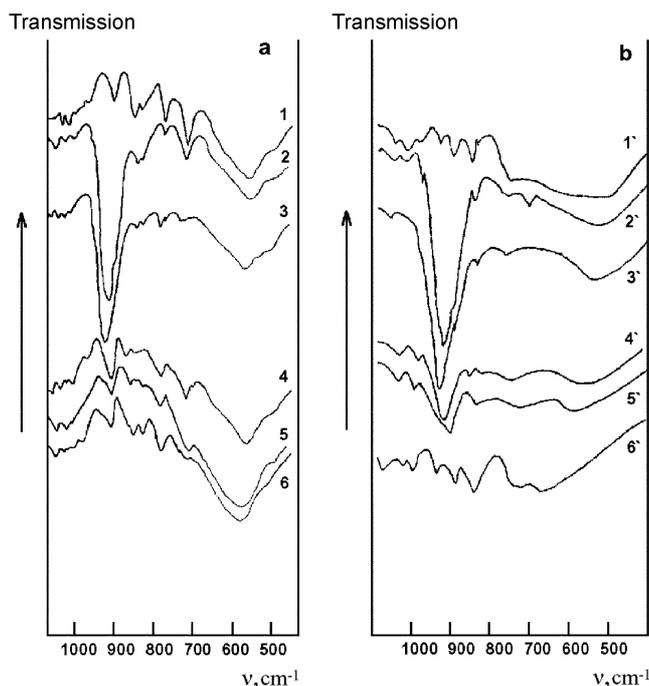
solutions in the presence of tin (II) chloride and potassium thiocyanate.

The dependence of rhenium distribution ratios on hydrochloric acid concentration for both anion exchangers studied is given in Figure 1. The sorption of rhenium (VII) depends on salt composition of solutions. In the system Re(VII)-HCl-RCl (RCl anion exchanger in the Cl<sup>-</sup> form), the recovery of rhenium is practically independent on type of functional

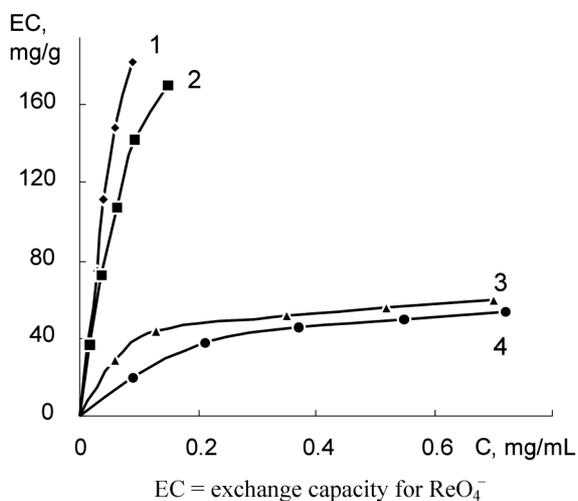
groups of sorbents (curves 1 and 1'). It should be noted that distribution ratios decrease with the growth in HCl concentration.

If HCl concentration is less than 1 mol/L, the perrhenate ions are sorbed, which is represented in IR-spectra of the anion exchangers investigated (Figure 2, spectra 2 and 2' as well as 3 and 3'). The narrow strong absorption band at 890-920 cm<sup>-1</sup> is characteristic for Re=O bond of ReO<sub>4</sub><sup>-</sup> anion.<sup>23</sup> The isotherms of rhenium sorption from solutions with pH > 1 (Figure 3, curves 1 and 2) are convex (*i.e.* sorption is selective). Therefore, rhenium (VII) can be almost fully recovered (97-99.9%) on anion exchangers AV-17-10P and AN-105-10P under these conditions (Table 2).

In the HCl concentration range of 3-5.5 mol/L, the



**Figure 2.** IR-spectra fragments of anion exchangers AN-105-10P (a) and AV-17-10P (b) after Re(VII) sorption from the solutions: ReO<sub>4</sub><sup>-</sup>-HCl (pH = 3) (2,2'); ReO<sub>4</sub><sup>-</sup>-HCl (pH = 1) (3,3'); ReO<sub>4</sub><sup>-</sup>-HCl (4 M) (4,4'); ReO<sub>4</sub><sup>-</sup>-HCl (4 M)-SnCl<sub>2</sub> (1 M) (5,5'); ReO<sub>4</sub><sup>-</sup>-HCl (4 M)-SnCl<sub>2</sub> (1 M)-KSCN (2 M) (6,6'). Spectra 1,1' = anion exchangers in the Cl<sup>-</sup> form. The initial rhenium (VII) concentration is 0.005 mol/L.



**Figure 3.** Isotherms of perrhenate sorption on anion exchangers AV-17-10P (1,3) and AN-105-10P (2,4) at pH = 3 (1,2) and in 4 M HCl (3,4).

**Table 2.** Dependence of rhenium sorption on HCl concentration

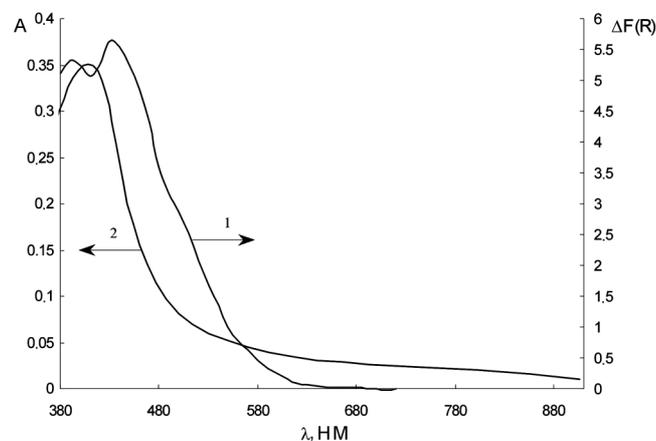
Salt system	C <sub>HCl</sub> , mol/L	Recovery degree, R %	Exchange capacity for rhenium, mg/g	Distribution ratios	Resin color change
<b>AN-105-10P</b>					
ReO <sub>4</sub> <sup>-</sup> -HCl	0.5	99.9	4.99	3350	
	1.1	98.1	4.89	1800	Light-brown
	1.6	96.3	4.82	1363	(without change)
	2.7	93.4	4.67	717	
	4.1	91.3	4.56	521	
ReO <sub>4</sub> <sup>-</sup> -HCl-SnCl <sub>2</sub>	5.5	88.3	4.41	376	
	0.5	87.7	4.38	357	
	1.1	84.9	4.25	281	From dark-green to green-brown
	1.6	82.7	4.13	239	
	2.7	79.1	3.95	190	
ReO <sub>4</sub> <sup>-</sup> -HCl-SnCl <sub>2</sub> -KSCN	4.1	77.0	3.85	167	
	5.5	74.1	3.71	143	
	0.5	83.6	4.19	255	
	1.1	65.0	3.26	93	From red-orange to green
	1.6	60.1	2.99	75	
<b>AV-17-10P</b>	2.7	50.0	2.49	50	
	4.1	47.9	2.40	46	
	5.5	45.7	2.29	42	
	0.5	97.0	4.84	1628	
	1.1	94.9	4.75	944	Light-yellow
ReO <sub>4</sub> <sup>-</sup> -HCl	1.6	93.0	4.64	639	(without change)
	2.7	90.6	4.52	477	
	4.1	87.7	4.38	357	
	5.5	86.3	4.32	314	
	ReO <sub>4</sub> <sup>-</sup> -HCl-SnCl <sub>2</sub>	0.5	89.1	4.45	405
1.1		82.7	4.13	239	From green to light-green
1.6		80.6	4.02	208	
2.7		76.3	3.82	161	
4.1		74.1	3.71	143	
ReO <sub>4</sub> <sup>-</sup> -HCl-SnCl <sub>2</sub> -KSCN	5.5	71.3	3.56	124	
	0.5	95.2	4.77	983	From red-orange to yellow
	1.1	78.1	3.91	179	
	1.6	68.3	3.41	108	
	2.7	60.1	3.00	75	
KSCN	4.1	54.0	2.70	59	
	5.5	51.6	2.59	53	

recovery of rhenium is gradually reduced to 86-88% (Table 2). It is known<sup>1,24</sup> that rhenium exists in these solutions mainly in the form of chloride complexes  $[\text{ReCl}_6]^{2-}$ ,  $[\text{ReOCl}_4]^{2-}$ ,  $[\text{Re}(\text{OH})_n\text{Cl}_{6-n}]^{2-}$ . That is why the quantitative recovery of rhenium is possible by means of larger anion exchanger quantities (no less than 0.5 g) because the exchange capacity of these sorbents is not high in these solutions (Figure 3, curves 3 and 4). The weak band at 890-915  $\text{cm}^{-1}$  in IR-spectra (Figure 2, spectra 4 and 4') corresponds to Re=O bond in the sorbed rhenium anion complexes.<sup>23</sup> Possibly there is a simultaneous sorption of the above-mentioned rhenium chloride complexes.<sup>23</sup>

The presence of tin (II) chloride and potassium thiocyanate in the systems investigated leads to the decrease in rhenium distribution ratios (Figure 1, curves 2 and 2' as well as 3 and 3'). The recovery degree of rhenium in these systems is on the level of 46-88% and 52-95% for AN-105-10P and AV-17-10P, respectively (Table 2). The weak bands at 890-915  $\text{cm}^{-1}$  in IR-spectra can not be attributed with confidence to Re=O groups of rhenium chloride complexes (Figure 2, spectra 5 and 5' as well as 6 and 6').

The formation of rhenium complexes with thiocyanate ions in solutions was determined by means of visible absorption spectroscopy: the absorption maximum is observed at 420 nm (Figure 4, spectrum 2). This is probably consistent with formation of such complexes as  $[\text{ReO}_2(\text{SCN})_2]^{2-}$ ,  $[\text{Re}(\text{SCN})_6]^{2-}$  or  $[\text{ReO}(\text{SCN})_n\text{Cl}_{4-n}]^{2-}$ .<sup>1,10,12</sup>

The sorption of rhenium from thiocyanate-containing solutions proceeds in the form of anionic complexes and depends on hydrochloric acid concentration in contacting solutions. In the HCl concentration range of 1-5.5 mol/L, the distribution ratios are changed slightly (Figure 1, curves 3 and 3'). IR-spectra (Figure 2, spectra 6 and 6') of anion exchangers at 1000-400  $\text{cm}^{-1}$  have no strong absorption bands of the sorbed complexes due to relatively low exchange capacity of the sorbents (absorption bands of Re=O bond take place at 850-920  $\text{cm}^{-1}$ ). The weak absorption is observed at 700-680  $\text{cm}^{-1}$  for C=S bond. For  $\text{SCN}^-$



**Figure 4.** Diffuse reflection spectrum of Re(VII) complex with thiocyanate ions on a surface of strong basic anion exchanger AV-17-10P (1) and absorption spectrum of this complex in solution (2). The initial rhenium (VII) concentration is 0.004 mmol/L.

groups, the strong absorption is observed at 2000-2100  $\text{cm}^{-1}$  (band maximum at 2050  $\text{cm}^{-1}$ ); the other absorption bands are at 350-200  $\text{cm}^{-1}$ .<sup>23</sup>

Therefore, the sorption recovery of rhenium from thiocyanate solutions is possible and depends on hydrochloric acid concentration in the initial solution.

**Development of rhenium (VII) determination method by means of diffuse reflection spectroscopy.** The spectral characteristics of rhenium (VII) complex compound with thiocyanate ion on a surface of anion exchangers investigated were studied by diffuse reflection spectroscopy. It should be noted that it is insufficient to obtain the reliable results (for both procedures of samples preparation) judging on the difference of diffusion reflection coefficients on a surface of AN-105-10P for the sorbed complexes and for blank tests. That is why the further investigation was carried out on strong basic anion exchanger AV-17-10P.

Figure 4 contains the diffuse reflection spectrum of the complex compound of rhenium with thiocyanate ions (spectrum 1). In comparison with absorption spectrum of this compound in solution (spectrum 2), the maximum bathochromic shift as well as the widening of sorbate absorption band are observed. The measurement of diffusion reflection coefficients was carried out at a wavelength of 470 nm. It should be noted that the spectral characteristics of rhenium complex compounds in the resin phase are identical for the samples prepared according to the procedures (1) and (2).

We have determined that the analytical signal maximum in the system Re-HCl-SnCl<sub>2</sub>-KSCN-RCl is achieved over a period of 30 min. Under the chosen optimal conditions, the calibration curves were plotted for rhenium determination in river-derived water and aqueous solutions.

The calibrations curves obtained are linear at the Re(VII) concentration range of 0.5-20.0 mg/L. The relative detection limit determined by 3 $\sigma$  method is 0.05  $\mu\text{g}/\text{mL}$  (1  $\mu\text{g}$ -absolute). The calibrations curves follow the equations:

$$\Delta F(R) = 0.0884 C_{\text{Re(VII)}} + 0.8766; \quad (4)$$

and

$$\Delta F(R) = 0.2498 C_{\text{Re(VII)}} + 1.2012. \quad (5)$$

for procedures (1) and (2), respectively.

It is obvious that expressions (4) and (5) are linear equations. Since the expression (4) represents more sensitive dependence between  $\Delta F(R)$  and  $C_{\text{Re}}$ , we decided to use this

**Table 3.** Sorption-spectroscopic Re(VII) determination in model solutions

Analysis object	Rhenium (VII) content, mg/L		Standard deviation, $S$	Relative standard deviation, $S_r$
	Added	Found		
MS 1 <sup>a</sup>	1.1	1.0 $\pm$ 0.3	0.1	0.10
MS 2	7.5	7.4 $\pm$ 0.7	0.3	0.04
MS 3	15	16 $\pm$ 3	1	0.07

<sup>a</sup>MS-model solution. n = 3; P = 0.95.

**Table 4.** Inhibitory effect of some foreign ions on rhenium(VII) determination by diffuse reflection spectroscopy

Foreign ion	Ratio of foreign ion to Re(VII)	Found Re(VII) concentration, mol/L·10 <sup>6</sup>	Relative error ε, %
Mo (VI)	15	4.5	+16
Cu (II)	20	4.8	+11
Fe (II)	400	5.8	-7
Ni (II)	400	5.3	+2
Zn (II)	400	4.9	+9
K <sup>+</sup>	3 × 10 <sup>3</sup>	5.6	-4
Na <sup>+</sup>	2 × 10 <sup>3</sup>	5.2	+4

<sup>a</sup>C<sub>Re(VII)</sub> = 5.4 × 10<sup>-6</sup> mol/L.

**Table 5.** Sorption-spectroscopic Re(VII) determination in river-derived water

Concentration of Re(VII), mg/mL		S <sub>r</sub>	$\pm \frac{t \cdot S}{\sqrt{n}}$	ε, %
Added <sup>a</sup>	Found			
1.1	0.9	0.10	0.2	-22
7.5	7.6	0.03	0.4	+5
10.0	9.8	0.06	0.2	-2

<sup>a</sup>n=3; P=0.95

**Table 6.** Sorption-spectroscopic determination of rhenium(VII) in industrial solutions obtained after dissolution of spent catalysts

Analysis object	Re(VII) found, mg/L	
	by sorption-spectroscopic method	by flame AAS method
IS 1 <sup>a</sup>	35.2 ± 1.1	34.7 ± 0.87
IS 2	38.7 ± 1.2	37.9 ± 1.1
IS 3	39.8 ± 1.9	39.2 ± 1.4

<sup>a</sup>IS industrial solution. n = 3; P = 0.95

particular calibration curve for our further experiment.

The reproducibility of the developed method was tested at sorption-spectroscopic Re(VII) determination in model solutions (Table 3). It can be seen from this Table that the standard deviation does not exceed 0.1.

The inhibitory effect of some accompanying elements on sorption-spectroscopic Re(VII) determination was studied and the results are shown in Table 4. As follows from these data, rhenium can be determined in the form of thiocyanate complexes in the presence of molybdenum(VI) and copper (II) (up to 10 mg/L), iron(II,III), nickel(II), zinc(II) (100-fold excesses), K<sup>+</sup> and Na<sup>+</sup> (1000-fold excesses).

Using the calibration curves obtained, we have determined rhenium (VII) content in river-derived water and in industrial solutions of spent catalysts (Tables 5 and 6).

The results obtained allow us to recommend the analytical systems on the basis of strong basic porous anion exchanger AV-17-10P for the ion exchange recovery of rhenium from the multicomponent solutions and for direct determination of rhenium in the sorbent phase.

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