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Received on 18.12.2006

UDC 543.253

DETERMINING RHENIUM IN CRUDE ORE BY THE METHOD OF X-RAY FLUORESCENCE ANALYSIS

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Optimal conditions of sorption concentration of perrhenate-ions with activated carbon have been considered. The possibility of rhenium determination with accompanying element is shown.

The analysis of geological rhenium samples is not an easy task owing to its low industrial contents as well as the presence of tungsten and molybdenum accompanying to it in ores. Rather complete review by the methods of rhenium determination in mineral raw materials is given in papers [1–3]. As rhenium is distributed nonuniformly over the analyzed sample then its determination is not possible without preconcentration. Sorption concentration of perrhenate-ions (ReO_4^-) with activated carbon (AC) is one of the most efficient methods of extracting ReO_4^- from solutions with high content of nonferrous and other metals salts. Increase of determination sensitivity is not the only and often not the main reason of concentration use. Concerning the method of X-ray fluorescence analysis (XFA) the concentration allows solving and decreasing acuity of the problem of obtaining calibration characteristics at single-type matrices [4].

The aim of the given work was to determine optimal conditions of perrhenate-ions sorption concentration at activated carbon and develop the technique of X-ray fluorescence rhenium determination in crude ore.

Experimental part

To study sorption characteristics the standard nitric acid solution Re(VII) in 3M HNO_3 with concentration of 100 mg/dm³ was used. After metal rhenium dissolution it is in solution in the form of perrhenate-ion (ReO_4^-).

Model mixtures containing different quantities of ReO_4^- ions were prepared by 3M HNO_3 dilution on the day of analysis. ReO_4^- sorption was carried out at activated carbon of BAU-A type with total pore water volume not less than 1,6 cm³/g and iodine adsorption activity not less than 60 %. For more uniform concentration sorbent granules were ground to powder in agathic mortar to the size of 50 mkm.

Influence of time contact of sorbent with solution on completeness of sorption of BAU-A ions was studied under the affect of ultra-violet radiation (UVR) of solutions and without it. Mercury lamp of high pressure DRT-220 without filter was used as a source of UVR. Distance from radiation source to the samples is 20 cm. Sorption of perrhenate-ions was carried out in static conditions. For this purpose 0,3 g of BAU-A was put into solution with volume of 10 ml. After concentration sorbent with sorbtive were filtered, the remainder was dried. Quantity of sorbed perrhenate-ions was determined by the method of XFA [5] using spectrometer «Spectroscan» (SPA «Spectron», Saint-Petersburg). The parameters of X-ray tube operation with molybdenum anode were as follows: voltage 40 kV, current 100 mA, crystallizer LiF. Time of one measurement was 200 s. $L_{\alpha 1}$, $L_{\beta 2}$ served as analytic lines at rhenium determination. Fluorescence radiation intensity at the stated lines was defined by subtracting the magnitude of background intensity.

Sorption completeness was controlled analyzing filtrate at voltamperometric analyzer TA-1 (SPA «Takhnoanalit», Tomsk) by the method of inverse voltamperometry by the technique [6]. Three-electrode cell in which main electrode represents graphite electrode impregnated by polyethylene prepared by the technique was used [6]. Saturated chloride-silver electrode served as the reference one. Platinum electrode was used as an auxiliary one.

Results and discussion

Taking out the experiments solution pH, process duration, UVR action were varied. As AC is capable of sorbing perrhenate-ions from acid and alkaline solutions, pH of solutions containing perrhenate-ions was changed from 0,5 to 13 adding concentrated solutions of HNO₃ and NaOH. Sorbent was researched after sorption by the method of XFA. It was stated that activated carbon has a pronounced dependence of sorbent capacity on pH of analyzed solution. Optimal value of pH at which static exchange capacity BAU-A by perrhenate-ions achieves maximal value amounts to 1,5...2,5.

One more factor influencing the completeness of perrhenate-ion sorption with activated carbon is contact time of sorbent with solution. After treating experimental data it was stated that the most complete sorption concentration of perrhenate-ions at BAU is achieved during 90 min of sorption. The possibility of intensifying the process of sorption due to sorption process carrying out from solutions irradiated by ultraviolet was studied.

The data of changing sorption kinetics of perrhenate-ions from nitro-acid solutions of AC of BAU-A type without solution irradiation and at UVR influence are given in Fig. 1. As it is seen from the Figure already after 10 min of radiation perrhenate-ions are sorbed by AC almost completely 95...99 %. Within the same period of time perrhenate-ions sorption without UVR does not exceed 80 %. The fact that complete extraction of Re(VII) by AC is possible without UVR but for longer period of time allows supposing that in natural conditions rhenium ion sorption may also occur owing to solution irradiation with light from visible spectrum.

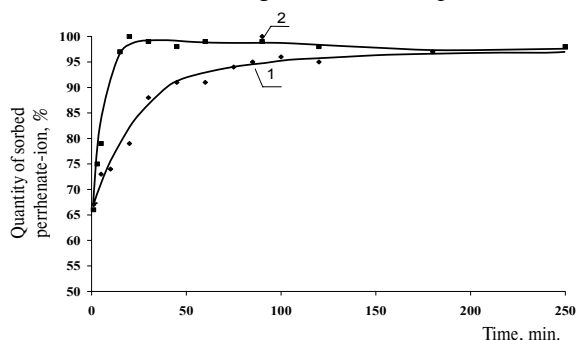


Fig. 1. Kinetics of perrhenate-ions sorption from nitro-acid solutions of AC of BAU-A type. Solution volume is 10 ml, sorbent mass is 0,3 g: 1) at UVR; 2) without influence

Adsorptive processes coursing at AC may be described mathematically by different isotherms. Determination of the type of adsorptive isotherm allows describing sorption mechanism, determining sorbent sorption capacity.

Sorption isotherm was plotted using solutions with concentration 50, 100, 150, 200, 250, 300, 350, 400, 450 mg/dm³. BAU-A batch amounted to 0,3 g. Sorption was carried out during 10 min with UVR.

To plot sorption isotherm it is necessary to calculate Γ adsorption in equilibrium conditions of sorption process. Quantity of sorbed substance was calculated by the formula (1) by the experimental data.

$$A_{\text{эксп}} = \frac{C_{\text{нач}} - C_{\text{равн}}}{m} \cdot V, \quad (1)$$

where $A_{\text{эксп}}$ is the experimental rhenium adsorption, $C_{\text{нач}}$ is the initial rhenium concentration in solution, mg/l, $C_{\text{равн}}$ is the residual rhenium content in solution after sorption, mg/l, m is AC mass equal to 0,3 g, V is the volume of solution for sorption, l.

On the basis of the data calculated by the formula (1) the sorption isotherm was plotted, Fig. 2.

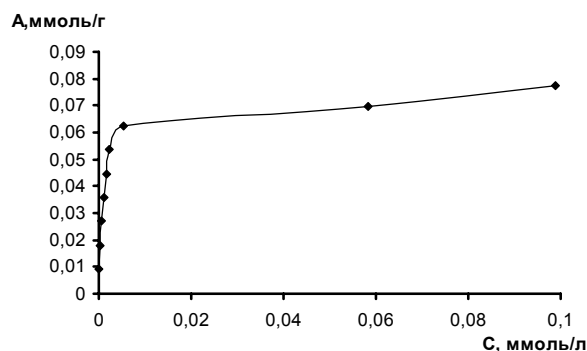


Fig. 2. Sorption isotherm of perrhenate-ions with activated carbon

The character of sorption isotherm given in Fig. 2 does not allow indicating definitely the type of adsorptive isotherm. Therefore, the experimental data were treated by the equation of Langmuir and Freundlich in their linear form.

As a result of calculations the Freundlich isotherm was plotted however the Freundlich equation turned out to be not appropriate for describing rhenium sorption as the dependence is nonlinear.

To check out the possibility of describing sorption processes by Langmuir isotherm:

$$\frac{C_{\text{равн}}}{A} = \frac{1}{kA_{\infty}} + \frac{C_{\text{равн}}}{A_{\infty}},$$

where A is the quantity of adsorbed substance; A_{∞} is the capacity of monolayer, k is the constant; $C_{\text{равн}}$ is the equilibrium concentration.

Let us introduce the notations:

$$a = \frac{1}{A_{\infty}}; b = \frac{1}{A_{\infty} \cdot k}; y = \frac{C_{\text{равн}}}{A},$$

then the equation

$$\frac{C_{\text{равн}}}{A} = \frac{1}{k \cdot A_{\infty}} + \frac{C_{\text{равн}}}{A_{\infty}}$$

has a form $y=ax+b$.

Isotherm of perrhenate-ion sorption with AC calculated by the Langmuir equation is given in Fig. 3.

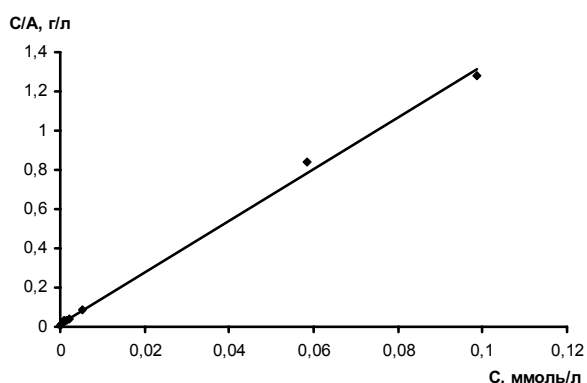


Fig. 3. Langmuir isotherm in linear coordinates for rhenium sorption

Static exchange capacity (SEC) of AC by rhenium $A_s=0,0763$ millimole/g or 14,2 mg/g was calculated.

The obtained experimental data showed that for describing sorption of perrhenate-ion by AC in the range of concentrations of 0,5...100 mg/dm³ the isotherm of monomolecular adsorption of Langmuir may be applied.

As in ores the main accompanying elements for rhenium are molybdenum, tungsten, aurum, argentum and a number of other metals their influence on the process of sorptive concentration of perrhenate-ions by AC was studied. For this purpose the solutions with content of different ratios of metals to rhenium were prepared, sorption at AC under UVR was carried out, the obtained systems were filtered, rhenium content in sorbent was measured by the method of XFA, Table 1.

Table 1. Influence of accompanying elements on the process of sorptive concentration of perrhenate-ions by AC

	Ratio Re:Me							
	1:1		1:30		1:50		1:100	
	Introduced Re, mg/l	Found Re, mg/l	Introduced Re, mg/l	Found Re, mg/l	Introduced Re, mg/l	Found Re, mg/l	Introduced Re, mg/l	Found Re, mg/l
Re : W	6	4,11	3,96	6	2,58	5	1,42	
		4,21	3,93		2,12		2,04	
		4,09	4,02		3,14		2,13	
Re : Mo	6	5,99	5,9	6	6,33	6	6,15	
		6,23	6,03		6,02		6,03	
		6,05	6,2		6,1		6,09	
Re : Au	10	8,58	9,43	10	8,32	9	7,32	
		9,14	9,68		7,95		6,94	
		9,83	9,05		8,36		7,22	
Re : Pt	10	9,45	9,24	10	7,49	9	5,59	
		10,1	9,76		8,04		5,75	
		8,96	9,87		8,06		5,99	

As a result of carried out works it was stated that molybdenum, aurum, argentum, copper at their ratio to rhenium 100:1, 30:1, 30:1, 30:1 respectively do not influence the determination of perrhenate-ions by the method of XFA therefore, rhenium determination by the method of XFA with these elements is possible. Presence of tungsten influences rhenium determination though their analytic lines are not juxtaposed. Tungsten

influence consists in absorbing rhenium fluorescent radiation and decreasing its analytical signal.

Found optimal conditions of rhenium concentration at BAU (pH=1,5...2; sorption time is 10 min; UVR; SEC =14,2 mg/g) allowed developing the technique of roentgen fluorescent determination of rhenium after its sorptive concentration by AC from nitro-acid solutions irradiated by ultraviolet [7]. The calibrating diagrams for rhenium determining in the range of concentrations of 0,5...100 mg/l in standard solutions (Fig. 5, a) and determination of rhenium in the range of concentrations of 0,25...5,0 mg/l with molybdenum and tungsten were obtained (Fig. 5, b).

Plotting the calibrating dependences for determining Re with W the standard solutions in which the ratio of concentration of Re to W amounts 1:50 were prepared. It is seen from Fig. 5, a that at the selected method of recording W influence the calibration equation Re remains linear even at fifty fold excess of W(VI) ions in the range of rhenium concentrations from 0,5 to 5 mg/dm³. Re determination at W presence at their ratio 1:1000 is possible according to the given dependences, Table 2.

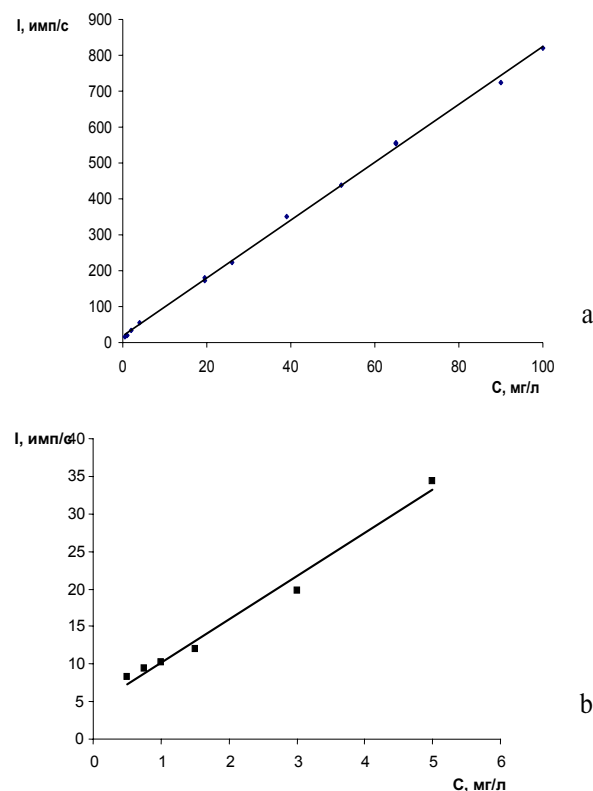


Fig. 5. Calibrating diagrams for determining Re(VII) and Re(VII) with W(VI) (Solution volume is 10 ml, pH=1,5...2,5, sorbent mass is 0,3 g, sorption time is 10 min at UVR influence): a) Re; b) Re with W

The obtained calibrating dependences allowed determining rhenium in real objects, in the given case in aurum-gold raw material, Table 3. The method of inversion voltamperometry was the comparison method (TPU, Tomsk).

Table 2. Validation of Re(VI) determination with W(VI) by the method of XFA

Introduced ReO_4^- , mg/l	Re:W	Found ReO_4^- , mg/l
1	1:50	1,228
		1,015
		0,968
4	1:100	3,940
		4,170
		3,981
3	1:1000	2,912
		2,876
		2,965

It is seen from Table 3 that the obtained results coincided satisfactorily with contents found by the method of TVA that indicates the possibility of applying the developed technique for determining rhenium in ores with accompanying elements by the method XFA.

Table 3. The results of determining Re in ores of different composition

Deposit	Ore material	XFA $\text{C} \cdot 10^5$, %	IV $\text{C} \cdot 10^5$, %
Nezhdaninskoe	Pyrite	$7,12 \pm 0,06$	$7,12 \pm 0,05$
Boko-Vasilievskoe	Sulfoarsenide	$10,20 \pm 0,02$	$9,61 \pm 0,06$
Akzhal	Sulphidized siltstone	$4,18 \pm 0,03$	$4,21 \pm 0,03$
Baladzhal	Black shales	$0,83 \pm 0,04$	$0,84 \pm 0,04$
Dzhumba	Pyrite	$0,95 \pm 0,04$	$0,96 \pm 0,03$
Bakyrchik	Sulphidized siltstone	$2,04 \pm 0,02$	$1,78 \pm 0,03$
Bolshevik	Pyrite and sulfoarsenides	$3,16 \pm 0,02$	$3,17 \pm 0,05$
Sukhoy log	Siliceous-carbonaceous siltstones	$0,56 \pm 0,05$	$0,37 \pm 0,04$
Nezhdaninskoe	Pyrite	$1,07 \pm 0,04$	$0,82 \pm 0,04$
Olimpiadinskoe	Black shales	$0,63 \pm 0,03$	$0,54 \pm 0,02$

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Received on 26.10.2006