=========== **ARTICLES** ===========

Determination of Rhenium in Gold-Containing Ores by X-Ray Fluorescence Spectrometry

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Abstract—A procedure is developed for determining rhenium in gold-containing ores by X-ray fluorescence spectrometry. The adsorption preconcentration of perrhenate ions on activated charcoal is studied. It is found that the pH of the solution, the time of exposing the adsorbent to the solution, UV irradiation, and the presence of associate elements (tungsten, gold, silver, and copper) affect the adsorption. The procedure is applied to the X-ray fluorescence determination of rhenium in gold-containing ores from different deposits.

The determination of rhenium in geological samples is difficult, because its industrial concentrations in them are low and because tungsten and molybdenum that are associated with rhenium in ores interfere with its determination by the available methods of analysis. The methods of determining rhenium in mineral raw materials are rather exhaustively reviewed in [1–3]. The adsorption preconcentration of perrhenate ions with activated charcoal (**AC**) is one of the most efficient techniques for recovering and preconcentrating ReO_4^- from solutions with high concentrations of nonferrous and other metal salts. The use of preconcentration to enhance the sensitivity of the determination is not the only and often is not a principal reason. Preconcentration is required when rare metals are inhomogeneously distributed in a sample and the representative test sample would be too large without preconcentration. Preconcentration also allows the analysis of geological samples that differ in composition to be unified. As far as X-ray fluorescence spectrometry (**XFS**) is concerned, preconcentration alleviates the challenge of obtaining calibration characteristics of similar type matrices [4].

The goal of this work is to choose the optimum conditions for the adsorption preconcentration of perrhenate ions on a BAU-A activated charcoal and to develop a procedure for the X-ray fluorescence determination of rhenium in gold-containing ores in the presence of tungsten and molybdenum.

EXPERIMENTAL

We used a standard (100 mg/L) solution of Re(VII) in 3 M HNO_3 to study the adsorption characteristics. After dissolving metallic rhenium, the latter occurred in the solution as ReO_4^- [1]. Model mixtures containing different amounts of ReO_4^-, were prepared by diluting the standard solution with a 3 M HNO_3 solution immediately before the analysis. ReO_4^- was adsorbed on a BAU-A activated charcoal with a total pore volume of at least 1.6 cm^3/g with respect to water and an adsorption activity of at least 60% with respect to iodine. Adsorbent granules we powdered in an agate mortar to sizes of less than 50 μm.

The effect of the time of exposing the BAU-A adsorbent to the solution on the recovery factor of ReO_4^- was studied under and without the ultraviolet irradiation (UVI) of solutions. As a source of UVI, we used a DRT-220 high-pressure mercury lamp. Perrhenate ions were adsorbed under static conditions. For this purpose, 0.3 g of BAU-A was added to a 10-mL portion of a solution. After adsorption, the adsorbent was filtered and the residue was dried. The amount of the adsorbed perrhenate ions was determined by XFS [5] using a Spektroskan spectrometer (NPO Spektron, St. Petersburg). The parameters of the X-ray tube with the molybdenum anode were as follows: voltage, 40 kV; current, 100 mA; and the analyzing crystal, LiF. The time of a single measurement was 200 s. The lines Lα1 and Lβ2 served as the analytical lines in the determination of rhenium. The intensity of the fluorescence at the specified lines was determined by subtracting the background intensity. The degree of adsorption was controlled by the stripping voltammetry of filtrate using a TA-1 voltammetric analyzer (NPO Tekhnoanalit, Tomsk) and following the procedure described in [6]. A three-electrode cell containing a graphite working electrode impregnated with polyethylene (**IGE**) that was prepared by the procedure [6], a saturated silver–silver chloride reference electrode, and a platinum auxiliary electrode was used.
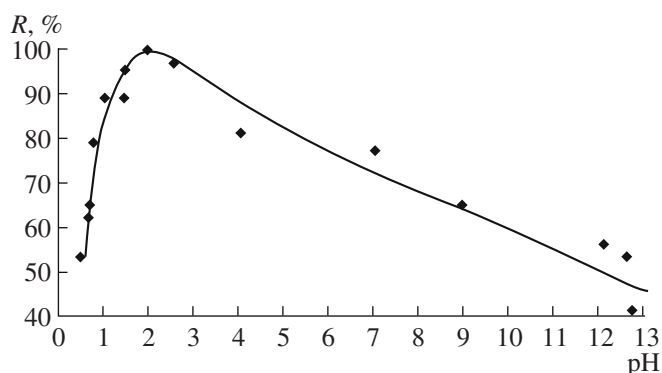
Fig. 1. Effect of the pH of a solution on the degree of perrhenate ion adsorption (R is the amount of adsorbed perrhenate ion, %).

Fig. 2. Effect of time on the adsorption of perrhenate ions with AC from nitric acid solutions (*1*) under UVI and (*2*) without UVI (the solution volume, 10 mL; the adsorbent mass, 0.3 g; R is the amount of adsorbed perrhenate ion, %).
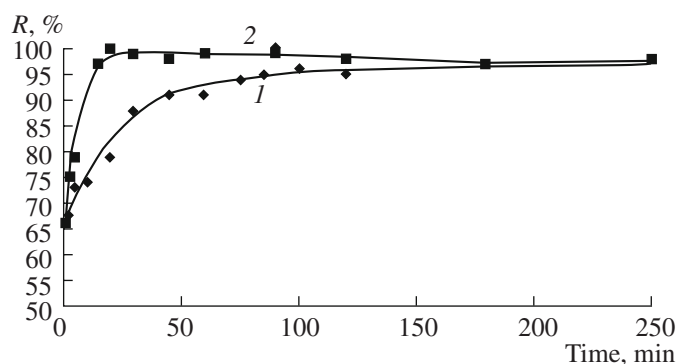
RESULTS AND DISCUSSION

The goal of our study was the choice of the optimum adsorption conditions: the pH of the solution, the time of the adsorption process, and the effect of the UVI.

It is known that AC can adsorb perrhenate ions from acidic and alkaline solutions. The pH of solutions containing perrhenate ions was varied from 0.5 to 13 by adding concentrated solutions of acid (HNO_3) or alkali (NaOH). After adsorption, the adsorbent was studied by XFS. The experimental data are graphically presented in Fig. 1. It is seen that the capacity of the adsorbent (activated charcoal) exhibited a clearly defined dependence on the pH of a test solution. The static exchange capacity of BAU-A with respect to perrhenate ions was maximum in the pH range 1.5–2.5.

The time of exposing the adsorbent to the solution is another factor that affects the extent of adsorption. The analysis of the experimental data (Fig. 2) shows that the highest degree of adsorption preconcentration of perrhenate ions on BAU (95–98%) was attained in a 90-min adsorption. Such a long time is unacceptable for routine analysis. Therefore, we studied the possibilities of intensifying the adsorption by the UVI of solutions during the adsorption preconcentration of perrhenate ions on BAU-A. Figure 2 graphically presents the adsorption of perrhenate ions from nitric acid solutions by BAU-A as a function of the UV-irradiation time.

As follows from Fig. 2, even after a 10-min irradiation, perrhenate ions were almost completely (95–99%) adsorbed by AC. In the absence of UVI, the adsorption of perrhenate ions for the same time was at most 80%. The fact that rhenium(VII) can also be completely recovered without UVI only for a longer time (90 min or longer) suggests that, under natural conditions, adsorption may occur under the irradiation of solutions with visible light.

Adsorption processes that occur on activated charcoal can be described by different isotherms. The determination of the type of adsorption isotherm suggests the adsorption mechanism and allows the adsorption capacity of the adsorbent to be determined.

The adsorption isotherm was constructed using rhenium solutions with concentrations of 50, 100, 150, 200, 250, 300, 350, 400, and 450 mg/L. The mass of the BAU-A sample was 0.3 g. The acidity of the solutions was maintained at pH 1.5–2.5. The time of adsorption under UVI was no longer than 10 min. The concentration of the adsorbed rhenium was calculated from experimental data by formula (1):

$$A_{exp} = \frac{c_{start} - c_{resid}}{m}V, \qquad (1)$$

where A_{exp} is the experimental adsorption of rhenium; c_{start} is the starting concentration of rhenium in the solution, mg/L; c_{resid} is the residual concentration of rhenium in the solution after adsorption, mg/L; m is the mass of AC (0.3 g); and V is the volume of the solution for adsorption, L.
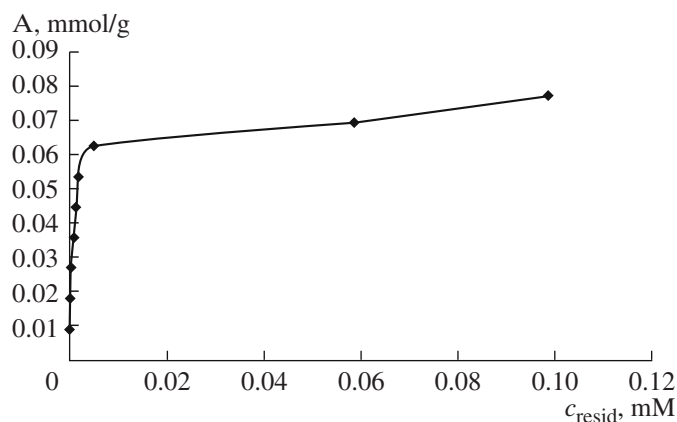
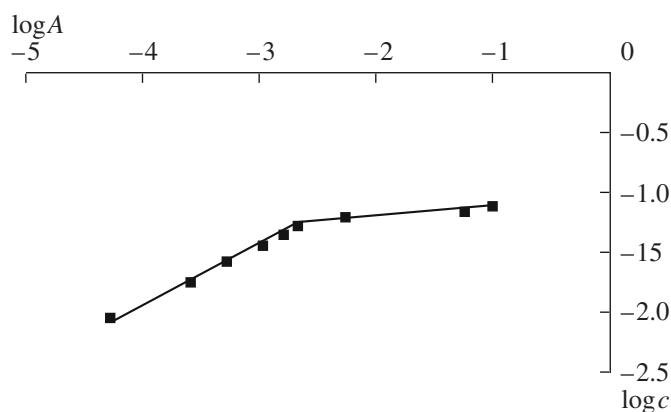**Fig. 3.** Isotherm of rhenium adsorption with activated charcoal.

Fig. 4. Isotherm of rhenium adsorption in the $\log A$–$\log c$ coordinates.
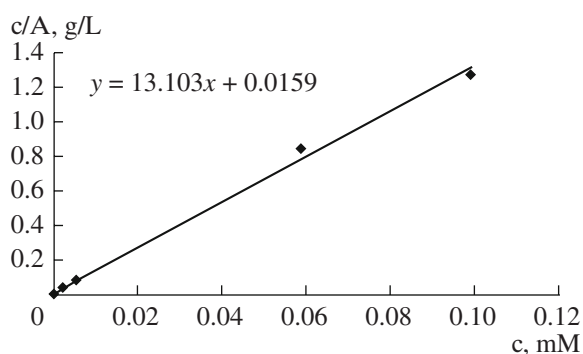

Fig. 5. Isotherm of rhenium adsorption in the (c/A)–c coordinates.

The adsorption isotherm was built using experimental data calculated by formula (1) (Fig. 3).

The character of the adsorption isotherm did not allow us to unambiguously determine its type. Therefore, the experimental data were processed by the Freundlich and Langmuir equations in linear forms.

The Freundlich equation has the following form:

$$A = \beta c^{1/n}, \qquad (2)$$

where β and $1/n$ are the empirical constants and c is the adsorbate concentration in the solution that is attained in the adsorption process at a given moment in time.

The constants β and n in equation (2) were determined graphically after logarithming

$$\log A = \log \beta + \frac{1}{n} \log c \qquad (3)$$

and constructing the $\log A$ – $\log c$ curve (Fig. 4).

It is seen that this dependence is nonlinear; hence, it follows that the Freundlich equation is inapplicable to the description of rhenium adsorption from nitric acid solutions under UVI.

The experimental data were presented in the (c/A)–c coordinates (Fig. 5) to verify the description of the process by the Langmuir isotherm:

$$\frac{c}{A} = \frac{1}{KA_\infty} + \frac{c}{A_\infty}, \qquad (4)$$

where A is the amount of the adsorbed substance; A_∞ is the capacity of a monolayer, that is, the maximum amount of the substance that can be adsorbed as a monolayer at the surface of a solid; and K is the constant of the adsorption equilibrium.

The obtained dependence with a correlation coefficient of 0.98–0.99 is a straight line, which points to the possibility of using it to describe the adsorption of perrhenate ions by AC.

It follows from Fig. 5 that $1/A_\infty = 13.103$ and, hence, $A_\infty = 0.076$ mmol/g or $A_\infty = 14.2$ mg/g. The found value is a static exchange adsorption capacity of BAU-A adsorbent with respect to perrhenate ion.

Because molybdenum, tungsten, gold, silver, and some other metals are the main elements that are associated with rhenium in ores, their effect on the adsorption preconcentration of perrhenate ions with AC was studied. It was found that molybdenum, gold, silver,
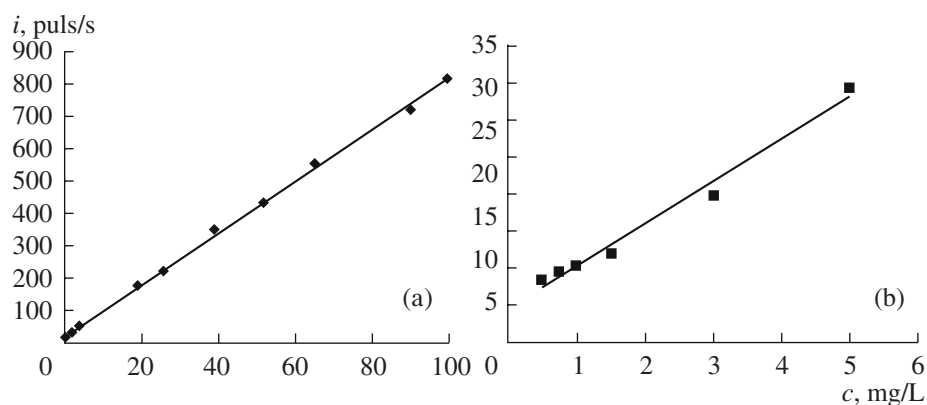
Fig. 6. Calibration graphs for determining rhenium (a) in the absence and (b) presence of tungsten (the solution volume, 10 mL; pH 1.5–2.5; the adsorbent mass, 0.3 mg; and the adsorption time under UVI, 10 min).

and copper taken in the ratios of 100, 30, 30, and 30, respectively, to 1 rhenium did not interfere with the determination of perrhenate ions by XFS. Hence, rhenium can be determined in the presence of these elements. However, the presence of tungsten affected the determination of rhenium, although their analytical lines were not superimposed. The effect of tungsten consisted in absorbing rhenium fluorescence radiation and reducing its analytical signal.

The found optimum conditions for rhenium preconcentration on BAU (pH 1.5 to 2; τ_{sorb} = 10 min; UVI; static exchange capacity = 14.2 mg/g) allowed us to develop a procedure for the X-ray fluorescence determination of rhenium after its adsorption preconcentration on activated charcoal from nitric acid solutions irradiated with UV light [7]. Calibration graphs were built for determining 0.5 to 100 mg/L rhenium in standard solutions and for determining 0.25–5 mg/L rhenium in the presence of molybdenum and tungsten (Fig. 6).

To construct calibration graphs for determining rhenium in the presence of tungsten, standard solutions with a rhenium-to-tungsten concentration ratio of 1 : 50 were prepared. Figure 6a demonstrates that, at the chosen way of taking the effect of tungsten into account, the calibration graph for rhenium determination was linear even in the presence of a 50-fold amount of tungsten(VI) in the rhenium concentration range from 0.5 to 5 mg/L. As follows from Table 1, rhenium can be determined from the calibration graph in the presence of tungsten at a ratio of Re to W of 1 : 1000 (Table 1).

The obtained calibration graphs allowed rhenium to be determined in real samples; in our case, in gold-containing raw materials (Table 2). The following procedure was used to pass rhenium from ore samples into a solution: depending on the rhenium content, a 1–10-g ore sample was treated with concentrated hydrofluoric acid upon heating to 150°C to the point of a dry residue to remove silicon fluoride. The residue was dissolved in concentrated nitric acid. Along with rhenium, molybde-

num, tungsten, and some other associate elements passed into the solution. Sample preparation was carried out in corundum crucibles. The solution obtained was cooled and filtered. Rhenium was adsorbed from it with BAU-A activated charcoal upon which it was determined by X-ray fluorescence spectrometry. For comparison, rhenium was determined by stripping voltammetry (TPU, Tomsk) (Table 2).

The comparison showed that the discrepancy between the results of analysis of the same sample was satisfactory. The results obtained demonstrate that our procedure is suitable for determining rhenium in ores of different compositions by X-ray fluorescence spectrometry.

Table 1. Verification of the accuracy of determining rhenium(VI) in the presence of tungsten(VI) by XFA

Added ReO_4^-, mg/L	Re : W	Found ReO_4^-, mg/L
1.000	1 : 50	1.228
		1.015
		0.968
4.000	1 : 100	3.940
		4.170
		3.981
3.000	1 : 1000	2.912
		2.876
		2.965

Table 2. Determination of rhenium in ores of different compositions by XFA

Deposit	Ore material	$C \times 10^{-5}$, % (XFA)	$C \times 10^{-5}$, % (SVA)
Nezhdaninskoe	Pyrite	7.12 ± 0.06	7.12 ± 0.05
Boko-Vasil'evskoe	Sulfoarsenides	10.20 ± 0.02	9.61 ± 0.06
Akzhal	Sulfidized alevrolit	4.18 ± 0.03	4.21 ± 0.03
Baladzhal	Black shale	0.83 ± 0.04	0.84 ± 0.04
Dzhumba	Pyrite	0.95 ± 0.04	0.96 ± 0.03
Bakyrchik	Sulfidized alevrolit	2.04 ± 0.02	1.78 ± 0.03
Bol'shevik	Pyrite and sulfoarsenides	3.16 ± 0.02	3.17 ± 0.05
Sukhoi log	Siliceous-carbon alevrolits	0.56 ± 0.05	0.37 ± 0.04
Olimpiadinskoe	Black shale	0.63 ± 0.03	0.54 ± 0.02

REFERENCES

1. *Analiticheskaya khimiya redkikh elementov* (Analytical Chemistry of Rare Elements), Ermakov, A.N., Ed., Moscow: Nauka, 1988.
2. Karpov, Yu.A., Kim, E.M., Ryazanova, L.N., and Shiryaeva, O.A., *Zavod. lab.,* 1990, vol. 56, no. 12, p. 1.
3. Losev, V.N., Buiko, E.V., Elsuf'ev, E.V., Belousov, O.V., and Trofimchuk, A.K., *Zavod. lab. diagn. mater.*, 2005, vol. 71, no. 2, p. 16.
4. Lebedev, K.B., *Renii* (Rhenium), Moscow: Metallurgizdat, 1963.
5. Kolpakova, N.A., Buinovskii, A.S., and Zhidkova, I.A., *Fizika*, 2004, no. 12, p. 147.
6. Kolpakova, N.A., Gol'ts, L.G., and Avgustinovich, O.V., RF Patent 2247369, *Byull. Izobret.*, 2005, no. 6.
7. Buinovskii, A.S., Gol'ts, L.G., Zhidkova, I.A., and Kolpakova, N.A., RF Patent 2272278, *Byull. Izobret.*, 2006, no. 8.