

UDC 546.26–162

## Determining the Mechanism of Gold Concentration from Solution on BAU-A Charcoal under Ultraviolet Irradiation

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(Received March 22, 2010; revised March 3, 2011)

### Abstract

Using the method of Fourier transform infrared spectroscopy, a study was performed concerning the composition of surface functional groups inherent in birch activated carbon BAU-A as well as changing their qualitative and quantitative composition in the course of gold sorption from chloride solutions with different composition under the action of ultraviolet irradiation and without it. It has been demonstrated that under the action of UV irradiation the amount of hydroxyl groups on the surface of birch activated carbon exhibits an increase, which results in an increase in its sorption capacity for  $[\text{AuCl}_4]^-$  anions. The method of EXAFS spectroscopy revealed that after the sorption from hydrochloric acid solutions, gold on the surface of birch activated carbon is in the form of dimers  $\text{Au}_2\text{Cl}_6$  both after ultraviolet irradiation and without it. The sorption mechanism is suggested to involve the following stages: ion exchange of surface hydroxyl groups for the complex ions  $[\text{AuCl}_4]^-$  as well as the formation of dimers  $\text{Au}_2\text{Cl}_6$  on the surface of carbon.

**Key words:** activated carbon BAU-A, oxygenated surface functional groups, ultraviolet irradiation, adsorption, tetrachloroaurate ion, Fourier transform infrared spectroscopy

### INTRODUCTION

The mechanism of gold sorption on activated carbon species [1] are under extensive discussion in the literature. In the case of the sorption of  $[\text{AuCl}_4]^-$  complexes from hydrochloric acid solutions onto the samples of birch activated carbon (BAU-A), the most probable mechanism [2–4] determining the ion exchange between  $[\text{AuCl}_4]^-$  and the surface functional groups (SFG) of coal, the formation complexes at the expense of the donor-acceptor interaction between the delocalized *p* electrons of carbon atom and the unoccupied *d* orbitals of gold [5] with further reducing the complex to form metal due to electron-donor properties of carbon. According to the authors of [3, 4], the

stage of tetrachloroaurate ion exchange occurs only with respect to hydroxyl ions formed in the course of operating the oxygen gas electrode. In this case, the authors of the papers ignored other oxygen-containing SFG, already present on the surface of activated carbon: phenol (hydroxyl), carbonyl, carboxyl, ester, enol, lactone, as well as sulphur- and nitrogen-containing groups [6, 7]. However, the specific sorption of complexes  $[\text{AuCl}_4]^-$  is also possible due to ion exchange with morphological oxygen-containing SFG and complexation with other SFG those do not contain oxygen.

Our studies performed earlier demonstrated that under the action of ultraviolet irradiation (UVI) the process of gold sorption from hydrochloric acid solutions onto carbon BAU-A

occurs faster and better than without it [8, 9]. The mechanism of this effect is under hypothesizing. The ultraviolet radiation could affect both on each of the stages of gold sorption onto BAU-A, and on each of the components involved in the system carbon sorbent-solution. Most likely, a great part of the radiation should be absorbed by the BAU-A as by a black body. In this connection, first of all UVI could act on the sorbent, rather than on the solution, as we proposed earlier in [8, 9]. Consequently, the action of ultraviolet irradiation should result in changing the characteristics of the sorbent such as appearing new surface groups or decaying those already exist. Consequently, there could be changing the adsorption capacity of BAU-A, its potential (and reductive ability), the polarity of the sorbent surface as well as a number of other properties.

Purpose of the work consisted in ascertaining the mechanism concerning gold sorption from hydrochloric acid solutions into the BAU-A, as well as the influence of ultraviolet irradiation on this mechanism.

## EXPERIMENTAL

In order to determine the SFG composition we used the method of Fourier transform IR spectroscopy.

The FT-IR spectra were obtained at the Scientific Analytical Center of TPU (Tomsk, Russia) with the use of a Nicolet-5700 FT-IR spectrometer in a transmission mode within the range of  $4400\text{--}390\text{ cm}^{-1}$ . The samples for analysis were prepared by pressing with KBr. The spectra of BAU-A samples were also registered at the Institute of Inorganic Chemistry of the SB RAS (Novosibirsk) employing a Bruker IFS-85 FT-IR spectrometer within the range of  $4000\text{--}400\text{ cm}^{-1}$  in transmission and absorption modes.

As the objects of investigation we used the samples of activated carbon BAU-A those contacted during a preset time (5–20 min) with 1 M HCl solution, model gold hydrochloric acid solutions ( $100\text{ mg/dm}^3$ ) as well as gold processing (technological) solutions under the influence of ultraviolet irradiation and without it. Further the coal samples were filtered and dried at room temperature. The technological solutions

represented the solutions of gold leaching from the concentrate by the mixture of sulphuric acid, sodium chloride (in an amount sufficient to form tetrachloroaurate ion) and manganese dioxide. The concentration of gold therein was equal to  $80\text{ mg/dm}^3$ , the residual concentration of sulphuric acid amounted to 2 M. As a source of UV we used a DRS-20 low-pressure mercury lamp. We also investigated a sample of BAU-A irradiated by means of high-pressure UV lamp XRD-250 W for 20 min in dry air.

The conclusions concerning the presence or absence of either functional group on the surface were made on the basis of studying a series of samples where the variation of the material treatment conditions naturally reflected in the dynamics of the FT-IR spectra. The interpretation of the spectra was performed according to the data from [1016].

Chemical gold species adsorbed on the surface of BAU-A samples were determined using EXAFS-spectroscopy according to the technique described in [17], employing an EXAFS unit at the IC of the SB RAS (Novosibirsk).

## RESULTS AND DISCUSSION

Figures 1–3 demonstrate the spectra of an intact (untreated) sample of activated carbon BAU-A wherein oxygen-containing groups were identified such as the OH group inherent in hydroxyl, carboxyl and phenol (a broad band at  $3435\text{--}3446\text{ cm}^{-1}$ ), secondary alcohol groups ( $1092\text{--}1099\text{ cm}^{-1}$ ). To a lesser extent the transmission spectra exhibited vibration bands inherent in carboxyl groups. More distinctly they could be observed only in the spectrum obtained

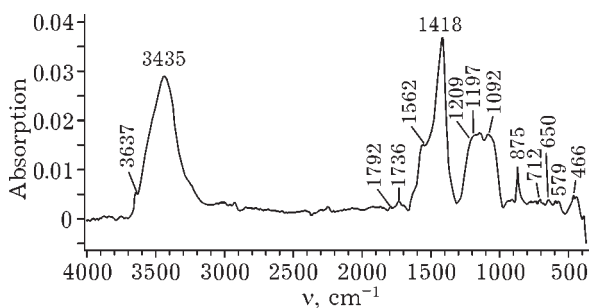


Fig. 1. Absorption spectrum of BAU-A sample obtained using a Bruker IFS-85 FT-IR spectrometer in an absorption mode.

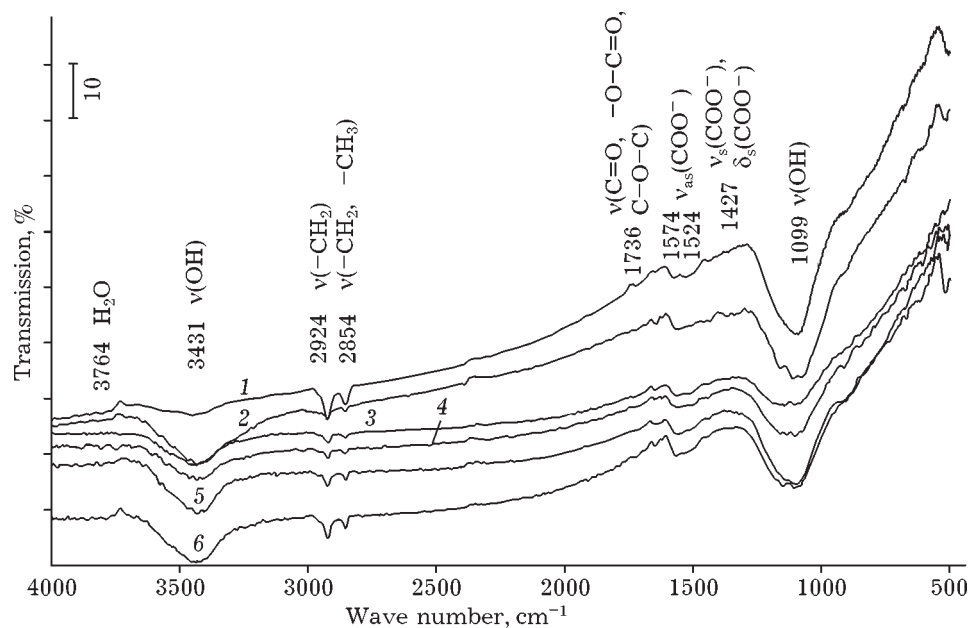


Fig. 2. Transmission spectra of the initial sample BAU-A, subjected to ultraviolet radiation (UVI) in dry condition, and sample BAU-A which was in contact with the 1 M HCl solution under the action of ultraviolet irradiation and without it: 1 – intact; 2 – exposed to ultraviolet irradiation in dry condition; 3, 4 – without UVI, contact time 10 and 20 min, respectively; 5, 6 – with UVI, contact time 10 and 20 min, respectively.

by a Bruker IFS-85 FT-IR spectrometer in an absorption mode (see Fig. 1). For their interpretation we used a procedure of stretching weak signals. It was revealed that the band centred at  $1562\text{ cm}^{-1}$  in the absorption spectra (see Fig. 1) and at  $1574$ ,  $1524\text{ cm}^{-1}$  in the transmission spectra (see Figs. 2, 3) correspond to asymmetric stretching vibrations of ionized carboxyl groups  $\text{COO}^-$ , the bands at  $1417\text{ cm}^{-1}$  in the absorption spectrum (see Fig. 1) and at  $1427\text{ cm}^{-1}$  in the transmission spectrum (see Figs. 2, 3) represent symmetric vibrations of  $\text{COO}^-$  groups. The line at  $1736\text{ cm}^{-1}$  in the absorption and transmission spectra (see Figs. 1–3) can be attributed to the vibrations of the  $\text{C}=\text{O}$  bond in the  $\text{COOH}$  group [11], or to the vibrations in lactone groups  $\nu(\text{C}-\text{O}-\text{C})$ , and  $\nu(-\text{O}-\text{C}=\text{O})$  [16]. The presence of lactone groups on the initial BAU-A surface is also confirmed by the presence of the bands at  $1209$  ( $\delta\text{ O}-\text{C}-\text{O}$ ) and  $875\text{ cm}^{-1}$  ( $\text{O}-\text{C}=\text{O}$ ) in the absorption spectra. We also identified the adsorbed water (at  $3637\text{ cm}^{-1}$  in the absorption spectrum and at  $3764\text{ cm}^{-1}$  in the transmission spectrum) and aliphatic groups such as  $-\text{CH}_2$  ( $2924\text{ cm}^{-1}$ ),  $-\text{CH}_2$ ,  $-\text{CH}_3$  ( $2854\text{ cm}^{-1}$ ) [10, 13]. No nitrogen- and sulphur-containing SFG were found by means of the FT-IR spectroscopy. Thus, in the case when the sorption of gold in-

volves such interaction as ion exchange or complex formation, the interaction should occur with oxygen-containing SFG or with coal matrix.

Figures 2–4 demonstrate the IR spectra of samples BAU-A (intact and rich in gold) obtained under contact with a solution of HCl with the action of ultraviolet irradiation and without it. The comparison of IR spectra demonstrated that the spectra of treated BAU-A samples exhibit all the main bands (with minor shifts) observed in the spectrum of the intact BAU-A. Basing on the data obtained, we revealed some regularities of changing the composition and amount of SFG depending on the conditions of BAU-A sample processing.

Firstly, when contacting the BAU-A with HCl solution the intensity of the peak at  $3430\text{ cm}^{-1}$  corresponding to the OH groups inherent in hydroxyl, carboxyl and phenol [11] exhibits an increase with time. For the samples irradiated with UV, these peaks are more pronounced comparing to the samples not subjected to UV irradiation (see Fig. 2). These changes indicate that new OH groups appear on the surface of the BAU-A when contacting with hydrochloric acid aqueous solutions and the UVI causes this process to be more intense.

The sorption of gold from model hydrochloric acid solutions without UV exposure results

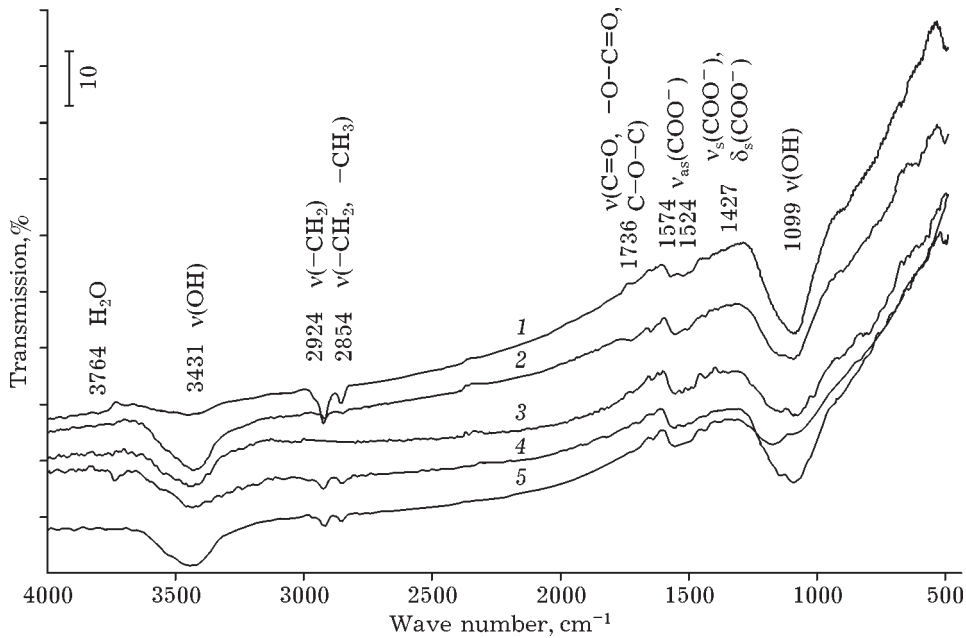


Fig. 3. Transmission spectra of BAU-A sample which was in contact with the model hydrochloric acid solutions of gold ( $100 \text{ mg}/\text{dm}^3$ ): 1 – intact; 2, 3 – contact time 5 min, no UVI and with UVI, respectively; 4, 5 – contact time 10 min, no UV and with UVI, respectively.

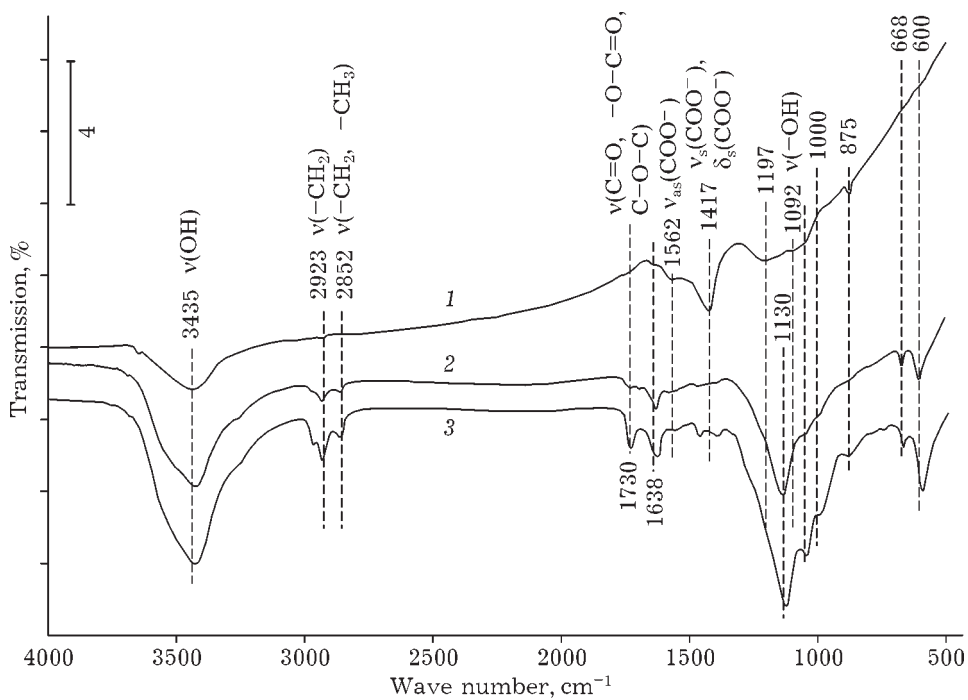


Fig. 4. Transmission spectra of BAU-A samples contacted with technological gold leaching solutions: 1 – initial; 2, 3 – contact time 10 min, no UVI and with UVI, respectively.

in the fact that the intensity of the peak corresponding to the vibrations of hydroxyl groups, slightly decreases with time (see Fig. 3), which may be interpreted as a result of the ongoing ion-exchange of surface OH groups for  $[\text{AuCl}_4]^-$  anions. The sorption of gold under the influence of ultraviolet irradiation the peak intensity value remains the same within 5 or 10 min. These data are consistent with the information obtained by the authors of [1, 22] concerning the fact that the sorption from model gold solutions in hydrochloric acid at such concentration values ( $100 \text{ mg/dm}^3$ ) results in a complete absorption of gold within the first 5–10 min. In addition, further increasing the amount of surface groups is not possible, since the surface of the sample BAU-A by this moment is already covered by adsorbed gold. With the sorption of gold from technological solutions (see Fig. 4) the peak at  $3435 \text{ cm}^{-1}$  ( $\nu(-\text{OH})$ ) is approximately three-fold increased without UV exposure being 3.5-fold increased under the action of ultraviolet irradiation. To all appearance, this indicates the surface oxidation of BAU-A in the presence of permanganate ion in sulphuric acid medium.

The irradiation of BAU-A samples in dry condition also results in significant changes: the peak at  $3431 \text{ cm}^{-1}$  ( $\nu(-\text{OH})$ ) exhibits a 4.7-fold increase compared to the intact (initial) one (see Fig. 2). This could be explained by the fact that the influence of ultraviolet irradiation gives rise to an additional formation of surface oxygen-containing functional groups.

Secondly, the IR spectra obtained exhibit the most intense of stretching vibration bands inherent in  $\text{OH}^-$ , C–OH and C–OX groups. According to [11], the group of peaks at 1050, 1100 and  $1150 \text{ cm}^{-1}$  characterizes the primary, secondary and tertiary alcohol OH groups, respectively. An intact BAU-A sample exhibits only an intense peak at  $1100 \text{ cm}^{-1}$ , which corresponds to the secondary alcohol OH group. With UVI of dry BAU-A sample, this peak splits into three peaks ( $1000$ ,  $1100$  and  $1130 \text{ cm}^{-1}$ ) of high intensity. Other samples demonstrate the peak at  $1100 \text{ cm}^{-1}$  (secondary) having a lower intensity than the intact sample. To all appearance, the action of ultraviolet irradiation could cause the  $-\text{CH}_3$  groups to undergo cleavage and the sec-

ondary alcohol groups to transform into the primary alcohol groups (see Figs. 2–4).

Thirdly, all the samples demonstrated peaks corresponding to the vibrations of aliphatic groups: the peak at  $2924 \text{ cm}^{-1}$  (symmetric and asymmetric stretching vibrations of  $-\text{CH}_2$ ) and  $2854 \text{ cm}^{-1}$  ( $\nu(-\text{CH}_2, -\text{CH}_3)$ ). These peaks are distinctly visible in the spectrum of the intact BAU-A sample and decrease when BAU-A being in contact with chloride solutions. We observed a 3-fold decrease with no UVI and a 1.5-fold decrease under the influence of ultraviolet irradiation. It should be noted that after contacting the BAU-A sample with the solution of HCl within 20 min under UV irradiation peak intensity exhibited its original value. One could see that when BAU-A sample is in contact with the hydrochloric acid solutions, the amount of aliphatic groups decreases, whereas the UV action on the system BAU-A–HCl– $\text{H}_2\text{O}$  either causes the process to decelerate, or results in the formation of new aliphatic groups.

The irradiation of dry BAU-A sample also results in three-fold decreasing the intensity of peaks corresponding to the vibrations of aliphatic groups, which could indicate the destruction of these groups under the influence of ultraviolet irradiation. Upon contacting the BAU-A sample with gold leaching solutions the intensity of peaks corresponding to the vibrations of  $-\text{CH}_2$ ,  $-\text{CH}_3$  increases (see Fig. 4). In addition, for the samples subjected to ultraviolet irradiation, this effect is 2–4 times more pronounced than for the samples without UVI exposure. To all appearance, in the sulphuric acid medium and in the presence of  $\text{MnO}_2$  as an oxidant there are processes occurring different from the processes inherent in chloride environments. The presence of an oxidant results in the oxidation of the carbon sorbent surface, promoting the emergence of SFG, as evidenced by the authors of [18].

Fourthly, the behaviour of lines belonging to the vibrations of the carboxyl group and its components was investigated. The peaks at  $1427$  and  $1574 \text{ cm}^{-1}$  in the transmission spectrum (symmetric and asymmetric vibrations of ionized  $\text{COO}^-$ ) are almost unchanged when dry BAU-A sample contacting the hydrochloric acid solutions as well as under its irradiation with

slight increasing with its contacting the technological solutions of gold leaching.

Other lines inherent in the carboxyl groups were found in the spectra obtained by means of a Bruker IFS-85 spectrometer. The line at 1730–1736  $\text{cm}^{-1}$  corresponds to the vibrations lactone groups  $\nu(\text{C}-\text{O}-\text{C})$  and  $\nu(-\text{O}-\text{C}=\text{O})$  (or  $\nu(\text{C}-\text{OH})$ ), those were almost not pronounced in the initial BAU-A sample and the samples those contacted with HCl. However, these vibrations become pronounced in the samples contacted with gold processing (technological) solutions, whereas under the influence of ultraviolet irradiation this effect is much more pronounced. According to [19, 20], the peak at 1722  $\text{cm}^{-1}$  corresponding to  $\nu(\text{C}=\text{O})$  appeared after the oxidation of carbon sorbent NUMS. The same peak is observed also in the spectra of BAU-A sample contacted with gold leaching technological solution without UVI and (the most pronounced) under the influence of UVI (see Fig. 4). This peak is almost insignificant in the spectra of BAU-A sample after contacting HCl under the UVI, and without irradiation (see Fig. 2, the peak at 1730  $\text{cm}^{-1}$ ). The peak at 1197  $\text{cm}^{-1}$  can be attributed to the vibrations of C-OX, or  $\nu(\text{C}-\text{OH})$ , or  $\nu(\text{C}-\text{O}-\text{C})$ . Comparing to the initial sample, this peak increases to a considerable extent in the case of BAU-A sample contacting with technological solutions: 4-fold without UVI action, 7-fold – under the action of UVI (see Fig. 4).

Thus, changing the amount of SFG is greatly affected not only the UVI action, but also the composition of the solution under contacting:

1. Sulphuric acid solutions containing an oxidizing agent, provide occurring the process of BAU-A oxidation to produce oxygen-containing groups, the formation of C=O, C-OX, C-O-C, O-C=O, C-O-H, whereas under the influence of UVI this process is much more intense. In addition, we observed the formation of alcohol and hydroxyl groups as well increasing the amount of carboxyl groups.

2. In the hydrochloric acid medium, the amount of carboxyl, carbonyl, lactone and alcohol groups decreases; especially this phenomenon is pronounced under the influence of UVI. This could be caused either by the abstraction of these groups from the surface of BAU-A, or by transforming them into other SFG. Only the amount of hydroxyl groups exhibits an increase, and under the influence of UVI this process is more intense. The formation of OH groups is likely to occur as a result of the following processes: the interaction between adsorbed (or dissolved) oxygen with water molecules (in the process of acting the oxygen gas electrode), water decomposition under the influence of UVI [21], the oxidation of aliphatic groups.

To all appearance, the UVI action promotes SFG to be abstracted from the surface of BAU-A, whereas on the active sites formed in this manner there are of processes occurring those depend on the composition of the aqueous solution. These processes could represent, in particular, the decomposition of water molecules and the reduction of oxygen to form new hydroxyl SFG in hydrochloric acid medium or oxidation processes with the formation of oxy-

TABLE 1

Results of studying BAU-A samples with sorbed gold by EXAFS method

Sorptions conditions	Gold content in the sample, mass %	Bond type	Coordination sphere composition	
			Number of atoms in the closest three coord. spheres	Distance to the central atom, nm
3 h, UVI	0.4	Au-Cl	0.5 Au	2.788
			2.9 Cl	2.925
			2.0 Au	4.100
3 h, no UVI	0.4	Au-Cl	0.2 Au	2.723
			2.5 Cl	2.298
			1.2 Au	4.134

gen-containing SFG (carbonyl, carboxyl, and lactone) in the oxidizing  $\text{H}_2\text{SO}_4$  atmosphere in the presence of  $\text{MnO}_2$ .

The composition of gold compounds adsorbed on the surface of the sample of BAU-A under the influence of UVI and without it was determined by means of EXAFS spectroscopy. The conditions for obtaining the samples and the results of the analysis are presented in Table 1. The composition of three nearest coordination spheres of the central atom (Au) and the distance between this atom and chlorine ligands surrounding it were determined.

Comparing these results with data concerning the structure of gold compounds [22], we concluded that the samples whereon the sorption of gold from its chloride solutions was performed during 3 h, both under the impact of UVI, and without it, exhibit gold species presented mainly as dimers  $\text{Au}_2\text{Cl}_6$ . Metal species, whose presence would be indicated by revealing the Au–Au bond as well as a significant amount of gold atoms in the nearest coordination sphere (about 10), were not detected.

These results reject our previous hypothesis [8, 9] that the effect of UVI consists in intensifying the stage of reducing the adsorbed complexes to yield metal. However, it should be noted that this method allows one to determine a relatively high concentration of substances (about 0.1 mass %). Consequently, the fact that the metallic form of gold was not determined by EXAFS spectroscopy, could not be unambiguously interpreted as the absence of reduced gold in the sample of BAU-A. It is likely (and data obtained by the authors of [2, 3] support our hypothesis) that gold is present in the sample, but the amount is not sufficient to be determined using the method of EXAFS spectroscopy. So, the duration of the sorption procedure (3 h) was sufficient for the complete extraction of gold from solution, but not sufficient for the complete reduction to produce the metallic state. On the other hand, it is likely that there is a reverse process of chloride complex formation occurring; such cases were described for palladium [23]. According to our data, the duration of the sorption amounting to 20–120 min can result in only 5–15 % of gold readily desorbed from the surface of coal using weak solutions of hydrochloric acid. Thus, as dem-

onstrated by EXAFS, the species of gold existing on the surface of BAU-A are affected by the duration of concentration procedure rather than UVI.

Thus, the adsorption of gold on the surface of the BAU-A occurs in at least two stages such as ion exchange and the formation of dimers. The kinetics of these processes requires for further investigation. It is obvious that the stage of gold reduction on the surface of BAU-A is the longest (rate determining), whereas UVI, to all appearance, results in increasing the rate of the first stage, the sorption of noble metals onto carbon materials.

## CONCLUSION

It is demonstrated that the sorption of gold from hydrochloric acid on the surface of BAU-A occurs, to all appearance, in two stages such as the ion exchange of surface hydroxyl groups for the complex ions  $[\text{AuCl}_4]^-$  and the formation dimers  $\text{Au}_2\text{Cl}_6$  on the surface of carbon.

It is proved that the UVI can affect the process of gold sorption from its hydrochloric acid solutions both with an oxidant, and without it, to accelerate its first stage, ion exchange.

It is demonstrated that the exposure to UVI results in increasing the amount of hydroxyl groups, which increases the adsorption capacity for  $\text{AuCl}_4^-$  anions.

## Acknowledgements

The authors express gratitude to the Director of the SAC of the TPU V. A. Tarbokov and the specialist N. I. Radishevskaya for the analysis of samples, as well as appreciation to the researchers of the IC of the SB RAS (Novosibirsk) D. I. Kochubey, B. N. Novgorodov and to the researcher of the NIIC of the SB RAS (Novosibirsk) L. A. Sheludyakova for the analysis and interpretation of experimental data.

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