Talanta 99 (2012) 750–757

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of gold in geological materials by carbon slurry sampling graphite furnace atomic absorption spectrometry

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ARTICLE INFO

Article history:
Received 20 April 2012
Received in revised form
25 June 2012
Accepted 5 July 2012
Available online 20 July 2012

Keywords:
Modified activated carbons
Enrichment
Gold determination
Slurry sampling graphite furnace atomic absorption spectrometry
Scanning electron microscopy-energy dispersive X-ray spectrometry
X-ray photoelectron spectroscopy.

ABSTRACT

A simple and cost effective preconcentration method on modified activated carbons is described for the determination of traces of gold (Au) in geological samples by carbon slurry sampling graphite furnace atomic absorption spectrometry (GFAAS). The basic parameters affecting the adsorption capacity of Au(III) ions on modified activated carbons were studied in detail and the effect of activated carbons modification has been determined by studying the initial runs of adsorption isotherms. The influence of chlorides and nitrates on adsorption ability of Au(III) ions onto the modified activated carbons for diluted aqueous solution was also studied in detail in respect to the determination of gold in solid materials after digestion steps in the analytical procedure, which usually involves the application of aqua regia. SEM-EDX and XPS studies confirmed that the surface reduction of Au(III) ions to Au(0) is the main gold adsorption mechanism on the activated carbon. Determination of gold after its preconcentration on the modified activated carbon was validated by applying certified reference materials. The experimental results are in good agreement with the certified values. The proposed method has been successfully applied for the determination of Au in real samples using aqueous standards.

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1. Introduction

Gold is one of the noble metals widely used in various areas. It is a toxic element, causing allergic eczematous dermatitis and some nephrotoxic effects on humans [1]. Owing to its increasing presence in the environment, a growing interest in the elucidation of its role in living organisms and the impact on human health, it is important to develop accurate and dependable analytic procedures for gold determination in the environmental samples [2].

Several analytical methods, such as flame (FAAS) [3] and graphite furnace (GFAAS) [4] atomic absorption spectrometry also with slurry sampling [5], inductively coupled plasma atomic emission spectrometry (ICP-OES) [6], inductively coupled plasma mass spectrometry (ICP-MS) [7], neutron activation analysis (NAA) [8], have been applied for accurate gold determination in geological materials. It is worth mentioning that gold occurs in geological materials at low concentrations and it is inhomogeneously distributed. Furthermore, because of variety of matrices and numerous interferences, direct application of even highly sensitive and selective spectrometric techniques is seriously limited. For these, much consideration has to be taken for the elimination of matrix effects, particularly those coming from common elements present in examined samples, when the AAS detection method is used [9]. Hence, a separation and preconcentration stage is often necessary for sensitive and interference-free gold determination [10]. Various techniques have been used for separation and preconcentration of gold, e.g. different extraction methods [11], liquid–liquid extraction [12], dispersive liquid–liquid microextraction [13], solid-phase extraction [14–17], cloud point extraction [18,19], coprecipitation [20], electrodeposition [21] and ion exchange [22]. Different sorbents such as Amberlite XAD resins [15], nanotubes [23], nanoclays [24], cotton fibers/chitosans [25], polyurethane foams [26], silica gels [27] have been used for preconcentration of Au(III) ions from various media. However, adsorption of heavy metals onto activated carbons seems to be the most effective for separation and enrichment of trace metals from aqueous solutions. Application of activated carbon offers high adsorption capacity, large surface area, micropore character and high degree of surface reactivity. What is more, the surface of activated carbons can be easily modified in various ways, which can give them adsorption capacity and selectivity for specific metal ions [28]. The most important phenomena, which influence the ion adsorption capacity, are ion exchange, nonspecific sorption, surface precipitation, redox reactions and formation of surface chelates. These have made desorption a critical step of an analytical procedure, especially when the main mechanism of adsorption is metal reduction to elemental state on the activated carbon surface [29]. For this

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http://dx.doi.org/10.1016/j.talanta.2012.07.016

reason, concentrated acid application is required for analyte elution causing severe interferences or leading to substantial sample dilution resulting in the decreasing preconcentration factor. This shortage can be eliminated by the solid sampling technique application, when loaded activated carbons can be directly introduced into the graphite furnace atomic absorption spectrometry in the form of slurry as well as solid samples [30].

The aim of this study was to develop a new analytical procedure for gold determination in geological materials using carbon slurry sampling graphite furnace atomic absorption spectrometry technique. In order to find the most effective sorbent, modification of powdered activated carbon by treatment with H_2O_2 and concentrated HNO_3 solution was proposed. The basic parameters affecting the adsorption capacity of Au(III) ions on the modified activated carbons were studied in detail and the effects of modification have been determined by setting the initial runs of adsorption isotherms. Taking further analytical application of the prepared carbons into account the influence of chlorides and nitrates, as the residue of solid materials digestion, on Au(III) adsorption and gold removal from the gold loaded activated carbons using inorganic acids were studied. Moreover, the morphology and the elemental surface composition of activated carbon was investigated by scanning electron microscopy (SEM)–energy dispersive (ED) X-ray spectrometry and X-ray photoelectron spectroscopy (XPS) to prove Au(III) adsorption mechanism.

2. Experimental

2.1. Reagents and materials

The powdered activated carbon, Medical Carbon (Carbo Medicinalis), produced from charcoal by Gryfskand in Hajnówka, Poland, after pretreatment with hydrochloric acid (POCH, Gliwice, Poland) using a Soxhlet apparatus made of quartz and with hydrofluoric acid in the Teflon vessel was used as the initial adsorbent. It was stated experimentally that this pretreatment reduced ash contents in carbon up to 0.01%.

Gold stock solutions were obtained by proper dilution of 1000 mg L^{-1} standard solution (Merck, Darmstadt, Germany). The calibration curve was established using the standard solutions of Au(III) prepared in 2 mol L^{-1} HCl by dilution from 1000 mg L^{-1} stock solution (Merck, Darmstadt, Germany). The calibration standard was not submitted to the preconcentration procedure. Hydrochloric acid Suprapure (36%) (Merck, Darmstadt, Germany), nitric acid Suprapure (65%) (Merck, Darmstadt, Germany), sodium chloride (POCH, Gliwice, Poland), potassium nitrate (POCH, Gliwice, Poland) were used. NaOH and HCl solutions were used for pH adjustment. Throughout all analytical work, Milli-Q water was used. All solvents and reagents were of analytical-reagent grade or better and the presence of gold was not detected in the working range.

The certified reference materials, SARM–7 and MA–2b, were purchased from the International Atomic Energy Agency, IAEA (Vienna, Austria) and the Canada Centre for Mineral and Energy Technology, CANMET (Ontario, Canada), respectively. Samples of magmatic rocks from Tajno (Mazurian District, Poland) were obtained from the Central Laboratory of the Polish Geological Institute in Warsaw.

2.2. Apparatus

Measurements of gold concentrations in the studied adsorption system were carried out with an AAS 3 (Carl Zeiss, Jena, Germany) atomic absorption spectrometer equipped with deuterium-lamp background correction, an EA 3 electrothermal atomizer and a MPE autosampler. The gold hollow cathode lamp (Narva, Germany) was operated at 5 mA current. The absorbances were measured using the pyrolytically coated graphite tube at 242.8 nm with 0.2 nm spectral bandpass. The optimized time/temperature program for determination of gold in the samples by slurry sampling GFAAS is presented in Table 1. pH measurements of initial gold solutions as well as of carbon suspensions were made using a glass electrode combined with a calomel electrode, GK2302B (Radiometer).

The topochemical inspection of Au(III) adsorption onto activated carbon was investigated by the scanning electron microscope Carl Zeiss Ultra Plus (Germany) equipped with an energy dispersive X-ray detector Bruker AXS (Germany). All experiments were carried out under recommended conditions (20-kV acceleration voltage and 5-nA probe current).

XP spectra were obtained using a Multi-Chamber Analytical System (Prevac, Poland) with monochromated K_α-Al radiation (1486.6 eV) (Gammadata Scienta, Sweden) and an X-ray power of 450 W. The binding energy (BE) scale was referenced against $C1s=284.7$ eV line. The vacuum in the analysis chamber was better than $8 \cdot 10^{-9}$ Pa. The high-resolution scans were performed over the 81–93, 282–294, 527–538 eV ranges for Au*4f*, C*1s* and O*1s* spectra, respectively.

2.3. Activated carbon modification and measurements

Two portions of the commercially available powdered activated carbon were chemically modified by oxidation with 13% of hydrogen peroxide and concentrated nitric acid. In both cases the oxidation procedures were as follows: 500 mL of 13% hydrogen peroxide or concentrated nitric acid were added to 50 g of the activated carbon and the suspension was heated at 90 °C until dry. The residue was washed with distilled water until conductivity of the water eluent was close to that of the distilled water. In this way three different carbons were obtained: A – discharging carbon, B – oxidized by 13% H_2O_2 carbon and C – oxidized by concentrated nitric acid carbon. The surface characteristics of the obtained carbons are summarized in Table 2. The reaction of the activated carbon with the oxidants can change either chemical nature of its surface or its texture characteristics. Carbon oxidation causes the decrease in the surface area. Probably, it is caused by micropores structure changes and/or by blocking macropores by acidic surface groups. Moreover, oxidation increases the cation exchange capacity and decreases the anion exchange one. This is

Table 1
Time–temperature program for gold determination by slurry sampling GFAAS.

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)	Air flow (mL min^{-1})
Drying I	80	20	3	240
Drying II	105	2	40	240
Ashing	800	200	5	240
Atomization	2100	FP[a]	5	0
Cleaning	2600	1000	2	280

[a] FP -“full power” - maximum of ramp.

Table 2
Basic parameters of modified activated carbons.

Carbon type	A	B	C
S_{BET} (m^2 g^{-1})	1200	1090	810
Anion exchange capacity (mmol g^{-1})	0.29	0.26	0.03
Cation exchange capacity (mmol g^{-1})	0.37	0.60	2.44

probably associated with an increasing amount of oxygen groups on activated carbon surface.

Optimization of Au(III) ions adsorption onto modified activated carbons was carried out at 25 °C. Individual measuring points were obtained for the adsorption system: 50 mL of proper concentration of Au(III) solution and 0.2 g of activated carbon. The equilibrium adsorption uptake in the solid phase a, (mg g^{-1}), was calculated as follows:

$$a=\frac{(c_i-c)\cdot V}{m} \qquad (1)$$

where c_i is the initial Au(III) concentration (mg L^{-1}), c is the equilibrium Au(III) concentration (mg L^{-1}), V is the volume of the solution (L) and m is the mass of the adsorbent (g). After the equilibrium was reached (20 min.), the liquid phase was separated by a centrifuge and gold was determined.

Prior to SEM-EDX and XPS analysis the powdered activated carbon sample after gold uptake (24.8 mg g^{-1}) was dried for 3 h at 120 °C.

2.4. Determination of Au in CRMs and real samples

The SARM–7, MA–2b and magmatic rocks samples were digested as follows: for the microwave digestion 0.5 g of each sample was weighted accurately into the Teflon vessel and 2 mL of HNO_3 and 6 mL of HCl were added. The above mixture was digested in microwave system (Mars 5, Matthews, USA). The blanks were prepared in the same way as the sample. The digested sample was evaporated almost to dryness and 2 mL of HCl were added. This step was repeated several times for thorough removal of NO_3^- ions and transforming Au(III) ions in their chloride complexes. Then the sample was made up to a volume of 50 mL with Milli-Q water and adjusted to the pH value of 1.5 with 1 mol L^{-1} of NaOH. The preconcentration-separation procedure given above was applied for the samples using 0.2 g of A carbon. After the equilibrium was reached, the suspension was filtered through the filter disk and dried in a laboratory dryer at 120 °C until the constant weight was obtained. Gold contents in the samples were then determined using the carbon slurry sampling graphite furnace atomic absorption spectrometry technique by preparing the carbon slurry in the range 20–50 mg per 1 mL of 5% HNO_3 as a liquid medium.

3. Results and discussion

3.1. Effect of pH

The effect of pH on Au(III) adsorption onto the modified activated carbons was studied at different initial pH values, keeping the other parameters constant. In Fig. 1 the adsorption abilities of gold as a function of the equilibrium pH are shown. The maximum Au(III) ions adsorption onto A carbon in the pH range from 0.5 to 2 and onto B carbon for pH about 2 is accomplished. For both carbons in the pH range 2–8 almost linear decrease of Au(III) ions adsorption is also observed and for pH higher than 8 it does not practically occur. Probably, it is caused by the complex ions formation at high pH, e.g. $AuOHCl_3^-$, $Au(OH)_2Cl_2^-$, $Au(OH)_3Cl^-$, $Au(OH)_4^-$ or $Au(OH)_5^{2-}$, which are not adsorbed onto A and B carbons. On the other hand, a slight decrease of Au(III) adsorption in acidic solutions ($pH<1$) may be result of undissociated molecules of $HAuCl_4$ formation. Moreover, the phenomenon of adsorption sites blocked by chloride ions, which prevents the gold complex ions interactions with the carbon surface may also occur. In the case of C carbon the plateau of Au(III) ions adsorption at equilibrium pH from 1.5 to 8 pH is observed. This phenomenon is probably caused by formation of surface chelates with the increasing pH values up to 9.

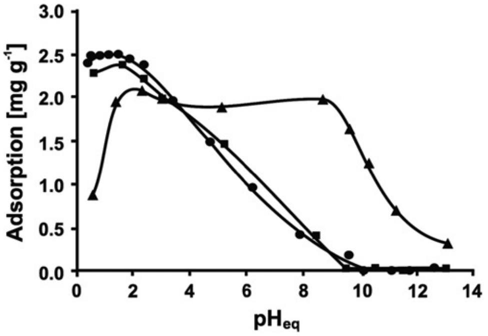

Fig. 1. pH influence on Au(III) adsorption onto A (●), B (■),C (▲); m=0.2 g, V=50 mL, C_{Au}=10 mg L^{-1}, t=20 min, T=25 °C.

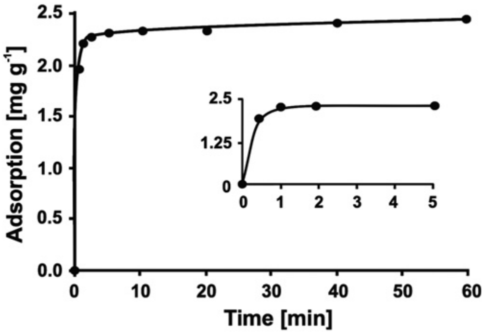

Fig. 2. Adsorption kinetics of Au(III) onto A carbon; m=0.2 g, V=50 mL, C_{Au}=10 mg L^{-1}, pH=1.5, T=25 °C.

3.2. Kinetic study

The effect of time on adsorption of Au(III) onto the A carbon is shown in Fig. 2. The studies suggest that the process of adsorption is quick and close to the equilibrium after 10 min. After that time, there are slight changes of adsorption values, which are within the precision limits of measuring technique. Finally, the shaking time of 20 min. was chosen to ensure adsorption equilibrium. Adsorption of Au(III) onto the powdered activated carbon is very quick in comparison to Au(III) adsorption onto the granular activated carbon reported by [17]. The equilibrium of Au(III) adsorption onto the single granular activated carbon for the studied system was reached after 20 h. Moreover, the authors observed that with the increasing sample volume the contact time increased dramatically. Application of powdered activated carbon results in significant shortening of time analysis.

3.3. Effect of NO_3^- and Cl^-

The excess of nitrates and chlorides in the sample, as a result of aqua regia application for digestion of solid materials, may influence the adsorption ability of activated carbons (the effect of ions competition for adsorption sites). For this reason, in order to assess the possibilities of practical applications of studied procedure, the effect of oxidants and reducing agents, e.g. NO_3^- and Cl^- on Au(III) adsorption was investigated. In Fig. 3 the effect of nitrates and chlorides on the adsorption of Au(III) ions onto A carbon is shown. In this case the effect of nitrates is quite different from that of chlorides. Not so much as 0.9 mol L^{-1} nitrates decreases about 10% of Au(III) adsorption. Due to this

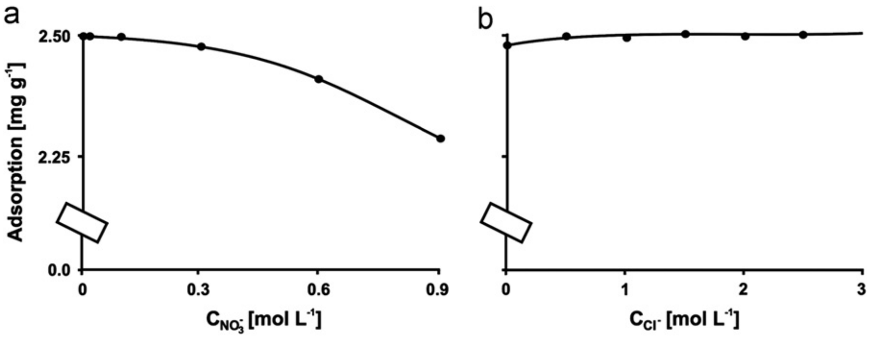

Fig. 3. Influence of (a) NO_3^- and (b) Cl^- on Au(III) adsorption onto A carbon; $m=0.2$ g, $V=50$ mL, pH$=1.5$, $C_{Au}=10$ mg L^{-1}, $t=20$ min, $T=25$ °C.

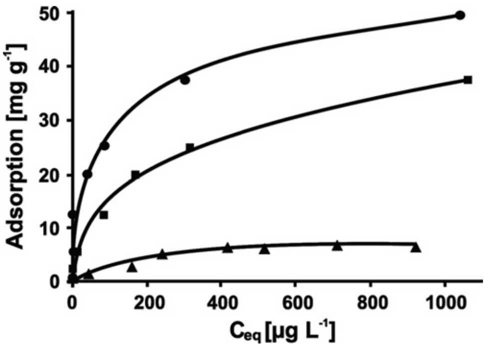

Fig. 4. Initial runs of adsorption isotherms of Au(III) onto A (●), B (■),C (▲); $m=0.2$ g, $V=50$ mL, pH$=1.5$, $t=20$ min, $T=25$ °C.

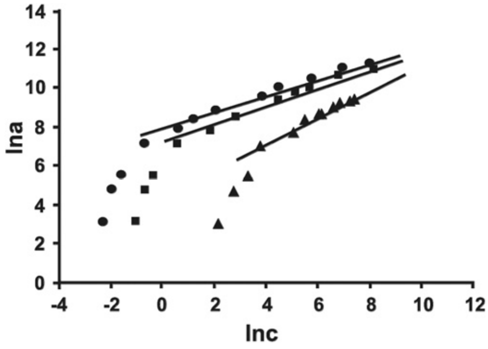

Fig. 5. Linear dependences plotted according to Eq. (4) for carbon A (●), B (■),C (▲).

effect removing of nitrates from the solution by sample evaporation almost to dryness and the addition of concentrated HCl solution (repeated twice) before enrichment step were applied.

3.4. *Equilibrium isotherm study*

The adsorption ability of the modified activated carbons has been determined by studying the initial runs of adsorption isotherms of Au(III) ions from the aqueous solutions, which are shown in Fig. 4. The equilibrium isotherm studies were carried out at the initial pH 1.5, temperature 25 °C and equilibrium time 20 min. The best sorption ability for gold ions is exhibited by A carbon and the worst by C carbon. The adsorption isotherms presented in Fig. 4 show the Langmuirian behaviour and may be described by the generalized Langmuir equation:

$$a = a_m \frac{(Kc)^n}{1+(Kc)^n} \qquad (2)$$

where a is the amount of Au(III) adsorbed onto the activated carbon [mg g^{-1}] at the equilibrium of Au(III) concentration c, a_m is the maximum adsorbed amount (sorption capacity), K is the Langmuir constant and n, varying from zero to unity, characterizes the quasi Guassian energetic heterogeneity of the adsorption system [31]. Assuming that $n=1$ Equation (2) becomes the classical Langmuir isotherm used for description of homogeneous adsorbents. For very low concentration, the factor $(Kc)^n$ can be neglected and Eq. (2) reduces to the Freundlich equation, which can be written in the linear form:

$$\ln a = \ln(a_m K) + n \ln c \qquad (3)$$

By including c_o denoting the Freundlich constant describing the sorption capacity and further substituting K by $(c_o)^{-n}$ Eq. (3) can be rewritten as follows:

$$\ln a = \ln[a_m (c_o)^{-n}] + n \ln c \qquad (4)$$

Table 3
Freundlich isotherm parameters for the studied adsorption systems.

Carbon type	a_m (mg g^{-1})	K ((L g)$^{-n}$)	n	c_0 (mg L^{-1})	R^2
A	75	61	0.413	1.8×10^{-4}	0.954
B	61	48	0.458	1.2×10^{-3}	0.962
C	12	45	0.679	6.5×10^{-2}	0.924

The above relation is presented in Fig. 5 and it can be observed that the studied isotherms are in good agreement with the linear form of the Freundlich equation for higher Au(III) concentrations. The adsorption heterogeneity increases when the value of n decreases to zero. The maximum sorption capacity evaluated from the adsorption isotherms presented in Fig. 4 equals to 75 mg g^{-1} for A carbon, 61 mg g^{-1} for B carbon and 12 mg g^{-1} for C carbon. The parameters K and n evaluated from Eq. (4) are summarized in Table 3. Additionally, the maximum sorption capacities for the studied carbons are listed in this table. The smallest value of n is obtained for A carbon and the greatest for C carbon. It means that energetic heterogeneity of the studied carbons is the greatest for A carbon nearly the same for B carbon and the smallest for C carbon. Moreover, Figs. 4 and 5 show significant similarities in the sorption properties of A and B carbons, which are largely different from those observed for C carbon. These differences are probably caused by surface ion-exchange groups which are completely removed in the oxidation process of C carbon [30].

It is important to note that the linear relationship between lna vs. lnc is satisfied for all but the lowest concentrations of Au(III). The reason is not quite clear at the moment, but one can expect that different mechanism of Au(III) adsorption may take place for very diluted samples regardless of carbon adsorption sites type.

3.5. *Desorption study*

Experimentally it was stated that the desorption kinetic of Au(III) from modified activated carbons with different concentrations of HCl and HNO_3 solutions was relatively slow and after about 60 min. the desorption equilibrium was reached. Moreover, the time of desorption equilibrium reaching did not depend on the carbon modification and the concentration of hydrochloric and nitric acids in the liquid phase. The desorption studies of Au(III) ions in relation to concentration of HCl and HNO_3 (Fig. 6) confirmed that even the application of concentrated nitric or hydrochloric acid did not cause the total desorption of studied ions from the modified activated carbons. The differences of gold desorption from each activated carbon come from the nature of their surface. Additionally, as it is shown in Fig. 6, the lowest desorption of gold by hydrochloric acid is observed for A carbon and the greatest for C carbon. It can be assumed that the main gold adsorption mechanism onto the modified activated carbons is associated with surface reduction of Au(III). However, in the case of concentrated HNO_3 application, differences in gold desorption from modified activated carbons are negligible and this is the result of significant oxidizing properties of the eluent used.

From the analytical point of view, due to the incomplete gold desorption from the activated carbons, the slurry sampling GFAAS technique is more preferable than the classical GFAAS for the determination of gold in the environmental samples after their separation/enrichment on the activated carbon.

3.6. SEM–EDX study of Au(III) adsorption onto activated carbon

The multi-method experimental studies including scanning electron microscopy investigations with secondary electron (SE) as well as backscattered electron imaging (BSE) and energy dispersive X-ray detection EDX for the topochemical inspection of Au(III) adsorption onto A carbon were applied. In Fig. 7(a) and (b) the examples of the SE images of gold loaded A carbon and the areas on the micrographs, from which the exemplary SEM–EDX spectra were taken (Fig. 8), are shown. The EDX spectrum confirms the non uniform presence of gold on the carbon surface. Additionally, the Au elemental mapping, presented in Fig. 7(c), shows the gold islands formation and the sites of 0.5–3 μm, but some larger islands with the dimensions of 5–8 μm can be occasionally seen (Fig. 7(d)). That confirms the heterogeneous nature of activated carbon and the existence of strong adsorption sites responsible for not uniform gold distribution.

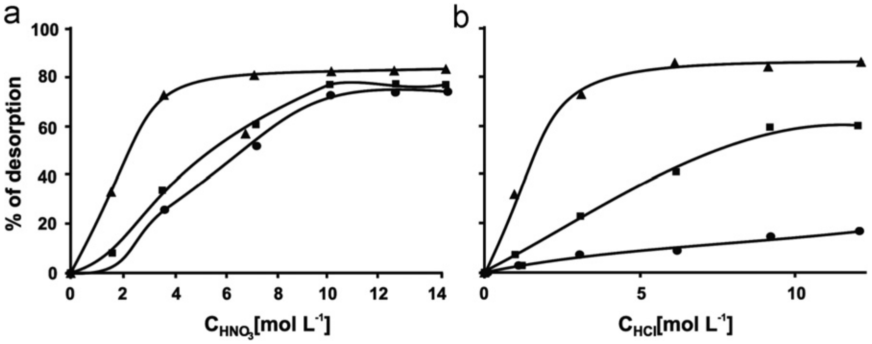

Fig. 6. Desorption of Au(III) from A (●), B (■),C (▲); in respect to (a) HNO_3 and (b) HCl concentration; $m=0.5$ g, $V=50$ mL, $A_{Au}=2.5$ mg g^{-1}, $t=60$ min, $T=25$ °C.

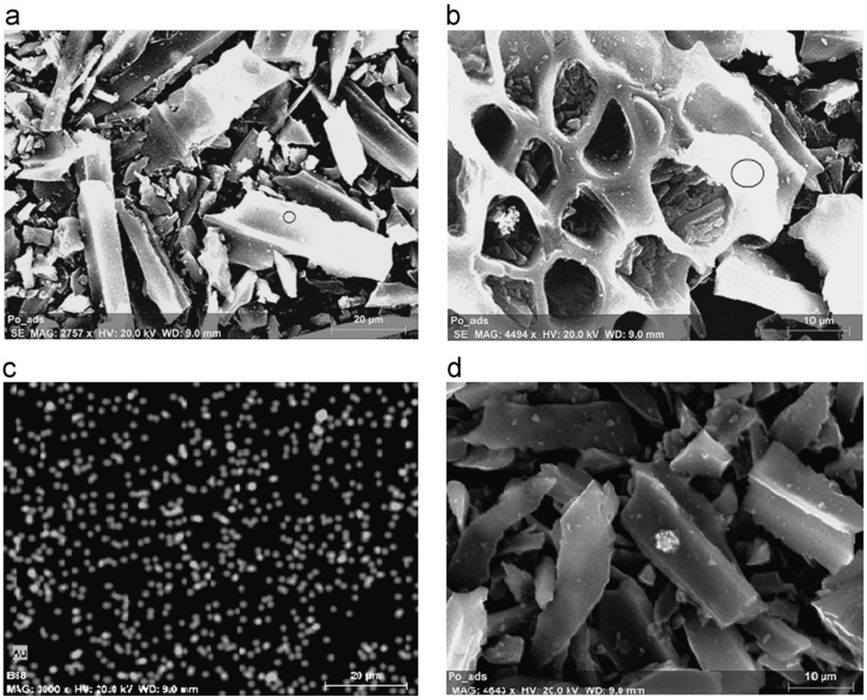

Fig. 7. SEM micrograph of an A carbon (a) region with Au at a magnification of × 2757 and (b) region without Au at a magnification of × 4494 using SE detector and (c) X-ray elemental mapping for Au loaded A carbon at a magnification of × 3000 and (d) region with Au at a magnification of × 4643.

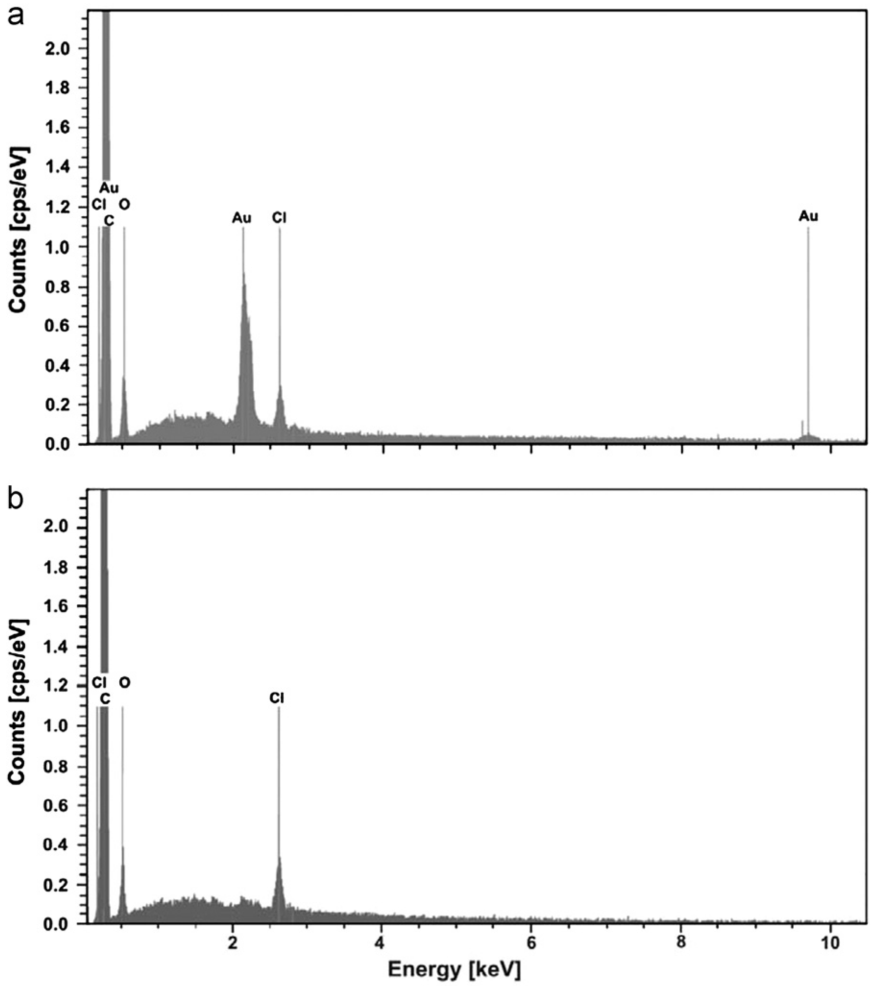

Fig. 8. SEM–EDX spectra of an A carbon (a) region with Au and (b) region without Au.

3.7. *XPS study of gold loaded carbon*

To understand the mechanism of Au(III) ions adsorption onto the activated carbon and their chemical transformations on its surface the XPS studies were carried out. In Fig. 9 the XPS spectrum of the Au4*f* region is shown. The fitted peaks for the Au4*f* region and their possible assignments indicate that the main species as result of the gold adsorption onto A carbon surface are metallic gold, Au compounds containing chlorine (AuCl) and $HAuCl_4$ precursor or even gold(III) (oxy)chloride species, which represent about 81%, 14.9% and 4.2% of the total Au, respectively [32,33].

According to the XPS data presented above the metallic gold is the most abundant species on the activated carbon surface. The XPS study proves that the main mechanism of gold adsorption onto A carbon is the surface reduction of Au(III) to Au(0), which determines its selectivity. Shamspur et al. [34], applying of modified multiwalled carbon nanotubes for Au(III) enrichment from aqueous solution, suggested limited selectivity of studied sorbent with respect to Al(III) ions. Because of the main gold adsorption mechanism this restriction is negligible in the case of A activated carbon.

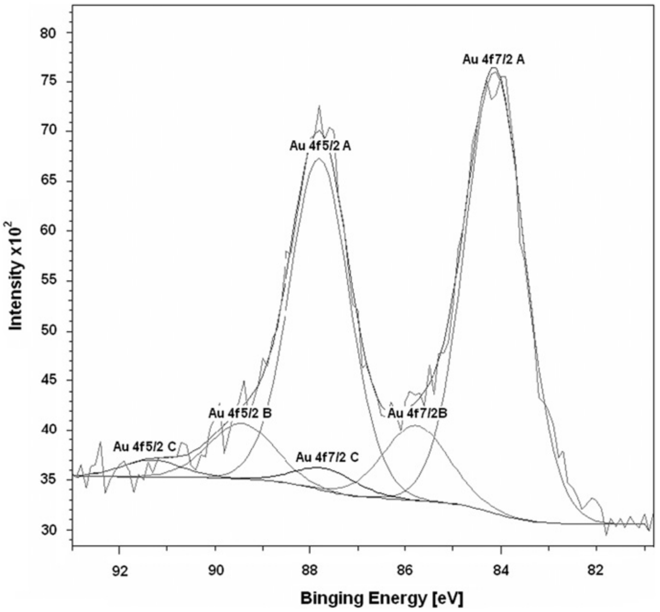

Fig. 9. Au4*f* XPS spectra of the A carbon.

3.8. *Analytical features*

The calibration curves for gold determination have been established with a blank and five calibration solutions in the range 1.0–70 $\mu g\, L^{-1}$. The comparison of calibration curve slopes obtained for aqueous solutions and various percentage of carbon slurries confirmed that in the case of the integrated absorbance measurements it was possible to use aqueous standards for

Table 4
Results of gold determination in CRMs and magmatic rocks samples by slurry sampling GFAAS technique after preconcentration on A carbon.

Sample	Certified value (mg kg^{-1})	Slurry sampling (mg kg^{-1})
SARM–7	0.310 ± 0.016	0.316 ± 0.019[a]
MA–2b	2.39 ± 0.05	2.42 ± 0.10[a]
Magmatic rocks1	–	0.241 ± 0.015[a]
Magmatic rocks2	–	0.162 ± 0.010[a]
Magmatic rocks3	–	0.242 ± 0.012[a]
Magmatic rocks4	–	0.075 ± 0.005[a]

[a] Relative standard deviation for seven replicate measurements.

quantitative determination of gold. The integrated absorbances of the same amount of gold injected into the graphite furnace either as aqueous solution or carbon slurry were equal. The gold loaded carbon slurry caused only Au signal shift and shape change. Owing to these effects integrated absorbance was chosen for all measurements. The detection limit (LOD) of gold (calculated as the average of 7 blank samples signals plus three times as large standard deviation of the signals obtained from 7 blank samples) for a 10% slurry sample was 4 ng L^{-1}. The characteristic mass, based on the integrated absorbance (amounts, in picograms, providing a signal of 0.0044 s), was 10.2 pg. A total enrichment factor of 25 was obtained with respect to 10% slurry sample. In passing, we would like to point out the experience on the direct introduction of gold loaded powdered activated carbon into electrothermal atomizer makes it possible to achieve higher enrichment factor, even up to 100. Comparing analytical parameters for the proposed method with others reported in the literature [13] one can conclude that in relation to the linear range, the LOD and enrichment factors are comparable to other methods using solid phase extraction. On the other hand, taking into account the type of materials dedicated and selectivity, proposed method can be considered as the method of choice.

3.9. *Applications*

The investigations on the analytical applicability of the prepared activated carbons indicated that A carbon is characterized by great sorption capacity and good selectivity for Au(III) ions. Owing to these unique properties A carbon has been selected for enrichment and determination of Au in the real samples. Because of not completed desorption of gold from the loaded carbon the slurry sampling GFAAS technique has been chosen for gold determination. Due to the lack of carbon slurry time stability (decrease of gold signal to 30% after 2 min), homogenization using ultrasonic mixing just before each measurement was applied. The proposed methodology was validated by applying two certified reference materials (SARM–7 and MA–2b). Additionally, that procedure was applied for separation and determination of gold in magmatic rocks samples. The analytical data are summarized in Table 4. The precision of gold determination in the geological samples by the presented method can be regarded as acceptable. Moreover, the good agreement of the determined content of Au in the certified reference materials confirmed the accuracy of the proposed method.

4. Conclusions

Application of the proper sorbent for Au(III) enrichment require a preliminary study to find the most effective and selective adsorbent. For this, the sorption of Au(III) onto the modified activated carbons was studied in details. The comparison of the activated carbons which undergo different modification leads to the conclusion that the amphoteric carbon (A carbon) possesses excellent adsorption ability with respect to Au(III) ions. The XPS data confirmed that the surface reduction of Au(III) ions to Au(0) is the main gold adsorption mechanism onto that activated carbon. This feature is very important because reduction mechanism makes the activated carbon very selective especially for noble metals ions. Additionally, in acidic solution (pH value around 1.5) efficient Au(III) adsorption process can be carried out and surface acidic groups are not ionized. It means that matrix elements e.g. Fe(III) ions will not be adsorbed on carbon as cations. Moreover, acidic condition prevents from precipitation of transition metal ions. This effect is especially important in the case of geological samples analysis. Because of not completed desorption of gold species from the activated carbon surface by strong acids, the slurry sampling graphite furnace atomic absorption spectrometry technique is advised for gold determination in the geological samples. The concentration of gold loaded carbon slurries up to 10% can be applied and it improves detection limit of that technique significantly. The application of more concentrated slurries may decrease the precision of that method. In order to get a higher preconcentration factor direct analysis of gold loaded carbon by the GFAAS technique can be considered. Summarizing, the application of activated carbon is a sensitive, useful and accurate method for the Au(III) preconcetration from aqueous solutions and their determination in the geological samples using the carbon slurry sampling graphite furnace atomic absorption spectrometry technique.

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