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Determination of Low-Content Gold by Complexing Polymer of Polystyrene-azo-thiazandithion-2,4 to Analyze in Copper Ore

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ABSTRACT

In present work, low content gold in copper ores was determined by using enrichment method. Complexing polymer sorbent (polystyrene-azo-thiazandithion-2,4) was used to increase the gold content for analysis of waste copper, copper ore and copper concentrate to upgrade the methodology. The optimum conditions of the volume capacity, pH, temperature, and time dependence enrichment of gold content were examined to increase analysis efficiency by using treatment of complexing polymer sorbent. The chemical interactions and molecular structure of PSTDT with gold were successfully determined using by FT-IR and theoretical calculations.

Keywords: polystyrene-azo-thiazandithion-2, gold, adsorption, infra-red, quantum chemistry calculation

INTRODUCTION

The atomic absorption spectroscopy (AAS) method is used to determine the low-content precious elements in biological [1] and geological samples [2]. The gold is one of the precious metal which can be enriched by activated carbon, ion exchange, extraction, assaying analysis and others. These methods are poor selectivity and to take a long time and to use toxic organic compounds. Comparison of differents gold recovery methods as amalgamation, cyanidation were investigated previously [3]. Hoffman et al. [2] have been described the gold analysis in geological samples by fire-assaying methods which include instrumental neutron activation, AAS, graphite furnace-atomic absorption or inductively coupled plasma mass spectroscopy (GF-AAS or ICP-MS).

The functional polymers can been used for determination of low-content gold in ores and minerals by using AAS such as silicon organic adsorbent PSTM-3T [4]. The PSTM-3T polymer also had been investigated for removal of copper and chromium ions from aqueous solution [5]. PSTM-3T polymer includes thiocarbamide functional group which forms the metal complexes.

The Erdenet Mining Corporation (EMC) is one of the largest copper and molybdenum mining and processing factories in the world that located on the northern of Mongolia. The copper is concentrated by using flotation method of sulfide minerals. The concentration of gold in copper concentrate has been determined by using the assaying analysis by GF-AAS in Central Laboratory of Chemistry of EMC which method is not efficiency.

Basargin et al. used the polystyrene-azo-thiazandithion-2,4 (PSTDT) polymer to determine the low-content gold in silicates, quartz, and sulfide ores [6]. The calcined powders were dissolved in conc. HNO_3, HCl and HF [6]. The PSTDT can been used to selectively determine the low-content gold in samples by using enrichment method.

In our study, we examined the method to enrich the low content gold in ores by using complexing polymer sorbent. The method is simple, selective and to fully separate low-content gold and to take a short time. In this present work, we determined the low-content gold in waste copper, copper ore and copper concentrate of EMC by using PSTDT.

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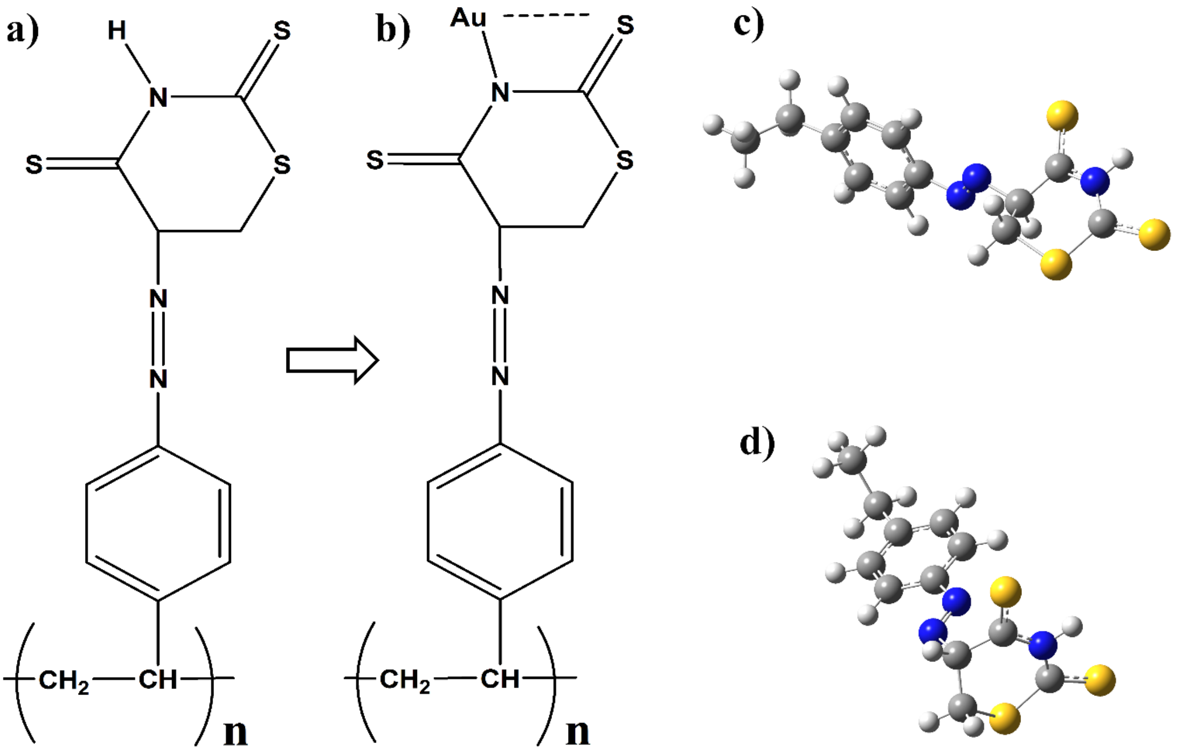

Figure 1. The PSTDT polymer without (a, c and d) and with (b) gold

EXPERIMENTAL

Materials

The gold standard solution of 1 mg mL^{-1}, (ACROS Organics, Geel, Belgium) were used to determine the optimum conditions as pH, temperature, time dependence and volume capacity of PSTDT polymer. The PSTDT polymer (Astra, Moscow, Russia) was used to determine the gold content in waste copper, copper ore and concentrate. The PSTDT polymer (**Figure 1a**) is not dissolve in water, acid, base and organic solvents.

The PSTDT includes functional group imine and thione in ortho position which forms a stable chelate complex with gold. The gold atom substitutes a hydrogen atom of imine group and connects with thione atom by coordination bond (**Figure 1b**).

Methods

Firstly, the optimum conditions as pH, temperature, time dependence and volume capacity of PSTDT for gold standard solution was determined before treatment of gold content that were 0.1, 20 °C, 15 min and 45.0 mg g^{-1}, respectively (**Figure 2**). In the sample decomposition stage, the samples were calcined at 650 °C then were dissolved in nitric acid and were evaporated the solution. The powder had been calcined at 450 °C to form the copper oxide. The formed oxide was dissolved in solution of H_2SO_4: H_2O_2(3 %, v/v) with ratio 1 : 10. The excess solution of hydrogen peroxide was added and boiled the solution then was added 5 mL NaCl and 1 mL KI with each concentration of 10 % (w/v) to precipitate the precious metals. This procedure was repeated until all gold, platinum, silver and palladium were precipitated. The precipitate was filtered and calcinated at 600 °C. The precipitate was dissolved in “Aqua regia” solution and evaporated then dissolved in 1 N hydrochloric acid. The ascorbic acid was added into the resultant solution to reduce the oxidation number of gold which can be produced the complex between Au^{1+} and PSTDT polymer.

In enrichment stage, 100 mg PSTDT polymer was added into solution and mixed at 20 °C then filtered. The precipitate was calcined at 550 °C and dissolved again 1 N hydrochloric acid.

In gold content determination stage, the gold content was analyzed in this solution by using GF-AAS. The gold content in prepared solution was determined by using GF-AAS (AAnalyst 800, Perkin Elmer, Rodgau, Germany). The sample burned by air-acetylene flame at 2125 – 2400 °C and measured the gold content at 242.7 nm wavelength.

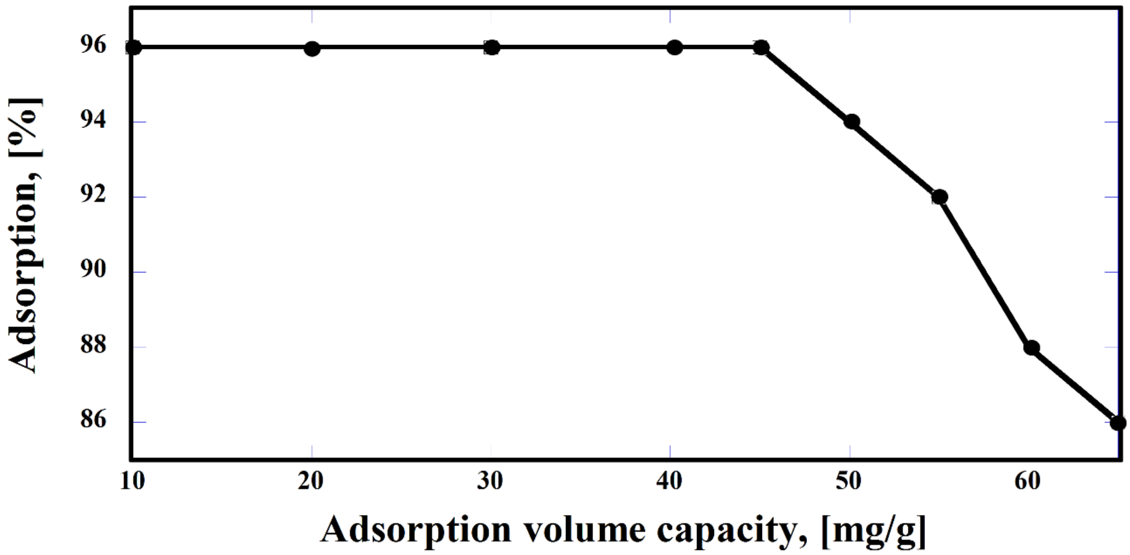

Figure 2. Adsorption volume capacity vs Adsorption

Table 1. The comparison of gold content [ppm] in waste copper, copper ore and concentrate by using different methods of CT-GF-AAS, AA-GF-AAS and ICP-MS

Samples	**Gold content, ppm**		
	CT-GF-AAS	**AA-GF-AAS**	**ICP-MS**
Copper ore	0.04	NA	0.05
Copper concentrate	0.48	0.40	0.44
Waste copper	0.005	NA	0.002

The chemical bond frequencies of functional groups of polymer before and after treatment of sample were analyzed by using Fourier-Transform Infrared (FT-IR) spectrophotometer (IRPrestige-21, Shimadzu, Tokyo, Japan). The powdered samples were mixed with KBr and made the pellets. The FT-IR spectra were obtained with frequency range of 4000 – 400 cm^{-1}. The molecular structures of PSTDT polymer were modeled with consideration of isomerization. Geometries of all the considered model molecules (**Figure 1c** and **d**) in this study were fully optimized by using density functional theory (DFT) with Becke`s three-parameter hydrid exchange function [7, 8] and the Lee-Yang-Parr correlation function [9] (B3LYP) and with the 6-31G(d, p) basis set [10] method in Gaussian 03 package [11]. Vibrational frequencies and absolute IR intensities of optimized structures were investigated with 6-311G(d, p) level. All the convergent precisions were the system default values, and the all calculations were carried out on the standard lab–level workstation with AMD Opteron 285 dual core CPU. Data visualization was carried out using Gauss View 3.0 [12].

RESULTS AND DISCUSSION

Firstly, we analyzed the gold content of certified reference material of OREAS13b with 0.211 ppm concentration of Au (Ore Research & Exploration, North Vic, Australia) using by PSTDT. All the certified reference materials and ore samples were prepared more than 20 samples and the averaged values of gold content were 0.207±0.0019 ppm which means that this method is suitable for the determination of gold content.

In this work, the sample decomposition stage were different with previous work by using PSTDT [6]. The adsorption optimum conditions of the volume capacity, pH, temperature and time dependence of PSTDT for gold adsorption were established as <45.0 mg g^{-1}, 0.1, 20 °C and 15 min, respectively (**Figure 2**). **Table 1** shows the averaged gold contents in copper ore, copper concentrate and waste copper by using our chemical treated (CT) GF-AAS compared to assay analysis (AA) GF-AAS and ICP-MS methods. The gold contents in copper concentrate and waster copper by using CT-GF-AAS were higher than by using ICP-MS method which mean that the low-content gold determination is enriched by the PSTDT are higher efficiency in analysis of copper mining industry.

The functional groups of PSTDT before (**Figure 3a**) and after (**Figure 3b**) treatment of gold samples were identified using FT-IR experiment and the spectrum. In **Figure 3c**, the difference of IR signals for PSTDT were 1537.5 and 3439.1 cm^{-1} for N–H, 1348.2 cm^{-1} for C–S. The IR signals were similar with the group frequencies [13]

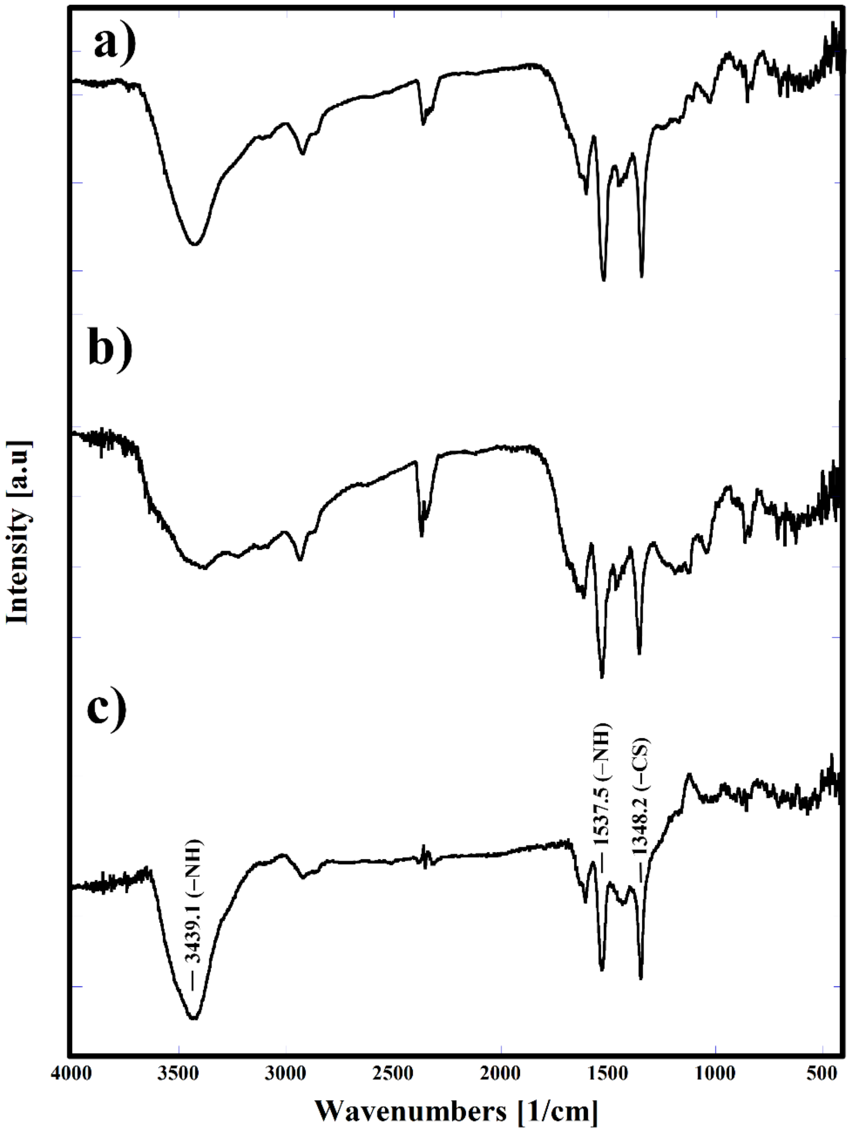

Figure 3. The IR spectra of PSTDT polymer with (a) and without (b) gold, and difference (c)

Table 2. The comparison of theoretical frequencies of PSTDT polymer and experimental frequency difference (Figure 3c) of before and after treated PSTDT polymer. The percentage of relative deviation of model in different frequencies is shown in parenthesis

Groups	Wavenumbers, [cm^{-1}]						
	Cal.						Exp.
	#1	Int.	Δ [%]	#2	Int.	Δ [%]	
N-H	3521.7	52.3	-2.4	3525.9	42.4	-2.5	3439.1
	1500.2	403.1	2.0	1508.6	431.8	1.5	1531.5
C-S	1210.9	56.5	10.2	1196.3	45.8	11.3	1348.2

vice versa the frequencies does not shown for PSTDT after treatments of the gold sample. The Au^{3+} is reduced to Au^{1+} by addition of ascorbic acid. Therefore, it shows that the gold atom substituted the hydrogen atom of imine group and connected with thione atom by coordination (**Figure 1b**). In this study, two possible isomers of model for PSTDT polymer (**Figure 1c** and **d**) were investigated using the density functional B3LYP method with 6-311G(d, p) basis set to compare the experimental results. In theoretical calculations, the values for N-H bond frequencies have relative deviation less than 2.5 % and the deviations of values for C-S bond frequency are not too more than 11 % (**Table 2**). The theoretical values are in good agreement with experimental values, the same as previous reports [5, 14]. Finally, the PSTDT polymer is a good enrichment of gold content to use the analysis of gold in copper concentrate and waste copper.

CONCLUSIONS

The low-content gold determination in samples of copper industry was clearly examined using CT-GF-AAS, FT-IR and ab initio calculations. The optimum conditions of the volume capacity, pH, temperature and time dependence of PSTDT for gold adsorption were <45.0 mg g-1, 0.1, 20 °C and 15 min, respectively. The analysis efficiency of gold determination was increased after treatment of PSTDT. The chemical interactions and moleculer structure of PSTDT with gold were successfully determined using by FT-IR and theoretical calculations.

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