

## Electrochemical Characterization of a Commercial Au-Ag-Cu Alloy in an Acidic Medium

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The voltammograms obtained by the cyclic voltammetry method show potentials at which current waves occur successively corresponding to the number and the quantity of the phases present in the alloy, which can be used for characterisation of the investigated alloys. All voltammograms for gold and gold containing alloys exhibit anodic waves corresponding to the formation of the first OH monolayer, low and high valence gold oxides or their hydrated forms. A well-defined cathodic wave can be observed indicating gold oxide reduction. In addition, the voltammograms for the gold-copper alloys exhibit the current waves corresponding to the formation of copper oxides in the anodic region and their reduction in the cathodic region. The voltammograms for the gold-silver alloy also contain the current waves indicating oxidation of silver in the anodic region and its reduction in the cathodic region. The electrodes were obtained metallurgically. This paper presents investigation results of the possibility of using cyclic voltammetry to determine the composition of an commercial gold alloy declared as 14-carat gold [58.5 % Au + the most common alloying elements Ag and Cu, in the proportion 1:1] as well as a verification of pure gold declaration.

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**Keywords:** Gold, Electrochemical characterization, Cyclic voltammetry, Gold alloys, Oxides

### 1. INTRODUCTION

Cyclic voltammetry [1] is a method that has been used in electrochemistry for characterization of two-component alloys and pure metals [2-12] for some time. However, according to the available literature, this method has not been used much for the characterization of multy component noble metal alloys. For that reason, this paper attempts to determine the possibility of using cyclic voltammetry for characterization of gold alloys in 1M sulphuric acid. Investigations were performed for 14-carat gold, since besides 18-carat gold (which contains 75 % of gold), it is the most commonly used alloy of gold, silver and copper with 58.5% gold content, whereas the other two metals are present most often in the proportion 1:1. Firstly, the voltammograms for pure metals comprising the alloy were recorded. Then, the voltammograms were recorded for two-component alloys having the

same gold content as in Au58.5-Ag20.75-Cu20.75 alloy and, finally, it was done for a three-component alloy.

Anodic polarization of gold electrode in acidic medium leads to the formation of an oxide layer on the electrode. This oxide has been well characterized as the Au<sub>2</sub>O<sub>3</sub>, or its hydrated form, Au(OH)<sub>3</sub>. The Au/Au<sub>2</sub>O<sub>3</sub> system is well defined [13] and the reversible potential set up by the following equilibrium has been measured:



The standard electrode potential vs. standard hydrogen electrode (SHE) is  $E^0=1.36$  V.

The mechanism of electrochemical oxidation of gold is very complex and proceeds through several steps [14] including AuOOH as a mean-product which can be formed by different reaction mechanisms. First of them is given by the following equations:



Reaction steps forming AuOOH can be also the following ones:



Further oxidation of AuOOH to Au(OH)<sub>3</sub> proceeds through the reaction:



Then, overall reaction is:



Dickermann et al. [15] noted the important differences among the single crystal and polycrystalline gold electrodes. The anodic oxide formation is very sensitive to the crystallographic nature of the electrode – every crystal plane exhibits only one anodic peak at the different potential, then the others. Anodic peak obtained on polycrystalline gold seems to be the sum of currents corresponding to all the planes on the electrode surface [16].

Anodic polarization of pure silver in unimolar sulphuric acid solution leads to the formation of a resistive porous silver sulphate layer on its surface via the reaction [17,18]:



During anodic polarization in sulphuric acid solutions pure copper dissolves in two step reaction [19,20]:



where the second reaction is slow step.

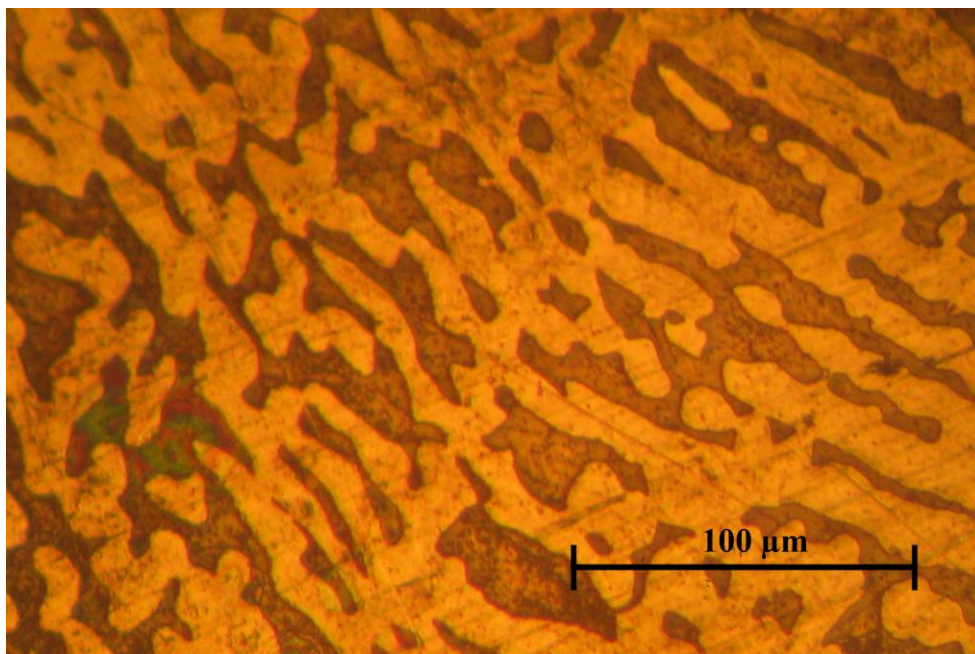
The aim of this investigation is to show how cyclic voltammograms may be used as a tool for fast preliminary checking the composition of gold alloys of unknown origin.

## 2. EXPERIMENTAL

The experiments were carried out in a system consisting of an electrochemical cell and hardware interface for computerized control and data acquisition. In a standard three-electrode

electrochemical cell, the working electrode was a pure metal or alloy (Au, Ag, Cu, Au58.5-Ag41.5, Au58.5-Cu41.5, Au58.5-Ag20.75-Cu20.75), which potential was controlled against saturated calomel reference electrode (SCE). Platinum foil served as a counter electrode. The computerized control (National Instruments card, NI-6251) and data acquisition software based on LabVIEW 8.2 platform, fully developed by Technical Faculty in Bor, were used to run the electrochemical experiments [21]. The investigations were performed at 25°C in 1 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>.

The working electrodes were formed from pure refined metals (Au, Ag and Cu) and their mixtures in the appropriate proportion, by smelting in a quartz furnace at a temperature of 1250<sup>0</sup>C, casting and subsequent cooling. The obtained castings were further treated with aqueous solution of HNO<sub>3</sub> (1:1) in order to remove the oxides formed during cooling, after which they were subjected to the processes of rolling and drawing to obtain wires of dimensions Ø = 1 mm and h = 150 mm. The central part of these wires was isolated with lacquer, whereas one end, whose surface was 0.1 cm<sup>2</sup>, served as an active work surface and the other as an electric contact. The alloys surfaces were studied using the microscope EPY TYPE2. Microphotography of the working electrode crosssection is presented in Figure 1 showing that the alloy has a dendritic microstructure revealing two types of grains – light, rich in silver, and darker, rich in copper. Gold alloys undergo separation into two or more phases depending on the alloying elements [22, 23].



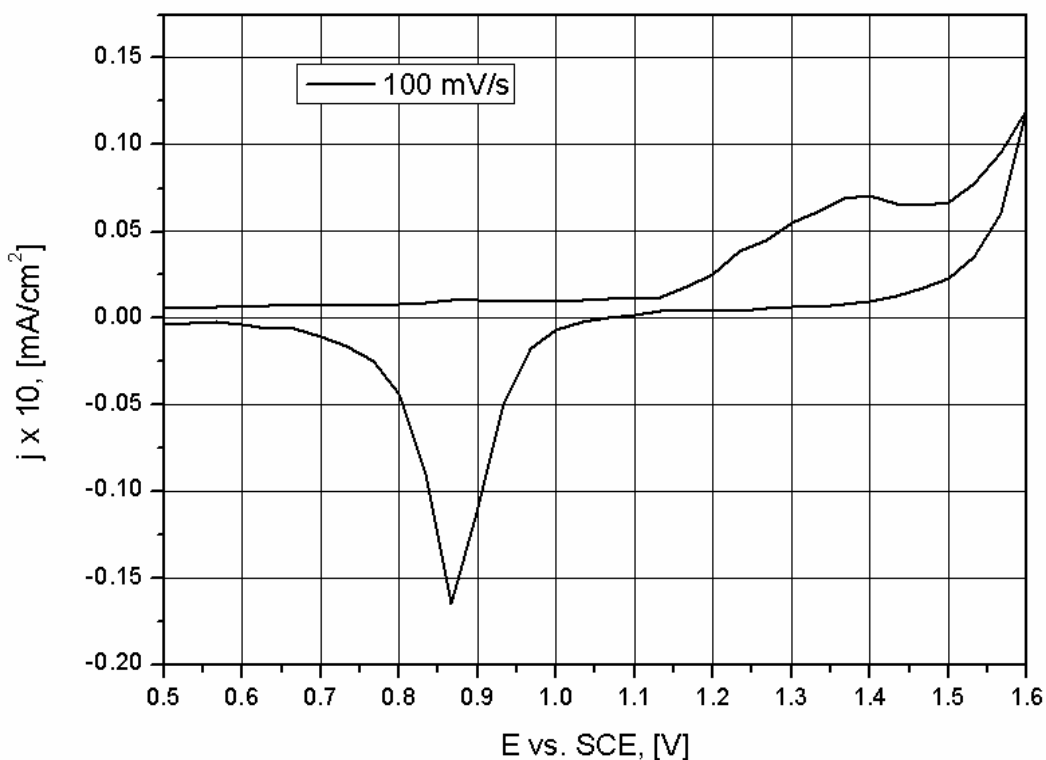
**Figure 1.** Microphotography of Au58.5-Ag20.75-Cu20.75 alloy

Prior to each experiment, preparations were done comprising the following procedures:

- double rinsing of the electrochemical cell, first with distilled water then with working solution, after which the working solution was poured into the cell:
- mechanical polishing of the working electrode first by using abrasive paper and then by using felt soaked into the suspension of distilled water and alumina.

### 3. RESULTS AND DISCUSSION

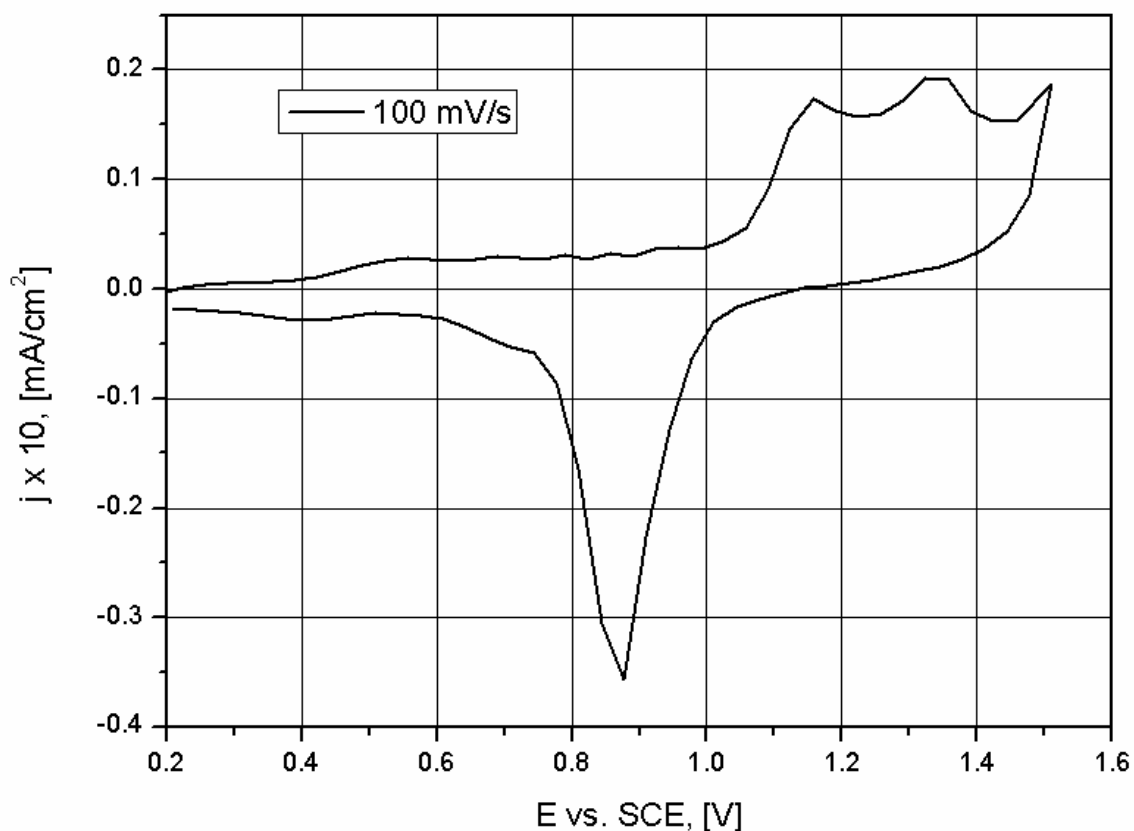
The results of the investigation of electrochemical behavior of 14-carat gold, the corresponding binary alloys as well as pure metals are shown in Figures 2-7. The voltammograms were obtained starting from the open circuit potential. The potential was scanned towards more positive values until the beginning of oxygen gas evolution, which corresponded to a sudden increase in the current density. Analysis of obtained cyclic voltammograms is performed with consuetude of Pourbaix diagrams [24] and other used literature.



**Figure 2.** Voltammogram recorded for pure gold at a scan rate of 100 mV/s in 1M sulfuric acid

Figure 2 shows voltammogram for pure gold obtained at scan rate of 100 mV/s, starting from the open circuit potential at 0.19 V vs. SCE. In the anode region, a current wave can be observed at about 0.9 V vs. SCE, which corresponds to the formation of the first OH monolayer on gold, that is, to the formation of low valence gold oxides (reactions 2 and 5). At a potential of 1.35 V vs. SCE the second current wave occurs corresponding to the formation of high valence gold oxides (reactions 3, 4, 6 and 7). Oxygen evolution begins at a potential of 1.45 V vs. SCE. In the cathode region a current wave occurs at about 0.86 V vs. SCE, which corresponds to the reduction of gold oxide. A.K. Vijn [13] cited in his book results of J.L. Miles et al. obtained by cyclic voltammetry for pure gold in 0.2 M sulfuric acid using rotating disc electrode. The shape of our and this voltammogram is similar, but anodic current waves potentials on our voltammogram are more negative than those recorded by Miles,

while the cathodic peak potential is a bit higher. Electrochemical behavior of gold and its alloys is much extensively investigated in alkaline media [25,26].

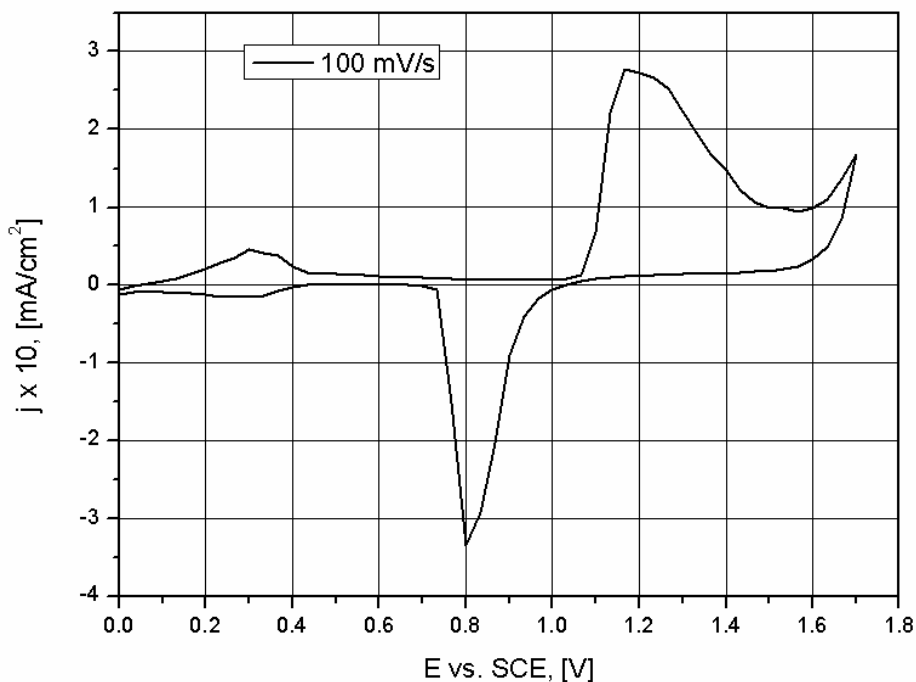


**Figure 3.** Voltammogram recorded for a Au58.5-Ag41.5 alloy at a scan rate of 100 mV/s in 1M sulfuric acid

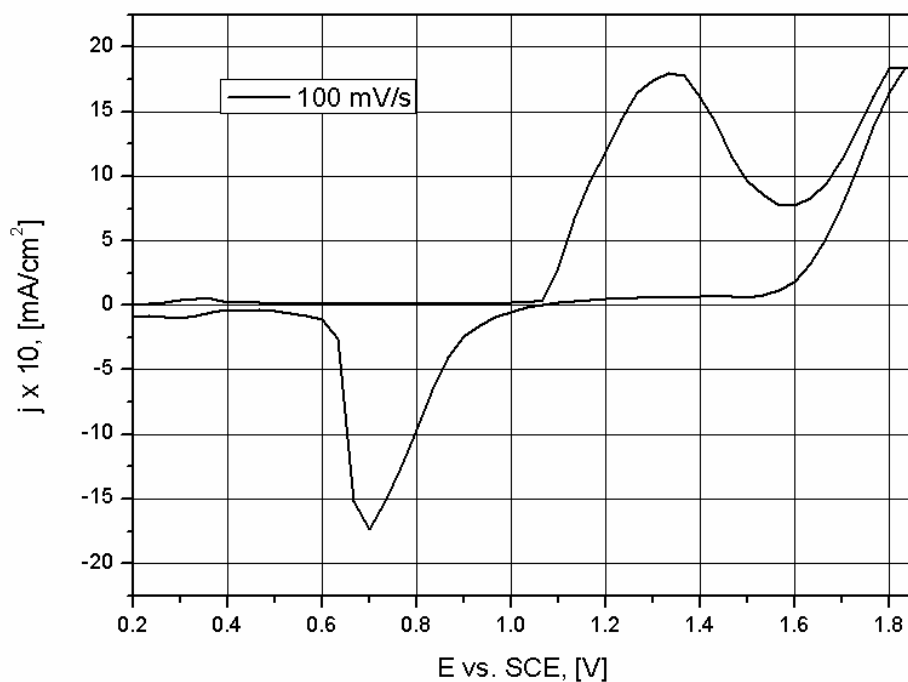
Figure 3 shows voltammogram recorded for a Au58.5-Ag41.5 alloy at scan rate of 100 mV/s. As it can be seen, on the anodic part of voltammogram at a potential of 0.55 V vs. SCE, a current wave occurs corresponding to the formation of silver oxide. At a potential of about 1.15 V vs. SCE the second current wave occurs, which is ascribed to the formation of low valence gold oxides and at a potential of about 1.35 V vs. SCE, the third wave occurs corresponding to the formation of high valence gold oxides. At a potential of about 1.4 V vs. SCE the evolution of oxygen begins. In the cathode region at a potential of about 0.86 V vs. SCE a current wave occurs indicating reduction of the formed gold oxides. At a potential of about 0.4 V vs. SCE a current wave appears which is not clearly defined and corresponds to silver oxide reduction.

Figure 4 shows voltammogram recorded for an Au58.5-Cu41.5 alloy at scan rate of 100 mV/s. In the anode region at a potential of about 0.35 V vs. SCE a current wave appears indicating copper oxide formation. This wave is followed by a wide passive zone. At a potential of 1.13 V vs. SCE another current wave appears indicating firstly the formation of low valence gold oxides, and then at 1.17 V vs. SCE high valence gold oxides as well. Oxygen evolution begins at about 1.5 V vs. SCE. In the cathode region at a potential of 0.8 V vs. SCE a peak appears associated with gold oxide reduction.

At a potential of about 0.25 V vs. SCE another current wave appears indicating copper oxide reduction.

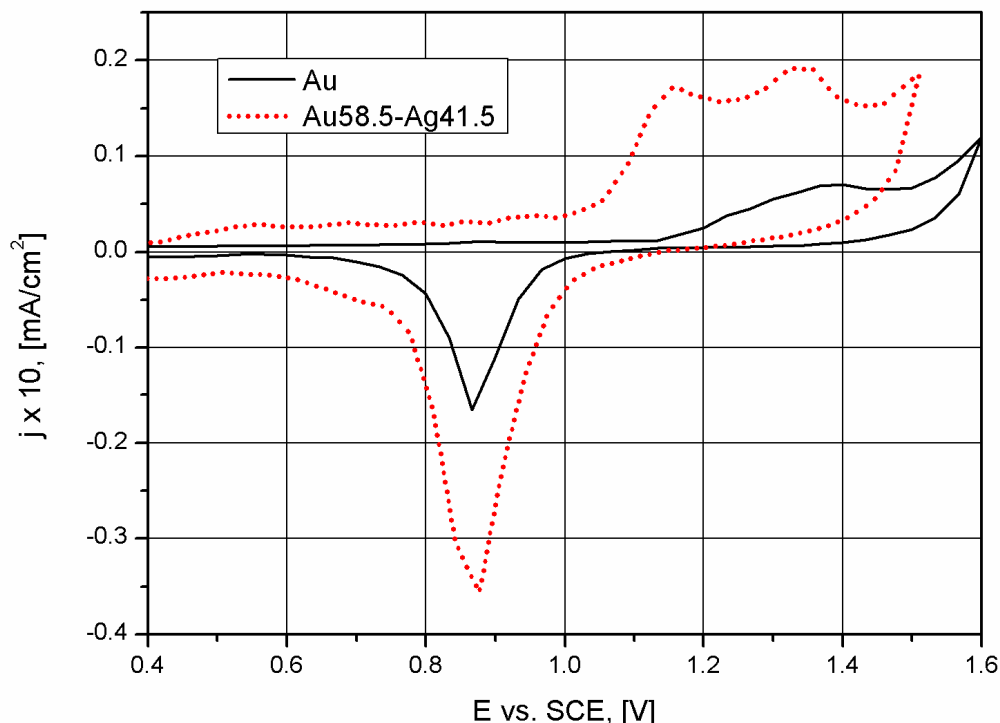


**Figure 4.** Voltammogram recorded for a Au88.5-Cu11.5 alloy at a scan rate of 100 mV/s in 1M sulfuric acid



**Figure 5.** Voltammogram recorded for a Au88.5-Ag20.75-Cu10.75 alloy at a scan rate of 100 mV/s in 1M sulfuric acid

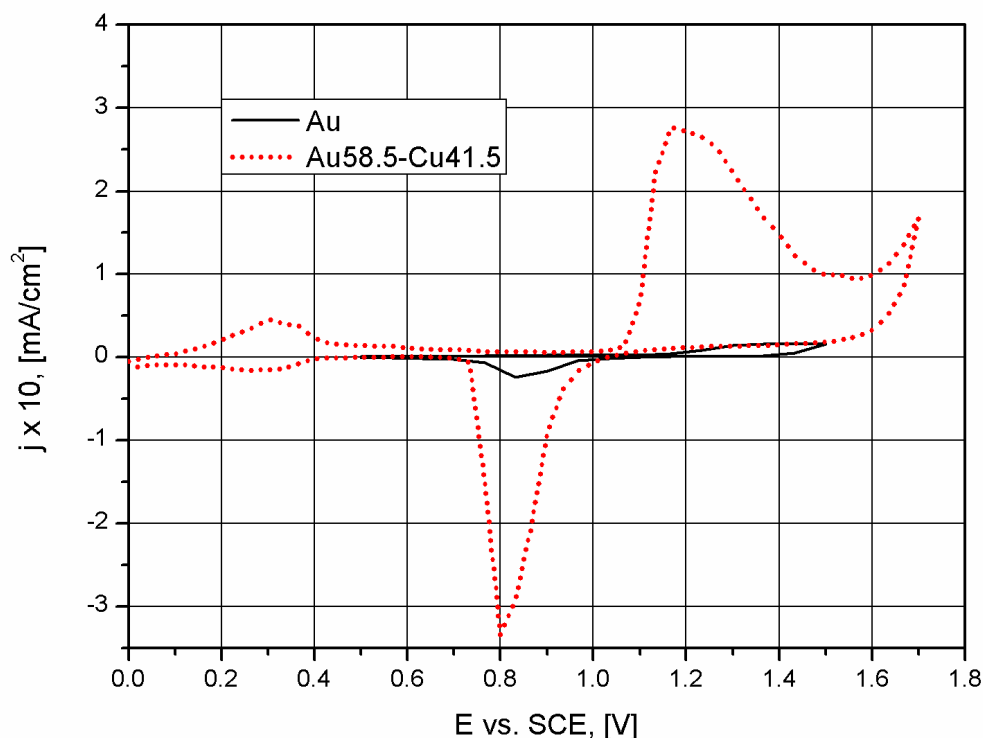
Figure 5 presents voltammogram recorded for an Au58.5-Ag20.75-Cu20.75 alloy at scan rate of 100 mV/s. In the anode region the first peak appears at about 0.33 V vs.SCE. This peak is associated with copper and silver oxidation. At about 1.33 V vs. SCE another wave appears characterized by more smaller peaks representing the formation of low valence gold oxides firstly and then the high valence ones. Oxygen evolution starts at 1.6 V vs. SCE. In the cathode region at about 0.7 V vs. SCE a wave indicating gold oxide reduction appears. At a potential of about 0.3 V vs. SCE the second wave is observed corresponding to the reduction of copper and silver oxides formed in the anode process.



**Figure 6.** Voltammograms recorded for pure gold and an Au58.5-Ag41.5 alloy at a scan rate of 100 mV/s in 1M sulfuric acid

Figure 6 shows voltammograms recorded for pure gold and for a Au58.5-Ag41.5 alloy at a scan rate of 100 mV/s in a 1M sulfuric acid. By comparing voltammograms obtained for pure gold and for a Au58.5-Ag41.5 alloy it can be seen that at all potential values the current density values for a Au58.5-Ag41.5 alloy are higher than the ones for pure gold. The voltammogram for a Au58.5-Ag41.5 alloy shows a current wave appearing at about 0.55 V vs. SCE indicating silver oxide formation. The second current wave appears at about 1.15 V vs. SCE representing formation of low valence gold oxides, whereas the third wave appears at about 1.35 V vs SCE and is associated with the formation high valence gold oxides. These two peaks are clearly defined, unlike the current wave appearing on the voltammogram for pure gold. Oxygen evolution begins at about 1.45 V vs. SCE. In the cathode region at about 0.86 V vs. SCE a current wave appears at both voltammograms representing gold oxide

reduction. The voltammogram for an Au58.5-Ag41.5 alloy shows current waves also appearing at 0.86 V vs. SCE and at 0.4 V vs. SCE, corresponding to the reduction of the phases formed in the anode part.



**Figure 7.** Voltammograms recorded for pure gold and an Au58.5-Cu41.5 alloy at a scan rate of 100 mV/s in 1M sulfuric acid

Figure 7 shows voltammograms for pure gold and an Au58.5-Cu41.5 alloy at a scan rate of 100 mV/s. By comparing these two voltammograms it can be observed that at all potential values the current density values for a 14k Au-Ag alloy are much higher than the ones for pure gold. Unlike the voltammogram obtained for pure gold, the voltammogram for an Au58.5-Cu41.5 alloy exhibits a current wave appearing first at 0.35 V vs. SCE, which corresponds to copper oxide formation. At a potential of 1.13 V vs. SCE another current wave appears indicating firstly the formation of low valence gold oxides, and then at 1.17 V vs. SCE high valence gold oxides as well. This wave can also be seen on the voltammogram obtained for pure gold. Oxygen evolution begins at about 1.5 V vs. SCE. In the cathode region a current wave appears at about 0.8 V vs. SCE on both voltammograms representing gold oxide reduction. The voltammogram obtained for an Au58.5-Cu41.5 alloy shows another current wave appearing at a 0.25 V vs. SCE associated with copper oxide reduction.

The data referring to the open circuit potential, the number of anodic and cathodic peaks as well as potential and density values of these peaks obtained in all the investigated alloys as well as in pure gold are summed up in Table 1. The table enables comparison of the results obtained experimentally on a sample declared to be pure gold or its 14k alloy in order to determine the validity of declaration.



**Table 1.** Characteristic parameters obtained by electrochemical measurements

Anodic part								
Electrode	Open circuit potential, [Vvs.SCE]	Number of anodic peaks	Anodic peak potential, [V vs. SCE]			Anodic peak current density, [mA cm <sup>-2</sup> ]		
Au	0.1865	2	$E_{Ia}$	$E_{IIa}$		$j_{Ia}$	$j_{IIa}$	
			0.9	1.35		0.1	0.69	
Au58.5-Ag41.5	0.1651	3	$E_{Ia}$	$E_{IIa}$	$E_{IIIa}$	$j_{Ia}$	$j_{IIa}$	$j_{IIIa}$
			0.55	1.15	1.35	0.29	1.7	1.9
Au58.5-Cu41.5	0.1604	3	$E_{Ia}$	$E_{IIa}$	$E_{IIIa}$	$j_{Ia}$	$j_{IIa}$	$j_{IIIa}$
			0.35	1.13	1.17	4.5	22.1	27.6
Au58.5-Ag20.75-Cu20.75	0.1708	2	$E_{Ia}$	$E_{IIa}$		$j_{Ia}$	$j_{IIa}$	
			0.33	1.33		4.7	179	
Cathodic part								
Electrode	Open circuit potential, [Vvs.SCE]	Number of anodic peaks	Cathodic peak potential, [V vs. SCE]			Cathodic peak current density, [mA cm <sup>-2</sup> ]		
Au	0.1865	1	$E_{Ic}$			$j_{Ic}$		
			0.86			-1.6		
Au58.5-Ag41.5	0.1651	2	$E_{Ic}$	$E_{IIc}$		$j_{Ic}$	$j_{IIc}$	
			0.86	0.4		-3.5	-0.28	
Au58.5-Cu41.5	0.1604	2	$E_{Ic}$	$E_{IIc}$		$j_{Ic}$	$j_{IIc}$	
			0.8	0,25		-33	-1.6	
Au58.5-Ag20.75-Cu20.75	0.1708	2	$E_{Ic}$	$E_{IIc}$		$j_{Ic}$	$j_{IIc}$	
			0.7	0,3		-174	-10	

#### 4. CONCLUSION

Cyclic voltammetry can provide data that clearly indicate whether the obtained voltammogram was recorded for pure gold, for some of its binary alloys with silver or copper, or it was done for ternary Au58.5-Ag20.75-Cu20.75 alloy. The differences are observable not only in the open circuit potential, but also in the current density values obtained at corresponding potential values as well as the number of anodic and cathodic current waves. Consequently, cyclic voltammetry with parallel recording of the open circuit potential proves to be a very fast and simple method enabling rough estimation of a gold alloy composition as well as a verification of pure gold declaration.

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