



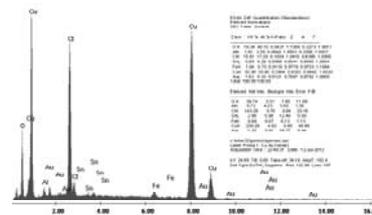
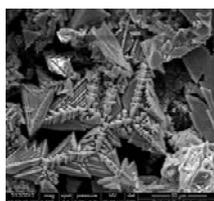
## STUDIES FOR GOLD AND SILVER RECOVERY FROM WASTE ELECTRONIC EQUIPMENT

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Printed circuit boards (PCBs) are very rich in copper and other precious metals. Cyclic voltammetry technique was applied for studies of gold and silver electrodeposition from synthetic solutions on graphite and copper electrodes. Different support electrolytes like: H<sub>2</sub>SO<sub>4</sub> 0.5M, HCl 0.1M and HNO<sub>3</sub> 1M were used. Studies were made in (-1200) to 500 mV interval at different scan rates and number of cycles. Tests for precious metals recovery from selected WEEE started with dissolution of wastes in nitric acid and aqua regia. Electrodeposition of gold and silver on different electrodes were performed. The metal deposits were characterized by scanning electron microscopy-energy dispersive-X-ray analyses. Decreasing of metals concentration from initial solutions was followed by atomic absorption spectrometry. In experiments, a new conceptual installation was using. Over 95% Au and 97% Ag were removed from real solutions by electrodeposition, but the metal deposits have not enough adherences on the electrode material.



### INTRODUCTION

Every year, in the European Union, more than 8 million tones of waste electronic and electrical equipments (WEEE) are generated.<sup>1-3</sup> Directive 2002/96/EC establish the categories of WEEE.<sup>4</sup> The European Commission's Waste Electronic and Electrical Equipments require sustainable activities for the re-use, recycle and recover the WEEE rather than the disposing of them in landfill sites. Nowadays, there are hydrometallurgical processes<sup>5-7</sup> and pyrometallurgical processes like: Noranda in Quebec-Canada, Umicore in Belgium, Rönnskär Smelter in Sweden used for treatment of tones WEEE /year,<sup>8-10</sup> but sometimes the costs of processes are higher than the value of precious

metals recovered. Printed circuit boards-PCBs are particularly rich in copper and precious metals. Difficulties on metals recycle appear due to the heterogeneous mix of organic materials, metals and glass fibers. Researchers proposed different methods for precious metal recovery like: solvent extraction,<sup>11, 12</sup> precipitation, adsorption/biosorption of metals,<sup>13</sup> ion exchange,<sup>14</sup> electrochemical processes,<sup>15</sup> biometallurgical processes with bacteria for gold, copper and other metallic ions,<sup>16-18</sup> etc.

Electrochemical approach can be considered a simple and clean method to recover metals from WEEE in their metallic state. Cathodic electrodeposition of precious metals can be a versatile, safe and beneficial process. The aim of this work was the recovery of Au and Ag from selected

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WEEE by leaching with acids and the electrochemical treatment of the resulting solutions.

## RESULTS

**Cyclic voltammetry.** Cyclic voltammetry technique was used for Au and Ag electrodeposition

studies. Cyclic voltammograms were recorded on interval (-1200) – (500) mV, at different scan rates and number of cycles. Low current densities are obtained in 0.5M H<sub>2</sub>SO<sub>4</sub> as supporting electrolyte. Figs. 1 and 2 present some results on copper electrode. Two methods based on leaching with acids were used in this work.

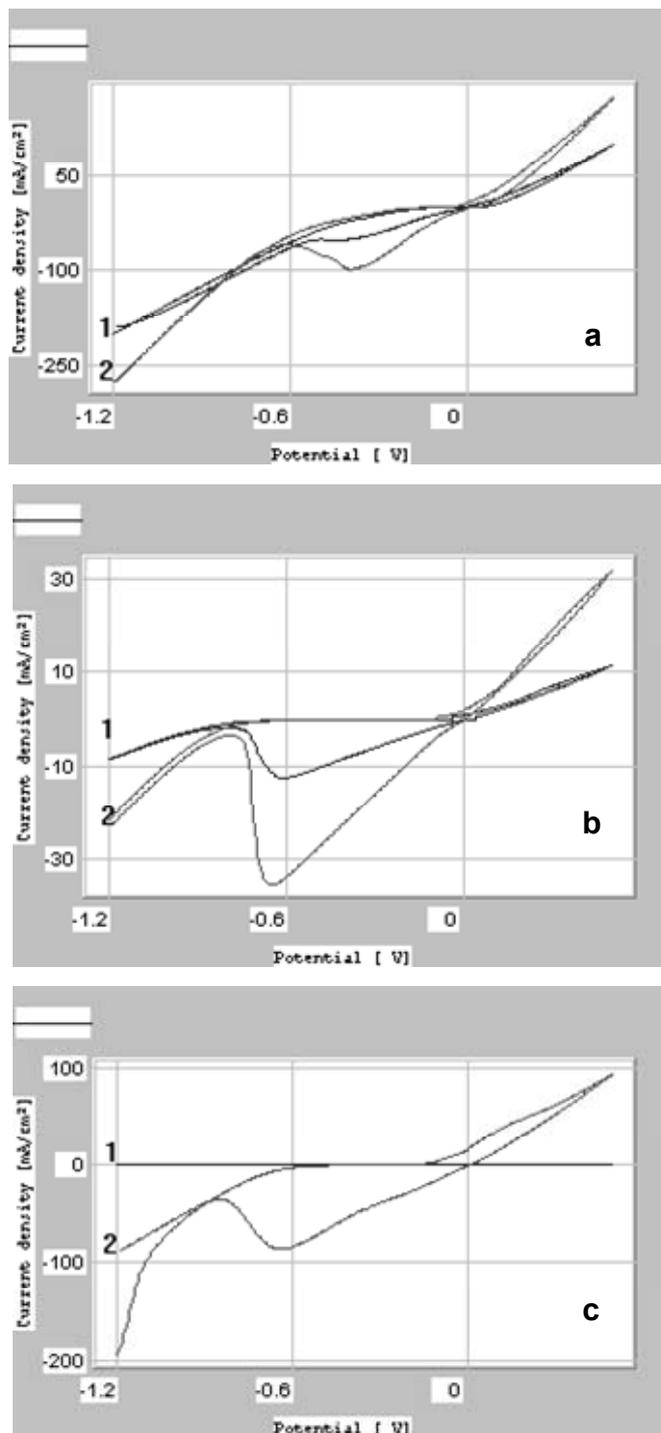


Fig. 1 – Cyclic voltammograms of 0.2 mM Au on copper electrode in different support electrolytes: a – HNO<sub>3</sub> 1M; b – HCl 0.1M; c – H<sub>2</sub>SO<sub>4</sub> 0.5M; 1 – supporting electrolyte; 2 – gold solution.

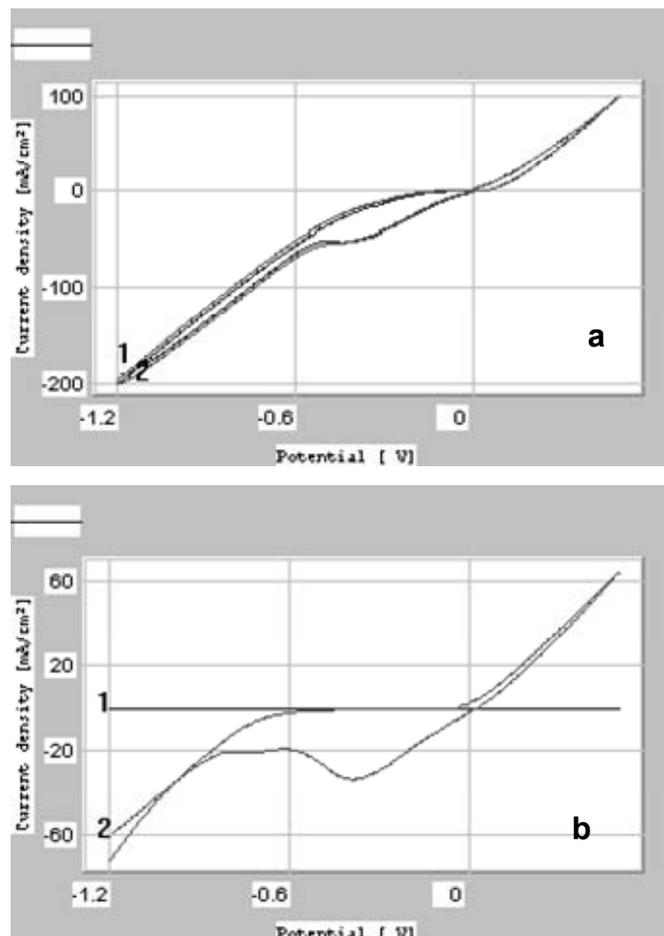


Fig. 2 – Cyclic voltammograms of 0.2 mM Ag on copper electrode in different support electrolytes: a – HNO<sub>3</sub> 1M; b – H<sub>2</sub>SO<sub>4</sub> 0.5M; 1 – supporting electrolyte; 2 – silver solution.

**Method I.** In order to recover the valuable metals, the electronic wastes from PC components have been treated with aqua regia for 4 hours (solid/liquid ratio was 1/10). After filtration of residues, solution composition was determined by atomic absorption spectrometry (AAS). The metals of interest concentrations were: 4132.50 mg/L Cu, 33.0 mg/L Au and 1.35 mg/L Ag.

The solution was diluted 1:15 v/v with HCl 0.1 M. Electrodeposition of metals from wastes

was conducted using a simple cell with two vertical fixed electrodes and a continuous current source LAB EC 3010. First, we used stainless steel anode ( $S=2\text{ cm}^2$ ) and graphite cathode ( $S=1.3\text{ cm}^2$ ), at 2.3 V and  $0.03\text{ A/cm}^2$ , during 20-50 min. Second, we used stainless steel anode ( $S=2\text{ cm}^2$ ) and copper cathode ( $S=1.3\text{ cm}^2$ ), at 1.9 V and  $0.02\text{ A/cm}^2$ , during 20-50 min.

The composition of solutions during the processes is presented in Table 1.

Table 1

The composition of solutions during the electrodeposition

Metal	Initial concentration [mg/L]	Concentration after 20 min (graphite cathode) [mg/L]	Concentration after 20 min (copper cathode) [mg/L]	Concentration after 50 min (graphite cathode) [mg/L]	Concentration after 50 min (copper cathode) [mg/L]
Cu	275.5	234.9	232.0	170.6	194.0
Au	2.2	1.8	1.8	0.9	*
Ag	0.09	0.08	0.08	*	*

\* under detection limit of apparatus

Table 2

Gold and silver concentrations during the process (copper cathodes)

No.	Time [min]	Gold concentration [mg/L]	Silver concentration [mg/L]
1.	0	102±10	4±1
2.	10	68±29	1±0
3.	20	45±10	1±0
4.	30	14±1	*
5.	40	10±1	*
6.	50	5±2	*
7.	60	4±0	*

\*under detection limit of apparatus

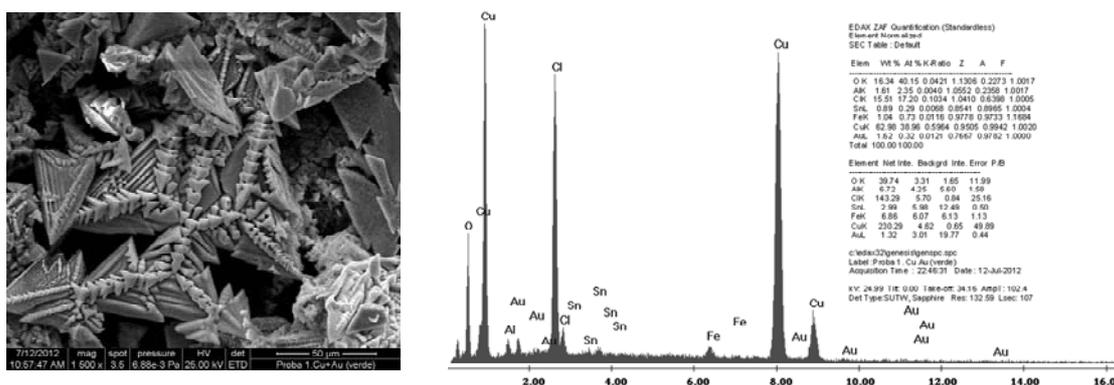


Fig. 3 – SEM image and EDAX spectrum for deposit on graphite cathode.

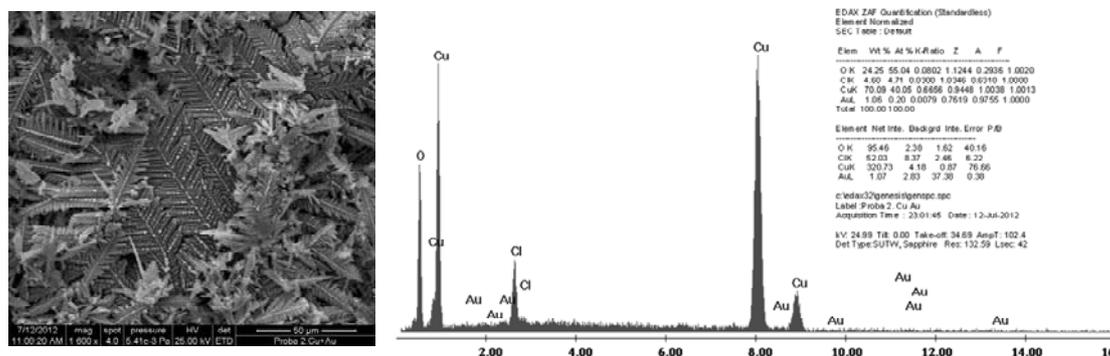


Fig. 4 – SEM image and EDAX spectrum for deposit on copper cathode.

**Method II.** PCBs were manually selected. They were dissolved in two steps: first in HNO<sub>3</sub> 30% for major elimination of copper – **solution 1** (solid/liquid ratio was 1/10), and then the residues were treated with aqua regia for gold and silver recovery – **solution 2** (solid/liquid ratio was 1/10). After non-metallic material filtration, solution 2 was processed using a new conceptual laboratory installation. The solution was diluted 1:6 with HCl 0.1 M. Concentration of precious metal during the process is presented in Table 2. AAS analyses showed a removal of 96% gold and 98% silver from solution (there are very small quantities of silver in WEEE).

The deposits obtained have not enough adherences on the electrode material and part of them dropped at bottom of the cell.

## DISCUSSION

Composition of WEEE regarding Cu, Au and Ag content varied very much as a function of sources and origin, age and types of devices. Therefore, composition of leaching solutions can vary very much. Method I was applied for small quantities of solutions (20 mL). The aspect of deposits is presented in Figs. 3 and 4. Very interesting dendritic deposits were obtained on graphite, but graphite cathodes are fragile.

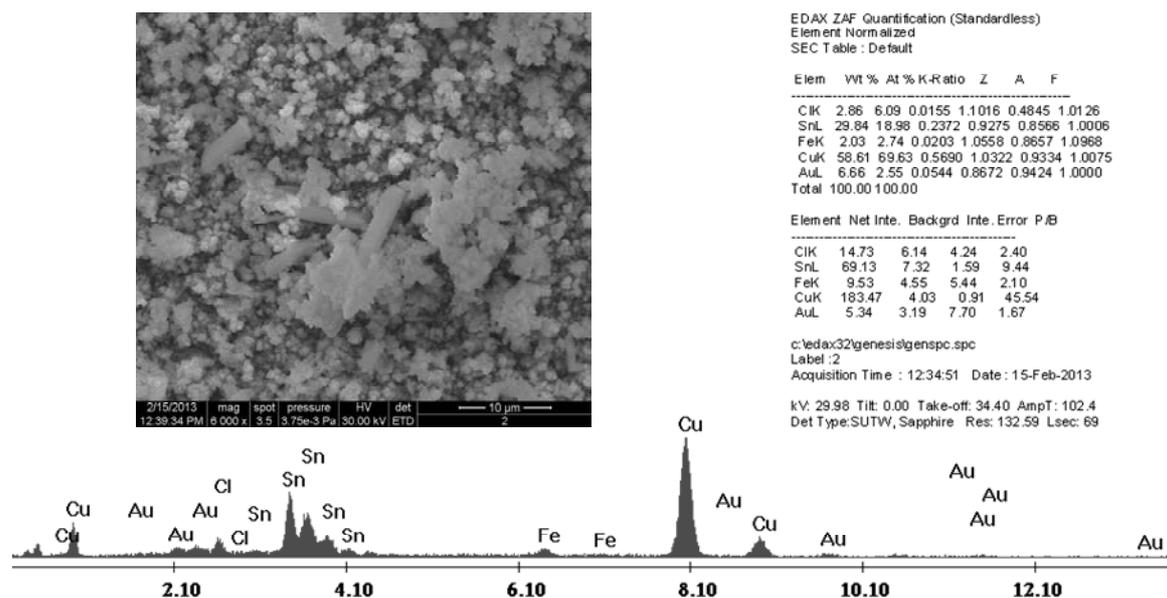


Fig. 5 – SEM and EDAX aspect of deposit obtained from *solution 2* in laboratory installation.

Method II was applied for large quantities of PBCs. *Solution 2* was processed in the laboratory installation. The up-down movement of cathodes determined permanently the renew of liquid surface contact with the electrodes and ensured reduction of the diffuse layer. The increasing of metal ions concentration near the cathodes determined the intensification of electrodeposition process. Unavoidably, other metallic ions like tin and iron appeared in deposits (Fig. 5).

## EXPERIMENTAL

### Materials

Materials for electrodes construction were purchased from local market. Hydrochloric acid 37%, sulphuric acid 95-97% and nitric acid 65% were purchased from Merck, Germany. AAS standard solutions for metals were purchased from Fluka, Germany. Ultrapure water for analyses was obtained by an EASypure® RoDi Barnstead system for laboratory water purification (USA). WEEEs were manually selected from old computers.

### Analyses

AAS analyses<sup>19</sup> were performed in order to determinate the decrease of gold and silver concentration in solutions. It was used a spectrophotometer novAA 400 G, Analytik Jena – Germany, equipped with graphite furnace, auto sampler MEP 60 and 3.17.0 WinAAS software for evaluation and control of the results. Calibration curves have been plotted using AAS standard solutions for metals (plots are not presented).

The metal deposits were characterized by scanning electron microscopy-energy dispersive-X-ray analysis (SEM – EDAX) using a Scanning Electron Microscope Inspect S + EDAX Genesis XM 2i, FEI Company, Netherlands..

### Electrochemical experiments

Initially, electrochemical experiments were carried out with a Voltalab 80 PGZ 402 apparatus-Radiometer Copenhagen, using a three-electrode electrochemical cell (carbon or copper interchangeable working electrode, a platinum wire as auxiliary electrode and a reference electrode Hg/Hg<sub>2</sub>Cl<sub>2</sub>/KCl sat.). Synthetic solutions of Au and Ag 0.2 mM were prepared from AAS standards in different electrolytes: H<sub>2</sub>SO<sub>4</sub> 0,5M and HNO<sub>3</sub> 1M and HCl 0.1M. Electrodes were cut as pills with same surface (S=0.24 cm<sup>2</sup>). After 200-300 cycles, the electrodes were inspected at microscope.

### Laboratory installation

A new conceptual installation was constructed in our lab. In a transparent plexiglass rectangular cell (0.1 L), three stainless steel anodes were fixed. Two cathodes (copper) were sandwiched between anodes and were moved up and down by a mechanical system. Distance between electrodes was 1 cm. Electrodes were mechanically cleaned with abrasive paper and then by ultrasonically treatment with HCl 3% for 5 min. before use. A current source LAB EC 3010, an ammeter and a voltmeter were connected with electrochemical cell. Active surface of cathodes was 36 cm<sup>2</sup>. Current was fixed at 0.7 A. The solution was processed at U=1.4÷1.5 V. Constant current density was maintained at 0.02A/cm<sup>2</sup>. Experiments were conducted at 23±2°C. The samples (0.5 mL) at the predetermined time periods are taken out from the same place of cell. Contents of Au and Ag were analyzed by AAS technique. Process was followed for 60 min. Deposits at the cathodes were washed with ultrapure water and left hanging in air to dry. The surface morphology of deposit was inspected by scanning electronic microscopy and energy dispersive X-ray spectroscopy.

## CONCLUSIONS

Cyclic voltammograms of synthetic solutions of gold and silver on interval (-1200)-500 mV

showed that the deposition of precious metals on graphite and copper cathode occurs at lower current density in H<sub>2</sub>SO<sub>4</sub> 0.5M and then in HNO<sub>3</sub> 1M and HCl 0.1M. Two techniques of WEEE processing were used: the dissolution directly in aqua regia and the dissolution in HNO<sub>3</sub> 30% for major elimination of copper, and then the residues treatment with aqua regia for gold and silver recovery. According to Method II, over 96% gold and 98% silver were removed from real solutions using a new conceptual laboratory installation for electrochemical process.

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