



Article

# Preliminary Study on Gold Recovery from High Grade E-Waste by Thiourea Leaching and Electrowinning

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**Abstract:** The present paper is focused on the extraction of gold from high-grade e-waste, i.e., spent electronic connectors and plates, by leaching and electrowinning. These connectors are usually made up of an alloy covered by a layer of gold; sometimes, in some of them, a plastic part is also present. The applied leaching system consisted of an acid solution of diluted sulfuric acid (0.2 mol/L) with thiourea (20 g/L) as a reagent and ferric sulfate (21.8 g/L) as an oxidant. This system was applied on three different high-grade e-waste, namely: (1) Connectors with the partial gold-plated surface (Au concentration—1139 mg/kg); (2) different types of connectors with some of which with completely gold-plated surface (Au concentration—590 mg/kg); and (3) connectors and plates with the completely gold-plated surface (Au concentration—7900 mg/kg). Gold dissolution yields of 52, 94, and 49% were achieved from the first, second, and third samples, respectively. About 95% of Au recovery was achieved after 1.5 h of electrowinning at a current efficiency of only 4.06% and current consumption of 3.02 kWh/kg of Au from the leach solution of the third sample.



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**Keywords:** gold; e-waste; connector; thiourea; electrowinning

## 1. Introduction

The exponential growth of waste electronic and electric equipment (WEEE) has increased over the years, especially in the last twenty years. This is mainly due to the great development of the technology relevant to personal computers (PCs), mobile phones, tablets, and, generally speaking, electronic equipment whose replacements with more advanced devices are very fast.

Recycling of WEEE implies several advantages, in particular, the recovery and reuse of metals and materials that can be re-introduced in the manufacturing chain of new electric and electronic equipment (EEE) or other devices, in the perspective of the new concept of the circular economy. There is also an additional environmental benefit, represented by avoiding the landfilling practices that can release heavy metals in groundwater tables due to the leaching action of rainwater [1].

EEE contain several metals of interest, like base (Cu, Fe, Pb, Sn) and precious (Au, Ag, Pd) metals. The latter ones are abundant in motherboards, connectors, and integrated circuit pins. Many of these components are assembled in printed circuit boards (PCBs) that, however, contain around 70%wt of plastic-composite materials like epoxy resins, glass fibers, and brominated compounds used as flame retardants [2].

A double stage leaching with H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> to extract Cu and Sn and a second stage with SC(NH<sub>2</sub>)<sub>2</sub>/Fe<sup>3+</sup>/H<sub>2</sub>SO<sub>4</sub> to dissolve Au and Ag was proposed by Birloaga et al. [3,4]. Among hydrometallurgical processes developed for spent PCBs, those using thiourea or other chemical mixtures like HCl/H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>COOH [5] are the most used, as they do not involve very hazardous and toxic compounds.

Several other processes were investigated to recover metals from PCBs [6–14], but, considering the circular approach of the full recycling concept, even the recovery of the

non-metallic fraction of PCBs was studied [10]. Debromination is a necessary treatment before any other recycling process. The research activity's development goes towards the circular economy approach of the full recycling of spent devices [15–17]. Furthermore, the recovery of the plastic fraction limits the spread of microplastics, which is another current environmental concern.

Thermal treatments are also applied to remove the plastic fraction and concentrate the metal fraction into the char [18], which hence undergoes hydrometallurgical treatments to dissolve, separate, and refine the most valuable and concentrated metals. The hydrothermal, as the thermal ones, also have the important role of detoxification of the materials, as PCBs contain brominated flame retardants that have to be removed from flue gas [19]. The hydrothermal treatment is a thermochemical conversion process, in the presence of water, at high temperature (200–375 °C) and high-pressure (up to 220 bar) [20]. It produces a liquid fraction containing organic compounds generated from the decomposition of plastics and a metal residue.

Moreover, waste PCBs are the sole valuable WEEE whose recycling is profitable [21], without any environmental fee [14].

Considering the technical aspects, PCBs are usually crushed and milled after the removal of special components, like small aluminum heat exchangers, capacitors, transistors, etc. The crushing pre-treatments, unfortunately, cause the loss of a considerable amount of gold and other metals of interest that are pulverized and sucked by the dedusting systems. Nevertheless, such concentrated powder can be recovered in cyclones or bag filters and treated in the hydrometallurgical section of the plant. One of the systems foresees the leaching of whole or large pieces of PCBs. Jadhav and Hocheng [22] removed the epoxy solder mask of PCBs by 10 mol/L NaOH solution and thus leached the large pieces by different acids, both organic and mineral. The dissolution of Au, Ag, Pd, and Cu was quantitative, although at least 24 h are required to achieve such a result. Other authors tried the biometallurgical approach using *Acidithiobacillus ferrooxidans* to maximize the dissolution of Cu, Fe, and Ni: 100% of the first two metals were dissolved, whereas the dissolution yield of Ni was only 54% [23].

An integrated process used the combination of ammonium thiosulfate and *Lactobacillus acidophilus* for selective biosorption of gold from the contact point of PCBs. This novel leaching-sorption method allows 85% of gold recovery [24].

Other authors concentrated on base metals contained in PCBs, increasing the circular approach using spent solutions from PCB manufacturing processes to recover Cu, Sn, and Pb [25].

In the past, the most used and efficient method for the extraction of gold from ores was cyanidation. One study even tested this process on PCBs. 10 g/L sodium cyanide solution at 40 °C is able to dissolve 95% of gold in 15 min. Gold was recovered from the leachate by adsorption onto charcoal [26].

There are some electric and electronic components that are much richer in precious metals over the household WEEE. These components like connectors, processors, integrated circuits, microchips, etc., coming from special equipment such as army and space applications, contains more Au, Ag, and Pd per mass unit.

The connectors are used in several applications depending on their requirements; they are made of different materials. The choice of base, insulation, and interface (plating) materials at the beginning of the connector design process essentially define the connector characteristics, determining how well the overall device or system will operate. Copper is the most used base material in the manufacturing of both input and output connectors. However, for certain connectors, copper is applied as a base alloy (i.e., brass, bronze, and aluminum bronze with nickel) or as underplating on base materials (steel, brass, aluminum zinc, and copper-beryllium) or as underplating for final plating (solder coatings and tin-nickel plate). Beryllium copper alloy (CuBe<sub>2</sub>) represents an alternative to pure or even silver-bearing copper, as it has a better corrosion resistance and has better machinability than copper, but not as good as brass.

However, as this alloy has a higher price, its use is limited to the following connector components: Contact sockets (electrical contacts) and spring elements. Bronze is the alloy between Cu and Sn, including some phosphorous and zinc complexes. It is considered a suitable alternative to other copper alloys, particularly when the connector technical specifications do not mandate CuBe<sub>2</sub>. Generally, this alloy is used for the production of the following connectors parts: large contact sockets, resilient contacts, and outer conductors. Brass is the alloy between copper and zinc and is normally plated either with gold, silver, or SUCOPLATE. This alloy is used in the housings, outer conductors, and contact pins of connectors. Stainless steel is used for applications that require a hard metal, i.e., the outer conductor. Generally, it is used as a base material for bodies and outer contacts.

Concerning plating materials, gold can be deposited on copper or nickel. However, in certain applications (military, space, etc.), the designer might want to apply a thicker layer of gold as the base plate. To minimize the cost of the connector, the thickness of the gold plating is usually kept to a minimum. Even if gold is corrosion-resistant, with the minimization of thickness, the risk of contamination (because of high porosity) and wear-through is detected. Therefore, the use of the gold plating variation SUCOPRO is considered a suitable alternative. Usually, connectors' gold-plated components are inner conductors, springs, and generally the bodies and outer conductors of PCB connectors (only for soldering). SUCOPRO is a thin gold plating layer with a nickel-phosphorus alloy (13% phosphorus) underlayer. Its main advantages are excellent wear and corrosion resistance, low contact resistance, very high strength of solder joints without embrittlement, and excellent wettability/solderability. Silver can be plated on base materials of most ferrous and non-ferrous metals and is found as a plated layer of the following connectors/cable components: conductors, contacts, and sleeves [27].

Besides these base and plating materials, various plastics and rubbers are used for the manufacturing of connectors. Polyethylene (PE) is used for turned insulators, wire, and cable insulation, cable jacket material, corrugated cables, and packaging. Polytetrafluoroethylene (PTFE) is used for insulators, gaskets, and anti-adhesive coatings. Polyether-Etherketone (PEEK) is used for radiation-resistant wire insulation, wire coating, and insulators. Polyphenylene oxide (PPO) is used for thermal and electrical insulator parts, switch housings, covers. Silicone rubber is used for gaskets.

All these characteristics of connectors are important to determine the best way of treatment of the spent connectors. In this paper, coaxial connectors constituted by brass as the base material, gold as a plating material, and PTFE as insulating were chemically characterized and studied in order to identify a technical and economically feasible process to recover industrial interest metals, focusing on gold for his higher economic value.

In the present paper, the application of the thiourea acidic leaching and electrowinning process for Au recovery from high-grade e-waste is presented. This study shows the preliminary results obtained in a wide experimental campaign whose aim is to design and optimize a recycling process for gold-rich materials.

## 2. Materials and Methods

### 2.1. Characterization of the Connectors

Three samples of high-grade e-waste were provided by a company located in central Italy (Arezzo, Italy). The samples underwent acid digestion with aqua regia (HCl:HNO<sub>3</sub> = 3:1) with a solid to liquid ratio (S/L) of 1:20 % wt/vol with Ethos Up Milestone microwave digestion system (Milestone Srl, Sorisole, Italy). The adopted digestion program included 20 min isotherm at 220 °C. The whole program lasted 2 h, a sufficient time for solubilization of the metal fraction: in this way, only the plastic fraction remained as residue. The solid residue obtained by the digestion was only the PTFE component. The acid solution was diluted to 50 mL with deionized water in a calibrated flask and stored to determine metals by inductively coupled plasma optical emission spectrometry (ICP-OES 5100) (Agilent Technologies, Cernusco sul Naviglio, Italy). To have a reasonable estimation of the content of the base and precious metals of interest, twenty replications were carried out on first

sample. The average concentration and the standard deviation of Au, Ag, Pd, Cu, Zn, Pb, and Sn were determined (Table 1).

**Table 1.** Average (Avg.) concentration and standard deviation (Std. Dev.) of metals in connectors, sample 1.

Metal Concentration	Au (mg/kg)	Ag (mg/kg)	Pd (mg/kg)	Cu (%wt)	Zn (%wt)	Pb (%wt)	Sn (mg/kg)
Avg.	1139	2417	15.4	53.5	32.7	2.2	385
Std. Dev.	317	707	3.9	1.4	1.0	0.3	321

The first sample (Figure 1) is visually composed of a plastic component covered by brass and the metallic part covered by gold.



**Figure 1.** First sample of connectors with partial gold-plated surface.

As shown in Figure 2, the second sample, constituted by different types of connectors, some of which are totally plated with Au and present a plastic part within connectors structure.



**Figure 2.** Second sample of connectors.

The third sample, Figure 3, is constituted by connectors and plates with the completely gold-plated surface.



**Figure 3.** Third sample of connector and plated with the completely gold-plated surface.

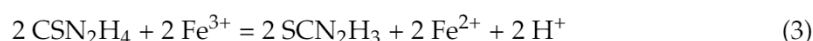
X-ray diffraction analysis were performed on the solid product obtained by electro-winning as confirmation of the results. PANalytical XPert PRO diffractometer (Malvern Products, Rome, Italy) equipped with XCellerator detector, and Cu X-ray source was used. The diffraction pattern is registered in the range of 10–70° 2Theta and 0.026° steps.

## 2.2. Leaching Procedure

The thiourea leaching system was tested on all three samples. The leaching mechanism of gold and silver leaching by thiourea in sulphuric medium and in presence of Fe<sup>3+</sup> ions is expressed by the following reactions [28]:



During this process, the oxidation of thiourea to formamidine disulfide (FDS) takes place (Equation (3)). This reagent is not stable in acid solution and oxidation conditions. Therefore, FDS decomposes irreversible to thiourea, cyanamide, and sulphur (Equation (4)).



Besides, if thiourea is not added in excess by ferric ion concentration, the reactive is lost according to the following reactions:



Fe<sup>3+</sup> ions are used as oxidant and thiourea as a complexing agent, whereas sulphuric acid assures that the pH remains acidic, avoiding iron precipitation. This treatment was chosen as the precious metals are on the connectors' surface, so the competition against copper in consuming thiourea is greatly reduced.

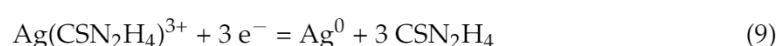
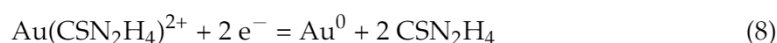
The runs for the first sample were carried out in 250 mL flasks, under magnetic stirring (300 rpm) with 0.2 mol/L H<sub>2</sub>SO<sub>4</sub> solution, 20 g/L of thiourea, and 21.8 g/L of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The S/L ratio was 10% wt/vol, and the reaction time was investigated up to 1.5 h, at the end of which the solution was filtered by a vacuum pump and a 0.45 μm paper filter and

stored for the analysis. These experimental conditions were chosen after the optimization was achieved after several tests carried out with PCBs [1–3].

The runs on the completely gold-plated connectors and plates (second sample) were carried out with (second sample) (100 rpm) and without magnetic stirring (third sample) for 1 h using the concentration of the above-presented reagents. Metals' concentration was determined by ICP-OES, and the dissolution yields were determined as a percentage of the content determined by acid digestion [29].

### 2.3. Electrowinning Procedure

During the electrowinning process into an acid solution of thiourea, gold and silver are reduced to cathode according to the following reactions:



Besides, as the thiourea process was performed in the presence of ferric ion, the resulted formamidine disulfide, at controlled cathode potential may be reduced back to thiourea according to the following reaction:



At the anode occurs the water decomposition reaction:



Most of all scientific works have been conducted on solutions obtained by stripping of gold from activated carbon with solutions of diluted sulfuric acid containing the only thiourea as reagent [30]; immersion of both gold and silver complexes within acidic thiourea solution [31]; dissolution of metallic gold within the solution of acidic thiourea with a small excess of hydrogen peroxide and with/without the presence of alcohol [32]. The authors have shown that both precious metals can be recovered efficiently from their solutions by this technology within these papers. However, it was shown in many articles that the current efficiency of the process is very low for the recovery of both elements. This is due to the parasitic reactions (e.g., reduction of hydrogen to the cathode and partial degradation of thiourea to anode) during the process.

The solution obtained by thiourea leaching from the first sample with gold and silver concentration of 20 mg/L and 250 mg/L, respectively, was subjected to electrowinning in order to recover gold and silver as metals. Since the current efficiency decreases with the increase of current density for gold electrowinning from thiourea solutions [33], a value of 40 A/m<sup>2</sup> of current density was adopted. The other operative conditions that allowed maximizing the gold recovery were the following: cylindrical graphite electrodes with a surface area of 6.8 cm<sup>2</sup>, room temperature, 100 rpm of stirring, and cell potential of 0.9 V. The recovery of gold and silver was investigated as a function of time carrying out the chemical analysis on the solution.

For other electrowinning tests (second sample), the influence of current-voltage parameters was studied. Runs were conducted in galvanic conditions at different current intensities (75, 100, and 200 mA) and corresponding cell potential (0.9, 1.2, and 1.5 V) on the solution achieved after treatment of connectors of the second sample. 100 mL of solution and two cylindrical electrodes of graphite with a surface area of 26.12 cm<sup>2</sup> each were used for all three runs. The experiments were performed under continuous magnetic stirring (100 rpm) for 1.5 to 3 h at room temperature at 2 cm distance between the electrodes and 41% of electrodes surface area immersed within the solution. The optimal conditions of electrowinning runs of the second sample were also tested for an electrowinning test with a cathode of copper and graphite as the anode of the same dimensions. Moreover, the same

optimal conditions of electrowinning were adopted for the treatment of solution achieved after leaching of the third sample with the graphite electrodes.

A laboratory rectifier (EA-PS 3016-20 B) with an output power of 0–16 V and output current of 0–20 A was used for these tests.

A sampling of the solution of each test was performed at predetermined time intervals and then analyzed by ICP-OES for Au and Ag content. The thiourea concentration determination within solution achieved after both leaching and electrowinning procedures was performed by titration with  $\text{KIO}_3$  and potato starch as indicator [34].

### 3. Results and Discussion

#### 3.1. Characterization of the Connectors

The concentration of the foremost metals of sample 1 is listed in Table 1.

The results showed that a gold average concentration of 1139 mg/kg was determined, the main components were copper and zinc: 53.5% and 32.7%, respectively. With regard to the other precious metals 2417 mg/kg of silver and 15.4 mg/kg of palladium were detected. Figure 4 shows the connectors before and after the chemical digestion.



Figure 4. Sample 1 before (right) and after (left) acid digestion.

Gold content of different type of connectors (sample 2) were reported in Table 2.

Table 2. Au content within different types of connectors (sample 2).








Type of Connector and Its Weight	Photographic Aspect	Au Concentration (mg/kg)
1—large round connector—13.22 g		885
2—thin and long connector—2.06 g		446.7
3—medium long and thin connector—1.77 g		524.7
4—long and very thin connector—0.84 g		726
5—squared connector—3.30 g		440
6—round and medium long connector—2.05 g		370

Table 2. Cont.

Type of Connector and Its Weight	Photographic Aspect	Au Concentration (mg/kg)
7—round and short connector—1.17 g		370

A gold average of 590 mg/kg was obtained by mixing all the above-presented connectors. Concerning the plates and the connectors with the completely gold-plated surface of the third samples a gold content of 7900 mg/kg was determined.

### 3.2. Thiourea Leaching of Gold from the First Sample

The results of the replicated thiourea leaching tests for the first sample were reported in Table 3. Au dissolution yield was 31% only after 1 h of reaction, whereas those of Ag and Cu were 76% and below 1%, respectively. The result was rather unsatisfying, so another test was carried out applying a counter-current leaching process with four stages: every stage, fresh reagents were added, according to the concentrations indicated in Section 2.2, to treat the same connectors sample.

Table 3. Gold and silver cumulative dissolution yields as a function of stage number.



Stage Number	Au Extraction (%)	Ag Extraction (%)
1	30.6	75.9
2	44.5	94.7
3	51.6	95.1
4	52.7	95.1

After the third stage, the total Au dissolution yield was 52%, whereas 95% and 5% of Ag and Cu were leached, respectively.

### 3.3. Thiourea Leaching of Gold from Second and Third Samples

The second sample with 590 mg/kg of Au was obtained by mixing all the types of connectors that were previously subjected to chemical attack, in order to evaluate the efficiency of thiourea leaching. The third sample, with a gold content of 7900 mg/kg was also leached within the conditions presented within Section 2.2. The recovery yields are reported in Table 4.

Table 4. Gold content within leaching solution and recovery.

Sample	Photographic Aspect of Solid Residue	Au Recovery (%)
2nd sample		93.9
3rd sample		49.0



The result of the leaching of completely gold-plated surface connectors demonstrates that this leaching process can efficiently recover about 94% of the gold content of these wastes. This fact demonstrates the suitability of this leaching system for gold dissolution. Not complete dissolution is achieved due to the fact that once the Au layer is dissolved, the copper metal substrate is exposed to leaching media (the sample has a copper content of 80%). This base metal determines both Au cementation and the degradation of thiourea to elemental sulfur that rapidly passivates the precious metal surface and prevents the gold dissolution [1–3]. Besides Au, 80.8 mg/L of Ag were detected within the leaching solution of the second sample. A relatively high gold dissolution was also achieved from the third sample. This was probably due to the very large content of Au within the solid material. So far, there is no data about the amount of Au that can be dissolved with this leaching system.

Moreover, no silver was detected within the leaching solution of this sample. This may be due to the fact that the gold layer was not completely dissolved, and, therefore, the substrate of the silver layer was not exposed to the leaching environment. The determined concentration of thiourea had a value of 12.2 and 12.5 g/L for the solution of leaching of the second and third samples, respectively. The high consumption of thiourea is due to its oxidation by ferric ion to formamidine disulfide. This complex is not stable in acidic solutions and decomposes irreversibly, producing elemental sulphur and cyanamide. Both solutions have been further subjected to the electrowinning process. The pH of all solutions was measured after each test using an electrode.

### 3.4. Electrowinning

#### 3.4.1. Electrowinning Test on Solution of First Sample Leaching

Gold and silver were recovered from the solution obtained by the first stage of thiourea leaching by electrodeposition. In Table 5, the results of gold and silver deposition as a function of time were reported.

**Table 5.** Gold and silver recovery as a function of time by electrowinning.

Time of Reaction h	Au Recovery (%)	Ag Recovery (%)
0.25	38.1	18.1
0.50	50.4	25.0
0.75	55.9	32.5
1.00	62.4	36.9
1.25	68.7	46.2
1.50	72.8	53.5
1.75	79.0	62.2
2.00	79.0	62.2

After 1 h of the process, the maximum difference between gold and silver recoveries was observed based on the obtained results. Hence, this time was selected in order to obtain a product with a higher gold grade. The current efficiency for gold was 10%, due to the low concentration of gold in the solution, and the average energy consumption was 12 kWh/kg of gold. The recovered metallic powder was dissolved by aqua regia to determine the chemical composition: Ag 85.7%, Au 11.8%, Cu 1.4%, and traces of other elements.

#### 3.4.2. Electrowinning Tests on Solutions of Second and Third Samples Leaching

As is presented within Section 2.3, three runs at different current intensities were performed on the solution obtained from the second sample treatment. The achieved recovery degrees for Au and silver are reported in Figures 5 and 6.

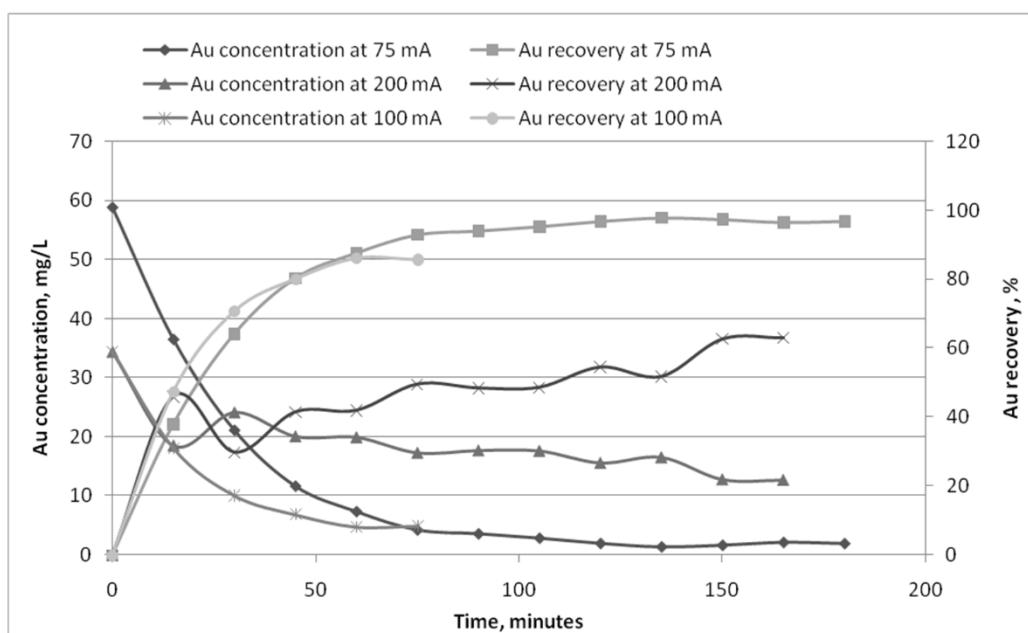


Figure 5. Evolution of Au concentration and recovery from solution at various current intensities vs. process time.

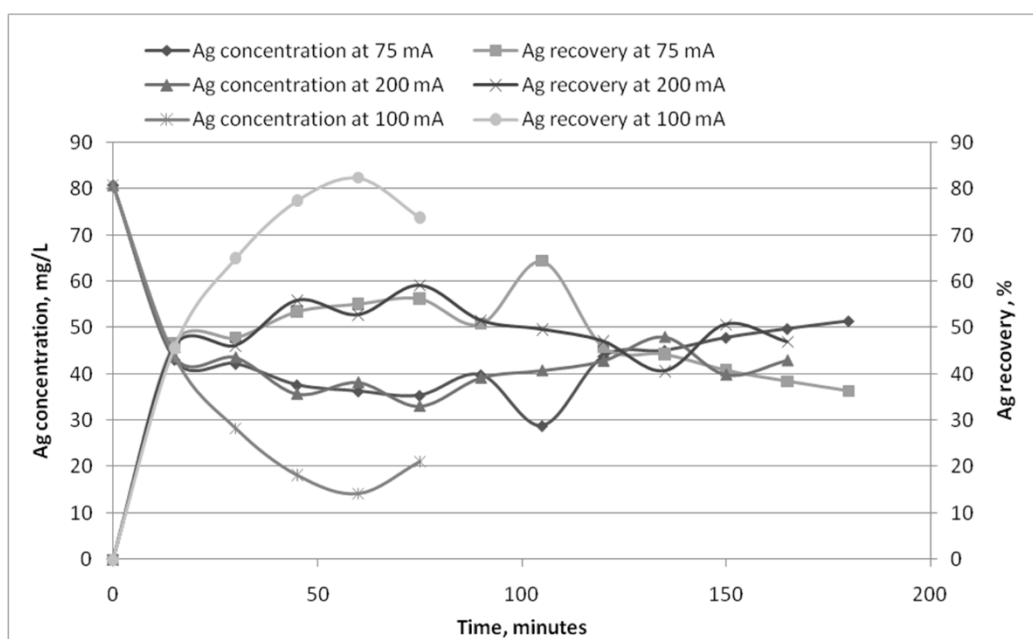


Figure 6. Evolution of Ag concentration and recovery from solution at various current intensities vs. process time.

As is shown in Figure 5, the process yield for gold increased linearly with time in the current limited regime as per Faraday’s law only for runs conducted at 75 and 100 mA. After 1 h of process, about 88 and 86% of gold recovery were achieved for the treatments performed at 75 and 100 mA, respectively. There was noticed in both of these runs that once the mass transport limited regime was approached, the rate of increase was slower, even stopped for the run conducted at 100 mA. This may be explained by the fact that the increase of current intensity determines the evolution of hydrogen at the cathode and possible partial oxidation of thiourea at the anode. Moreover, at 200 mA, the kinetics of the process for the gold reduction was much slower, and only 60% of gold was recovered from the solution after three hours of the process. For silver, only within the experiment with 100 mA there was a linear increase of recovery yield till one hour of the process. It was

noticed after this process time that silver tends to be dissolved again within the solution. The other two experiments have shown that the applied conditions ensure only about 50% of Ag recovery, even after 3 h of the process. This may be due to the resistance of the Ag deposit, which does not allow the electrons to transfer from the cathode to the silver-thiourea complex.

The determined values of thiourea within solutions after each run have shown that at 75 mA, the thiourea was regenerated within the solution at a percentage of 10.65%. For the other runs, there was noticed a diminishing of thiourea concentration with 5.73% (test with 100 mA) and 13.11% (200 mA). These results are a confirmation of the possibility to regenerate thiourea by reduction of FDS content of the solution and also for the thiourea degradation by increasing current intensity.

Furthermore, the current efficiencies for both Au and Ag recovery and specific energy consumption for each run were calculated. The current efficiency of an electrochemical process is given as the ratio of electrical charge used to form the desired product over the total charge passed during the electrochemical process. This is given by the following equation based on Faraday's Law:

$$\phi = m \cdot n \cdot F / q \quad (12)$$

where  $m$  is the molar amount of starting material (mole),  $n$  is the number of electrons involved in the electrode reaction,  $F$  is the Faraday constant (96485 C/mol), and  $q$  is the charge passed (C·s).

The specific energy consumption of an electrochemical process relates to the electrical energy consumed per mass of product, and is given as follows:

$$E_s = -n \cdot F \cdot E_{\text{CELL}} / (\phi \cdot M) \text{ (kWh/kg)} \quad (13)$$

where  $n$  is the number of electrons involved in the electrode reaction,  $F$  is the Faraday constant (96485 C/mol),  $E_{\text{CELL}}$  is the cell voltage (V),  $\phi$  is the current efficiency (%), and  $M$  is the mass of product (kg). The determined current efficiencies and specific energy consumptions vs. process time for Au and Ag are shown in Figures 7 and 8.

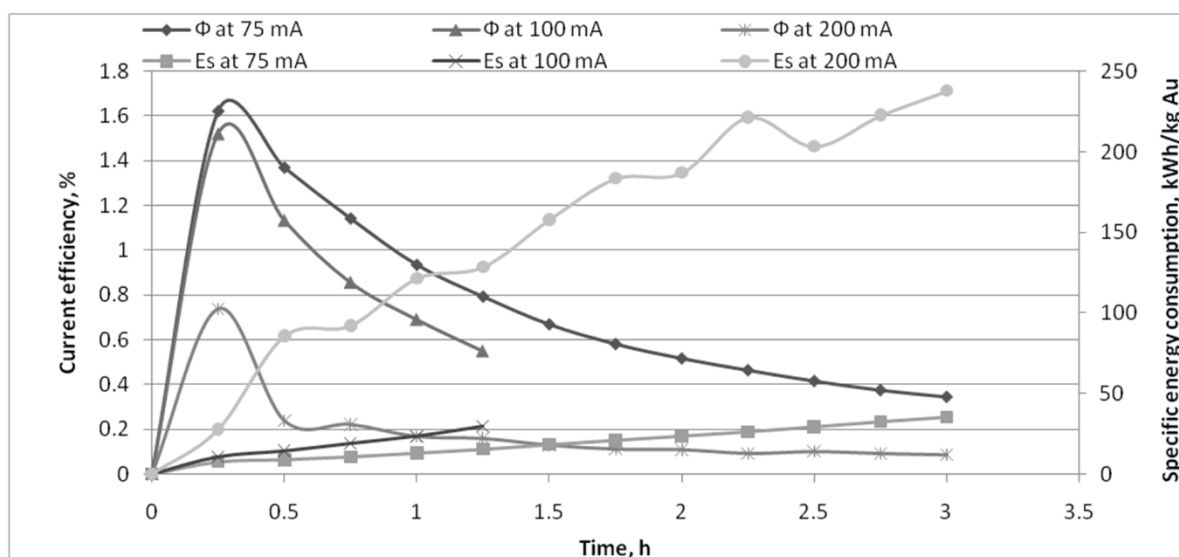
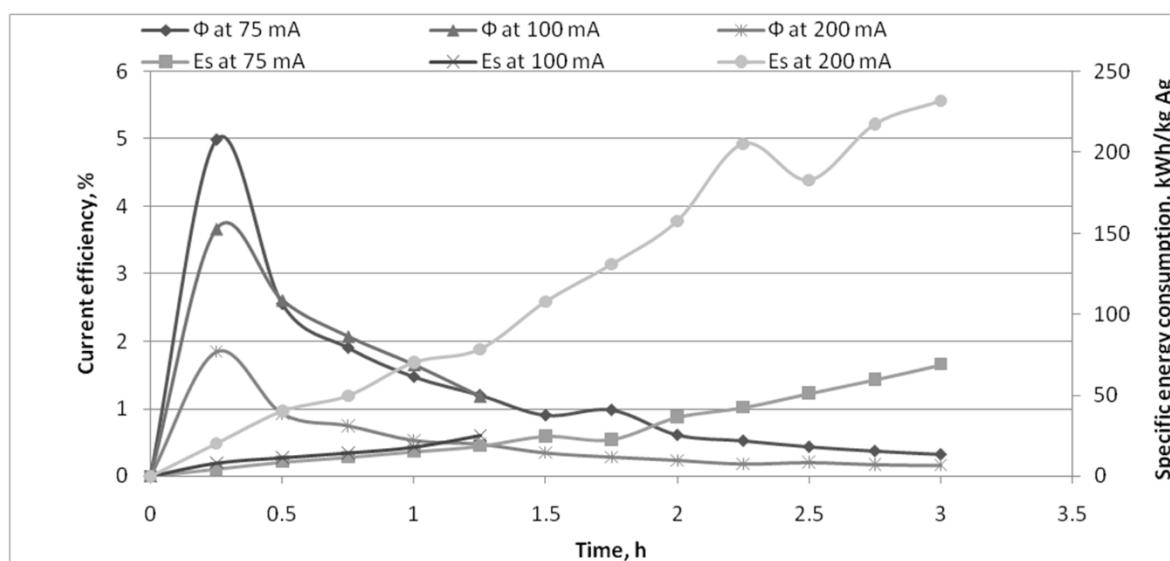


Figure 7. Current efficiency and specific energy consumption at different current intensity vs. time for Au.



**Figure 8.** Current efficiency and specific energy consumption at different current intensity vs. time for Ag.

From Figures 7 and 8, it can be inferred that the current efficiency was very low for both elements' recovery. The highest current efficiencies were achieved within the first 15 min of reaction: 1.6, 1.4 and 0.76% for Au and 4.48, 3.67 and 1.84% for Ag during the runs performed at 75, 100 and 200 mA, respectively. Moreover, as the experimental runs proceeded to the point where over 85% (1 h of reaction for runs conducted at 75 mA and 100 mA) of gold was recovered from the solution, overall current efficiency decreased to 0.55% and 0.79%, respectively. For the other run, where the recovery yields of both precious metals were lower than in the other two experiments, the current efficiency after 2.5 h (at the largest recovery yield of Au and Ag of this test), the current efficiency was decreased to 0.1%. For the energy consumption, which varied between 18–200 kWh/kg of metal recovered (depending on process time and applied current intensity), it is clear that the optimal condition for Au recovery was achieved during the experiment with the lowest level of current intensity (75 mA). About 94% of Au was recovered from solution after 1.5 h of reaction and specific energy consumption of 18 kWh/kg of Au. Instead, for better efficiency of Ag recovery, a larger current intensity is required. About 83% of Ag recovery was obtained after one hour of process at 100 mA with a current efficiency of 1.65% and current consumption of 18.04 kWh/kg.

The efficiency of process conditions that were observed as optimal for Au recovery was tested on the same leaching solution using a copper electrode and a graphite electrode as anode. The achieved results for Au and Ag recovery are shown in Tables 6 and 7.

**Table 6.** Data on Au recovery by electrowinning with Cu cathode and graphite anode.

Time of Reaction (h)	Concentration (mg/L)	Recovery (%)	Current Efficiency (%)	Energy Consumption (KWh/kg)
0	58.9	0.00	0.00	0
0.25	38.0	35.40	1.51	8.10
0.50	22.7	61.50	1.31	9.32
0.75	14.1	75.98	1.08	11.32
1.00	9.3	84.26	0.90	13.61
1.25	5.9	89.93	0.77	15.94
1.50	5.9	89.95	0.64	19.12

Table 6. Cont.

Time of Reaction (h)	Concentration (mg/L)	Recovery (%)	Current Efficiency (%)	Energy Consumption (KWh/kg)
1.75	4.2	92.86	0.57	21.61
2.00	12.3	79.14	0.42	28.98
2.25	10.4	82.36	0.39	31.33
2.50	9.6	83.77	0.36	34.22
2.75	11.6	80.37	0.31	39.24
3.00	12.6	78.55	0.28	43.80

Table 7. Data on Ag recovery by electrowinning with Cu cathode and graphite anode.


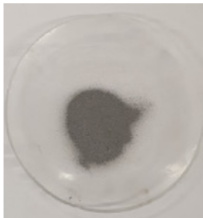
Time of Reaction (h)	Concentration (mg/L)	Recovery (%)	Current Efficiency (%)	Energy Consumption (KWh/kg)
0	80.8	0.00	0	0
0.25	53.8	33.37	3.57	6.26
0.50	33.7	58.30	3.12	7.16
0.75	24.4	69.79	2.49	8.98
1.00	18.6	76.93	2.06	10.86
1.25	15.2	81.23	1.74	12.86
1.50	9.7	87.98	1.57	14.24
1.75	33.5	58.58	0.90	24.95
2.00	32.5	59.72	0.80	27.98
2.25	33.5	58.54	0.70	32.11
2.50	38.8	51.93	0.56	40.22
2.75	40.5	49.85	0.49	46.08
3.00	42.2	47.77	0.43	52.46

The results presented within these Tables reveal that both precious metals have the same recovery yields (89.95% for Au and 87.98% for Ag) after 1.5 h of reaction. This is probably also due to the cathode of copper metal that favors the cementation of both metals. The main inconvenience in using this electrode's metal is its susceptibility to react with thiourea and decompose it. At the end of the process, the concentration of thiourea was decreased by about 20%. Similar to other experiments, the current efficiency was low, and the specific current consumption was 12 kWh/kg.

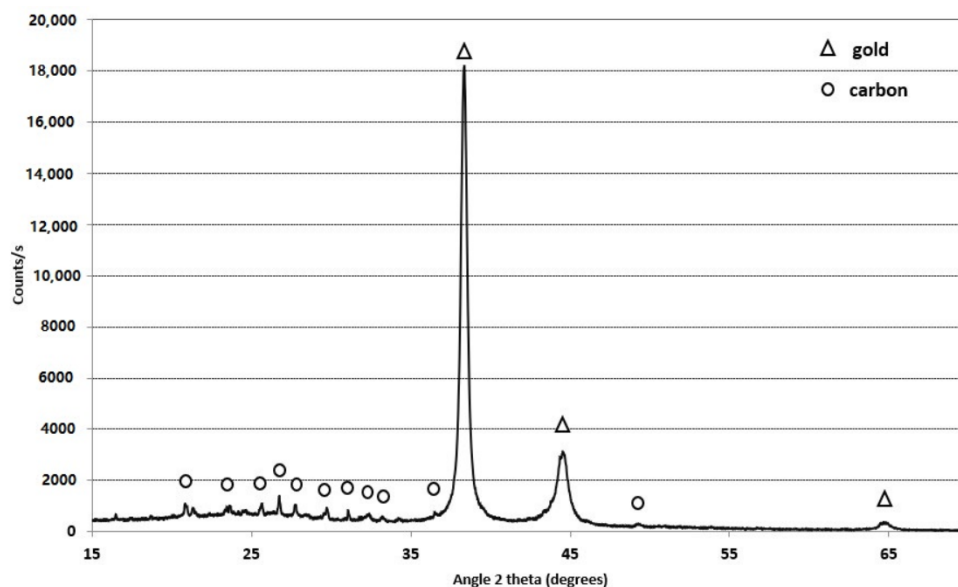
It is worth mentioning that the pH of both leaching solutions (1.2) has not suffered considerable modification during the electrowinning process; the measured pH values of the solution after electrowinning were within the range of 1–1.3.

Gold electrowinning from the third sample's solution was performed for 1.5 h with 75 mA and 0.9 V. 18.2 mg/L of gold were detected within the final solution at the end of the experiment and 13.1 g/L of thiourea. Accordingly, the adopted process conditions were suitable for both Au recovery from solution and to avoid degradation of thiourea. In order to determine the gold content within the achieved deposit, this was manually removed from the cathode, weighted, and then digested with aqua regia. The deposited gold is shown in Table 8, a similar gold deposit was achieved by Urbansky et al. [32].

**Table 8.** Photographic aspect of gold deposit on graphite cathode and purity.

Cathode after Gold EW	Recovered Gold—58.9 mg	Purity
		57%

Gold content of 57% was determined within the solid product. No copper or other element was detected within the solid product. The rest of the material is carbon from the graphite cathode that was detached during the manual removal of Au from the electrode surface. X-ray diffraction analysis, as shown in Figure 9, confirmed that only gold and carbon were detected.



**Figure 9.** X-ray diffraction pattern of solid product obtained by electrowinning.

According to the analysis of the solution, the final recovery yield of Au was 95%. The determined current efficiency after 1.5 h was 4.06%, and the specific energy consumption was 3.02 kWh/kg of gold. The consumption of energy was considerably reduced due to the much higher Au content within the leaching solution. The technology may be further improved to achieve the almost complete recovery of Au and Ag from this type of e-waste.

**4. Conclusions**

This paper showed the preliminary results obtained in the extraction of gold from military equipment connectors. These electronic components are used for special applications, and thus have to guarantee long-life reliability and duration. There was shown that thiourea acid leaching, much less polluting than traditional cyanide processes, may be successfully applied on completely gold-plated components. Precious metals are selectively dissolved by using a single stage of leaching. The best gold dissolution yield was nearly 94%. Gold was recovered from the solution by electrowinning process with high recovery yields; a recovery of 95% on graphite cathode was achieved after 1.5 h of reaction with a current consumption of 3.02 kWh/kg. The final solid product has a purity of 57 %, since only carbon was detected as impurity; a thermal treatment can increase the grade.

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