


## Article

# Technoeconomic Assessment of Organic Halide Based Gold Recovery from Waste Electronic and Electrical Equipment

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**Abstract:** Waste Electronic and Electrical Equipment (WEEE) is one of the fastest growing waste streams worldwide, with significant economic value due to the precious metals contained within. Currently, only a small share of the total globally produced quantity produced is treated effectively and a large amount of valuable non-renewable resources are being wasted. Moreover, the methods currently applied in industry on a large scale are not always environmentally friendly. Thus, an economically viable and environmentally friendly method that would achieve high recovery of certain elements is sought. The objective of this paper is to assess four different organic halides as leaching agents for gold recovery from WEEE. Two of them have been previously tested (namely *N*-bromosuccinimide, NBS, and *N*-chlorosuccinimide, NCS) and have shown promising results, whereas the other two are novel and were selected due to their lower toxicity levels (trichloroisocyanuric acid, TCICA, and tribromoisocyanuric acid, TBICA). Both commercially supplied pure gold powder and WEEE dust from a recycling company were used as the gold source. Results show that from a technical standpoint, the NBS is a superior solution with both substrates, reaching 61% and 99% extraction efficiency from WEEE dust and pure gold, respectively. The other three methods recorded lower recovery efficiency (with the highest value reaching 36% for NCS, 53% for TCICA and 29% for TBICA). However, taking into account the price of gold and the expenses of the extraction process, only three of the lixiviants tested (NBS, NCS and TCICA) could be potentially profitable and viable on a larger scale.

**Keywords:** waste electronic and electrical equipment (WEEE); technoeconomic assessment; gold recovery; organic halides



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## 1. Introduction

Consumer electronics are utilised globally by an ever-increasing proportion of the world's population, with more and more devices being produced, sold and ultimately disposed of every year. This is exacerbated by the mentality of today's society focusing on single use products and the annual release of new models for every device (e.g., mobile phones), leading to the disposal of a considerable amount of waste electronic devices, termed Waste Electronic and Electrical Equipment (WEEE).

Currently, WEEE is one of the waste streams with the highest growth rate in terms of quantity generated [1]. Approximately 40–50 million tonnes of WEEE are generated globally per year [2,3], whereas only within the European Union over 8 million tonnes of WEEE are produced each year [4]. However, only 15% of global WEEE is treated formally and between 25% and 40% of WEEE is officially treated in the EU [5]. Treatment usually involves separation of the WEEE into different fractions that are reusable, by dismantling the waste and removing easy to access high value materials. The remainder is either disposed in a landfill or exported to developing countries, with Asia being the major destination [6]. Recently, Africa has emerged as an alternative solution, due to the recent changes of Chinese waste importation legislation, which will ban solid waste importation,

including wastepaper and scrap metal, by the end of 2020, and the institutional and legislative framework established in India towards a sustainable WEEE management [7]. However, due to its categorisation as a hazardous solid waste stream, WEEE disposal in landfills is not an appropriate option, due to potential leaching of chemicals [8].

Moreover, until recently, WEEE in the receiving developing countries was usually poorly treated through methods such as open burning or acid leaching, thus leading to both low metal recovery and significant environmental issues. Such countries are not only receivers of electronic waste but also represent a significant producer of consumer electronics worldwide; thus, both internally produced and externally imported WEEE have to be successfully managed [9]. Only during the last few years, sustainable urban mining towards WEEE recycling has become an issue of concern for developing countries [6,10,11].

### *1.1. Metal Composition of WEEE*

WEEE holds significant economic value due to the precious metals that it contains, as a result of their desirable properties, including low reactivity and high electrical conductivity. In addition to the more commonly used metals (gold and silver), other elements present within WEEE include palladium and indium, which are often utilised in LCD panels and mobile phones. Precious metals within these devices generally provide between 40 and 70% of their overall value. The concentration of precious metals within such devices can range from 10 ppm up to 10,000 ppm depending on the types of devices making up the WEEE [12,13].

It has been estimated that approximately 6800 tonnes of gold (up to 16% of the world's reserves), 60,000 tonnes of silver (22% of global reserves) and 1700 tonnes of indium (15.5% of global reserves) are contained within WEEE reserves currently accumulating in local landfills or within "urban mines" [5]. Based on current market prices, this means approximately GBP 213 billion gold, GBP 22 billion silver and GBP 613 million Indium lay inactive in urban mines.

Focusing on gold, many types of electronic waste contain gold, with the concentration varying from 1 ppm (for a mobile telephone) to 25 ppm (for a personal computer) [13]. These values can be significant if the estimation is based on the total mass of the printed circuit boards (PCB) and can exceed 250 ppm [12]. Taking PCB as an example, the amount of gold available is significantly greater than the typical concentration within gold ores. Currently, the existing gold ores are low grade, and the typical gold content is about 1 ppm, with the exception of a few underground mines that contain high gold ores, but the reserves are limited. This makes utilising PCBs as a feedstock an attractive prospect for processes seeking to extract these materials from the waste since they will yield significantly greater quantities of precious metals.

### *1.2. Precious Metal Extraction Methods from WEEE*

Numerous alternative methods are currently employed on an industrial scale for the extraction of precious metals such as gold. As reviewed by [14], these can be split into two main categories: hydrometallurgy and pyrometallurgy. Moreover, both pyrometallurgical and hydrometallurgical methods require a pre-treatment stage (either physical or mechanical) to remove impurities and maximise the recovery efficiency. Pyrometallurgy utilises high temperatures, applied in various alternative options (e.g., blast furnace, plasma arc furnace, sintering, melting, high temperature gas reactions) to remove impurities and extract valuable materials [15]. However, pyrometallurgical methods usually act as a first separation stage and need to be combined with hydrometallurgy to achieve the recovery of a wide range of components [1].

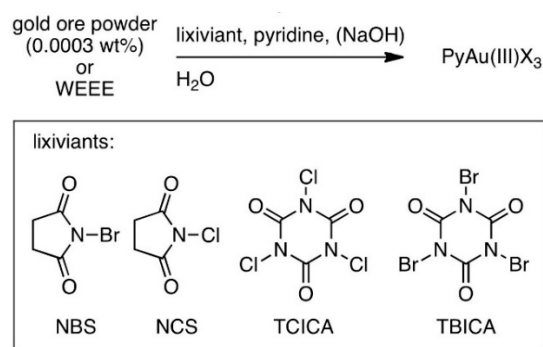
Hydrometallurgical methods consist of a two-step procedure: a chemical leaching step (with one or multiple stages), where precious metals are extracted through dissolution in a particular leaching agent, and a metal recovery step, where the metal precipitates and can be recovered in a solid state. Various reagents can be used for the leaching process and its economic and environmental viability depends on the nature of the chemicals used.

The reagents that are more widely used (e.g., aqua regia, i.e., a mixture of hydrochloric and nitric acid) may be cheaper and more efficient, reaching an extraction efficiency of 97% [16], but are very toxic, corrosive and hazardous to the environment [17]. Thus, other options with lower environmental impact that will improve the overall sustainability of the process are constantly sought, either by using an alternative leaching agent or by introducing a completely different process (such as biotechnology-driven microbial recycling [18]).

One promising group of alternative leaching agents are organic or inorganic halogens. Halogens, such as chlorine [19] or iodine [20], have been used as lixiviants but have not been widely adopted due to their high toxicity and the need for specialist equipment. Less toxic lixiviants have been also tested and the most promising method reported in the literature, so far, is the use *N*-bromosuccinimide (NBS), for the conversion of gold metal to water soluble gold salts, in the presence of pyridine [21]. More specifically, NBS and pyridine reacted with gold at pH 8.2 and room temperature, forming a solution of aqueous gold ( $\text{Au}^{3+}$ ). This solution was reduced and refined to obtain solid gold, which was then weighed to assess the recovery ratio. They also examined the optimal NBS and pyridine concentration values with the extraction efficiency varying between 20% and 90% [21]. They concluded that if 1 tonne of the waste CPUs was processed then an estimated 162 g of gold could be recovered, which, at today's gold market prices (using average values for January 2021, from the London Metal Exchange), would be worth approximately GBP 6700.

This method can definitely give a high yield of water-soluble gold salts. However, alternative organohalides are still being sought which could have additional benefits. One such possible alternative lixiviant is trichloroisocyanuric acid (TCICA), a chemical substance which is currently used as a pool cleaner and whose dehalogenated by-product (cyanuric acid) has been classified as essentially non-toxic. Another similar option could also be tribromoisocyanuric acid (TBICA), a stable chemical substance, which can be synthesised using cyanuric acid, potassium bromide (KBr), and oxone<sup>TM</sup> [22]. Regarding the environmental aspect of the process, TBICA is better since it can transfer three atoms of bromine to the substrate, compared to the other *N*-bromo compounds [23].

The objective of this paper is to assess both the technical efficiency and the economic viability of this process using different organohalogen-based routes. Four alternative lixiviants are tested and assessed (Figure 1). Two of them have not been used before for gold recovery (TCICA, TBICA) whereas the remaining two (*N*-bromosuccinimide (NBS) and *N*-chlorosuccinimide (NCS)) have proven to be quite successful and are used for comparative purposes.



**Figure 1.** Organohalogen lixiviants for the extract of gold from gold powder/ waste electronic and electrical equipment (WEEE).

There have been a few similar studies, assessing the economic feasibility of metal recovery [24,25], which, however, consider pre-treatment of the WEEE stream (through dismantling and separation). In our case, two different types of substrates are used for the analysis: pure gold powder and dust from the grinding process of a WEEE recycling company without previous pre-treatment, in order to test the methods in both an ideal and a non-ideal environment.

## 2. Materials and Methods

### 2.1. Materials

Gold powder, sodium hydroxide, pyridine, trichloroisocyanuric acid, *N*-chlorosuccinimide, and *N*-bromosuccinimide were purchased from Sigma-Aldrich and used directly from the supplier without further purification. TBICA was synthesised using sodium carbonate, potassium bromide and oxone<sup>TM</sup>, also purchased from Sigma-Aldrich and used directly. The 3D structure of the pure gold powder was determined by scanning electron microscopy (SEM; available in the Supplementary Material, Figure S1).

The WEEE dust used in this research was obtained from a recycling company and was composed of the residue from their shredding process. It was filtered through a sieve to remove any large substances. The metal composition of the WEEE dust was determined via inductively coupled plasma (ICP)-MS using the protocol described in Section 2.2. The dust was found to contain on average 10 ppm of gold along with several other metals. The detailed composition of the WEEE dust is available in the Supplementary Material (Table S1).

Table 1 illustrates the concentration of noble metals as well as that of the main components of the WEEE dust sample. The 3D structure of the WEEE dust was analysed using SEM (available in the Supplementary Material, Figure S2). The WEEE dust is composed of a vast mixture of materials each with a different structure including many shard-like pieces. This is in contrast to the relatively uniform nature of the gold powder.

**Table 1.** Metal composition of WEEE dust.

Metal	Concentration (in %w/w or ppm)
Gold	10 ppm
Sliver	95 ppm
Other Noble Metals (Pt, Rt, Os, Ir)	<10 ppm in total
Iron	23%
Zinc	10%
Aluminium	3%

The dust sample is used to simulate a non-ideal real-life system, indicative of the substrate that would be produced if waste electronic components were crushed and ground to a fine powder. On the contrary, gold powder can be considered the “ideal” scenario, where there are no interactions with other components. It might not be realistic but allows us to eliminate any combinations that under perform under these conditions. For those reasons, all four lixivants are initially assessed using the pure gold powder and only those that showcase a significant extraction efficiency are further examined using the dust samples.

### 2.2. Methods

#### 2.2.1. Synthesis of TBICA

To a stirred solution of cyanuric acid (0.5 g; 87 mmol) in water (56.2 mL) were added NaOH (0.47 g; 11.61 mmol), potassium bromide (1.38 g; 11.61 mmol) and sodium carbonate (0.62 g; 5.81 mmol). To this solution was added dropwise a solution of oxone<sup>TM</sup> (1.77 g; 11.61 mmol) in water (46.4 mL). The resultant mixture was then cooled in an ice bath in a round bottomed flask to encourage further precipitation.

#### 2.2.2. Reaction of Gold Pellets with Various Sources of Halides

It should be mentioned that the experiment was set up based on the optimised conditions for the NBS–pyridine system, as reported by [19]. The molar ratio between the gold, halide and pyridine was 1:10:75 and an adequate amount of sodium hydroxide was added for controlling the pH at approximately 8.2. However, based on a set of pre-experiments performed using TCICA, the use of an alternative ratio of 1:10:100 was chosen [26].

NBS—Method 1 (Molar ratio between gold, halide and pyridine 1:10:75): To a suspension of gold powder (10 mg; 0.05 mmol) in water (50 mL) at room temperature were added pyridine (0.31 mL, 3.8 mmol), NaOH (2.0 mg, 0.001 mmol) and NBS (90 mg, 0.51 mmol). The resultant mixture was stirred at room temperature and 400 rpm for 24 h. The solids were removed via filtration and the filtrate was subjected to inductively coupled plasma (ICP-OES) analysis.

NBS—Method 2 (Molar ratio between gold, halide and pyridine 1:10:100): To a suspension of gold powder (10 mg; 0.05 mmol) in water (50 mL) at room temperature were added pyridine (0.41 mL, 5.1 mmol), NaOH (2.0 mg, 0.001 mmol) and NBS (90 mg, 0.51 mmol). The resultant mixture was stirred at room temperature and 400 rpm for 7 days. The solids were removed via filtration and the filtrate was subjected to ICP-OES analysis.

NCS—Method 1 (Molar ratio between gold, halide and pyridine 1:10:75): To a suspension of gold powder (10 mg; 0.05 mmol) in water (50 mL) at room temperature were added pyridine (0.31 mL, 3.8 mmol), NaOH (2.0 mg, 0.001 mmol) and NCS (68 mg, 0.51 mmol). The resultant mixture was stirred at room temperature and 400 rpm for 24 h. The solids were removed via filtration and the filtrate was subjected to ICP-OES analysis.

NCS—Method 2 (Molar ratio between gold, halide and pyridine 1:10:100): To a suspension of gold powder (10 mg; 0.05 mmol) in water (50 mL) at room temperature were added pyridine (0.41 mL, 5.1 mmol), NaOH (2.0 mg, 0.001 mmol) and NCS (68 mg, 0.51 mmol). The resultant mixture was stirred at room temperature and 400 rpm for 7 days. The solids were removed via filtration and the filtrate was subjected to ICP-MS analysis.

TCICA—Method 1 (Molar ratio between gold, halide and pyridine 1:10:75): To a suspension of gold powder (10 mg; 0.05 mmol) in water (50 mL) at room temperature were added pyridine (0.31 mL, 3.8 mmol), NaOH (2.0 mg, 0.001 mmol) and TCICA (118 mg, 0.5 mmol). The resultant mixture was stirred at room temperature and 400 rpm for 24 h. The solids were removed via filtration and the filtrate was subjected to ICP-MS analysis.

TCICA—Method 2 (Molar ratio between gold, halide and pyridine 1:10:100): To a suspension of gold powder (10 mg; 0.05 mmol) in water (50 mL) at room temperature were added pyridine (0.41 mL, 5.1 mmol), NaOH (2.0 mg, 0.001 mmol) and TCICA (118 mg, 0.5 mmol). The resultant mixture was stirred at room temperature and 400 rpm for 7 days. The solids were removed via filtration and the filtrate was subjected to ICP-MS analysis.

TBICA—Method 1 (Molar ratio between gold, halide and pyridine 1:10:75): To a suspension of gold powder (10 mg; 0.05 mmol) in water (50 mL) at room temperature were added pyridine (0.31 mL, 3.8 mmol), NaOH (2.0 mg, 0.001 mmol) and TBICA (182 mg, 0.5 mmol). The resultant mixture was stirred at room temperature and 400 rpm for 24 h. The solids were removed via filtration and the filtrate was subjected to ICP-MS analysis.

TBICA—Method 2 (Molar ratio between gold, halide and pyridine 1:10:100): To a suspension of gold powder (10 mg; 0.05 mmol) in water (50 mL) at room temperature were added pyridine (0.41 mL, 5.1 mmol), NaOH (2.0 mg, 0.001 mmol) and TBICA (182 mg, 0.5 mmol). The resultant mixture was stirred at room temperature and 400 rpm for 7 days. The solids were removed via filtration and the filtrate was subjected to ICP-MS analysis.

### 2.2.3. Reaction of WEEE Dust with Various Sources of Halides

In this set of experiments, the amounts of pyridine and halide used were different than before. A set of pre-experiments was performed in order to find the optimal ratio between the gold in the WEEE dust, the pyridine and the halide [26]. Based on these results, the molar ratio between the gold, halide and pyridine in this set of experiments was chosen to be 1:500:7500.

NBS—Method 1: To a suspension of WEEE dust (100 mg, 0.0005 mmol Au) in water (50 mL) at room temperature were added pyridine (0.3 mL, 3.8 mmol) and NBS (45 mg, 0.26 mmol). The resultant mixture was stirred at room temperature and 400 rpm for 24 h. The solids were removed via filtration and the filtrate was subjected to ICP-MS analysis.

Method 2: To a suspension of WEEE dust (200 mg, 0.001 mmol Au) in water (50 mL) at room temperature were added pyridine (0.6 mL, 7.7 mmol) and NBS (92 mg, 0.52 mmol).



The resultant mixture was stirred at room temperature and 400 rpm for 7 days. The solids were removed via filtration and the filtrate was subjected to ICP-MS analysis.

NCS—To a suspension of WEEE dust (100 mg, 0.0005 mmol Au) in water (50 mL) at room temperature were added pyridine (0.3 mL, 3.8 mmol) and NCS (35 mg, 0.26 mmol). The resultant mixture was stirred at room temperature and 400 rpm for 24 h. The solids were removed via filtration and the filtrate was subjected to ICP-MS analysis.

TCICA—Method 1: To a suspension of WEEE dust (100 mg, 0.0005 mmol Au) in water (50 mL) at room temperature were added pyridine (0.3 mL, 3.8 mmol) and TCICA (60 mg, 0.50 mmol). The resultant mixture was stirred at room temperature and 400 rpm for 24 h. The solids were removed via filtration and the filtrate was subjected to ICP-MS analysis.

Method 2: To a suspension of WEEE dust (200 mg, 0.001 mmol Au) in water (50 mL) at room temperature were added pyridine (0.62 mL, 7.7 mmol) and TCICA (120 mg, 0.50 mmol). The resultant mixture was stirred at room temperature and 400 rpm for 7 days. The solids were removed via filtration and the filtrate was subjected to ICP-MS analysis.

#### 2.2.4. ICP-MS Analysis

A solution of aqua regia was prepared by pipetting 80 mL of trace-metal hydrochloric acid into a 100-mL plastic volumetric flask to equal volume with trace-metal nitric acid. The solution was allowed to stand at room-temperature for 30 min prior to use. In triplicate, approximately 100 mg of WEEE dust was weighed via microbalance into a plastic tube. Following the addition of 5 mL of aqua regia, the solution was sonicated for 10 min and allowed to stand at RT for 24 h to ensure maximum digestion. To the solution was then added 10 mL ultra-pure water. Any undissolved material was collected by filtering the solution via a sintered silica funnel (previously washed with aqua regia), washing through with ultra-pure water. The filtrates were collected and measured to volume in a 50-mL plastic volumetric flask with ultra-pure water. The sample solution was then transferred to ICP vials analysed via semi-quantitative ICP-MS.

#### 2.2.5. ICP-OES Analysis

Following the migration to the use of gold powder as a substrate for the extraction experiments, it was determined that inductively coupled plasma—optical emission spectrometry (ICP-OES) should be used for the analysis of the samples. ICP-OES allows better analysis by providing more accurate results when working with elements in higher concentrations (10–100 ppm), whereas ICP-MS is better suited for concentrations between 10 and 100 ppb. The gold was present in concentrations up to 10 ppm in the WEEE, whereas, when using the gold powder, the concentration was approximately 200 ppm. The concentration of the samples was measured following a standard procedure. To a 28-mL vial was added a 1-mL reaction sample followed by 100  $\mu$ L (0.1 mL) of a 100 ppm Rhodium solution, 200  $\mu$ L (0.2 mL) Aqua Regia and 8.7 mL Ultra-Pure (18.2 M $\Omega$ ) H<sub>2</sub>O. This made the sample up to 10 mL, which could then be fed into the ICP-OES inlet, compared against a standardised solution and analysed for gold concentration in parts per million. The extraction yield was then determined using the known initial gold concentration of 200 ppm as follows:

$$\text{Extraction Yield} = 100 \times \text{Sample Au Concentration} / 200 \text{ ppm} \quad (1)$$

### 3. Results

#### 3.1. Gold Recovery from Pure Gold Powder

Initially, all four combinations were assessed using the pure gold powder. Samples were collected every 15 min for the first hour, every hour for the next three hours and then every 24 h for the duration of the experiment. Table 2 presents the average and the maximum gold extraction (in the form of PyAu(III)X<sub>3</sub>, where X is the lixiviant) achieved by the four different methods, using gold powder as the substrate. It can be observed that, first of all, the NBS–pyridine combination is the best method from a technical point of view and the achieved extraction efficiency is comparable to the previously reported one.

However, as previously mentioned, the experiment was set up based on the optimised conditions for the NBS–pyridine system. The same values were used for all the other systems; thus, these are expected to probably underperform, since these were not optimised.

**Table 2.** Gold recovery using pure gold powder as the substrate.

Lixiviant	Average Gold Recovery	Maximum Gold Recovery
TCICA	2%	8% <sup>a</sup>
TBICA	11%	29% <sup>b</sup>
NBS	92%	99% <sup>c</sup>
NCS	12%	15% <sup>c</sup>

<sup>a</sup> reaction stirred for 15 min; <sup>b</sup> reaction stirred for 90 min; <sup>c</sup> reaction stirred for 7 d.

Although TBICA seems promising in terms of gold recovery, compared to the other two novel systems (excluding the NBS–pyridine system), a preliminary economic assessment combined with the high production cost of this halide reagent revealed that this option is economically non-viable (for more details see Section 4). Thus, it was decided to carry on the experiments for the non-ideal system using only three of the previously tested systems (NBS, NCS and TCICA).

### 3.2. Gold Recovery from WEEE Dust

The gold content of WEEE dust is very small and the composition of each sample is not uniform, so greater variations are expected among the different experiments, compared to the gold powder. Similarly to the pure gold powder, Table 3 presents the average and, in parentheses, the maximum gold extraction achieved (in the form of  $\text{PyAu(III)X}_3$ , where X is the lixiviant) for the three different methods, using the WEEE dust as the substrate.

**Table 3.** Gold recovery using non-ideal WEEE dust as the substrate.

Lixiviant	Gold Recovery
TCICA	5% (53%) <sup>a</sup>
NBS	26% (61%) <sup>a</sup>
NCS	36% <sup>b</sup>

<sup>a</sup> reaction stirred for 7 d; <sup>b</sup> reaction stirred for 24 h.

It can be seen from the results presented in Table 3 that the NBS–pyridine system is the most superior combination, even under non-ideal conditions. However, in this case the variability between experiments is much higher and the error is mostly due to non-uniform nature of the WEEE dust sample. Even so, NCS and NBS have a smaller range of extraction recovery compared to TCICA, which varied between 5% and 53%.

A magnetic pre-treatment of the WEEE dust was considered, in order to remove some of the unwanted chemical compounds, but the idea was not taken forward as it would reduce the non-ideal nature of the sample. Alternative gold, halide and pyridine molar ratios (1:100:5000, 1:100:7500) were also examined but there was no significant impact of that ratio to the gold recovery. Moreover, because the experiments were carried out in room temperature during the entire year, it was also decided to assess the temperature impact on the extraction process. Three alternative temperatures were selected (Room Temperature, 25 °C and 50 °C) and the experiments were carried out using method 1. However, again there was not an obvious trend that would allow us to determine a positive or negative correlation between the extraction ratio and the temperature.

In summary, using both WEEE dust and pure gold powder, the NBS–pyridine system proved to be superior from a technical point of view, reaching 61% and 99% extraction efficiency, respectively. The other assessed combinations were not equally successful, with the corresponding values being 15% and 36% for the NCS–pyridine system and 8% and 53% for the TCICA–pyridine system.

#### 4. Discussion—Profitability Analysis

Since the results using the non-ideal samples were not conclusive, it was decided to perform a preliminary profitability analysis, in order to determine the optimal gold recovery ratio, under which the alternative methods would be profitable. Table 4 presents the prices for all the chemical compounds used in all four different halide combinations, from the websites of major UK suppliers at the time of writing the manuscript (November 2020). When there were different packages/quantities available for a chemical compound, the largest one was intentionally chosen in order to determine the price in pounds per kilogram, since, due to the economy of scale, the price that a large-scale facility would have to pay for a bulk purchase would be closer to that value. Regarding TBICA, the production cost was calculated to be 432.2 GBP/mol or equivalently 1181.5 GBP/kg, based on the method presented in Section 2 and the prices of the corresponding reagents.

**Table 4.** Prices for the chemical compounds used.

Chemical Compound	Price (in GBP/mol)	Price (in GBP/kg)
Trichloroisocyanuric acid (TCICA)	16.2	69.6
N-Bromosuccinimide (NBS)	11.7	65.7
N-Chlorosuccinimide (NCS)	15.3	114.6
Pyridine	6.8	85.4
Sodium Hydroxide	0.90	22.4
Cyanuric Acid	1.5	11.9
Oxone™	4.8	15.6
Sodium Carbonate	7.3	68.6
Potassium Bromide	18.6	156.0

Regarding the operating costs, the electricity and water expenses were included. The overhead stirrer capacity was 60 W and it was assumed that, during the experiments, it operated at 30% of full capacity for the whole duration of the experiment. The electricity price was assumed to be GBP0.01/kWh. Deionised water was used for all the experiments, with an average price of GBP0.2/L. The overall expenses of the process were calculated as the sum of the cost of the reagents together with the electricity and water expenses. In order to calculate the profit, an average price for gold was assumed to be GBP30/g (with the current gold trading price being GBP31450/kg at the time of writing the manuscript).

Based on these assumptions, Table 5 presents the minimum required extraction efficiency in order to make the process profitable (when expenses are equal to the expected profit). It can be seen that for three of the reagents, the profitability limit is relatively low. More specifically, for NBS, NCS and TCICA, the minimum required yield is approximately 15%. In all three cases, this value is lower than the maximum achieved extraction yield, and, in two of these (NBS, NCS), it is also lower than the average achieved extraction yield. However, for TBICA, due its much higher production cost, the minimum required yield for this process is above 50%. That was the reason why the TBICA–pyridine system was not assessed using the non-ideal system.

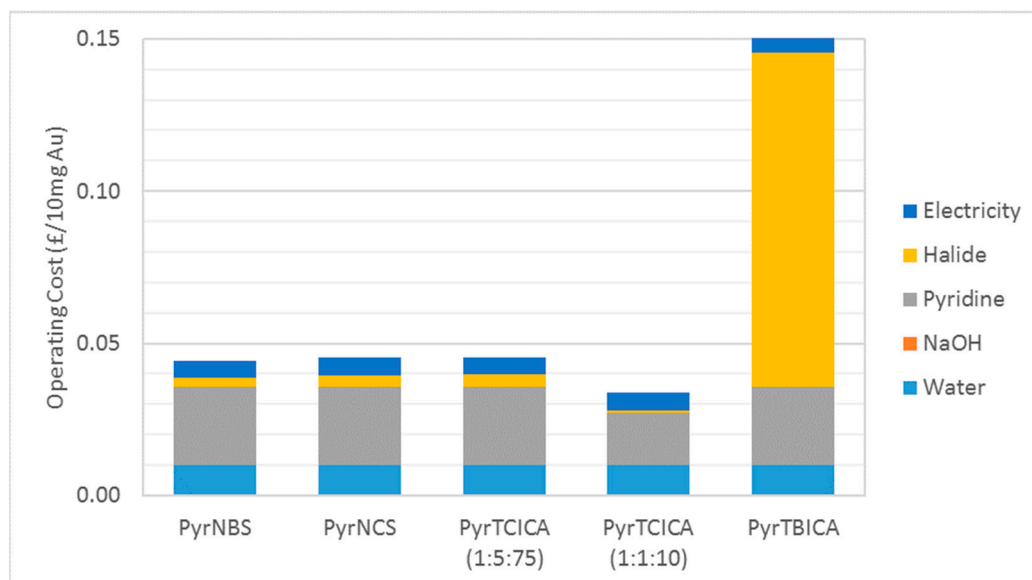
**Table 5.** Minimum profitable yield for each system (assuming a gold price of GBP30/g).

System	Minimum Profitable Yield
Pyridine–NBS	14.8%
Pyridine–NCS	15.1%
Pyridine–TCICA (1:5:75)	15.2%
Pyridine–TCICA (1:1:50)	11.2%
Pyridine–TBICA	50.4%

In order to assess the margin for further profit, a breakdown of the operational cost was performed (Figure 2). It is apparent that, apart from the TBICA system, in all other cases the pyridine cost is the most critical contributor to the expenses. Taking into account

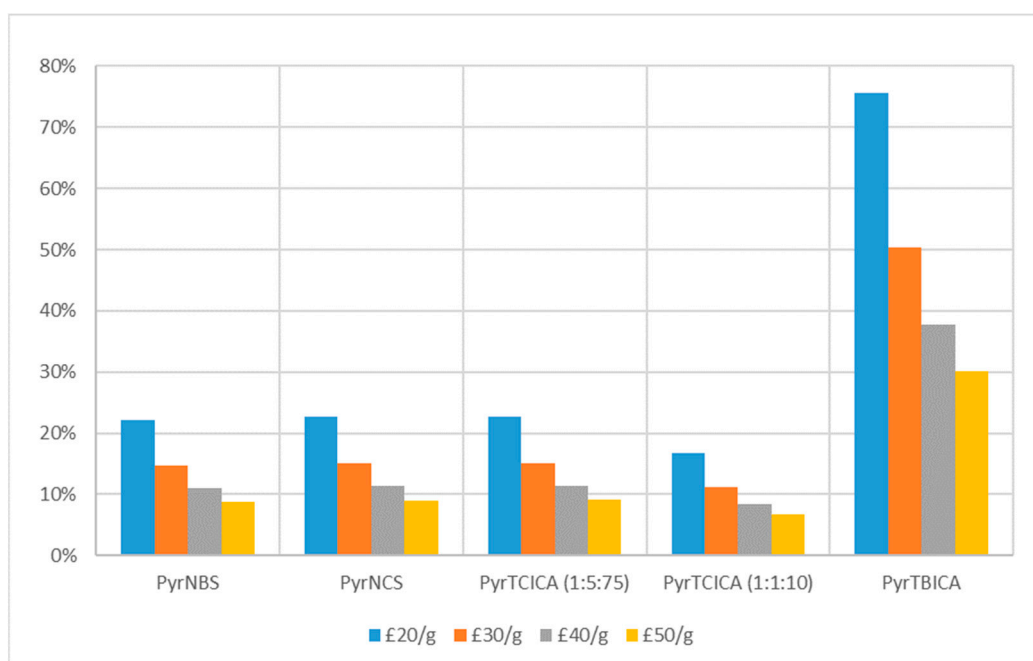


as well the toxicity potential of pyridine, it is advised that an alternative solvent should be sought, which should be cheaper and less toxic. TCICA, as a cheaper and more common reagent compared to the *N*-bromo or chloro compounds, can also contribute to overall cost reduction, when the process is further optimised.



**Figure 2.** Operating cost breakdown (expressed in GBP/10 mg of processed Au) for the minimum profitable yield for each system.

The profitability of the process is also closely related to the price of gold, which was assumed to be GBP 30/g. However, over the last 10 years, the price of gold ranged from USD 864/oz (approximately GBP23/g in current prices) to USD 2062/oz (approximately GBP 56/g), using historical data retrieved from online resources. These fluctuations make the gold price the parameter with the highest uncertainty in the profitability analysis performed. For that reason, a sensitivity analysis of the minimum profitable yield was performed with the price of gold ranging between GBP 20/g and GBP 50/g. The results show that even in the worst case (by gold price reaching an historical low), the minimum profitable yield for all three methods does not exceed 25% (Figure 3). This enhances the previously drawn conclusions that a potential scaled-up facility using NBS–pyridine as the main gold extraction system would be profitable and more environmentally friendly than the currently used ones. Moreover, less toxic solutions (e.g., use of a common pool cleaner/TCICA) cannot be disregarded. Although, the achieved extraction is lower compared to the *N*-bromo or chloro compounds, the fact that it is slightly cheaper and has a smaller toxicity impact could affect the final decision.



**Figure 3.** Uncertainty analysis of the minimum profitable yield based on the selling price of gold.

## 5. Conclusions

Four alternative methods for gold recovery from WEEE were assessed for their technical performance and their economic long-term viability. These methods are more environmentally friendly compared to the methods currently used in industry. Based on the results, three of these methods (NBS–Pyridine, NCS–Pyridine and TCICA–Pyridine) are potentially profitable and viable on a larger scale. More specifically, the NBS–Pyridine system reached a gold recovery efficiency above 90%, which agrees with the current literature, and is well above the minimum profitable yield for this specific system (22% in the worst-case scenario).

The other two methods (NCS–Pyridine and TCICA–Pyridine) showcased lower recovery efficiency with the highest value reaching 36% for the NCS–pyridine system and 53% for the TCICA–pyridine system. In both cases, though, these values are higher than the minimum profitable yield under current conditions (15% in both cases). It should be also mentioned that these systems were not optimised and the optimal conditions for the NBS–pyridine systems were used. On the other hand, a scaled-up plant for the recovery of gold from WEEE would need to have a profit margin of at least 10% in order for the business plan to be implemented, so the current recovery efficiency is still low. However, both of these methods have the potential to be economically viable on a large scale when optimised in terms of molar ratios used and reaction conditions.

## 6. Suggestions for Further Research

Apart from the technical performance and economic viability of the alternative methods, their environmental impact also needs to be assessed before moving to large-scale implementation. The use of TCICA as a pool cleaner illustrates its reduced environmental impact compared to both the currently used methods in industry (e.g., aqua regia) and the *N*-bromo or chloro compounds. However, a proper environmental impact assessment needs to be performed, focusing especially on the ecotoxicity and human toxicity indicators. The specialised nature of the reagents and the lack of the corresponding environmental factors that can quantitatively describe the impact, as part of a Life Cycle Assessment framework, makes such a comparison more difficult. Thus, further experiments need to be performed focusing on the characterisation of the waste streams. Alternatively, a methodology could be formulated that can characterise the toxicity impact of a stream based

on their descriptive hazard and precaution statements from the Safety and Documentation Sheet, similarly to the methodology described by [27] on assessing the toxicity of a mining facility's waste streams.

As already mentioned, the use of pyridine needs to be reassessed, since it both contributes significantly to the toxicity of the process and accounts for the biggest share of the reagents' cost. The role of pyridine in this process is mainly to promote formation of the water soluble pyridium salts ( $\text{PyAu(III)X}_3$ ), which can be easily separated from the residue solids via filtration. Bioderived pyridines, such as pyridine 2,5-dicarboxylic acid [28,29], are an attractive renewable alternative that could be explored in subsequent work. In addition, investigations into use of bio-available co-solvents [30,31] such as Cyrene™ [32–35],  $\gamma$ -valerolactone and isosorbide dimethyl ether as well as alternatives to the use of sodium sulfite for the final reduction should be undertaken.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/2079-9276/10/2/17/s1>, Figure S1: SEM Images of the pure gold powder at 1000 $\times$  (left) and 5000 $\times$  (right), Figure S2: SEM Images of the WEEE dust at 30 $\times$  (left) and 500 $\times$  (right), Table S1: WEEE Dust Composition via semi quantitative ICPMS.

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## References

- Ilankoon, I.; Ghorbani, Y.; Chong, M.N.; Herath, G.; Moyo, T.; Petersen, J. E-waste in the international context—A review of trade flows, regulations, hazards, waste management strategies and technologies for value recovery. *Waste Manag.* **2018**, *82*, 258–275. [CrossRef] [PubMed]
- Zhang, L.; Xu, Z. A review of current progress of recycling technologies for metals from waste electrical and electronic equipment. *J. Clean. Prod.* **2016**, *127*, 19–36. [CrossRef]
- Ding, Y.; Zhang, S.; Liu, B.; Zheng, H.; Chang, C.; Ekberg, C. Recovery of precious metals from electronic waste and spent catalysts: A review. *Resour. Conserv. Recy.* **2019**, *141*, 284–298. [CrossRef]
- Cyganowski, P.; Garbera, K.; Leśniewicz, A.; Wolska, J.; Pohl, P.; Jermankowicz-Bartkowiak, D. The recovery of gold from the aqua regia leachate of electronic parts using a core-shell type anion exchange resin. *J. Saudi Chem. Soc.* **2017**, *21*, 741–750. [CrossRef]
- Zhang, S.; Ding, Y.; Liu, B.; Chang, C. Supply and demand of some critical metals and present status of their recycling in WEEE. *Waste Manag.* **2017**, *65*, 113–127. [CrossRef] [PubMed]
- Gunarathne, N.; de Alwis, A.; Alahakoon, Y. Challenges facing sustainable urban mining in the e-waste recycling industry in Sri Lanka. *J. Clean. Prod.* **2020**, *251*, 119641. [CrossRef]
- Pathak, R.; Srivastava, R.R. Assessment of legislation and practices for the sustainable management of waste electrical and electronic equipment in India. *Renew. Sustain. Energy Rev.* **2017**, *78*, 220–232. [CrossRef]
- Li, Y.; Richardson, J.B.; Bricka, R.M.; Niu, X.; Yang, H.; Li, L.; Jimenez, A. Leaching of heavy metals from E-waste in simulated landfill columns. *Waste Manag.* **2009**, *29*, 2147–2150. [CrossRef] [PubMed]
- Sthiannopkao, S.; Wong, M.H. Handling e-waste in developed and developing countries: Initiatives, practices, and consequences. *Sci. Total Environ.* **2013**, *463–464*, 1147–1153. [CrossRef]
- Borthakur, A.; Govind, M. Emerging trends in consumers' e-waste disposal behaviour and awareness: A worldwide overview with special focus on India. *Resour. Conserv. Recy.* **2017**, *117*, 102–113. [CrossRef]
- Yong, Y.S.; Lim, Y.A.; Ilankoon, I. An analysis of electronic waste management strategies and recycling operations in Malaysia: Challenges and future prospects. *J. Clean. Prod.* **2019**, *224*, 151–166. [CrossRef]
- Chancerel, P.; Meskers, C.; Hagelaken, C.; Rotter, V. Assessment of Precious Metal Flows during Preprocessing of Waste Electrical and Electronic Equipment. *J. Ind. Ecol.* **2009**, *13*, 791–810. [CrossRef]

13. Wang, M.; Tan, Q.; Chiang, J.; Li, J. Recovery of rare and precious metals from urban mines—A review. *Front. Environ. Sci. Eng.* **2017**, *11*. [[CrossRef](#)]
14. Hsu, E.; Barmak, K.; West, A.; Park, A. Advancements in the treatment and processing of electronic waste with sustainability: A review of metal extraction and recovery technologies. *Green Chem.* **2019**, *21*, 919–936. [[CrossRef](#)]
15. Cui, J.; Zhang, L. Metallurgical recovery of metals from electronic waste: A review. *J. Hazard. Mater.* **2008**, *158*, 228–256. [[CrossRef](#)] [[PubMed](#)]
16. Young, J.P.; Derek, J.F. Recovery of high purity precious metals from printed circuit boards. *J. Hazard. Mater.* **2009**, *164*, 1152–1158. [[CrossRef](#)]
17. Syed, S. Recovery of gold from secondary sources—A review. *Hydrometallurgy* **2012**, *115–116*, 30–51. [[CrossRef](#)]
18. Ilyas, S.; Srivastava, R.; Kim, H.; Das, D.; Singh, V. Circular bioeconomy and environmental benignness through microbial recycling of e-waste: A case study on copper and gold restoration. *Waste Manag.* **2021**, *121*, 175–185. [[CrossRef](#)]
19. Gokelma, M.; Birich, A.; Stopic, S.; Friedrich, B. A Review on Alternative Gold Recovery Re-agents to Cyanide. *J. Mater. Sci. Chem. Eng.* **2016**, *4*, 8–17. [[CrossRef](#)]
20. Konyratbekova, S.; Baikonurova, A.; Ussoltseva, G.; Erust, C.; Akcil, A. Thermodynamic and kinetic of iodine–iodide leaching in gold hydrometallurgy. *Trans. Nonferr. Metals Soc.* **2015**, *25*, 3774–3783. [[CrossRef](#)]
21. Yue, C.; Sun, H.; Liu, W.J.; Guan, B.; Deng, X.; Zhang, X.; Yang, P. Environmentally Benign, Rapid, and Selective Extraction of Gold from Ores and Waste Electronic Materials. *Angew. Chem. Int. Edit* **2017**, *56*, 9331–9335. [[CrossRef](#)]
22. Esteves, P.; de Mattos, M.; de Almeida, L. Tribromoisocyanuric Acid: A New Reagent for Regioselective Cobromination of Alkenes. *Synlett* **2006**, *10*, 1515–1518. [[CrossRef](#)]
23. de Almeida, L.; Esteves, P.; de Mattos, M. Tribromoisocyanuric acid as a green reagent for benzylic bromination of alkylarenes. *Tetrahedron Lett.* **2015**, *56*, 6843–6845. [[CrossRef](#)]
24. Talens Peiró, L.; Castro Girón, A.; Gabarrell i Durany, X. Examining the feasibility of the urban mining of hard disk drives. *J. Clean. Prod.* **2020**, *248*. [[CrossRef](#)]
25. He, P.; Feng, H.; Hu, G.; Hewage, K.; Achari, G.; Wang, G.; Sadiq, R. Life cycle cost analysis for recycling high-tech minerals from waste mobile phones in China. *J. Clean. Prod.* **2020**, *251*. [[CrossRef](#)]
26. Angelis-Dimakis, A.; Mapesa, K.; Blackburn, J.; Camp, J. Economic Assessment of Halide Based Gold Recovery from Waste Electrical and Electronic Equipment. In *Proceedings of the 5th International Symposium on Green Chemistry, Sustainable Development and Circular Economy, Skiathos island, Sporades, Greece, 30 September–3 October 2018*; Kungolos, A., Schramm, K.W., Eds.; Grafima Publications: Thessaloniki, Greece, 2018.
27. Apostolopoulou, E.; Mylona, E.; Kourtis, A.; Adam, K.; Papassiopi, N. Ecotoxicity evaluation of mine waste using geochemical and biological tests. In *Proceedings of the 5th International Symposium on Green Chemistry, Sustainable Development and Circular Economy, Skiathos island, Sporades, Greece, 30 September–3 October 2018*; Kungolos, A., Schramm, K.W., Eds.; Grafima Publications: Thessaloniki, Greece, 2018.
28. Mycroft, Z.; Gomis, M.; Mines, P.; Law, P.; Bugg, T. Biocatalytic conversion of lignin to aromatic dicarboxylic acids in *Rhodococcus jostii* RHA1 by re-routing aromatic degradation pathways. *Green Chem.* **2015**, *17*, 4974–4979. [[CrossRef](#)]
29. Pellis, A.; Comerford, J.W.; Weinberger, S.; Guebitz, G.M.; Clark, J.H.; Farmer, T.J. Enzymatic synthesis of lignin derivable pyridine based polyesters for the substitution of petroleum derived plastics. *Nat. Commun.* **2019**, *10*, 1762. [[CrossRef](#)] [[PubMed](#)]
30. Clarke, C.J.; Tu, W.C.; Levers, O.; Brohl, A.; Hallett, J.P. Green and Sustainable Solvents in Chemical Processes. *Chem. Rev.* **2018**, *118*, 747–800. [[CrossRef](#)]
31. Gu, Y.; Jerome, F. Bio-based solvents: An emerging generation of fluids for the design of eco-efficient processes in catalysis and organic chemistry. *Chem. Soc. Rev.* **2013**, *42*, 9550–9570. [[CrossRef](#)]
32. Bousfield, T.W.; Pearce, K.P.R.; Nyamini, S.B.; Angelis-Dimakis, A.; Camp, J.E. Synthesis of Amides from Acid Chlorides and Amines in the Bio-based Solvent Cyrene<sup>TM</sup>. *Green Chem.* **2019**, *21*, 3675–3681. [[CrossRef](#)]
33. Camp, J.E. Bio-available Solvent Cyrene: Synthesis, Derivatization, and Applications. *ChemSusChem* **2018**, *11*, 3048–3055. [[CrossRef](#)] [[PubMed](#)]
34. Mistry, L.; Mapesa, K.; Bousfield, T.W.; Camp, J.E. Synthesis of Ureas in the Bio-Alternative Solvent Cyrene. *Green Chem.* **2019**, *19*, 2123–2128. [[CrossRef](#)]
35. Camp, J.E.; Nyamini, S.B.; Scott, F.J. Cyrene is a Green Alternative to DMSO as a Solvent for Antibacterial Drug Discovery against ESKAPE Pathogens. *RSC Med. Chem.* **2020**, *11*, 111–117. [[CrossRef](#)] [[PubMed](#)]