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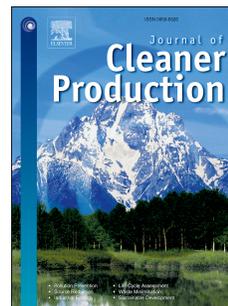
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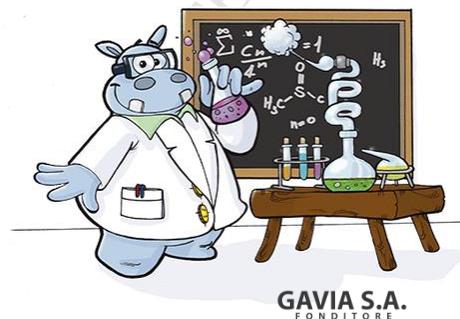
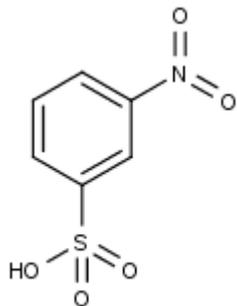
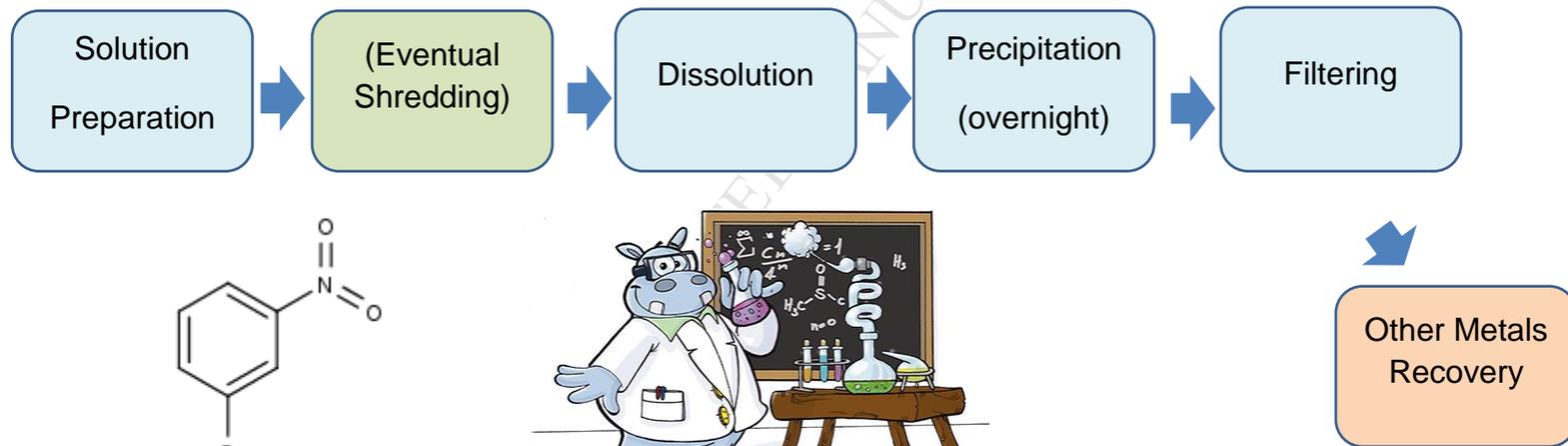
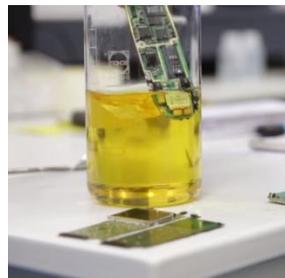
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## Reduction of potassium cyanide usage in a consolidated industrial process for gold recovery from wastes and scraps

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### Abstract

The main purpose of the present work is to improve the understanding of an industrial process that exploits the synergic action of cyanide ion and three-nitrobenzene-sulphonate for the selective removal of precious metals from various matrices. It has been observed that the cyanide dissolves first gold from the surface, forming dicyanoaurate gold complexes, but this reaction alone is not sufficient to dissolve gold with the observed velocity. A deeper knowledge of the chemical mechanisms can potentially improve the process competitiveness. Important reaction factors have been identified and analyzed. It has been demonstrated that the cyanide amount presently utilized is excessive. Possible reduction products have been also identified. The results can help the search for cyanide reduction and substitution. Yield and velocity optimization, together with a solution toxicity reduction can pave the way to eco-friendly processes for the leaching of noble metals.

*Keywords:* gold, cleaner recovery, scrap, potassium cyanide, nitrobenzene sulfonate

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## 1. Introduction

### 1.1. Gold recovery: a growing industry

With new technological innovation, the replacement of any kind of equipment is persistently accelerating. Consequentially the global amount of WEEE (Waste Electric and Electronic Equipment) produced and disposed is increasing over the last decades: the annual global growth has been estimated at 8.8% (2004-2011) and 17.6% (2011-2016) calculating for 2016 a global volume of 93.5 millions of tons (Alzate et al. (2016); Yu et al. (2014)). Subsequently precious metal recycling industries are growing globally, demanding new, sustainable, low environmental impact methodologies.

Gold is one of the most valuable metal that can be recycled from scrap and waste. The collection and proper treatment is regulated in the European Community through the WEEE Directive (2012). Environmental and economic issues demand the adoption of green technologies and of alternative bio-solutions for recycling. Many recent publication have deeply analyzed the state of the art of the current progress of recycling technologies for metals from WEEE, see for example Ghosh et al. (2015); Zhang and Xu (2016); Hester and Harrison (2009).

Generally the purified metals and alloys provided by the recycling industry are still a small proportion of the primary production. The estimated End Of Life (EOL) recycling rates for precious metals for the main end-use sectors is decreasing. Jewelry has a very high EOL percentage rate, while other kinds of waste, especially from the electronic scrap, offer ample room for improvement. Current global EOL recycling rates for over sixty metals can be found in the E-book: International Resource Panel (2013), gold is one of the few metals with a EOL higher than 50%. Sun et al. (2016) give an interesting evaluation of various types of urban waste, focused on determine metal recovery potential. When prices are perceived by the market to be low the share of recycled material in total gold supply stands at about a third. When prices are high, it can climb to as much as 80% of supply. According to industry players, on average, recycled material accounts for over half of total gold supply (Mudd (2007)).

### 1.2. Main recovery technologies

Hydrometallurgical extraction, thoroughly described by Rao (2006) and by Free and Moats (2014) is one of the main technologies for the recovery

of precious metals from scrap and waste materials, the other one is represented by pyrometallurgical processes, well introduced by Hayes and Jak (2013). The hydrometallurgical methodologies have several advantages: relatively low capital cost, reduced environmental impact (e.g. no hazardous gases/dusts) and high metal recoveries with good suitability for small scale applications, as it is well illustrated by Tuncuk et al. (2012). However, complete extraction is not yet achieved and traditional operations require highly corrosive media due to the chemical inertness of the noble metals toward most acids and bases. *The Chemistry of Gold Extraction* by Marsden and House (2006) extensively analyze industrial processes for gold recovery: despite the toxicity issues and the fact that the dissolution process is usually very slow, technologies based on alkaline solutions or alkali-metal cyanides (e.g. sodium cyanide, potassium cyanide) are widely adopted to dissolve gold under aerated conditions. Hilson and Monhemius (2006) examine the most widely-researched alternative lixivants for gold ores, showing that still nowadays none has yet made any significant inroad into the dominant position of cyanide.

### 1.3. Cyanide toxicity issues

The toxic effect of cyanide is considerable. Hazards to plants and animals from gold mining are examined by Eisler and Wiemeyer (2004). Donato et al. (2007) have reviewed the effects of gold cyanide-bearing tailings solutions on wildlife, clearly identifying limits of knowledge. Kuyucak and Akcil (2013), after analyzing the environmental problem, present commercially available and emerging methods for removing cyanide from waste streams in gold mining and metallurgical processes. In a recent review of the literature on occupational and environmental health hazards of formal e-recycling facilities, Ceballos and Dong (2016) underline that even in the high-tech formal e-recycling facilities, challenges still remain in assessing and controlling chemical exposures regularly. They conclude that overall, formalization is a desirable direction for the e-recycling industry. Johnson (2015) emphasizes that with respect to cyanide dispersal from gold leach operations, the widest margins of environmental safety will be achieved if operations are designed so that time for volatilization, aeration, and sunlight exposure are maximized if cyanide-bearing solutions are released inadvertently.

#### 1.4. Cyanide alternatives

Increasing environmental pressure on the use of cyanide has motivated researchers and scientists together with industries to test other possible lixivants, see Akcil et al. (2015); Hilson and Monhemius (2006). Cyanidric compounds are also used in certain stages of electroplating processes: in Scarazato et al. (2015) electroplating cyanide is replaced by 1-hydroxyethane 1,1-diphosphonic acid (HEDP). Applications and current status of the most attractive alternative lixiviant processes to cyanide are reviewed by Aylmore (2005). Most work has focused on thiosulfate, thiourea, and halide processes. Despite the research interest and pilot plant trials on many of the noncyanide gold lixivants, the majority are still at the development stage.

Other corrosive reagents are regularly adopted. Hot aqua regia, a mixture of nitric acid and hydrochloric acid, is extensively used in small and medium operations, examples are given by Sheng and Etsell (2007). Chlorine water or bromine water use is instead less common. The main inconvenience of treatment with these compounds is the production of toxic gas, a major hazard for workplace environments. Other reagents have been employed or tested: for a complete analysis of all the various methodologies used in the recovery of gold from secondary sources we recommend Syed (2012) review.

Bioleaching is hydrometallurgy employing microorganism, extensive reviews are provided by Olson et al. (2003) and by Rohwerder et al. (2003). In recent year bioleaching has significantly improved and has been already commercially applied, but unfortunately it is not yet as competitive as traditional techniques (Brierley and Brierley (2013)).

The adoption of hydrometallurgical processes for precious metals recovery that can reduce the cyanide hazardous effect drives our current research.

#### 1.5. Gold cyanidation process

Leaching gold via cyanidation reaches a high recovery rate, besides the cyanide toxicity and the serious threats to the natural habitat and to the industry personnel. Gold cyanidation is an electrochemical process: gold dissolves in the alkaline cyanide solution and forms gold cyanide complex. The overall reaction can be summarized in the following (Eq.1) Dorin and Woods (1991).



The oxidant employed is atmospheric oxygen: increasing the dissolved oxygen concentration increases the gold dissolution rate, as showed by Raphulu and Scurrrell (2015). Air/oxygen presence is essential for high extraction of metals, palladium in particular, as highlighted by Yazici and Deveci (2013). In Wadsworth et al. (2000) work a model able to predict gold dissolution behavior as a function of cyanide and oxygen concentration is elaborated and tested: model predictions are in good agreement with observations.

The main factors that influence the solubility of gold in cyanide solution are oxygen and cyanide concentration, temperature, pH, surface area, stirring rate and presence of other anion/cations. The cyanide hydrolyzation depends on the pH of the leaching environment. Approximately at pH 9.3, half of the total cyanide is present as free cyanide and the other half is as toxic hydrogen cyanide, Young and Jordan (1995). Lowering the pH leads to higher solution, a pH higher than 9.0 is recommended for the safety of the workers. The electrochemical behaviour of  $\text{CN}^-$  in contact with gold electrodes has been extensively studied, refer to Bozzini et al. (2007); Gómez-Díaz et al. (2010). Active and passive behaviors of pure gold with cyclic voltammetry and potentiodynamic polarization is described by Bas et al. (2015). Raphulu and Scurrrell (2015) propose several likely roles for cyanide, the interaction between cyanide and gold catalysts shows promise for elucidating further the structure and action of gold catalysts.

An innovative small company, active in the field of precious metals recovery and refining from more than ten years, patented a methodology that exploits the synergic action of cyanide ion and three-nitrobenzene-sulphonate for the selective removal of precious metals from various matrices (Tschanen (2008)). The process is competitive on small quantities, but cannot replace traditional methodologies as the actual process yield is not very high. The yield has already shown space for improvements, albeit the comprehension of the critical parameters that control the process is still poor. An accurate process characterization that considers and tunes all the variables would certainly improve the process yield and possibly reduce the environmental impact. A deep understanding of the process could speed up the development of research on the eco-friendly leaching of metals from electronic waste, suggesting possible cyanide substitutes.

To the best of our knowledge there are no studies that investigate the synergic action of cyanide ion and 3-nitrobenzene-sulphonate (NBS) to remove selectively precious metals from various matrices.

## 2. The industrial process

As described in the patent, Tschanen (2008), potassium cyanide (KCN) and 3-nitrobenzene sulphonic acid sodium salt are used for the dissolution of gold and of other precious metals. It is well known that potassium cyanide has the capability to dissolve gold, following the reaction described in Eq. (1) and forming the water-soluble dicyanoaurate(I) gold complex. However this reaction is very slow, cyanide dissolves gold in a time of the order of magnitude of days. As seen in the chemical equation, the oxidant in the redox is the oxygen, present in air. The dissolution is in fact carried out in air, at atmospheric pressure and at room temperature. The sodium salt of 3-nitrobenzenesulphonic acid, whose structure is reported in Fig. 1, has the capability to dissolve gold, forming a complex with unknown stoichiometry; as with cyanide alone, the reaction is very slow. Using potassium cyanide and 3-nitrobenzenesulphonic acid sodium salt together, the oxidation of gold becomes much and much faster, passing from days to minutes.

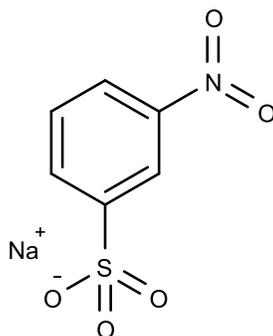
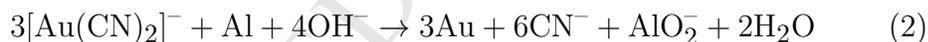


Figure 1: Scheme of 3-nitrobenzenesulphonic acid sodium salt.

The solution is prepared dissolving in hot tap water (303-308 K)  $8 \times 10^{-3}$  kg per  $1 \times 10^{-3} \text{ m}^3$  of 3-nitrobenzenesulphonic acid sodium salt and  $20 \times 10^{-3}$  kg per  $1 \times 10^{-3} \text{ m}^3$  of potassium cyanide, the concentration of free cyanide is about  $8 \text{ kg/m}^3$ , and is controlled by potentiometry. The addition of reagents to water should follow this order, because the organic salt is only slightly soluble in water, while potassium cyanide is heavily soluble. In the preparation steps, tap water should be preferably hot, to enhance the solubility of the sodium salt. Tap water becomes pale-yellow colored after the addition of the organic salt but pH does not have significant variation

since this salt is a very weak base (it is the conjugated base of a strong acid). On the other hand, the addition of potassium cyanide raises pH from near neutrality to about 12. If left to air, the solution slowly oxidizes, becoming darker. Waste and e-scrap materials containing gold are placed in a roto barrel and in a tank containing the solution; the barrel is left rotating until no more gold is present on the surface of the material; the absence of gold from surface can be controlled by X-ray fluorescence.

The solution can dissolve up to 20 kg/m<sup>3</sup> of gold, but in normal operating conditions this concentration is never reached, because although being very selective for gold, also other metals, like silver, palladium, copper, nickel, chromium, tin etc. are dissolved. Increasing the total amount of metals in solution, the dissolution process becomes slower. In practical conditions, when a concentration of 2-2.5 kg/m<sup>3</sup> of gold is reached, no more material is put into the roto barrel. When gold concentration reaches the maximum value, the dissolving solution is treated with sodium hydroxide solution (30-32% by mass); the volume of solution added is about 10% of the total volume. The addition of sodium hydroxide blocks the possible formation of toxic hydrogen cyanide and is needed in the reduction process. Aluminum plates from e-scrap are used as reductant. The redox reaction occurring has the following stoichiometry:



This reaction is followed by AAS (Atomic Absorption Spectroscopy) and aluminum plates are removed when gold residual concentration goes below  $1 \times 10^{-3}$  kg/m<sup>3</sup>. Under this value it has been observed that aluminum begins to precipitate as hydroxide.

The treated solution is then pumped away in another tank and the gold containing slurry is collected at the bottom of the settler tank; this sludge is filtered on a vacuum filter until a dry black powder is obtained. This powder is then burned into a graphite crucible in an induction oven and when all the organic residual part is removed, an ingot is obtained, with a typical gold amount of 80-85%. This ingot can be further purified with the aqua regia process or sold to a foundry. The rest of the solution is treated with chemical processes, filtering heavy metals. Then the solution, containing only sodium, potassium, chloride and sulphite is evaporated. The saline content is discarded, while the remaining water can be discharged in sewer. Fig. 2 illustrates the industrial process flow diagram.

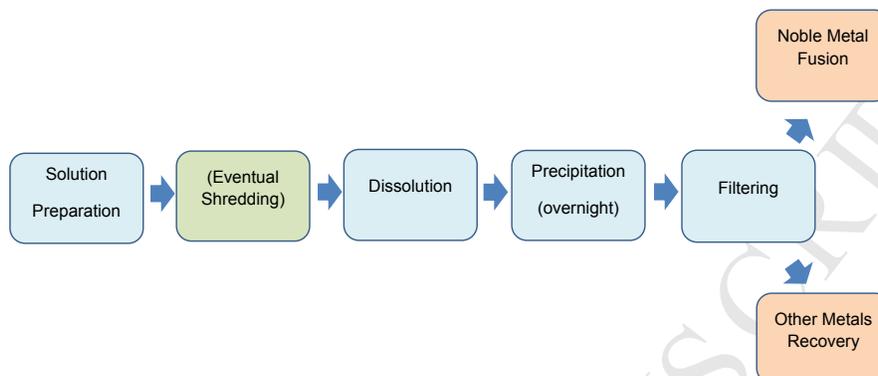


Figure 2: Gavia industrial process flow diagram.

### 3. Results and discussion

#### 3.1. Preliminary consideration

The dissolving solution is prepared as follows:

- dissolution of about  $20 \text{ kg/m}^3$  of KCN in water which corresponds to 65.1163 molecular weight, i.e.  $20/65.1163 \text{ mol/}1 \times 10^{-3} \text{ m}^3 = 0.31 \times 10^{-3} \text{ mol/m}^3$
- dissolution of about  $8 \text{ kg/m}^3$  of NBS in the previous solution which corresponds to 225.155 molecular weight, i.e.  $8/225.155 \text{ mol/}1 \times 10^{-3} \text{ m}^3 = 0.04 \times 10^{-3} \text{ mol/m}^3$

This means that there is ca. 1 NBS mole for 8 KCN moles dissolved in water. The solution is prepared dissolving first KCN in water. Cyanide salts dissolve in water and form free cyanide ions:

By itself, cyanide dissolves gold according to Eq. (1). In case of the solely cyanide reaction the oxidant agent is the oxygen. After the addition of KCN to water the pH of the solution reaches the value of 12. As already said at pH about 9.3 cyanide exist half as hydrogen cyanide and half as free cyanide ions. Higher pH than 9.3 increases the amount of free cyanide in solution (because the concentration of  $\text{OH}^-$  decreases). Besides, hydrogen cyanide and free cyanide can be oxidized to form undesirable cyanate  $\text{CNO}^-$  which does not dissolve gold and hence reduces the free cyanide concentration.

Based on the real solution adopted by the company, the experiments planned in the present work aimed at studying the interaction and synergistic effects between NBS and KCN in solution. In particular we were interested in studying why the presence of NBS speeds up the gold recovery process, and how. We started from the following observations:

- The molar ratio  $\text{CN}^-$  : NBS used in the standard process is 8:1 (standard condition): large excess of  $\text{CN}^-$  ions in solution compared to NBS
- Due to smaller size, the negatively charged  $\text{CN}^-$  ions, product of the dissociation of KCN, diffuse faster than NBS in solution

From these preliminary observations, it was reasonable to hypothesize that, as a first step, gold cyanidation occurs. In fact, the faster and smaller  $\text{CN}^-$  ions, in large excess respect to NBS, will rapidly cover and coordinate the gold surface. The gold cyanidation process by KCN can be summarized as composed of multiple steps: (i) migration of the  $\text{CN}^-$  ions to the gold surface, (ii)  $\text{CN}^-$  coordination with the Au atoms and (iii) separation of the Au atoms from the surface in the form of  $\text{Au}(\text{CN})_2^-$  complexes. Step (iii) exposes, in turn, new surface Au atoms to the solution, ready to be coordinated and sequestered by other  $\text{CN}^-$  ions. While gold cyanidation reasonably occurs first in solution, the process presents a considerable speed-up respect to normal cyanidation.

Grounding on these observations we hypothesized that the presence of NBS could facilitate step (iii) in the cyanidation process, accelerating the separation of the Au atoms from the surface. In this perspective, we were interested in understanding if NBS in solution could somehow interact with the  $\text{Au}(\text{CN})_2^-$  complexes, product of Au cyanidation or if NBS plays as oxidant in the process, substituting or helping oxygen that is the oxidant in classical cyanidation process. Two potential NBS reduction products are shown in Figs. 3a and 3b.

### 3.2. Characterization of working solutions

The first set of experiments to better understand the process have been conducted in standard condition, using small 1 gr coins. The coins have been immersed in a probe with distilled water solution of KCN (Sigma-Aldrich, technical  $\geq 96\%$ ) and NBS (Sigma-Aldrich 98%). The temperature was controlled thanks to a thermostatic bath whilst constant agitation was made to maintain homogeneity. All the experiments have been conducted with new

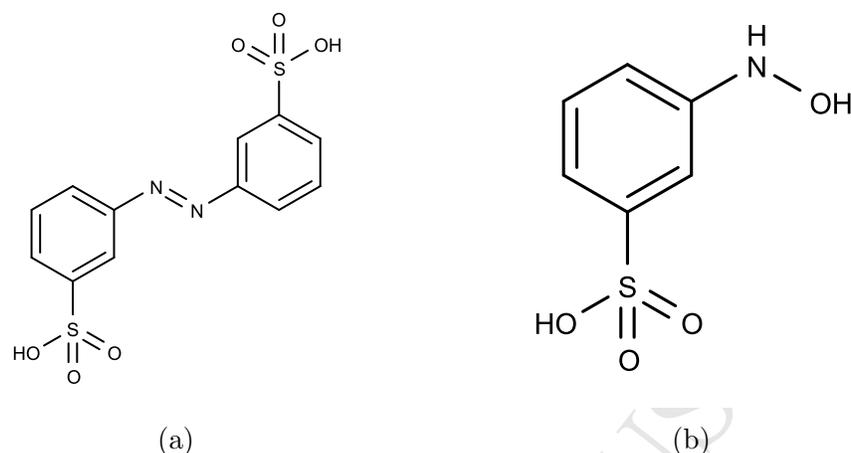


Figure 3: Two potential NBS reduction products.

coins, to avoid systematic error due to surface modifications and a new solution has been prepared just before the test. All the data were collected taking into account the weight variation. Different concentrations have been tested to check the rate of dissolution limits.

In Fig. 4 the results with concentration 8:1,  $20 \text{ kg/m}^3$  CN :  $8.65 \text{ kg/m}^3$  NBS are summarized, each experiment has been repeated three times, measuring the concentration variation over time. An inexplicable high variability can be observed.

A thin layer chromatography has been executed to verify if it was possible to identify in solution products derived by NBS reaction. A silica plate as stationary phase has been used and it has been chosen as mobile phase  $\text{CH}_3\text{CN}$  plus a little quote of  $\text{CH}_3\text{OH}$ . Forecasting a high polarity of the products a polar eluent has been preferred.

The following four samples have been analyzed by TLC:

- BLANK Standard Solution 8:1 without gold
- 1A Solution 8:1 with gold dissolute
- 1C Solution 8:1 with gold dissolute
- NBS only NBS in water

1A and 1C solutions were independently prepared. For all the sample the retention rate detected by TLC ( $R_f$ ) was 0.42, corresponding to the NBS

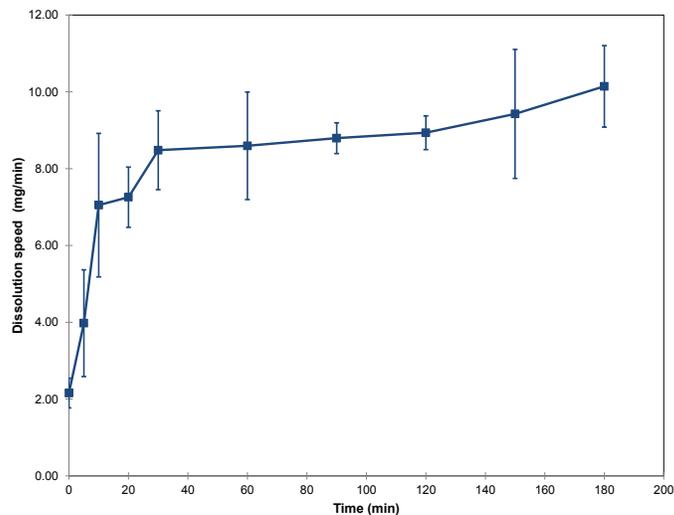


Figure 4: Average of the three experimentation with  $1 \times 10^{-3}$  kg coins with standard deviation.

species in solution. It was not possible with this technique to detect other compound than NBS. As could be expected TLC could neither identify  $\text{CN}^-$  nor the Au complex. Then a ultra violet analysis in the UV-visible region was executed on the four samples, as detailed in Fig. 5.

Apart from the differences in the height of the peak at circa 270 and 210 nm arising from concentration differences among the prepared solutions, the interesting feature of the spectra was that by UV spectrophotometry there are no evidences of the stoichiometric formation of azo compounds that could result from the reduction of NBS. Small sample quotes have been evaporated to reach a solid product. On that an IR spectrophotometry analysis (Fig. 6) was performed showing that also in the solid phase there are no significant differences between the BLANK, the 1A and 1C compounds and the NBS. This means that also in the solid phase no NBS reduction products are detectable.

In order to deepen the possible presence of NBS reduction products in solution, an NMR analysis was carried out. The dried BLANK, 1A, 1C and NBS samples were dissolved in  $\text{D}_2\text{O}$  and analyzed by means of a 400

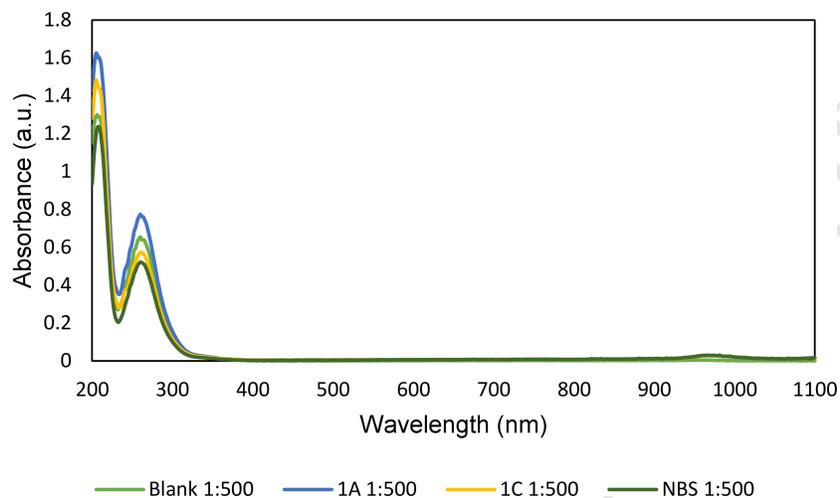


Figure 5: UV analysis of the selected samples, overlapping lines is an evidence that no new species are present in solution.

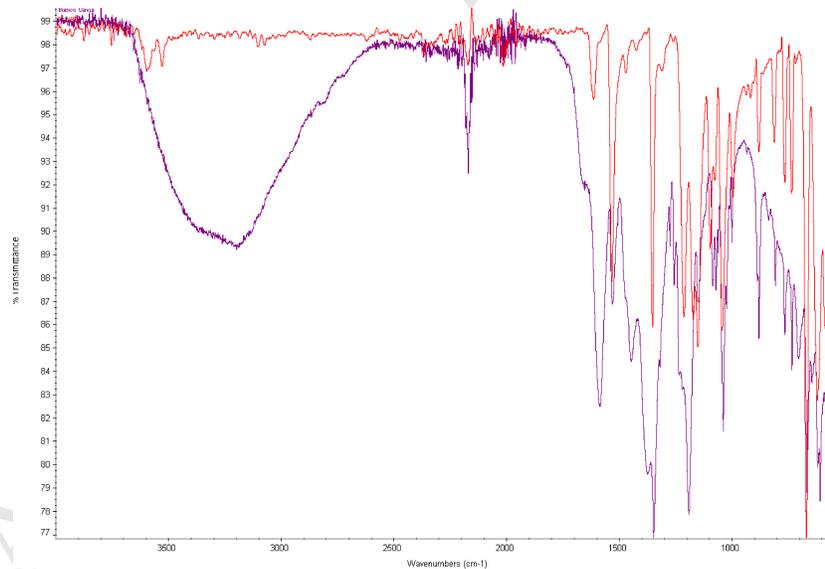


Figure 6: IR spectra of NBS (red) and BLANK (violet), transmittance % vs wave numbers cm<sup>-1</sup>.

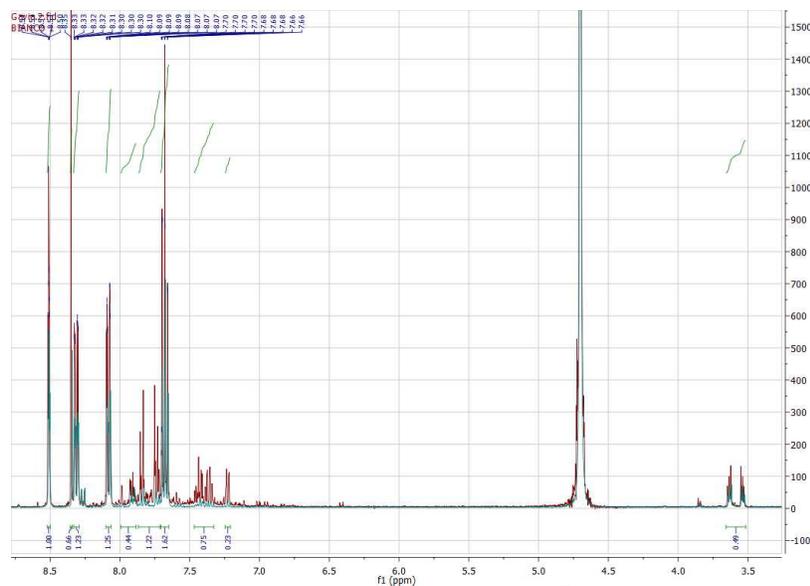


Figure 7: Superimposed NMR spectra of 1C and NBS: it cannot be identified any difference before or after gold addition, and as forecasted the presence of a reduction species bearing the NH-OH group can be excluded (ppm vs arbitrary units).

MHz Bruker Avance instrument. Also from the NMR differences cannot be identified, before or after gold addition. In particular, as forecasted in Fig. 3b, NMR excludes the presence of a reduction species bearing the NH-OH group, see Fig.7.

Mass spectrometry analyses were performed both on BLANK solution and on 1C solution. From the mass spectra it is possible to detect the unreacted NBS and the cyanoaurate compounds, but no NBS reduction species are detectable. It was very difficult to explain the high variability of dissolution data with different sample with the same concentration. We hypothesized that the surface had a role, meaning that the surface type prevalence was leading to a different reaction rate. So it was planned to perform the dissolution experiments with a powder, to exclude this possibility, in order to have a statistical distribution of the crystallographic faces on the gold surface. A  $1 \times 10^{-3}$  kg granulometry powder of edible gold ( $\text{Au} = 961,5\%$ ,  $\text{Ag} = 38,5\%$ ) was used to replicate the experiments and the characterization. The test have been performed in triplicate both in atmospheric and in inert conditions. The water used for the experiments was degasified and the reagents additions were done under nitrogen streaming to avoid oxygen entrance. The

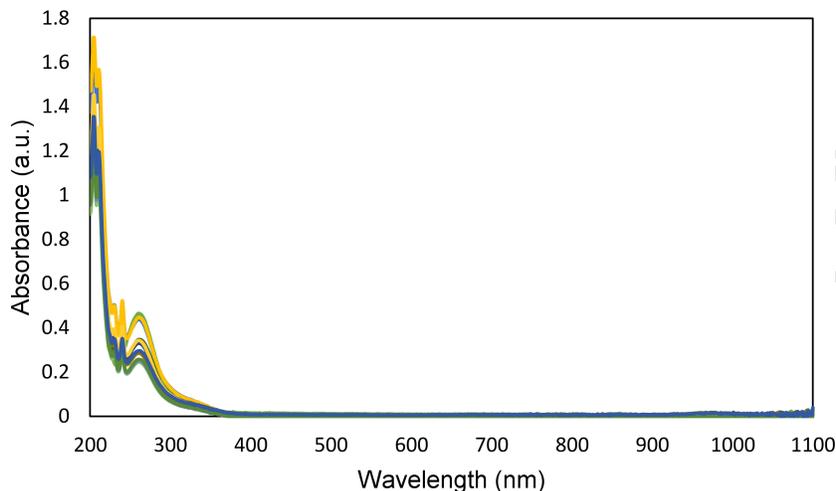


Figure 8: UV spectra of NBS (2 highest lines) and solutions containing gold and cyanide used to dissolve gold powder (3 spectra for each of the three replicates) under atmospheric conditions.

first interesting observation was that gold quickly dissolved in both conditions even if with different rates: 900 s in normal atmosphere, 1800 s in inert atmosphere. This behavior strengthened our supposition that the variability of dissolution rates data of the experiment performed on gold coins was effectively due to the predominance of crystallographic planes on the surface of gold coin grains. Using gold powder, with the same concentration, a higher surface area was available, leading to higher dissolution easiness. In the experiments performed under inert atmosphere, an intensification of the solution color passing from light yellow to yellow / orange was observed, then returning to a pale yellow color when the reaction completed. This behavior is compatible with the UV signal detectable at 310 nm, different from the 260 nm of the NBS. It can be hypothesized that NBS is able to oxidize gold alone, but if oxygen is present, also in traces, it could cooperate in the metal oxidation and a part of oxygen could re-oxidate the NBS reduced. This could explain some UV data variability observed, Fig.8 and 9.

With respect to the experiment performed under atmospheric conditions, the UV analyses of the experiments performed without oxygen show the 310 nm shoulder more intense. This behavior let us suppose that molecular oxygen plays a role (even if not exclusive) in the oxidation process. It is also possible to observe a decreasing of the presence of NBS in solution with

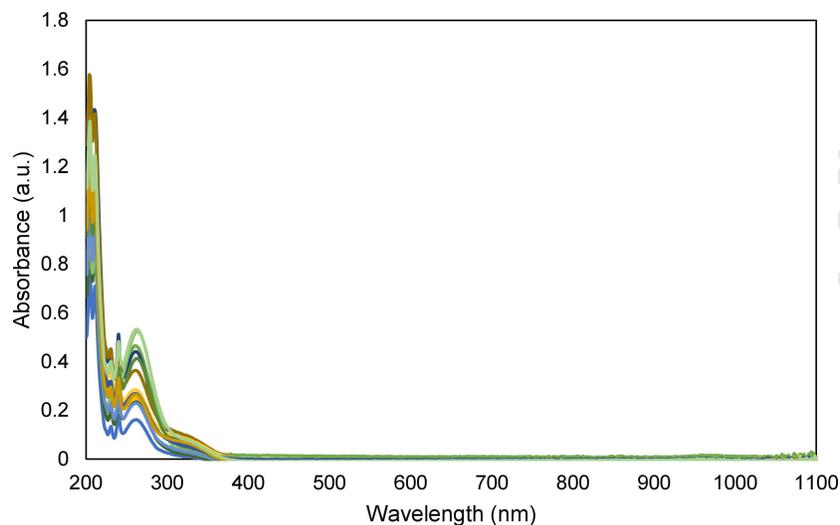


Figure 9: UV spectra of NBS and solutions containing gold and cyanide used to dissolve gold powder without oxygen.

time, until reaching a plateau, after the complete gold dissolution. As all the gold completely dissolved, ICP was not necessary to quantify it in solution. To deepen the comprehension of the species in solution, NMR analyses were performed. NMR shows two types of signals (Fig.10). One is attributable to NBS unreacted, as expected; and another type of signals attributable to a similar species. The interesting fact is that quantitatively the two species are approximately one 20% of the other. One of the two is NBS, and the other probably is its reduction product after the reaction with gold. NMR is not fully diagnostic, but it gives an interpretation consistent with an azolike structure as predicted in Fig.3a, in which the N=N bond is compatible with the effect of the shoulder seen at 310 nm in the UV spectrum.

To confirm the species hypothesized in solution, ESI-mass spectrometry analyses were performed, Fig.11. The negative ion spectrum shows only unreacted NBS and the gold complex that is produced. The positive ion spectrum gives a series of signals including the molecular peak (the strongest signal, 327 m/z ) that could be a fragment of the azo-compound in Fig. 3a arising from the reduction process of NBS (less an oxygen atom, plus H<sup>+</sup> ). Probably, the identified azo compound is not the only reduction product.

Despite the knowledge of the cyanidation process leading to gold dissolution, the mechanisms beyond the oxidation of this noble metal are still

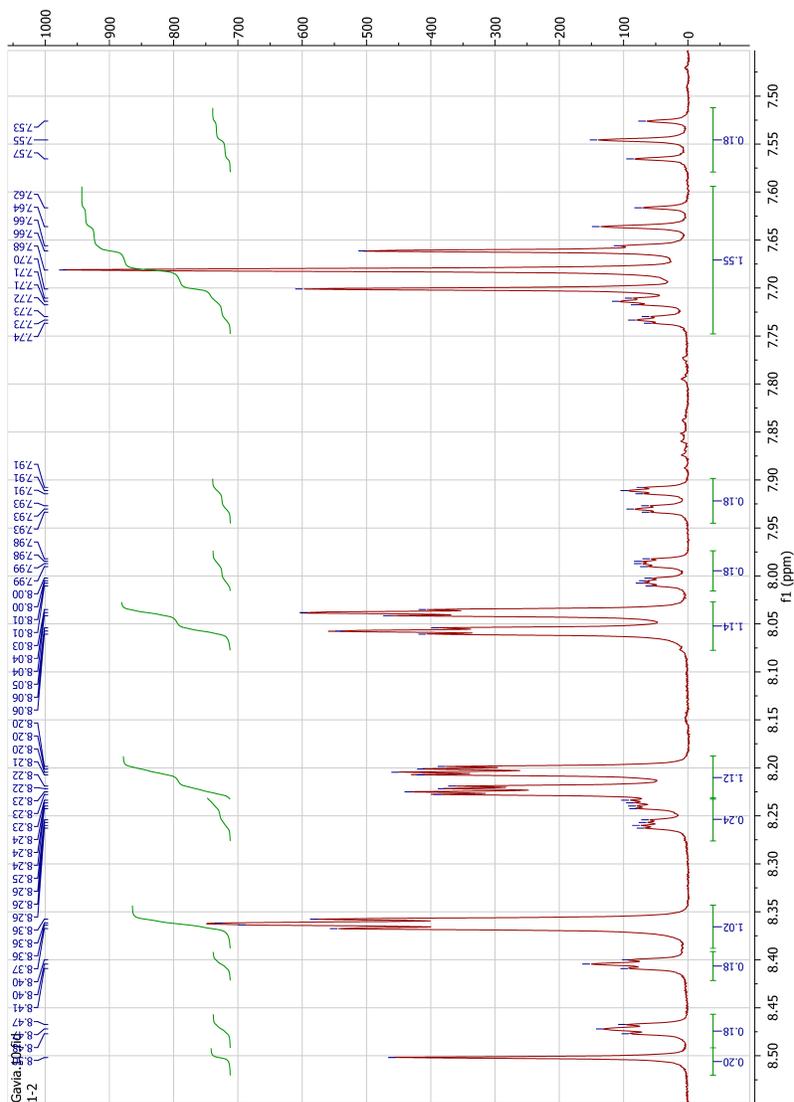


Figure 10: NMR spectrum of the solution containing the gold complex, cyanide ions, two types of signals are present, one is attributable to NBS unreacted the other of its reduction product (ppm vs arbitrary units).

object of interest. According to our findings, it seems that the presence of planes with different crystal orientation, as well as crystal defects of lower

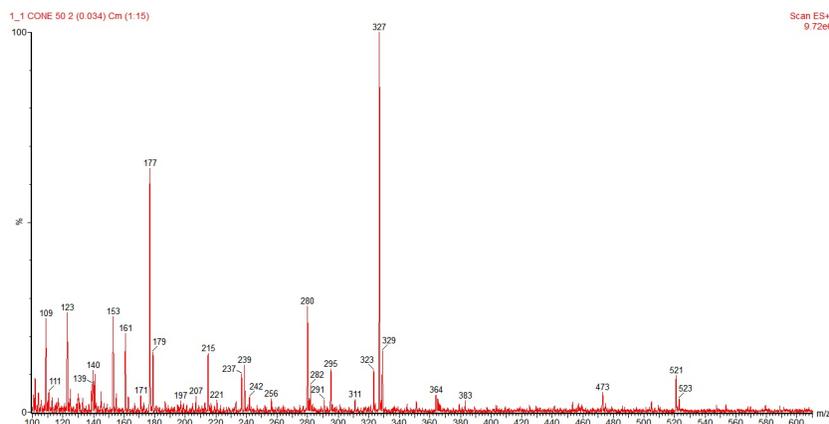


Figure 11: ESI-mass spectrum of the dissolution solution of the gold powder ( $m/z$  vs relative abundance of the analyzed ion).

coordination number, plays an important role in the gold dissolution process. Gold dissolution and subsequent passivation predominantly occur on the (100) and (111) crystal planes, respectively, as it has been also observed by Cherevko et al. (2013); Kirk et al. (1980). These data support our finding on the readiness of dissolution of gold powder with respect to gold coin. The results also explain why a mechanical waste disintegration before the chemical treatment, can further enhance the industrial processes. The cooperation of NBS in gold dissolution is evident, but its role is not yet well understood. We suppose that it plays a role in the oxidation process leading to reduction products mainly containing azo derivatives, as already suggested by Gomi et al. (2011). We also determined the free cyanide ions in solution by titration with silver nitrate. We confirmed that the cyanidation process was complete, and as expected, a large amount of cyanide still remained in solution.

#### 4. Conclusions

The present work is just a first step towards the whole comprehension of the synergic action of cyanide ion and 3-nitrobenzene-sulphonate to remove selectively precious metals from e-scrap and waste. Thanks to our experiments and analysis we have reached the following conclusions: NBS has a low solubility in water and no-intermediate complex are present in solution; cyanide dissolves first gold from the surface, forming dicyanoaurate gold com-

plexes, gold attaches to one of the sulphonate oxygen group of NBS, leaving the cyanide ions free to dissolve gold from Au surface. Other mechanism can be possible. Accordingly is important to analyze the system at the end of the process. We also can state that there is an important relation between the crystallographic plane and the yield. In fact executing experiments with powder has decreased the variability observed with coins, smaller pieces with higher free surface bring to higher yield. Oxygen in an influential factor, is not fundamental, but cooperates. Experimentally there is an evidence that with good probability between the two reduction products proposed what is formed is the azo compound (the *double*), in Fig. 3a. The dilemma remains the relative amounts. For a complete and better characterization of the NMR product further experimentation is required. At the end of the project it was clear that the ratio between the NBS and KCN was not optimal. The cyanide used is definitely too much: this is in part transformed into hydrogen cyanide, which should be avoided whenever possible. Decreasing the pH to a basic value would decrease the cyanide because it stabilizes. Probably the large amount required is due to the fact that in aqueous solution NBS passes to acid which liberates hydrogen cyanide from cyanide and does not make it available for gold. Using excess cyanide generates high pH due to hydrolysis and partly makes up for the fact that some goes as hydrogen cyanide, but its use is just excessive.

New guidelines for improving the process with increased efficiency and sustainability have been suggested to the company: reducing the cyanide content; increasing the grinding and the temperature, when the additional costs in the process is of course convenient.

Starting from the present results further studies on the reduction of cyanide usage in gold dissolution are envisaged. Even if  $\text{NBS}^- \text{CN}^-$  coupling leads to good results, an interesting way to improve the industrial process could be the search for NBS alternative, mostly able to better coordinate gold and further reduce  $\text{CN}^-$  content. A complete identification of the reduction product and of the mechanism beyond the dissolution process could lead to identify also a cyanide substitute, finally leading to cyanide-free environment-friendly process.

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Dear Editor and Reviewer,

These are our paper highlights:

- The interaction of potassium cyanide (KCN) ion and three-nitrobenzene-sulphonate (NBS) in solution for the selective removal of gold is investigated.
- Important factors are identified, and probable reaction products are proposed.
- Oxygen role and crystallographic plane exposure influence process the yield.
- New industrial guidelines, with a reduced KCN, improving the process with increased efficiency and sustainability have been suggested to the company.