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Hi-Tech waste as "Urban Mines" of precious metals: new sustainable recovery methods

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Abstract. Precious metals (PMs) are valuable components of Hi-Tech goods such as electrical and electronic equipment, catalysts, advanced materials. These relatively recent applications and the growth of their market due to the fast technological development, heavily contribute to the high rate of element consumption and Hi-Tech waste accumulation of the modern consumer society. Looking at these wastes with new eyes, encouraged by the recent world-wide regulations aimed to the sustainable waste management and raw materials preservation, we can appreciate the value contained in and turn them in secondary resources of raw materials. In this context, a sustainable approach in PMs recovery from Hi-Tech waste, built on *green chemistry* principles and addressed to find a ready technological transfer, is described here.

Keywords. Green processes, circular economy, secondary sorces, noble metals recovery, waste electrical and electronic equipments.

OVERVIEW

One of the main aspects related to the modern consumer society is the fast technology development and the inevitable production of high and increasing amount of waste it entails. The assets, especially the Hi-Tech ones, play an essential role in our daily life and their life cycle gradually decreases. Electronic equipment, automotive devices and advanced materials, often contain significant quantities of valuable and even toxic materials which would be destined to landfill, thus generating a serious environmental issue, if not valorized in a different way, *e.g.* through reuse or recycling. European and several other countries regulations on Waste Electrical and Electronic Equipment (WEEE),[1,2] End-of-Life Vehicles (EoLV)[3] and batteries & accumulators,[4] the fastest growing and pollution generating waste streams in the world, ban the uncontrolled disposal of these goods at the end of their life encouraging the implementation of a virtuous circular economy model where the recovered materials, obtained as output of waste valorization processes, are the input raw materials for new productions.[5–7] Sustainable recovery processes are also urged in order to prevent pollution and further waste generation.

In this context, PMs play a key role. Indeed, they are widely used in Hi-Tech goods because of their physical and physicochemical properties. High electrical and thermal conductivity and high resistance to the oxidation (they belong to the noble metals family characterized by high reduction potentials), coupled with their malleability and ductility, make these materials particularly appealing for industrial application mainly as conductors in long lasting high technologies. Besides that, they have limited natural availability and high economic value. For these reasons, and due to the relatively high PMs concentration in Hi-Tech scraps (where often they are present in concentration even higher than in their ores),[8,9,10] their recovery may represent the *driving force* for the profitability of more comprehensive materials recovery processes.

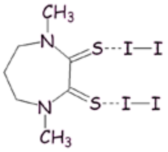
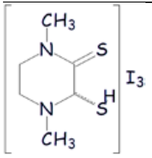
Currently the main methods used industrially to recover valued metals from the main Hi-Tech wastes have been mostly inherited from the well-known processes conventionally applied on ores and jewelry ashes and are mainly based on pyrometallurgy and hydrometallurgy.[11,12] The former, which operates by smelting and refining, generates high financial and environmental costs, while the latter, less energy-intensive, more tunable and predictable but often based on the use of toxic and aggressive substances (*e.g.* cyanides, strong oxidizing acids), can heavily affect the environment, biodiversity and human health, if not strictly controlled for reactants and wastewaters production. A wide research effort is hence required to find new ways for recovering and recycling materials from Hi-Tech scraps able to combine effectiveness to environmental sustainability. A multidisciplinary environmental science approach is needed to face this challenge. The last two decades have seen environmental scientists with different background (*e.g.* chemists, engineers, biologists) and complementary skills, at work for turning this issue into a market, scientific and environmental opportunity. Some interesting results, both in terms of effectiveness and environmental sustainability, have been obtained in the last two decades by Deplano's group of coordination chemists, for gold, palladium and platinum recovery from Hi-Tech wastes by using safe leaching agents and mild condition processes.[13] Here we describe the results obtained for two different families of Hi-Tech waste, following a new *greener* approach, exploiting the interaction between the complexing and oxidizing species in the reaction environment which promotes an effective NMs leaching.

THE CASE OF WEEE

The WEEE family contains all the devices that work with electric current or electromagnetic fields, such as: personal computers, mobile phones, TVs, printers, refrigerators, washing machines, photovoltaic panels, lamps and other small and large appliances. This type of waste contains a variety of different materials that stimulate interest on recycling profitability. At the same time, they make recovery processes a really complex issue. In particular they can contain plastics, glass, copper, aluminum, iron, as well as noble materials, especially metals (*e.g.* gold, silver, palladium), and other critical elements such as "rare earths", often beside toxic substances such as mercury, cadmium and lead, extremely hazardous for the environment and for human health. To understand the greatness of the WEEE phenomenon, it is worth mentioning that world production of WEEE in 2016 was around 45 million tons (+8% by 2014). According to the ONU, this trend is expected to grow further to 52.2 million tons (+17%) by 2021, the fastest increasing rate in the world's solid urban waste.[14] But there is still much to do for turning them into value, recovering materials in an environmentally friendly manner differently from currently used industrial methods. Conventional methods often give a not satisfactory (in terms of recovery rates) and costly (both in terms of economic and environmental impact) answer to this need. An interesting promising contribution in the field of NMs recovery from WEEE - in particular small appliances, Printed Circuit Boards (PCBs), printer cartridges and smartcards - comes from the smart use of coordination chemistry in finding sustainable reactants able to combine oxidizing and complexing properties in a single molecule. It is well-known, indeed, that the presence of a complexing agent is necessary to lower the reduction potential and make feasible the oxidation of metals with highly positive reduction potential such as gold, palladium and platinum (as in the case of cyanides and aqua regia).[11] Molecules coupling complexing and oxidizing moieties show enhanced reactivity with respect of the "free" reagents, as demonstrated in the 1990s by the McAuliffe's group in a pioneering study on the reactivity of $R_3D{\cdot}I_2$ (R = Alkyl; D= As, P) Charge-Transfer (CT) complexes towards crude inactivated metal powders.[15] On these basis, with the view to find safer and more effective leaching agents able to overcome the sustainability issues put by conventional methods, Deplano's group started an extensive study on the use of sulfur-donor/dihalogen CT complexes. In particular, dihalogen/interhalogen adducts of cyclic and acyclic dithiooxamides (DTO), soft chelating ligands bearing two vicinal thionic groups able to favor the square planar geometry preferred by d^8 metal ions, demonstrated to be a powerful class of non-cytotoxic and easily handled lixiviants towards gold,[13,16,17,18] palladium,[13,19] copper,[13] silver,[13,21] and platinum,[22] under very mild conditions, mainly providing complexes of general formula $[M(DTO)_2]^{n+}$ and/or $[M(DTO)I_2]^{(n-2)}$ (M = NM; n = charge of the metal cation) as shown in Table 1.

Among them, the bis-diiodine adduct of the N,N’-dimethyl-perhydrodiazepine-2,3-dithione ($Me_2dazdt\cdot 2I_2$) behaved as the most effective in the one-pot gold dissolution at room temperature and pressure in common organic solvents, and it was employed fully satisfactorily for the sustainable gold recovery phase in WEEE treatments as patented by the group in the last decade for the lab scale.[23,24] Figure 1 summarizes the patented three-step sustainable process for the treatment of a test specimen consisting in a thin metal powder (diameter=0.4mm) obtained by small appliances and PCBs comminution and deprived by aluminum, ferrous metals and vitreous-plastic materials, consisting in the selective dissolution and recovery of i) base metals; ii) copper; iii) gold.

Table 1. Summary of the reactions between cyclic dithioxamides/I_2 leaching agents and Au, Pd, Pt, Ag, Cu powders under mild conditions: room temperature, 2:1 molar ratio; acetone (or THF or CH_3CN).

Leaching agent	Metal	Main product	Ref.
	Au	$[Au(Me_2dazdt)I_2]I_3$	13,16,17
	Ag	-[a]	13
	Pd	$[Pd(Me_2dazdt)_2]I_6$	13,19
	Pt	-[b]	13
$Me_2dazdt\cdot 2I_2$	Cu	$[Cu(Me_2dazdt)_2]I_3$	13
	Au	$[Au(Me_2pipdt)I_2]I_3$	13
	Ag	$[Ag(Me_2pipdt)I]_2$	13,20
	Pd	$[Pd(Me_2pipdt)_2]I_6$	13
	Pt	$[Pt(Me_2pipdt)_2]I_6$[c]	22
$[HMe_2pipdt]I_3$	Cu	$[Cu(Me_2pipdt)_2]I_3$	13

[a]Unidentified product; [b]unreacted metal; [c]obtained under solvent reflux.

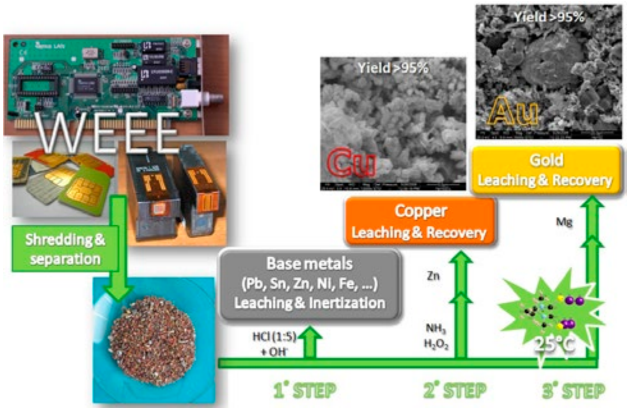


Figure 1. Schematic representation of the Deplano’s group Cu and Au recovery method from comminuted WEEE, based on the use of $Me_2dazdt\cdot 2I_2$ as gold leaching agent.[22,24]

The described process is based on the use of safe reagents. It is selective and easy to be implemented and managed consisting in just few steps which require mild operative conditions. Moreover, it is effective in the recovery of noble metals, which are obtained almost quantitatively in form of elemental metal by chemical (cementation) or electrochemical (electrowinning) reduction. From the other side, $Me_2dazdt\cdot 2I_2$, though recyclable at the end of the process, is a reagent not yet available on the market and which works in organic solvent. In order to promote *green chemistry* processes able to meet *green engineering* principles as well for a faster technology transfer on industrial scale,[11,25,26] several changes in the process were studied and implemented as improvements. In particular:

- 1st step: a refluxing citric acid solution was used in place of HCl, in order to promote the use of weaker natural acids and increase selectivity;
- 2nd step: an alkaline I^-/IO_3^- mixture, able to combine oxidizing with coordinative capability, was used, in the presence of ammonia, as a more reliable alternative to H_2O_2, avoiding effervescence phenomena and promoting in one time the copper leaching and the separation of silver from the solution in form of AgI precipitate;
- 3rd step: a I_2/I^- water solution was used as leaching agent for gold in turn of the $Me_2dazdt\cdot 2I_2$ solution in organic solvent. Although the demonstrated lower reactivity of the I_2/I^- mixture, the lower cost of the reagents, their availability on the market and, remarkably, the easy recyclability of I_2, make this process really promising for a sustainable application on a large scale.

Satisfactory results (almost quantitative yields in NMs recovery) were obtained on the cited test specimen through this new process design, pursuing a virtuous cycle able to limit the wastewater production.[27] Remarkably, this process demonstrated to be applicable satisfactorily also on coarser materials like shredded PCBs, where a heterogeneous size distribution and the presence of composite materials are present.[28] These last results demonstrate the robustness of the approach which seems appealing also from a costs/benefits ratio point of view(1) and open the way for further larger scale experimentations.

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[1] The mechanical comminution and separation pre-treatments of the incoming material represent one of the heaviest costs of the whole recovery process

THE CASE OF THREE WAY CATALYSTS (TWC_S)

TWCs are exhaust emission control devices applied to the exhaust of vehicles in order to significantly reduce the polluting emissions (essentially of CO, unburnt hydrocarbons and NO_x), favoring oxidation and/or reduction reactions with formation of non-harmful compounds. Thanks to modern regulations that impose strict limits on vehicles emissions, from the 1st January 1993 the use of TWC is mandatory for all cars in all European countries. Every year, between 6 and 7 million of EoLV, corresponding to 7 and 8 million tonnes of waste, are generated in the European Union which should be managed correctly. Well-known procedures for managing EoLV, reuse of still working parts and processes for the enhancement of bulky materials such as iron, aluminum, glass, etc., have being implemented. Differently, it is still an issue to enhance materials from electronic apparatus, batteries, car fluff (complex mixture of non-ferrous materials including plastics, foam, textiles, rubber and glass residue from car demanufacturing) and catalytic converters.

Among them, in the specific field of noble metals reclamation, catalytic converters represent a rare opportunity. Indeed, they typically consists in a metal case containing the substrate (ceramic or metallic, with a "honeycomb" structure) coated by the wash-coat(2) which supports from 5 to 8g (for petrol and diesel engines, respectively) of highly dispersed catalytically active phase formed by a mix of metal platinum, palladium and rhodium. These metals are able to promote the oxidation of carbon monoxide to carbon dioxide and that of unburnt hydrocarbons to carbon dioxide and water (Pd and Pt), and the reduction of nitrogen oxides to nitrogen (Rh).[29] Notably, Pd-only technology has been introduced in catalytic converters in the last years.[30] It is estimated that the car industry alone, which puts about 40 million new cars on the market every year, represents a potential annual resource of \$1 billion of Pd recovery.[29] Currently significant but still low (~30%) noble metals recycling from spent car converters[29] is done by non-selective unattractive methods involving unselective pyrometallurgical chlorination[30] or dissolution with strong oxidizing acids[30] in the crucial metal-dissolution step.[31,32] Based on the promising results described above on the use of dithioxamide/I_2 adducts with crude metal palladium, a joint project by Deplano's group, from University of Cagliari, and Graziani's group, from University of Trieste, allowed to check the effectiveness of $Me_2dazdt{\cdot}2I_2$ on model TWCs consisting in a Pd(2.8%)-CeO_2–ZrO_2/Al_2O_3 material underwent simulated aging (1050°C, 200h) for assessing its potential in Pd recovery from spent car converters.[33,19] Almost quantitative Pd-dissolution and recovery rates were achieved through the selective metal leaching by refluxing a Methyl Ethyl Ketone (MEK) solution of the molecular adduct in the presence of the cited test specimen in form of powder for 168 hours, has been patented and summarized as follows (Figure 2).

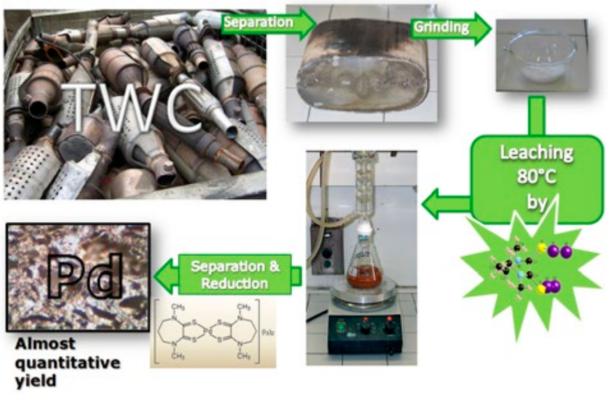

Figure 2. Schematic representation of the Deplano's group Pd recovery method from model aged TWCs based on the use of $Me_2dazdt{\cdot}2I_2$ as palladium leaching agent.[33]

The main recovered product was the $[Pd(Me_2dazdt)_2]I_6$ complex. Pd metal was quantitatively obtained by both chemical and thermal degradation of the molecular compound. Differently, Pd metal recovery attempts by chemical or electrochemical reduction were unsuccessful as expected because of the dithiolenic nature of the dicationic compound.(3) Nevertheless, $[Pd(Me_2dazdt)_2]I_6$ complex demonstrated to be successfully applicable in his molecular form as valuable homogeneous catalyst for C-C coupling reactions[34] and as precursor of effective photo-catalysts for H_2 production.[35]

As a cheaper alternative, we recently studied the use of safe fully organic triiodides (organic cations: tetrabuthylammonium, TBA^+; tetraphenilphosphonium, Ph_4P^+; 3,5-bis(phenylamino)-1,2-dithiolylium, $(PhHN)_2DTL^+$) as Pd leaching agents in organic solvents. The presence of an organic cation in the triiodide salt showed to dramatically improve its Pd-leaching properties with respect to those of the fully inorganic KI_3 salt, hampering the formation of PdI_2 coating passivation (typically present in these cases and limiting the leaching reaction to go ahead) by promoting the formation of stable and soluble ionic couples of gen-

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[2] High specific surface layer 40-50 mm thick, of g-alumina or CeO_2–ZrO_2/Al_2O_3 in current technologies

[3] In this class of complexes, the reduction event involves the whole molecule without achieving dissociation into metal and ligand components.

eral formula $Org_2[Pd_2I_6]$.[36] Although the recovery rates achieved using the cited triiodide salts were found slightly lower than those found by $Me_2dazdt{\cdot}2I_2$ solutions in analogous experimental conditions (98%, 83%, 73% for $(PhHN)_2DTLI_3$, Ph_4PI_3 and $TBAI_3$, respectively, *vs* almost quantitative for $Me_2dazdt{\cdot}2I_2$), these reactants seem really appealing for practical application due to their low cost and environmental impact, mild reaction conditions, market availability (or easy synthetic procedures), as well as for the easy metal Pd and reagents recyclability.

CONCLUSIONS AND PERSPECTIVES

The present work highlights how coordination chemistry, which is traditionally involved in the recovery/refining processes of NMs, can give a relevant contribution in designing molecular-level methods able to combine effectiveness with low environmental impact, as promoted by green chemistry principles and required by new legislation. On these basis multidisciplinarity seems the key approach to grew up molecular to industrial scale processes meeting both green chemistry and engineering requirements in order to balance sustainability with economic development. Here, a new promising sustainable approach based on the combined coordinative and oxidizing capability of safe, easy to handle and working in mild conditions charge-transfer compounds towards NMs, has been presented. A further effort is required to the *Environmental Sciences* community for implementing these methods on a larger scale in order to promote the conversion of *Trash into Resource* making the "circular economy" model feasible.

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