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Advances in Recovering Noble Metals from Waste Printed Circuit Boards (WPCBs)

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KEYWORDS. Hydrometallurgy; WPCBs; Noble metals; Recycling; Green Chemistry; Iodine.

ABSTRACT. An extensive investigation on the NMs content in different classes of WPCBs (Random Access Memories, RAMs; Network Interface Controllers, NICs; motherboards; TV, DVD/CD player, hard-drive and mobile phone PCBs) has been performed to define the most appropriate case study and provide a robust database

useful for workers in the waste valorisation field. Following accurate selection, mechanical comminution, representative sampling, quantitative digestion and analytical characterization (ICP-AES), RAMs and mobile phone PCBs confirmed to be the "richest" source, while TV PCBs the "poorest" one in term of NM content. Accordingly the RAMs case study has been employed for the application of a new Noble Metals (NMs) recovery method, previously set-up on finely comminuted WEEE underwent materials enrichment by mechanical separation. Despite the very large amount of vitreous-plastic and metallic materials present in the mixture, satisfactory NMs recovery yields (Cu 70%, Ag 92%, Au 64%) with limited by-products formation have been obtained using safe and recyclable reagents in mild conditions: citric acid for base metal leaching; ammonia in oxidizing environment for Cu and Ag separation and recovery; triiodide aqueous solution for gold recovery; room pressure; 25-100°C. The reported results provide useful quantitative parameters for assessing the profitability of an industrial scale-up of the new sustainable NMs recovery method.

Introduction

One of the great modern-days challenges of our society is to give a "new life" to the obsolete goods which are destined to landfill if not differently managed. Today, regulations from several governments world-wide, addressed to face the concern of waste accumulation and Earth-planet pollution, encourage a more environmentally respectful waste management and the preservation of natural reserves of raw materials through secondary raw materials enhancement and sustainable reclamation processes in a *circular economy* vision.[1,2,3,4] Waste Electric and Electronic Equipments (WEEE) are the object of a specific attention in that sense, due to the amount of waste generated by year (with a ≥5% growth by year, it has been recognized as the fastest growing waste stream in the world)[5] and the consequent drawbacks of their disposal.[6] Indeed, the production of modern electronics involve the use of both hazardous and "critical" materials,[7] among them a great deal of scarce and expensive resources (e.g. around 10% of total gold worldwide is used for their production). This represents an environmental concern, thinking on the related pollution and human health risks they

can generate and on the depletion of limited raw materials. At the same time, it may be turned into a value when the end-of-life goods are reprocessed to enhance the materials they are constituted off. A great interest in metals recovery is growing up worldwide at industrial and research level and it is demonstrated by the numerous and increasing conventions and research papers on this topic in the last five years.[8–11] Among WEEE, Waste Printed Circuit Boards (WPCBs) are the most intriguing and challenging source of valuable raw materials because of their qualitative and quantitative metal composition. Thus, in the last decades they were recognized and named as “urban mines”, because the amount of precious and “critical” metals they contain, often larger than in their ores.[12,13,14,15,16] In this context, Noble Metals (NMs) play a crucial role in materials recovery due to their peculiar properties and for their high economical value which often represents the economical *driving force* to make the whole recovery process affordable. Gold, silver, palladium and copper are the most widely employed valuable metals in PCBs manufacturing. They combine high electrical and thermal conductivity with high resistance to the oxidation. These features, coupled with their malleability and ductility, make these materials particularly appealing for

industrial application as conductors in long lasting high technologies.[17] Gold, the noblest one, is widely used as an external metallization in electrical contacts where high reliability is required and can be appreciably found in PCBs, but also in Central Processing Units (CPU), printer cartridges, and sim and smart cards. Silver, the most conductive among metals, is often used in PCBs as solder alloy or paste but its most peculiar role is in creating electrical pathways and high sensitive silver membrane switches. Palladium can be used as an alternative plating material to gold, or used in small amount in conductive tracks in hybrid integrated circuits (HIC) often paired with silver, but its most important application in PCBs is in multi-layer ceramic capacitors (MLCC). Copper, the most massively NM employed in PCBs, is widely used for circuit pathways, magnetic induction coils and windings, contacts and connections. Platinum and other Platinum Group Metals (PGMs; primarily Ir, Rh) are used as well in some extent, mainly in electrode coatings and fiberglass. They are also used in EEE for liquid crystals, flat-panel displays and cathode ray tubes manufacture. Despite the industrial interest and growing recovering rates, NMs are still scarcely recovered[18,19,20] and the recovery is mainly performed by conventional, often energy and environmentally

demanding, processes inherited by ore mining.[20] Typically, companies working in the field of NMs production and/or treatment by means of conventional methods, adapted their industrial process to the recovery purposes. The most diffused industrial practices for NMs recovery from WPCBs are based on pyrolysis and electrolysis.[21] Hydrometallurgical methods are industrially applied as well, but the widespread of their application is limited by the use of harmful reagents (i.e. cyanidation and aqua-regia leaching) and by the heterogeneous and composite composition of the scraps which makes the process poorly effective and selective.[21,12] The high costs and, often, harmfulness of the recovering processes, heavily discourage new actors interested in this field to entry into the market. Nevertheless more sustainable NMs recovery from complex matrix such as WPCBs is a very challenging issue not satisfactorily solved yet. In this context, new hydrometallurgical methods recently set-up on lab or pilot scale, seem to give a promising contribution for designing new industrial plants able to combine effectiveness and low environmental impact accordingly to *green chemistry & engineering principles*.[17] Among them, we found high effectiveness and selectivity, in high purity NMs recovery by using benign, selective and recyclable reagents in very

mild conditions from a mixed metallic fraction of WEEE obtained by means of shredding and electrostatic and magnetic separation techniques.[22] This method consists of a sequence of steps involving the selective leaching of the different metals from the comminuted sample by using: (1) a refluxing aqueous citric acid solution able to dissolve Sn, Zn, Pb, Ni, and other base metals; (2) NH_3 in combination with an IO_3^-/I^- mixture allowing either the oxidation of Cu and Ag, and their separation by selective AgI precipitation; (3) an I^-/I_2 mixture able of leaching quantitatively Au metal from the solid residue. Each step is followed by a further treatment, typically a chemical or electrochemical reduction, for obtaining high-rate metal and reagent recovery. The "chameleon" behavior of iodine, which shows versatile redox/complexing/precipitating capabilities, allows one to achieve the selective NM leaching and the reagent and metal recovery, towards a potentially "zero waste" process. Nevertheless the very heterogeneous composition of WEEE and the inefficiency of commercial mechanical pre-treatments plants, in terms of loss of valuable materials during the shredding and separation phases and their cost, still limit the industrial application of sustainable NMs recovery methods. It is worth noting that the number of companies able to produce a

coarse comminuted WPCBs material on their own is greatly increasing, while just few of them are currently able to produce good quality enriched metallic fractions obtained as the output of a selective mechanical separation process. On these basis, the recent project #Recovery #Green #Metal, involving Italian companies operating in WEEE management, is addressed to face specific, still open, scientific and technological issues which affect the robustness (applicability on a wide range of different materials), the sustainability (environmental but also technological and economical) and scalability (applicability on a different scale) of the process, in order to assess the potential profitability and promote the technology transfer of the proposed recovering method.

Here we report the results of an important part of this study involving: i) the accurate gold, silver, palladium and copper characterization by means of quantitative chemical analysis, by a selection of WPCBs samples underwent combined mechanical (shredding) and chemical (leaching) processes, in order to build a robust database functional to this work and useful as a reference for researchers and companies interested in waste valorisation; and, as a case study, ii) the preliminary results on the application of our sustainable NMs recovery process on a shredded sample of Random

Access Memories (RAMs) provided by companies, highly heterogeneous in terms of size distribution and composition, in order to test the selectivity and effectiveness of the method on a very coarse sample and when the vitreous-plastic support and the ferrous materials are still present in the mixture.

Materials and methods

Reagents and solvents for chemical digestion, characterization and leaching of the samples, were purchased from Sigma-Aldrich (except citric acid anhydrous FU-E 330 from ACEF, Italy) and used without further purification. WPCBs of different origin were supplied by companies (see acknowledgments).

WPCBs comminution and characterization

Comminution The size-reduction of WPCBs was performed by the STIIMA-CNR De-manufacturing Pilot Plant – Cell 3 – Mechanical Recycling, under dry conditions in two

different stages after the removal of some minor components (i.e. motor and rotating supports, fasteners and ferrous parts) not containing NMs. A preliminary comminution was performed with a single shaft shredder Erdwich M600/1-400. The output product of this preliminary size-reduction (10 mm) was thus subjected to a further shredding process with cutting mill (rotor speed: 1500 rpm), adopting grates of 2 mm. The second comminution stage was performed by means of a Retsch SM300 equipment using hardmetal-made cutting tools (WC-based material). An internal cleaning of the machines and the collection of all the sub-aliquotes of the obtained powdered material was performed after each treatment.

Sampling Given the heterogeneous nature of the material, all fractions of the same type of sample were gathered into a single flat-bottom container and underwent homogenization and leveling. Sampling was made by coring with a glass cylindrical manual corer providing around 1g aliquots, applied to different regions of the sample (e.g. in the centre of each ideal quarter of material and in the geometrical centre of the sample as reported in Figure 1, in order to obtain representative sample aliquots for the subsequent treatments.

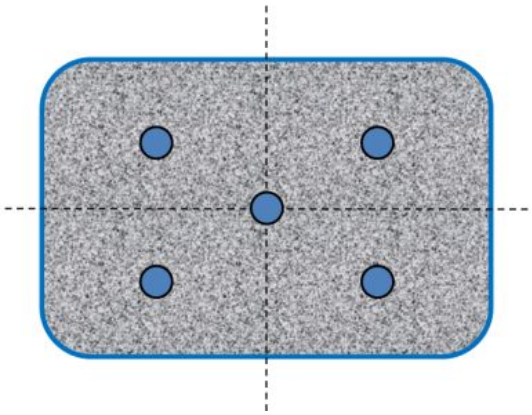


Figure 1. Schematic top-view of the WCPB shredded sample collected, homogenized and leveled in the flat-bottom container. Dotted lines (---) indicate the edges of the ideal quarters of the sample and circles (O) the coring points.

In particular, for each sample, the following aliquots were collected:

a. n. 5 1g aliquots, to be submitted to microwave mineralization in acid environment;

b. n. 1 20g aliquot, obtained by gathering twenty 1g corings, to be submitted to acid digestion under room conditions.

Sample digestion The aliquots referred to in point *a*, were weighted, then underwent microwave mineralization by introduction of the solid in TFM vessels containing a mixture of HNO_3 (65%, 2 mL), HCl (37%, 6 mL) and H_2O_2 (30%, 0.5 mL), and treatment in a Milestone Ethos 1 Microwave digester, equipped with an HPR1000/10S high pressure segmented rotor, an ATC-400CE automatic temperature control and a Terminal 640 with easyCONTROL software. The treatment was performed by applying

a microwave program consisting of two steps lasting 10 and 20 minutes, respectively, at a temperature of 220 °C and microwave power up to 1000 W. Differently, the bulky corings referred to in point *b*, were subjected to a prolonged digestion (24h) in a open flask at room temperature under magnetic bar stirring, preliminarily by slowly added HNO_3 65% (250mL), and subsequently, after filtration on a glass funnel filter and collection of the leaching solution, by freshly prepared aqua-regia (HNO_3 conc. – HCl conc. 1:3 mixture, 200mL). At the end of the digestion process, each sample was filtered off by the solid residue and the resulting clear solution properly diluted for the analysis with a 1% HNO_3 (aq) blank.

ICP-AES characterization The diluted solutions were analyzed by means of a Varian Liberty 200 Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). Specifically, metals were detected with respect to 5-point calibration plots in the 1–50 ppm range for copper and in the 1–10 ppm range for the other metals (correlation coefficient for single element calibration line > 0.9999). Elemental standards were prepared by dilution from 1000ppm mother solutions stabilized in HNO_3 5% for Cu, Ag and base metals (except for Sn), and HCl 5% for Au, Pd and Sn.

NMs leaching on RAM #R#G#M sample

RAMs milling 200 g of RAMs of different origin were milled for 24 hours in a stainless steel jar by means of *hardmetal* balls (Ø 6 mm, 1.4 Kg) in a planetary apparatus (4-stages Retsch mill, 300rpm) in the presence of Carbsyn 110 (250 mL). Carbsyn 110 is a non-flammable viscous liquid used as an auxiliary for the milling in ball mills. It belongs to the Carbsyn family of fluids which are safe-to-use, non-hazardous, odorless, non-flammable without a flash point and do not require an ATEX environment. At the end of the process, the slurry was separated by the *hardmetal* balls using sieves with grates of 4 mm. Then, Carbsyn was recovered by distillation and the milled sample collected and dried.

Characterization of the sample N. 4 aliquots of about 1.5 g each of RAM #R#G#M were sampled, digested under microwaves, and characterized for the most significant metals (Ni, Zn, Sn, Pb, Al, Cr, Mn, Fe, Au, Ag, Cu) by ICP-AES as described in paragraphs 2.1.2 - 2.1.4.

Leaching and recovery processes The selective NMs leaching and recovery procedure under study, was adapted from ref. 22 and applied to RAM #R#G#M sample

(selected sample of the project #Recovery #Green #Metal, see Acknowledgements) as following detailed and summarized in Figure 2. 10g of sample were reacted with 300mL of citric acid (H_3Cit) 3M at the refluxing temperature (100-120°C) for 48 hours. The solution turned from colorless to light green and gaseous H_2 developed when the reaction went off. Due to the H_2 production during the reaction, an inert atmosphere is desirable for safety reasons. Afterwards, the cleared and reddish solid residue was separated from the solution by filtration under vacuum, washed by water and then by acetone, dried and weighted. The leaching solution underwent digestion and chemical analysis for copper, gold and silver determination as described in 2.1.2 - 2.1.4. Base metals content was estimated by weight loss. The dried sample was then reacted, at room temperature under magnetic bar stirring, with NH_3 (aq) 33% (15 mL) in the presence of $(NH_4)_2SO_4$ (13.0 g). A solution prepared dissolving I_2 (25 g) in NaOH (aq) (1.5 M, 150 mL) was added dropwise to the mixture, readily turning the solution from colorless to blue. After 48 hours the solid residue was filtered. The procedure was repeated other 2 times (24 hours cycles) until the solution stop to turn to the blue. During the reaction, the yellowish AgI precipitation occurred. All the obtained leaching

solutions were gathered in the same flask for Cu recovery. The solid residue, was then leached by a $Na_2S_2O_3$ aqueous solution (0.06 M, 35 mL) at room temperature and the leachate filtered and collected for silver recovery. Finally the last solid residue were leached by a I_2 (1.04 g)/KI (3.68 g) water solution (80mL) for 30 minutes at room temperature under stirring. The solid residue was filtered off the solution, digested under microwaves and analyzed for unreacted NMs (see 2.1.2-2.1.4). The leaching solution was collected, diluted and directly analyzed by ICP-AES for gold. Cu(s) recovery was performed from the leaching solution by addition of an excess of Zn metal (5 g, powder, 20 mesh, freshly washed by HCl dil.) under stirring at room temperature. Zn grains slowly dissolved, red copper flakes precipitated and the blue solution cleared when the cementation reaction went on. The solution was separated from the solid by decantation and Cu metal was recovered, washed three times by HCl dil., then by water, dried and weighted (yield: 70%). Ag(s) and Au(s) recovery were performed by electrowinning from the thiosulfate and triiodide leaching solutions, respectively. Electrowinning experiments were performed by an apparatus constituted by two metallic electrodes (Pt-wire for the anode and Cu-wire for the cathode) connected, to their respective ends, with an

external electron supply (Thurlby Thandar Instruments, mod. PL 310) which drives the process (see Scheme 5 for the cell). Ag(s) and Au(s) recovery yields: 92% and 65%, respectively, by applying 2.50 mV for 1 hour without adding any support electrolyte to the cell. Due to the technological limitations of the available apparatus, the electrowinning processes were not optimized. Nevertheless, performed experiments were suitable to demonstrate the feasibility of the metal recovery by electrochemical reduction & deposition.

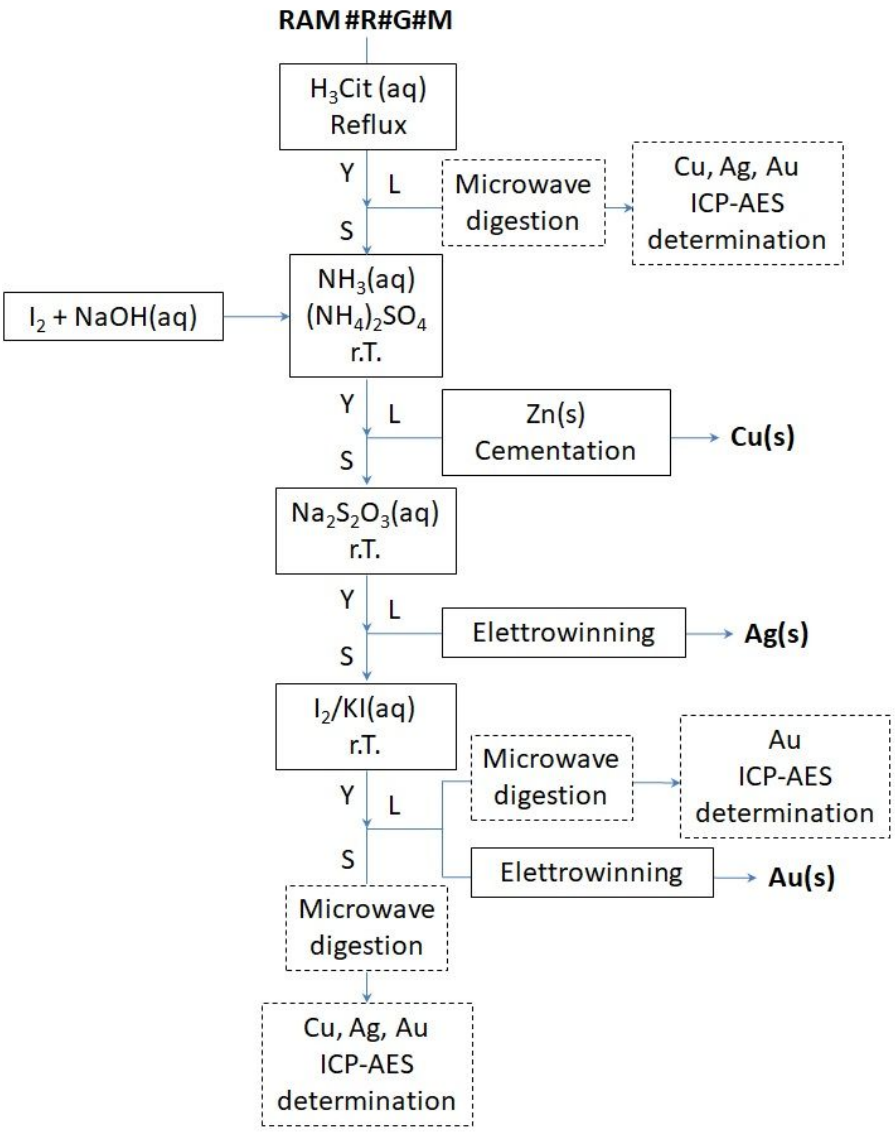


Figure 2. Integrated processing chart for the NMs recovery and analytical controls performed in the present study. R.T. = room temperature; Y = filtration; S, L = Solid, Liquid phase.

Results and discussion

Materials characterization and test specimen selection

WPCBs were selected as target WEEE for the activity, due to their wide availability and "richness" in terms of NMs, mainly gold, content. Different typologies of WPCBs

currently in use were hence collected and characterized in terms of NMs content as described in the following. The accurate characterization of such a complex materials is a challenging issue, requiring great control in operations, representative samplings, correct treatments of materials and quantitative chemical analysis data interpretation. Quite a few papers report WPCBs composition,[23,24,13,15] but a further effort sounded useful to build a robust database of strictly controlled data focusing on the different kind of PCBs available on the market.

Physical processes Table 1 summarizes the number, weight and typologies of WPCBs supplied by companies underwent comminution and the amount of powdered sample obtained through mechanical treatments. Size-reduction treatments were performed by the STIIMA-CNR Demanufacturing Pilot Plant – Cell 3 – Mechanical Recycling, are summarized in Figure 3. They consisted in a preliminary comminution with a single shaft shredder which provided a 1st stage shredded material (average size: 10 mm) which underwent a further shredding process with cutting mill (rotor speed: 1500 rpm), providing a thinner powdered sample (2nd stage material, sieve grates = 2 mm).

Table 1. List of PCB samples underwent comminution.

Typology	n.	Starting weight	Weight after shredding: 1st stage (g)	Weight after shredding: 2nd stage (g)	Weight loss (%)	Elements removed

		(g)				before shredding
DVD/CD players PCB	7	220.0	220.0	214.8	2.1	Motors and rotating supports (334g)
NIC[a]	13	642.6	639.6	635.1	1.2	Fastners (14.4g)
RAM[b] white fingers	50	703.3		702.6	0.1	
RAM[b] gold fingers	40	676.5		667.1	1.4	
Hard drive PCB	5	98.3	98.0	95.5	2.9	Heads and motors (768.3g)
Mother boards[c]	5	2525.4	2510.8	2486.7	1.5	
TV PCB	5	1985.3		1947.4	1.9	Ferrous parts (142.3g)
Mobile phone PCB	30	695.7		694.1	0.2	

[a]Network Integrated Controllers; [b]Random Access Memories; [c]Shredded with connectors

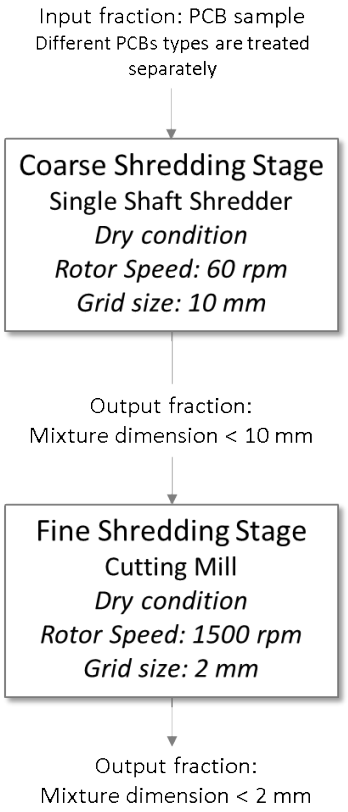


Figure 3. Schematic view of mechanical size-reduction treatments.

The size-reduction treatments were performed under dry conditions after the removal of some minor components not containing NMs (i.e. motor and rotating supports, fasteners and ferrous parts), to avoid machine jamming and damages. In order to obtain the most accurate results, all available WPCBs for each different typology were gathered and submitted to comminution, preventing material loss as much as possible

(maximum materials loss accounted for: 2.9%). Given the heterogeneous nature of the samples, they were treated separately and an internal cleaning of the machine was performed by using a vacuum cleaner after each treatment, in order to avoid loss of precious materials and samples contamination. Moreover, further separation procedures, addressed to concentrate the metallic value into a fraction, were avoided in order to limit the loss of NMs which is typically observed during eddy current and magnetic separations. Indeed, NMs, in particular gold, often consist of a very thin layer paired with magnetic elements like nickel. By shredding, NMs are reduced to a very thin powder which can be dispersed in the separation phases. Typically, it can follow nickel in magnetic separations. The whole amount of the shredded samples (2nd stage out-put) was then collected and stored to be following submitted to representative sampling and characterization.

Sampling and characterization In order to obtain accurate results, the following operations were carefully performed to pursue sample representativeness as much as possible. The whole amount of comminuted sample for each WPCB typology was collected in a flat-bottom box, homogenized and leveled. Then it was sampled by

manual coring in order to overcome material layering. Due to the really heterogeneous nature of the sample, 5 different samplings about 1g each were performed by manual coring in different areas of the sample as schematized in Figure 1. The different aliquots were then digested by a mixture of HNO_3, HCl and H_2O_2 under microwave oven conditions as detailed in 2.1.3 section. In order to compare the analytical results obtained by these 5 low amount aliquots (common microwave digestors can operates just on small amount of material) with a bulkier one, a larger amount (20g) of material was then massively sampled and leached in two steps by means of an excess of HNO_3 65% solution, then with aqua-regia on the solid residue, both under stirring at room conditions for 24 hours. Finally all the digested fractions were filtered and the solutions properly diluted by a 1% HNO_3 blank and measured for Au, Cu, Ag and Pd over five-points calibration plots (see 2.1.4). For clarity, Figure 4 summarizes the different sampling and treatments applied on each WPCB sample, up to the ICP-AES characterization. The results obtained for the two kind of sampling and treatments mostly agreed.

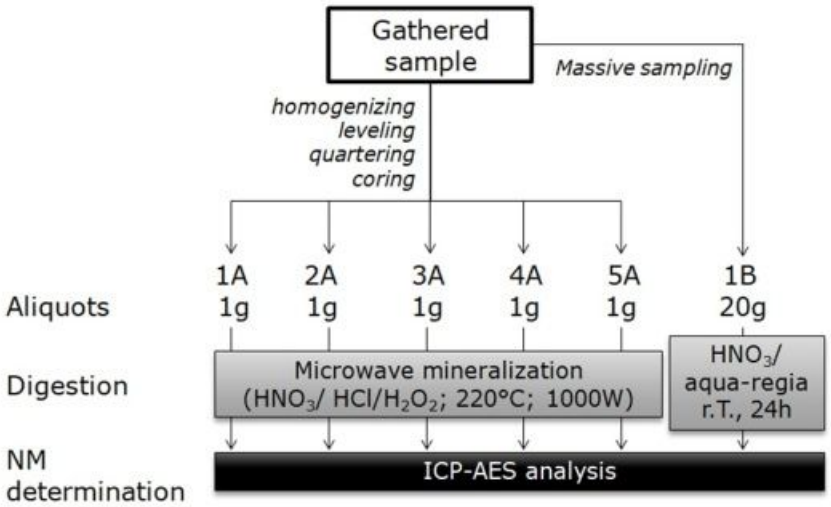


Figure 4. Summary of sampling, digestion and NM-analysis of the shredded WPCBs.

Table 2 summarizes the metal content percentages, calculated as the weighted average of the measured values by the different analyzed aliquots. In agreement with the literature, the results identified RAMs and mobile phone PCBs as the “richest” classes of PCBs, while TV PCBs as the “poorest” in term of NMs content. Because of their NMs content and sample availability by companies, waste RAMs were selected as target WPCBs for the present study.

Table 2. NMs content of different typologies of WPCBs determined by ICP-AES measurements.

WPCB sample	NMs content - %(SD)			
	Pd	Au	Ag	Cu
DVD/CD players	<0.01*	0.01(±0.01)	0.08(±0.05)	16.2(±4.4)
NIC	<0.01*	0.02(±0.01)	0.03(±0.01)	19.1(±2.3)
RAM white fingers	0.04(±0.03)	0.03(±0.01)	0.10(±0.06)	16.6(±1.9)
RAM gold fingers	0.01(±0.01)	0.07(±0.01)	0.05(±0.01)	17.1(±1.2)
Hard drive	0.02(±0.02)	0.03(±0.01)	0.06(±0.05)	23.6(±4.9)

Mother boards	<0.01*	0.01(±0.01)	0.04(±0.02)	26.7(±5.4)
TV	<0.01*	<0.01*	0.03(±0.01)	13.0(±7.4)
Mobile phone	0.06(±0.02)	0.07(±0.01)	0.14(±0.05)	33.8(±1.1)

RAM #R#G#M sample as a case study

Sample comminution and characterization RAM #R#G#M sample is a coarse material obtained by a planetary ball milling of a selection of RAMs (mix, 200g) for 24 hours in a stainless steel jar by means of *hardmetal* balls (Ø 6 mm, 1.4Kg) in the presence of Carbsyn, as detailed in 2.2.1 (Figure 5).

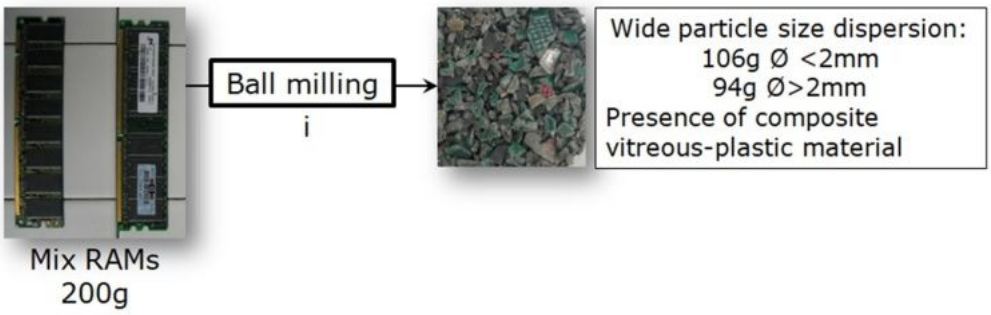


Figure 5. Preparation of the RAM #R#G#M sample. i = 24h, room temperature; stainless steel jar planetary apparatus: 4-stages mill, 300 rpm; *hardmetal* balls Ø = 6 mm, weight = 1.4 Kg; solvent: Carbsyn, 250 mL.

Carbsyn, due to its low flammability, was used as milling media with the aim to dissipate the heat produced during the milling process. Negligible erosion phenomena on the *hardmetal* balls were observed, with a weight loss of 5 g during the 24 hours treatment (weight loss = 0.35%). The obtained RAM #R#G#M sample is characterized by a wide particle size dispersion (diameters spanning from <1mm to several mm, where 106g Ø <2mm and 94g Ø>2mm) and by the presence of a huge amount of composite vitreous-plastic support material (around 70% w/w). Four portions of the described material were sampled and characterized for gold, copper, silver and palladium, and for the main base metals, by means of ICP-AES analysis, on the solutions prepared by microwave-assisted digestion as previously described.

Table 3 summarizes the metal content of the sample, which almost agreed, for NMs, with the previous RAMs characterization and with literature values for the other metals (Table 2).[13,15]

Table 3. Noble and base metals ICP-AES characterization of RAM #R#G#M sample. SD = Standard Deviation.

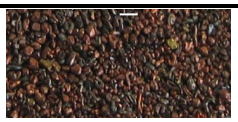
Element	RAM #R#G#M Content %(SD)
Au	0.08 (±0.03)
Ag	0.04 (±0.01)
Pd	0.06 (±0.04)
Cu	15 (±1)
Ni	4.2 (±0.7)
Fe	7 (±3)
Al	1.4 (±0.2)
Cr	<0.01*
Mn	0.06 (±0.02)
Pb	0.8 (±0.5)
Zn	<0.01*
Sn	1.9 (±0.3)

*Below Limit of Detection (LoD)

The relatively high standard deviation values are representative of the really heterogeneous nature of the sample and highlight how the sampling might affect the accuracy, in terms of precision, of the results. For comparison purposes, the reference sample A, obtained as the output of a mechanical de-processing plant, where a selection of WPCBs and small electronic equipments were shredded and submitted to mechanical pre-treatments in order to separate the incoming mixture into homogeneous particle flows with a high concentration of aluminum, ferrous metals, vitreous-plastic materials and non-ferrous metals, was taken into consideration. A comparison between the RAM #R#G#M sample and the reference sample A is reported in Table 4.

Table 4. Metal content and main features of the RAM #R#G#M and the reference Sample A.

Metal content (% w/w)			Sample features	
RAM #R#G#M		Ref.	RAM	Ref.
a	*b*	Sample A	#R#G#M	Sample A

Au	0.08	0.3	0.01		
Cu	15	49	79		
Ag	0.04	0.1	0.06	Coarse material from RAMs	Thin metallic powder from mixed WEEE
Ni	4.2	14	0.5	Metallic fraction: ~ 30% of the sample	Deprived by ferrous and non-metallic materials
Fe	7	23	1	Presence of ferrous and vitreous-plastic materials (~ 70%)	Costly treatments and equipments
Al	1.4	4.6		Low cost pre-treatments	Huge loss of valued materials
Cr	-*	-*		Limited loss of materials	
Mn	0.06	0.2			
Pb	0.8	3	7		
Sn	1.9	6.2	10		
Zn	-*	-*	2		

[a]On the whole sample; [b]On the metal fraction. *Below LoD.

The comparison between the two samples highlights that, as expected, RAM #R#G#M sample, deriving from a selection of high value WPCBs, is the “richest” in terms of NMs content with respect to sample A, obtained instead from mixed small EEE. At the same time the former contains a lower percentage of copper and lead. Furthermore, being the separation phase avoided, light metals (Al) and ferrous (Fe, Ni) and vitreous plastic materials are still present.

Selective leaching and NM recovery A portion of the RAM #R#G#M sample underwent the full leaching & recovery procedure previously applied to the reference sample A.[22] The main focuses of the experiment on the RAM #R#G#M sample were intended to point out: i) how the effectiveness in NMs recovery, in terms of yields and metal leaching times and conditions would be affected by the heterogeneous nature of the sample; ii) whether the process would occur selectively as observed in the previous case or if it would be affected by formation of by-products. The process, summarized in

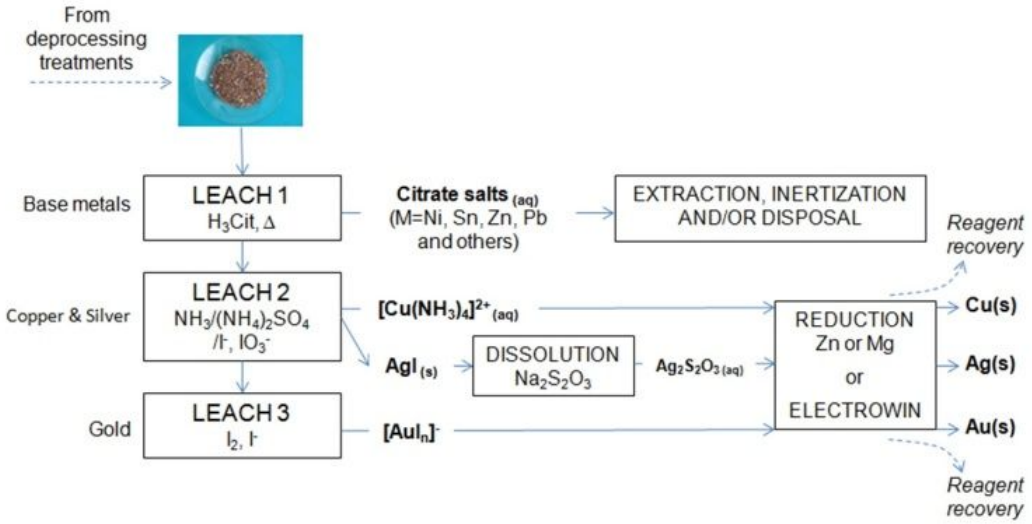


Figure 6, consisted of three main consecutive leaching phases (Leach 1: base metals; Leach 2: copper & silver; Leach 3: gold), based on the use of safe reagents (Citric acid – H_3Cit; $NH_3/(I^-,IO_3^-)$; I_2/I^-; respectively) in mild conditions, followed by NMs and reagents recovery phases in order to pursue a potential "zero waste" process.

Figure 6. Flow chart for the NM recovery process as in ref. 22. Almost quantitative NMs recovery.

When applied on the RAM #R#G#M sample, times and reagents concentration were normalized for the composition of the sample. Table 5 summarizes the experimental conditions (see details in 2.2.3) and the results obtained for the reference sample A and RAM #R#G#M sample in the leaching phases 1-3.

Table 5. Summary of the results obtained in leaching phases 1-3 for the reference sample A (**A**) and for the RAM #R#G#M (**RGM**) sample.

LEACH phase	Leached metals	Leaching conditions	Sample	Metal (%)	Time (h)		Main leaching products	Obtained result or further treatments
					Exp[a]	Obs[b]		
1	Base metals	Citric Acid 3M, Δ	**A**	~20	48	48	Citrate salts of base metals, H_2	Almost quantitative base metal dissolution
			RGM	~20		48		Almost quantitative base metal dissolution (+25% Cu)
	Copper	NH_3/NH_4	**A**	Cu		48		Solution: to

2	Silver	$^{+}$ I^-/IO_3^-		~80 Ag 0.06	48		$[Cu(NH_3)_4]^{2+}$(aq) AgI(s)	copper and reagents recovery (see Scheme 3) Solid residue: to silver leaching and recovery (see Scheme 4)
			RGM	Cu ~15 Ag 0.04		96		
3	Gold	I^-/I_2 (aq) 5:1	**A**	0.01	0.5	0.5	$[AuI_2]^-$ (aq)[c]	Solution: to gold and reagents recovery (see Scheme 5)
			RGM	0.08		0.5		

[a]Expected leaching time on the basis of previous results; [b]Experimental observation time; [c]See refs. [25] and [26].

In Leach 1, 10g of RAM #R#G#M were reacted firstly with approximately 300mL of a H_3Cit water solution (3M) (Liquid/Solid ratio, L/S=30) under stirring and reflux for 48 hours for base metal leaching with consequent formation of base metals citrate complexes and gaseous H_2 development. The solution turns from colorless to greenish when the reaction went off. Afterwards, the solid residue was separated from the solution by filtration, washed by water and then by acetone and dried. The found weight loss (~30%) of the solid sample was compatible with the full leaching of base metals plus a slight amount of copper, in agreement with the green color of the solution.

Quantitative copper determination onto the leaching solution found that 0.37g of Cu (representing the 3.7% of the sample and the 25% of the whole Cu content of the sample) dissolved in those conditions. On the basis of this result, in order to obtain higher selectivity, shorter leaching times and/or working under inert atmosphere might be advisable. In Leach 2, the dried sample was reacted with a NH_3 33% water solution in the presence of $(NH_4)_2SO_4$ (L/S ≅ 2), slowly adding a solution prepared by dissolving I_2 in aqueous NaOH 1.5 M, at room temperature (final L/S ≅ 20). The solution promptly turned from colorless to blue as the oxidizing IO_3^- specie was added to the mixture and the copper leaching went on forming the $[Cu(NH_3)_4]^{2+}$ complex, as summarized by the following equations:

Eq. 1) $I_2 + 2OH^- = I^- + IO^- + H_2O$; Eq. 2) $IO^- + O_2 = IO_3^-$; $E°(IO_3^-/I^-) = 0.26V$

Eq. 3) $3Cu + 12NH_3 + IO_3^- + 3H_2O = 3[Cu(NH_3)_4]^{2+} + I^- + 6OH^-$; $E°([Cu(NH_3)_4]^{2+}/Cu) = -0.05V$

After 48 hours, the solid residue was filtered and the solution collected for copper recovery. To ascertain that complete copper dissolution was achieved, the procedure was repeated on the solid residue until a colourless solution appeared. The whole

copper dissolution was achieved in approximately 96 hours. Meanwhile, the silver leaching and precipitation of AgI occurred by the reaction:

Eq. 4) $6Ag + IO_3^- + 3H_2O + 5I^- = 5AgI\downarrow + 6OH^-$; $E°(AgI/Ag) = -0.152V$

All the copper-containing solutions were gathered and copper was recovered from the solution by cementation with an excess of Zn metal at room temperature obtaining a 70% Cu metal recovery yield by weight after washing the red Cu flakes by HCl dil. (Figure 7).

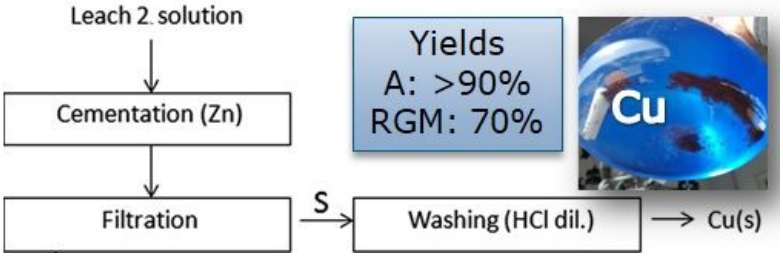


Figure 7. Leach 2 solution: copper recovery processes. Cu recovery yields for reference sample A (**A**) and RAM #R#G#M (**RGM**). S = solid phase.

It is noteworthy that the copper leaching time for this sample was expected to be 2-times shorter than that found. This finding is reasonable considering copper is the most abundant among the metals in the sample and also its recovery is the most affected by

the coarse nature of the sample due to its inclusion into the vitreous-plastic support matrix (being the main metal used for circuit pathways). Moreover, in contacts and connections, it is covered by gold.

Figure 8 summarizes silver metal recovering processes.

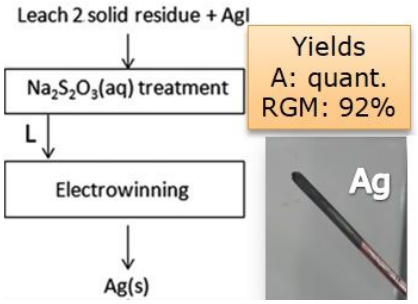


Figure 8. Leach 2 solid residue: silver recovery process. Ag(s) recovery yields for reference sample A (**A**) and RAM #R#G#M (**RGM**). L = liquid phase.

AgI was leached away from the Leach 2 solid residue by washing it with a $Na_2S_2O_3$ water solution at room temperature. After filtration, silver metal was recovered in high yield (92%) from the leaching solution containing the $[Ag(S_2O_3)_2]^{3-}$ complex, by electrowinning as a coating deposition on a Cu cathode (see details in 2.2.3). Finally, the solid residue underwent gold leaching by using 80mL of a water solution containing

I_2/I^- ($E°(I_3^-/I^-)$ = +0.54V) in a 1:5 molar ratio (4.1 and 22.2 mmol, respectively), for 30' at room temperature under stirring following the reaction:

Eq. 5) $2Au + I_2 + 2I^- = 2[AuI_2]^-$; $E°([AuI_2]^-/Au)$ = +0.58V.

After leaching, H_2O_2–HCl were added to the solution in order to oxidize iodide and recover I_2 (Figure 9). Metal analysis on the leaching solution showed that a 64% gold leaching yield was found for RAM #R#G#M sample in the applied experimental conditions with respect to the almost quantitative occurred in the case of reference sample A. This data was in agreement with the amount of gold deposited by electrowinning from the resulting chloride solution on a copper wire working as cathode.

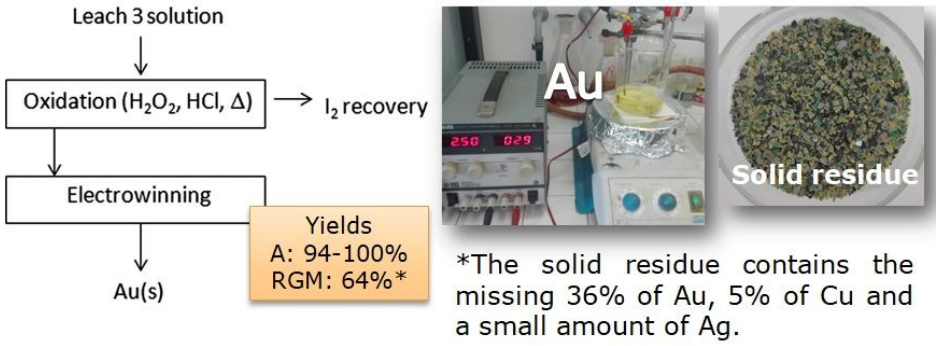


Figure 9. Leach 3 solution: gold recovery process. Au(s) recovery yields for reference sample A (**A**) and RAM #R#G#M (**RGM**).

Nevertheless, wide improvements in gold reclamation are expected by prolonging the leaching time for the "richest" last cited sample (gold content: sample A = 0.01%; RGM = 0.08%). In agreement, the missing 36% of gold was found in the final solid residue. Beside gold, 5% of copper and a small amount of silver were found in the final solid residue as well, highlighting that, according to the previous findings, copper remains partially included in the support matrix and it is exposed gradually to the leaching.

No interfering by-products were isolated and/or identified along the whole leaching and recovery process.

A comparison between the proposed method and the more conventional ones, e.g. based on the direct use of HNO_3 and/or aqua regia solutions,[27] highlights that the use of the selected leaching agents promote a slightly less efficient, in terms of recovering times and rates, but more selective and sustainable NMs recovery. Indeed, besides the slight loss in efficiency which can be faced improving the degree of comminution and prolonging the leaching times, the method described here pursues and obtains the phase-by-phase dissolution and recovery of metals using leaching agents specifically selected for coupling the highest affinity towards each metal class with the lower

environmental impact. At the contrary, the more aggressive conventional methods, beside a high efficiency of the leaching phase (potentially nearly quantitative in short times), achieve no or very low selectivity (HNO_3 dissolves all the metals with standard reduction potential <0.96V, then including copper and silver; aqua regia dissolves gold as well) which heavily affects the following metal recovery phase, produce abundant toxic emissions (mainly NO_x, besides other gaseous by-products), related to the strong oxidative action of HNO_3 and or Cl_2 towards metals and plastics, and wastewaters, which require strict industrial set up, risk assessment and qualified staff, for being managed.

Conclusions

As well-known, hydrometallurgical methods clearly benefit from prior comminution and separation, able to reduce bulk volume, to expose a greater surface area of contained metals to the leaching and to limit interfering reactions. This important pre-treatment becomes more helpful for improving effectiveness when selective non-aggressive reactants are used to meet sustainability requirements, as shown by the preliminary results here described. Nevertheless, these treatments remain the most expensive and technologically concerning part of the whole recovery process pointing out the need to balance the comminution and separation effort with the following leaching and recovery processes. The robustness of an innovative NM recovery

method from WPCBs coupling "greenness" with effectiveness, was demonstrated by its application on a coarse sample of shredded RAMs. Indeed, though the limited low-cost mechanical pre-treatments underwent by the sample, satisfactory NMs recovery yields (Cu 70%, Ag 92%, Au 64%) are found applying an effective three phases leaching process where i) a refluxing citric acid aqueous solution achieves base metals leaching in 48 hours; ii) ammonia in oxidizing environment operates Cu and Ag leaching and separation in one pot in almost 96 hours; and iii) a triiodide aqueous solution dissolves gold in about 30'; followed by a cementation or electrochemical deposition of the different NMs. This process provides a clean separation with limited by-products formation using safe and recyclable reagents in mild conditions. Consequently, it is worth noting the coarse nature of the sample does not seem jeopardize the whole metal recovery process. A further effort in combining the pre-treatment set up with the subsequent leaching processes would help in obtaining the optimal conditions to meet the effectiveness and sustainability required for practical application as aimed by green chemistry & engineering principles, and open the way to the scale-up phase on a pilot plant.

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Author Contributions

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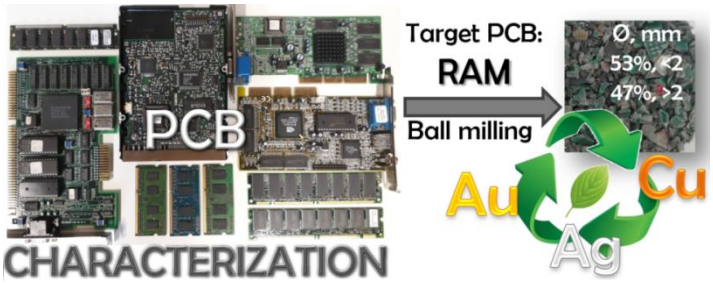
TOC & SYNOPSIS

Towards circular economy: application of a “green” NMs recovery process from WPCBs with high metal recovery rate and low-cost pre-treatments.