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

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ABSTRACT: An extensive investigation on the noble metal (NM) content in different classes of waste printed circuit boards (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 valorization 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 are the "poorest" one in term of NM content. Accordingly, the RAM case study has been employed for the application of a new NMs recovery method, previously set up on finely comminuted waste electric and electronic equipment underwent materials enrichment by mechanical separation. Despite the very large amount of vitreous-plastic and metallic materials present in the mixture, satisfactory NM recovery yields (Cu 70%, Ag 92%, Au 64%) with limited byproduct 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, at room pressure, and 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.

KEYWORDS: Hydrometallurgy, WPCBs, Noble metals, Recycling, Green chemistry, Iodine
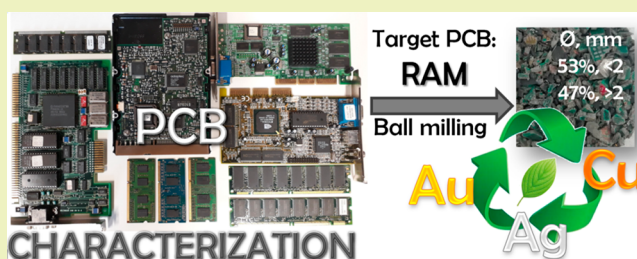
INTRODUCTION

One of the great modern-day 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 worldwide, 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.[1−4] Waste electric and electronic equipment (WEEE) is the object of 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 involves 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 of the related pollution and human health risks they can generate and of 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 from. Great interest in metals recovery is growing worldwide at the industrial and research level, and this is demonstrated by the numerous and increasing conventions and research papers on this topic over the past 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, over the past decades they were recognized and named as "urban mines", because of the amounts of precious and "critical" metals they contain, which are often larger than in their ores.[12−16] In this context, noble metals (NMs) play a crucial role in materials recovery due to their peculiar properties and for their high economic value which often represents the economic *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 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 for 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 highly sensitive silver membrane switches. Palladium can be used as an alternative plating material to gold, or used in a small amount in conductive tracks in hybrid integrated circuits (HIC) often paired with silver, but its most important application in PCBs is in multilayer ceramic capacitors (MLCC). Copper, the most massively employed noble metal 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 to some extent, mainly in electrode coatings and fiberglass. They are also used in EEE for liquid crystals, flat-panel displays, and cathode ray tube manufacturing. Despite the industrial interest and growing recovering rates, NMs are still scarcely recovered[18−20] and the recovery is mainly performed by conventional, often energy and environmentally demanding, processes inherited from ore mining.[17] Typically, companies working in the field of NM production and/or treatment by means of conventional methods adapted their industrial process to recovery purposes. The most diffused industrial practices for NM recovery from WPCBs are based on pyrolysis and electrolysis.[21] Hydrometallurgical methods are industrially applied as well, but their widespread 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 enter the market. Nevertheless, more sustainable NM recovery from complex matrices 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 provide a promising contribution for designing new industrial plants able to combine effectiveness and low environmental impact accordingly to *green chemistry and engineering principles*.[17] Among them, we found high effectiveness and selectivity, in high-purity NM 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; and (3) an I^-/I_2 mixture able to quantitatively leach Au metal from the solid residue. Each step is followed by an additional 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 selective NM leaching and reagent and metal recovery, toward a potentially "zero waste" process. Nevertheless, the very heterogeneous composition of WEEE and the inefficiency of commercial mechanical pretreatments plants, in terms of loss of valuable materials during the shredding and separation phases and their cost, still limit the industrial application of sustainable NM recovery methods. It is worth noting that the number of companies able to produce a coarse comminuted WPCB material on their own is greatly increasing, while just a few of them are currently able to produce high-quality enriched metallic fractions obtained as the output of a selective mechanical separation process. On these bases, 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 the scalability (applicability on a different scale) of the process, in order to assess the potential profitability and promote the technology transfer of the proposed recovery 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 WPCB samples that 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 NM recovery process on a shredded sample of random access memories (RAMs), provided by companies, that are 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).

WPCB Comminution and Characterization. *Comminution.* The size reduction of WPCBs was performed by the STIIMA-CNR Demanufacturing 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 hard-metal-made cutting tools (WC-based material). An internal cleaning of the machines and the collection of all the subaliquotes 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 approximately 1 g aliquots, applied to different regions of the sample (e.g., in the center of each ideal quarter of material and in the geometrical center of the sample as reported in Figure 1) in order to obtain representative sample aliquots for the subsequent treatments.
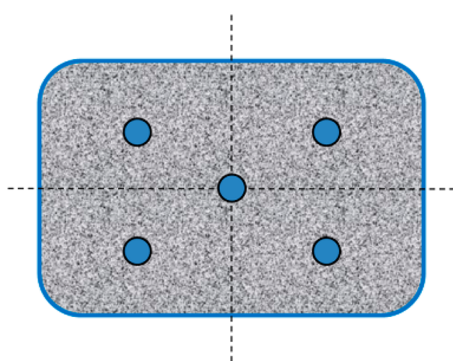
Figure 1. Schematic top-view of the WCPB shredded sample collected, homogenized, and leveled in the flat-bottom container. Dotted lines (---) indicate the edges of the ideal quarters of the sample, and circles (○) indicate the coring points.

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

(a) Five 1 g aliquots, to be submitted to microwave mineralization in acid environment;
(b) One 20 g aliquot, obtained by gathering 20 1 g corings, to be submitted to acid digestion under room conditions.

Sample Digestion. The aliquots referred to in point (a) were weighed, and then they 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 easy-CONTROL software. The treatment was performed by applying a microwave program consisting of two steps lasting 10 and 20 min, 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 (24 h) in a open flask at room temperature under magnetic bar stirring, preliminarily by slowly added HNO_3 65% (250 mL), 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, 200 mL). 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 1000 ppm 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.* A 200 g portion of RAMs of different origin was milled for 24 h in a stainless steel jar by means of hard metal balls (Ø 6 mm, 1.4 kg) in a planetary apparatus (4-stages Retsch mill, 300 rpm) in the presence of Carbsyn 110 (250 mL). Carbsyn 110 is a nonflammable 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, nonhazardous, odorless, nonflammable, without a flash point, and do not require an ATEX environment. At the end of the process, the slurry was separated by the hard metal 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. Four 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 above.

Leaching and Recovery Processes. The selective NM leaching and recovery procedure under study was adapted from ref 22 and applied to the RAM #R#G#M sample (selected sample of the project #Recovery #Green #Metal, see Acknowledgments) as detailed and summarized in Figure 2. A 10 g sample was reacted with 300 mL of 3
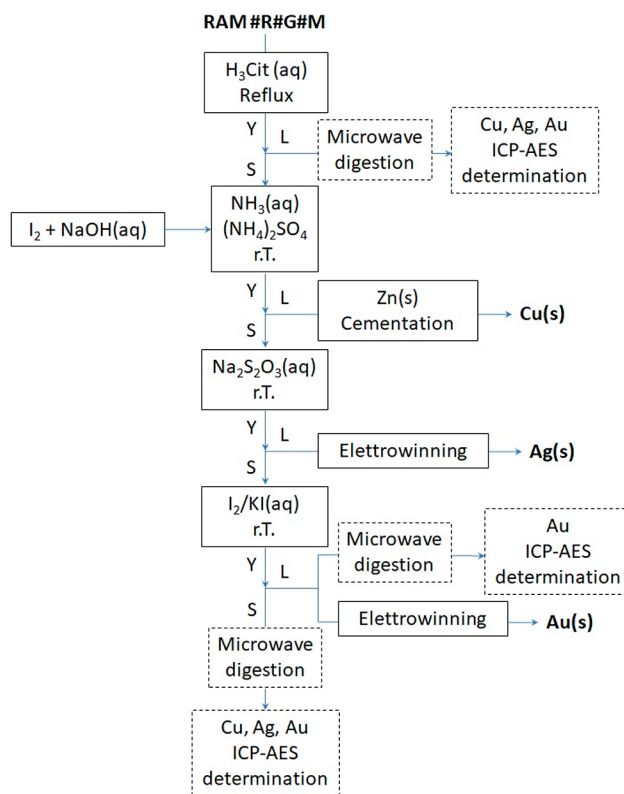
Figure 2. Integrated processing chart for the NMs recovery and analytical controls performed in the present study. R.T. = room temperature. Y = filtration. S, L = solid, liquid phase.

M citric acid (H_3Cit) at the refluxing temperature (100−120 °C) for 48 h. 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. Afterward, the clear and reddish solid residue was separated from the solution by filtration under vacuum, washed by water and then by acetone, dried, and weighed. The leaching solution underwent digestion and chemical analysis for copper, gold, and silver determination as described above. Base metal 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

Table 1. List of PCB Samples That Underwent Comminution

typology	no.	starting weight (g)	weight after shredding		weight loss (%)	elements removed before shredding
			1st stage (g)	2nd stage (g)		
DVD/CD players PCB	7	220.0	220.0	214.8	2.1	motors and rotating supports (334 g)
NIC[a]	13	642.6	639.6	635.1	1.2	Fastners (14.4 g)
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 (768.3 g)
motherboards[c]	5	2525.4	2510.8	2486.7	1.5	
TV PCB	5	1985.3		1947.4	1.9	Ferrous parts (142.3 g)
mobile phone PCB	30	695.7		694.1	0.2	

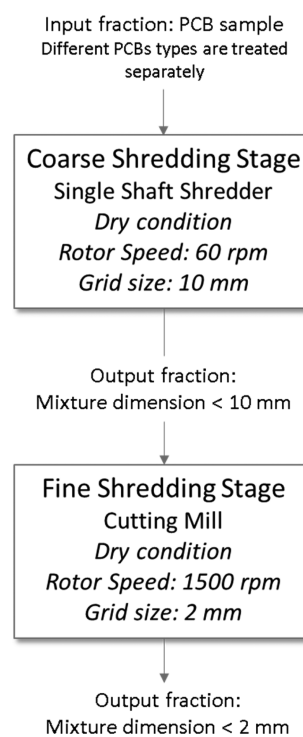[a]Network integrated controllers. [b]Random access memories. [c]Shredded with connectors.

dropwise to the mixture, readily turning the solution from colorless to blue. After 48 h the solid residue was filtered. The procedure was repeated another 2 times (24 h cycles) until the solution stopped turning 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 was leached by a I_2 (1.04 g)/KI (3.68 g) water solution (80 mL) for 30 min at room temperature under stirring. The solid residue was filtered off the solution, digested under microwaves, and analyzed for unreacted NMs (see above). 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 and then by water, dried, and weighed (yield 70%). Ag(s) and Au(s) recoveries 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, model PL 310) which drives the process (see Figure 9 for the cell). Ag(s) and Au(s) recovery yields 92% and 65%, respectively, by applying 2.50 mV for 1 h 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 and deposition.

■ 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 NM, 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 material 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 that underwent comminution and the amount of powdered sample obtained through mechanical treatments. Size-reduc-

tion treatments were performed by the STIIMA-CNR Demanufacturing Pilot Plant—Cell 3—Mechanical Recycling, are summarized in Figure 3. They consisted of a preliminary


Input fraction: PCB sample
Different PCBs types are treated separately

↓

Coarse Shredding Stage
Single Shaft Shredder
Dry condition
Rotor Speed: 60 rpm
Grid size: 10 mm

↓

Output fraction:
Mixture dimension < 10 mm

↓

Fine Shredding Stage
Cutting Mill
Dry condition
Rotor Speed: 1500 rpm
Grid size: 2 mm

↓

Output fraction:
Mixture dimension < 2 mm

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

comminution with a single shaft shredder which provided a first 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 (second stage material, sieve grates = 2 mm).

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 damage. 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 sample

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 (second 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 representation 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 of about 1 g 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 the Sample Digestion 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 those from a bulkier one, a larger amount (20 g) of material was then massively sampled and leached in two steps by means of an excess of HNO_3 65% solution, and then with aqua regia on the solid residue, both under stirring at room conditions for 24 h. 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 the ICP-AES Characterization section). For clarity, Figure 4 summarizes the different sampling and
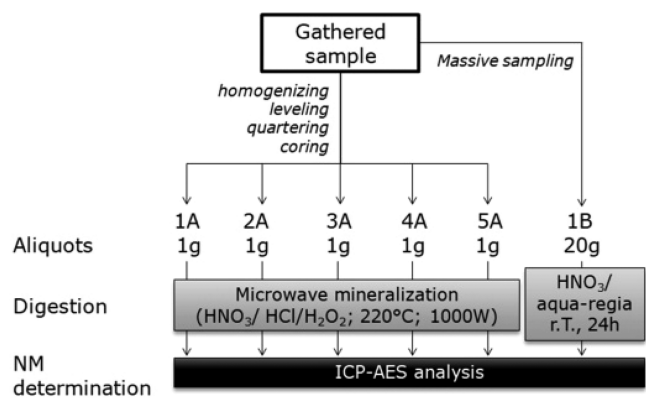
Figure 4. Summary of sampling, digestion, and NM analysis of the shredded WPCBs.

treatments applied on each WPCB sample, up to the ICP-AES characterization. The results obtained for the two kinds of sampling and treatments mostly agreed.

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, with TV PCBs as the "poorest" in term of NMs content. Because of their NM

content and sample availability by companies, waste RAMs were selected as target WPCBs for the present study.

RAM #R#G#M Sample as a Case Study. *Sample Commination and Characterization.* The RAM #R#G#M sample is a coarse material obtained by a planetary ball milling of a selection of RAMs (mix, 200 g) for 24 h in a stainless steel jar by means of hard metal balls (Ø 6 mm, 1.4 kg) in the presence of Carbsyn, as detailed in the RAMs Milling section (Figure 5).

Carbsyn, due to its low flammability, was used as the milling medium with the aim of dissipating the heat produced during the milling process. Negligible erosion phenomena on the hard metal balls were observed, with a weight loss of 5 g during the 24 h treatment (weight loss = 0.35%). The obtained RAM #R#G#M sample is characterized by a wide particle size dispersion (diameters spanning from <1 mm to several millimeters, where 106 g Ø < 2 mm and 94 g Ø > 2 mm) 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]

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, reference sample A, obtained as the output of a mechanical deprocessing plant, where a selection of WPCBs and small electronic equipment was shredded and submitted to mechanical pretreatments, in order to separate the incoming mixture into homogeneous particle flows with a high concentration of aluminum, ferrous metals, vitreous-plastic materials, and nonferrous metals, was taken into consideration. A comparison between the RAM #R#G#M sample and the reference sample A is reported in Table 4.

The comparison between the two samples highlights that, as expected, the RAM #R#G#M sample, derived from a selection of high-value WPCBs, is the "richest" in terms of NM content with respect to sample A, which was obtained instead from mixed small EEE. At the same time, the former contains a lower percentage of copper and lead. Furthermore, with 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 and 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 byproducts. The process, summarized in Figure 6, consisted of three main consecutive leaching phases (leach 1, base metals; leach 2, copper and 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

Table 2. NM Content of Different Typologies of WPCBs Determined by ICP-AES Measurements

WPCB sample	NM content, % (SD)			
	Pd	Au	Ag	Cu
DVD/CD players	<0.01[a]	0.01 (±0.01)	0.08 (±0.05)	16.2 (±4.4)
NIC	<0.01[a]	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)
motherboards	<0.01[a]	0.01 (±0.01)	0.04 (±0.02)	26.7 (±5.4)
TV	<0.01[a]	<0.01[a]	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)

[a]Below limit of detection.
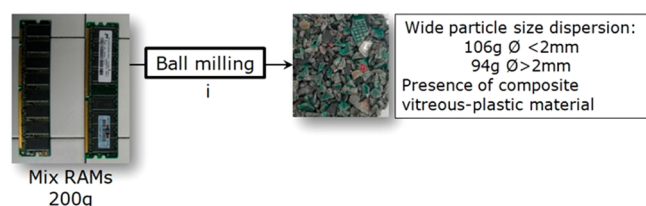
Figure 5. Preparation of the RAM #R#G#M sample. Conditions identified as i = 24 h, room temperature. Stainless steel jar planetary apparatus: 4-stage mill, 300 rpm; hard metal balls Ø = 6 mm, weight = 1.4 kg. Solvent: Carbsyn, 250 mL.

Table 3. Noble and Base Metal ICP-AES Characterization of RAM #R#G#M Sample[a]

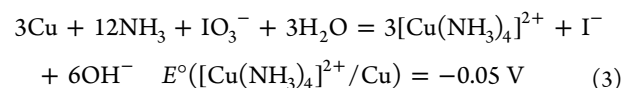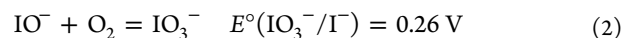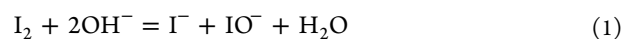| element	RAM #R#G#M content, % (SD)
Au	0.08 (±0.03)
Ag	0.04 (±0.01)
Pd	0.06 (±0.04)
Cu	15 (±1)
Ni	4.2 (±0.7)
Fe	7 (±3)
Al	1.4 (±0.2)
Cr	<0.01[b]
Mn	0.06 (±0.02)
Pb	0.8 (±0.5)
Zn	<0.01[b]
Sn	1.9 (±0.3)

[a]SD = standard deviation. [b]Below limit of detection (LoD).

conditions, followed by NMs and reagents recovery phases in order to pursue a potential "zero waste" process.

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.

In leach 1, 10 g of RAM #R#G#M was reacted first with approximately 300 mL of a H_3Cit water solution (3 M) (liquid/solid ratio, L/S = 30) under stirring and reflux for 48 h for base metal leaching with consequent formation of base metal citrate complexes and gaseous H_2 development. The solution turns from colorless to greenish when the reaction went off. Afterward, 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 0.37 g 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 an 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^- species 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:

$$I_2 + 2OH^- = I^- + IO^- + H_2O \tag{1}$$

$$IO^- + O_2 = IO_3^- \quad E°(IO_3^-/I^-) = 0.26 \text{ V} \tag{2}$$

$$3Cu + 12NH_3 + IO_3^- + 3H_2O = 3[Cu(NH_3)_4]^{2+} + I^-$$
$$+ 6OH^- \quad E°([Cu(NH_3)_4]^{2+}/Cu) = -0.05 \text{ V} \tag{3}$$

After 48 h, 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 colorless solution appeared. The whole copper dissolution was achieved in approximately 96 h. Meanwhile, the silver leaching and precipitation of AgI occurred by the following reaction:

$$6Ag + IO_3^- + 3H_2O + 5I^- = 5AgI \downarrow + 6OH^-$$
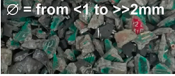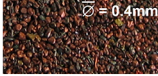$$E°(AgI/Ag) = -0.152 \text{ V} \tag{4}$$
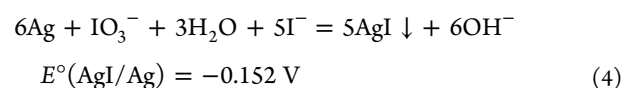
All the copper-containing solutions were gathered, and copper was recovered from the solution by cementation with an excess of Zn metal at room temperature obtaining a 70% Cu metal recovery yield by weight after washing the red Cu flakes by HCl dil (Figure 7).

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.

**Table 4. Metal Content and Main Features of the RAM #R#G#M and Reference Sample A**

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

[a]On the whole sample. Asterisks indicate below LoD. [b]On the metal fraction. Asterisks indicate below LoD.
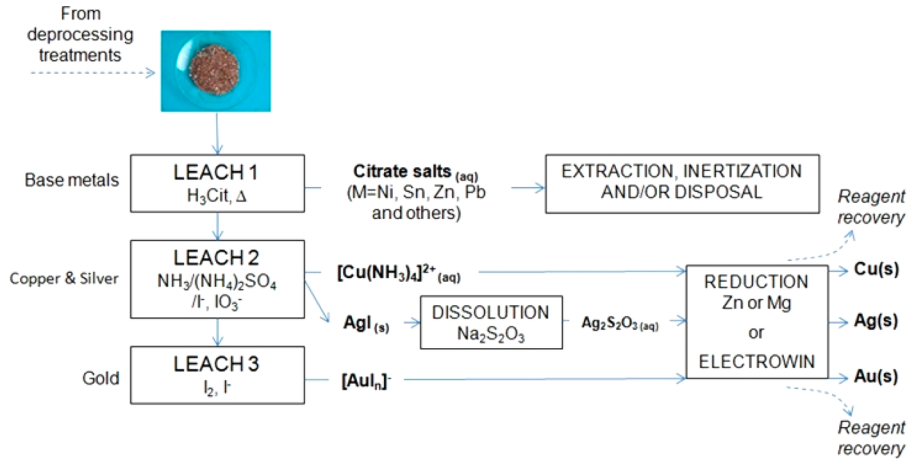
Figure 6. Flowchart for the NM recovery process based on process from ref 22. Almost quantitative NM recovery.

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 the Leaching and Recovery Processes section). Finally, the solid residue underwent gold leaching by using 80 mL of a water solution containing I_2/I^- ($E°(I_3^-/I^-)$ = +0.54 V) in a 1:5 molar ratio (4.1 and 22.2 mmol, respectively), for 30 min at room temperature under stirring following the reaction

$$2Au + I_2 + 2I^- = 2[AuI_2]^- \quad E°([AuI_2]^-/Au) = +0.58 V$$
(5)
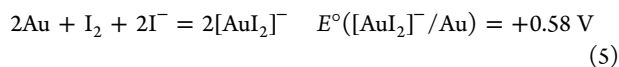
After leaching, H_2O_2−HCl was added to the solution in order to oxidize iodide and recover I_2 (Figure 9). Metal analysis on the leaching solution showed that a 64% gold leaching yield was found for the RAM #R#G#M sample in the applied experimental conditions with respect to the almost quantitative reaction that 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.

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. Besides gold, 5% of copper and a small amount of silver were found in the final solid residue as well,

Table 5. Summary of the Results Obtained in Leaching Phases 1−3 for the Reference Sample A and for the RAM #R#G#M (RGM) Sample

| LEACH phase	leached metals	leaching conditions	sample	metal (%)	time (h) expt[a]	obsd[b]	main leaching products	obtained result or further treatments
1	base metals	citric acid 3 M, 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)
2	copper	NH_3/NH_4^+	A	Cu ~80	48	48	$[Cu(NH_3)_4]^{2+}(aq)$	solid residue: to silver leaching and recovery (see Figure 8)
	silver	I^-/IO_3^-		Ag 0.06				
			RGM	Cu ~15		96	AgI(s)	solution: to copper and reagent recovery (see Figure 7)
				Ag 0.04				
3	gold	$I^-/I_2(aq)$	A	0.01	0.5	0.5	$[AuI_2]^-(aq)^c$	solution: to gold and reagents recovery (see Figure 9)
		5:1	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.
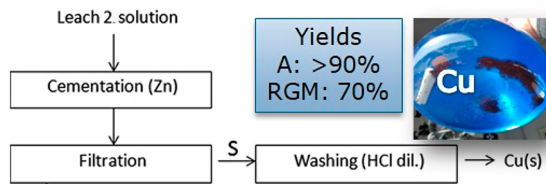
Figure 7. Leach 2 solution: copper recovery process. Cu recovery yields for reference sample A (A) and RAM #R#G#M (RGM). S = solid phase.
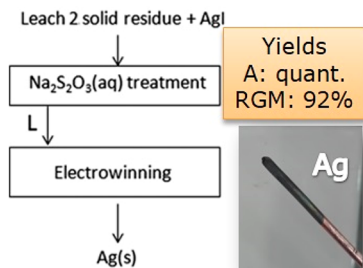
Figure 8. Leach 2 solid residue: silver recovery process. Ag(s) recovery yields for reference sample A (A) and RAM #R#G#M (RGM). L = liquid phase.
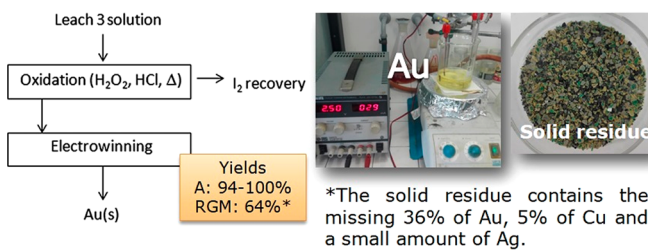
Figure 9. Leach 3 solution: gold recovery process. Au(s) recovery yields for reference sample A (A) and RAM #R#G#M (RGM).

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 byproducts 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 promotes a slightly less efficient, in terms of recovering times and rates, but more selective and sustainable NM recovery. Indeed, besides the slight loss in efficiency which can be faced by 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 toward each metal class with the lower environmental impact. On the contrary, the more aggressive conventional methods, besides 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 <0.96 V, then including copper and silver; aqua regia dissolves gold as well) which heavily affects the following metal recovery phase and produces abundant toxic emissions (mainly NO_x, besides other gaseous byproducts), related to the strong oxidative action of HNO_3 and or Cl_2 toward metals and plastics, and wastewaters, which require strict industrial set up, risk assessment, and qualified staff, for being managed.

CONCLUSIONS

As is well-known, hydrometallurgical methods clearly benefit from prior comminution and separation, and the ability to reduce bulk volume, to expose a greater surface area of contained metals to the leaching and to limit interfering reactions. This important pretreatment becomes more helpful for improving effectiveness when selective nonaggressive reactants are used to meet sustainability requirements, as shown by the preliminary results described here. 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 pretreatments were undergone by the sample, satisfactory NM recovery yields (Cu 70%, Ag 92%, Au 64%) are found applying an effective three phase leaching process where (i) a refluxing citric acid aqueous solution achieves base metal

leaching in 48 h; (ii) ammonia in oxidizing environment operates Cu and Ag leaching and separation in one pot in almost 96 h; and (iii) a triiodide aqueous solution dissolves gold in about 30 min, followed by a cementation or electrochemical deposition of the different NMs. This process provides a clean separation with limited byproduct formation using safe and recyclable reagents in mild conditions. Consequently, it is worth noting that the coarse nature of the sample does not seem to jeopardize the whole metal recovery process. A further effort in combining the pretreatment setup with the subsequent leaching processes would help in obtaining the optimal conditions to meet the effectiveness and sustainability required for practical application as targeted by green chemistry and engineering principles, and open the way to the scale-up phase on a pilot plant.

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Notes
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