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Abstract

As one of the most valuable components in waste electrical and electronic equipment (WEEE), the recovery of spent printed circuit boards (PCBs) is economically and strategically relevant. However, their composition drastically changes depending on location, year and the type of appliance in which they were used. For the development of new treatment processes, representative sampling of spent PCBs from large samples is necessary and their raw material compositions should be accurately determined. This study aimed at characterizing spent PCBs by implementing milling, sampling and leaching with an adequate reagent. Sampling was performed on 526 kg of spent PCBs, to obtain different samples milled at 750 µm in order to achieve metal accessibility. These samples were leached by aqua regia and metal contents in the leach solutions were determined. Metal analyses in 40 grams-samples of spent PCBs showed limited

composition variation for most metals towards the different samples. Furthermore, a good accordance was found with other studies reported in the literature.

Keywords sampling; characterization; printed circuit boards; e-waste.

1. Introduction

Many countries including the European Union (EU) are highly dependent on imports of raw materials that are crucial for a strong industrial base. The increasing global demand for minerals and metals and the price volatility of certain raw materials, as well as the market distortions imposed by some countries on several raw materials, have highlighted the importance of raw materials for the global economy (UNEP, 2013). Furthermore, the supply of raw materials is also threatened by the depletion of many primary deposits that are easily accessible and easy to process. Consequently, the recycling of secondary resources such as waste electronic and electrical equipment (WEEE) is a good opportunity to diversify raw material supply. In particular, metals contained in spent printed circuit boards (PCBs) are economically and strategically relevant and make them one of the most valuable components in WEEE (Goosey and Kellner, 2003).

Presently, pyrometallurgy is the most common technology implemented to recover metals from e-waste. In pyrometallurgical processes, spent PCBs are treated with ores in smelters to recover mainly copper and precious metals. This technology presents several disadvantages, such as metals losses in the slags (rare earth elements, tantalum), high energy consumption, toxic emissions, *etc.* (Cayumil et al., 2018; Cui and Zhang, 2008). Furthermore, only high-grade PCBs, containing high gold concentration (> 400 $mg.kg^{-1}$; Hagelüken, 2006), are processed in the pyrometallurgical route, as the addition of PCBs

46 in smelters represents at most 15% of the inlet flow of materials, the rest being ores
47 (Ghosh et al., 2015; Goosey and Kellner, 2003). Goosey and Kellner (2003) estimated
48 that, in the United Kingdom in 2003, only 15% of PCB scraps were subjected to any
49 forms of recycling, the rest being consigned to landfill.

50 Printed circuit boards composition is dependent on the location, year and the type of
51 appliance in which they were used. The average composition of PCBs is 40% of metals,
52 30% of ceramics and glasses and 30% of plastics (Kumar et al., 2018).

53 Many works are dedicated to the development of the different operations involved in
54 WEEE recycling (Akcil et al., 2015; Ghosh et al., 2015) such as dismantling, mechanical
55 treatments (crushing, grinding), physical separation (magnetic separation, electrostatic
56 separation, gravimetric separation), leaching and bioleaching, chemical separation and
57 extraction (liquid-liquid and liquid-solid extraction). In addition to these conventional
58 processes, original dedicated technologies are currently under development to address the
59 specificities of e-wastes. As an example, non-classical reagents can be used such as
60 supercritical CO_2 for the extraction of polymers (Calgaro et al., 2015) and molten salts
61 for the dissolution of glasses, oxides and the destruction of plastics without oxidizing the
62 most valuable metals (Flandinet et al., 2012). The use of ionic liquids have also been
63 investigated for the dissolution of epoxy resins (Zhu et al., 2012). Usually these unit
64 operations are combined in a common treatment flowsheet, which gives a wide diversity
65 of alternative processes that might be used for WEEE recycling. For instance, Mäkinen
66 developed recently a process relying on the combination of flotation and bioleaching
67 (Mäkinen et al., 2015).

68 The development of the complex above-mentioned operations involves the
69 establishment of material balances in order to assess and optimize the recovery of
70 valuable elements in PCBs. Consequently, it is necessary to know accurately the raw
71 material compositions and to be able to get reproducible sampling at the laboratory scale.
72 The Gy sampling theory was developed to ensure a good reproducibility and
73 representativeness of samples from primary resources at various scales (Gy, 1992). This
74 theory enables an estimate of the error generated by dividing samples into smaller
75 samples. Some other studies dealt with sampling of municipal waste, plastics,
76 metallurgical powders, or soils, with adjustments from Gy theory. Likewise, the
77 International Organization for Standardization or other organisms published methods for
78 sampling various materials, such as soils (ISO 23909:2008 from AFNOR, 2008), plastic
79 wastes (XP CEN/TS 16010 from AFNOR, 2013), metallurgical powders (ISO 3954:2008
80 from AFNOR, 2008), particulate materials (ISO 11648-2:2001 from AFNOR, 2001), *etc*.
81 These methods often also describe analytical methodologies to obtain reliable
82 characterization. However, there is no similar theory applied to e-waste sampling and
83 more especially PCBs sampling. Today, the implementation of reproducible and
84 representative sampling of e-waste remains a great challenge because of their huge
85 heterogeneity.

86 PCBs sampling relies also on the implementation of an efficient method to reduce
87 the particle size of PCBs in order to release metals from PCB matrix. Yamane et al.
88 (2011) reported that above 1 mm, metals were not completely accessible from polymers
89 and ceramics. In order to achieve an efficient metal release, Wang et al. recommended
90 using an impact or knife milling (Wang et al., 2005). However, several issues were

reported with shredding due to the presence of ductile metals (Ernst et al., 2003; Wienold et al., 2011; Yamane et al., 2011). Unfortunately, very few data are available from the recycling industry concerning the sampling procedure, including size reduction, material division and the methods implemented to evaluate PCBs composition of large samples.

Spent PCBs can be characterized by dry techniques and wet techniques. For the sake of illustration, some of the techniques used to prepare samples and analyze them are reported in Table 1. It could be of great interest to combine several methods to have a full characterization of the wastes (metal contents, elemental speciation, *etc.*) since these techniques are usually complementary. The combination can include various analytical methods such as elemental analyses after digestion with adequate reactive, X-Ray Fluorescence spectroscopy (XRF), Scanning Electron Microscopy with Energy-Dispersive X-ray spectroscopy (SEM-EDX) and Transmission Electron Microscopy (TEM). However, some of these techniques (particularly XRF analysis or microwave-assisted digestions) characterize only very small amounts of materials (below 1 g); this can lead to issues of representativeness and reproducibility, and therefore large errors of characterization. Due to high temperatures, techniques such as calcination and fusion are not compatible with the characterization of volatile elements. With an easy implementation and the possibility to treat large quantities of PCBs, aqua regia digestion is the most frequently used technique in the literature. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or inductively coupled plasma-mass spectrometry (ICP-MS), as well as atomic absorption spectroscopy (AAS), are widely used to analyze leachates of spent PCBs digestion.

The aims of the present work are (i) to establish and evaluate a sampling procedure from a large sample of spent PCBs in order to obtain reproducible sub-samples and (ii) to develop a methodology to determine the metal composition of the PCBs. The experimental protocol proposed, tested and assessed in this study was designed specifically to be applied to large amounts of PCBs that are further used for the development of dedicated metallurgical treatments, from laboratory to pilot scale. The objective was to produce subsamples of the same composition from a few grams to several kilograms, which then enables the calculation of mass balances at every step of the process and the assessment and the comparison of the efficiency of the metal recovery. The protocol developed in this study includes several milling steps, the division of the materials in subsamples and the determination of metal contents, as well as their partitioning in the different size fractions. This protocol was applied to 526 kg of spent PCBs and the accuracy of the analytical methods and the reproducibility of the subsamples was assessed. The developed methodology was evaluated according to the following requirements:

- Concerning the reproducibility, less than 10% of variation of metal concentrations between two samples was expected.
- Concerning their characterization, to obtain the closest metal concentration to the true value, the most complete digestion possible was required. 98% (in mass) of metal digested was considered satisfactory.

2. Materials and methods

2.1. Electronic scrap sample

135 A sample of 526 kg of medium-grade spent PCBs from the small waste electrical
136 and electronic equipment category (sWEEE) was collected and provided by the WEEE
137 sorting center "Envie 2E Midi-Pyrénées" (France). The grade of the sample, which was
138 medium (with 100 to 400 $mg.kg^{-1}$ of gold; Hagelüken, 2006), was estimated by the
139 sorting center from the origin of the PCBs (type of appliances), and not by elemental
140 analyses. These PCBs were collected from small appliances such as information
141 technology (IT) equipment, audio and video appliances, toys, personal care products,
142 culinary equipment, *etc*.

143 *2.2 Samples preparation*

144 Figure 1a shows the successive steps of milling and sampling procedure
145 implemented in the present study : (i) PCBs were shredded to reduce the particle size
146 below 30 mm with a shear shredder from Bohmier Maschinen GmbH; (ii) the particles
147 were afterward shredded to a size less than 10 mm with the same equipment; (iii) particle
148 size reduction was then carried on using a laboratory knife mill (Retsch SM-2000) with
149 bottom sieve mesh size of 750 µm. Intermediary bottom sieves with mesh sizes of 10
150 mm, 4 mm, 2 mm and 1 mm were used for this step. To reduce the particle size to smaller
151 diameter, the following apparatuses were tested on two 500 g-samples: laboratory knife
152 mill (Retsch SM-2000) with bottom sieve mesh size of 500 µm and disk mill (Bico Inc).
153 In each reduction steps, particles retained on the bottom sieve of the mill were added to
154 the ground sample in order to ensure a good representativeness.

155 After size reduction steps at 30 mm, 10 mm and 750 µm, the milled samples were
156 divided into smaller samples so that the final mass of the final samples was equal to
157 approximately 4 kg (initial mass of the batch = 526 kg). The details of these sample

158 divisions are given in Figure 1b. These operations were carried out with a rotary divider
159 for large samples (fraction 30 mm) and a riffle-divider for smaller ones (fractions 10 mm
160 and 750 µm) with openings of the riffle-divider larger than three times the particle size
161 (see supporting information).

162 For the sake of comparison of sampling procedures, the Umicore procedure is also
163 presented in Figure 1a. To our knowledge, this procedure is the only industrial
164 methodology published in the literature until now (Hagelüken, 2006). At each step of the
165 procedure, the size reduction and mass ratios obtained in this study were in the same
166 order of magnitude than those reached in the Umicore's procedure.

167 *2.3 Particle size distribution*

168 Particle size distributions were determined for three samples: (i) a sample reduced
169 with bottom sieve mesh size of 750 µm (step 3), (ii) a sample reduced with bottom sieve
170 mesh size of 500 µm (step 4) and (iii) a sample ground with disk mill (alternative step 4).
171 These distributions were obtained by wet sieving of 290 g samples at 1.25 mm, 1 mm,
172 800 µm, 400 µm, 200 µm, 100 µm and 63 µm. Each size fraction was dried at 40 °C
173 before weighting and performing any analyses.

174 *2.4 Analyses*

175 Considering the particles' size, analysis should be performed on 40 g-samples (see
176 Section 3.2). However, for safety reasons, aqua regia digestions were performed on 5 g-
177 samples. Consequently, initial 40 g-samples were divided into 8 sub-samples by
178 quartering method. 5 g-PCBs samples were leached by 56 mL of aqua regia (HNO_3:HCl
179 1:3) prepared by mixing 42 mL of 32%w HCl with 14 mL of 67-69%w HNO_3, or reverse

aqua regia (HNO_3:HCl 3:1) (14 mL of 32%w HCl+42 mL of 67-69%w HNO_3). Nitric acid (67-69%w, trace metal grade) and hydrochloric acid (32%w, certified for analysis) were provided by Fisher Chemical. The leaching reactors were heated to 200 °C during 2 hours by means of a Kjeldatherm-Gerhardt digestion system. After cooling, solid/liquid filtration was performed with cellulose nitrate membrane filters (Sartorius Stedim Biotech, pore diameter=0.45 µm) in order to separate the leaching solutions and the residues. The residues were rinsed with water and dried at 40 °C. Metal concentrations in the filtrate were determined after dilution in 0.5 $mol.L^{-1}$ HNO_3 prepared by dilution of concentrated nitric acid in milliQ water (resistivity= 18.2 MΩ.cm). A Varian SpectrAA-300 flame atomic absorption spectrometer (FAAS) was used to determine Fe, Cu, Zn, Pb, Co and Ni concentrations. An ICP-AES Horiba Jobin Yvon Ultima 2 or an ICP-MS Thermo Scientific X Series were also used to determine other metals concentrations : Ag, Al, Au, Cr, Ga, Ge, In, Mg, Mn, Mo, Pd, Sb, Sn, Ta, V and W.

After characterizing these 8 subsamples by the methodology above-mentioned, metal concentrations in 40 g-samples were calculated by using the following equation:

$$m_{40g}x_{40g} = \sum_{i=1}^{8} m_{i_{5g}}x_{i_{5g}} \quad [1]$$

Where m_{40g}, x_{40g}, m_{i5g} and x_{i5g} denote effective mass of the 40 g-sample, metal concentration in the 40 g-sample, effective mass of 5 g-subsample *i* and metal concentration in 5 g-sub-sample *i*, respectively.

The same methodology was used for reverse aqua regia digestion of one 40-g sample and for reverse aqua regia digestion of each size fraction.

Solid residues resulting from partial leaching by aqua regia were ground for 20 min at 710 rpm in a planetary mill containing ferro-chromium grinding bowls (Siebtechnik). After grinding, the solid residues were leached a second time by using two different methods: (i) 5 g of residues were leached by aqua regia in triplicate in the same conditions as the first digestion and (ii) 200 mg of residues were leached by a mixture of 1 mL hydrofluoric acid (Merck, 40%w for analysis), 1 mL hydrochloric acid (Fisher, 32%w certified for analysis) and 3 mL nitric acid (Fisher, 67-69%w, trace metal grade) in duplicate at 150 °C under 125 bars during 20 min and, afterward, at 260 °C under 125 bars during 2 hours. Leachates were analyzed by ICP-MS. Some samples of these residues were also examined by scanning electron microscopy (SEM HIROX-SH 3000 with integrated EDS Bruker Nano).

3. Results

3.1. Sampling

The initial sample of 526 kg was entirely reduced to 30 mm except 41 kg of large pieces, mostly corresponding to heat sinks and coils that were removed because it was not possible to shred them. The ground material was then divided by quartering in 4 samples of respectively 110 kg, 142 kg, 108 kg and 122 kg (see Figure 1b). The differences obtained between the samples masses might be explained by the formation of clusters of copper wires that led to changes of incoming flow rate of materials in the rotary divider. In this step, 3 kg of materials were lost (0.6% of the total mass). Only one of the four samples (122 kg) was afterward used for this study. In the step 2, this sample was entirely shredded to 10 mm and divided to obtain sub-samples of 4 kg. Unlike in step 1, the mass of the sub-samples obtained throughout the different quartering operations of

224 step 2 were similar and closed to targeted value. Clusters were not observed anymore,
225 since copper wires were cut during this step. Consequently, the material was better
226 distributed. During the step 3, 4 of these 4 kg-samples were milled by means of a
227 laboratory knife mill with bottom sieve mesh size of 750 µm. Some particles did not go
228 through the bottom sieve (7,9% in mass) but were gathered with the ground sample. Less
229 than 0.6% of the mass of the initial sample was lost when grinding was performed from
230 10 mm to 750 µm. This result is promising. For a sake of comparison, Wienold et al.
231 (2011) reported 0.05% (mass) of material losses during the grinding of 4 kg of PCBs
232 from 1.5 mm to 500 µm with an ultra-centrifugal mill cooled by a continuous flow of
233 liquid nitrogen. Finally, during step 4, some samples were afterward milled with a disk
234 mill or a laboratory knife mill with smaller bottom sieve mesh size (500 µm) in order to
235 further reduce the particle size. 20% of the mass of the sample ground with Retsch SM-
236 2000 with bottom sieve of 500 µm did not go through the sieve, while 2.0% of the
237 material was lost. Concerning the sample ground with the disk mill, the material loss was
238 less than the weighing scale precision (1 g).

239 Particle size distribution of the samples obtained after the step 3 and the step 4 is
240 given in Figure 2. The d_{80}, 80th percentile of the particle size distribution, was equal to
241 750 µm when using the laboratory knife mill with bottom sieve mesh size of 750 µm,
242 equal to 700 µm when using the same device with bottom sieve mesh size of 500 µm and
243 equal to 850 µm after the 4th milling with disk mill. The use of a bottom sieve mesh size
244 of 500 µm did not enable to reduce the larger particles' size under 700 µm. Even after 2
245 hours of milling, a large number of particles did not cross the 500 µm-sieve. As said
246 previously, particles that did not cross the bottom sieve were added to the ground sample

247 to preserve the representativeness of the subsample. Conversely, the disk mill had a
248 negative impact, since it was responsible for an increase of the d_{80} of the ground sample.
249 The samples used in the next sections of the present paper were those obtained at the end
250 of step 3, using the Retsch SM-2000 with bottom sieve mesh size of 750 µm.

251 *3.2. Analyses*

252 As explained above, the grinding methodology proposed in this study did not enable
253 to reduce the size of the spent PCBs particles under 500 µm. Such fine grinding is
254 probably not required to obtain complete accessibility of metals, but it decreased the
255 heterogeneity of composition, which allows reducing the mass of the sample that will be
256 used to perform the chemical analysis of the metal content. In our study, based on the
257 empirical formula [2] used in BRGM (French geological survey) for the characterization
258 of complex materials (unpublished data), 40 grams of samples were analyzed.

259 $$Sample\ mass\ for\ analysis = 0.06 \times d_{80}\ (\mu m) \qquad [2]$$

260 Table 2 shows the metal concentrations determined by ICP-AES, ICP-MS and
261 FAAS analyses in three samples of 40 g after aqua regia digestion. For Fe, Cu, Ni, Zn, Co
262 and Pb, leachates concentrations were measured with both FAAS and ICP-AES and it
263 gave similar results. These three samples were taken from two different samples of 4 kg
264 to determine the variability of metal contents, as given in Figure 1b. The sample n°3 was
265 only analyzed by FAAS.

266 Relative standard deviation (RSD), defined as the ratio of the standard deviation to
267 the mean value, was lower than 2% for Cu and Fe and comprised between 5% and 10%
268 for Zn, Pb, Ni and Co. When only a duplicate was analyzed, RSD were not calculated but

the relative difference between the two obtained values was evaluated. For Al, Ga and Ta, this relative difference was limited (0.9% for Ga, 6.8% for Al, 11.8% for Ta), while high discrepancies in metal concentrations between samples were obtained for Sn and Au (31.3% for Sn and 46.9% for Au).

Metal concentrations obtained after aqua regia digestion were compared with those obtained after digestion with reverse aqua regia, which is supposed to be more oxidative than aqua regia (Figure 3a). The same metal concentrations were obtained except for Ag whose concentration was 60 times lower than that obtained with aqua regia. Likewise, a factor of 15 between aqua regia and reverse aqua regia was observed for Pd. With these results, the use of aqua regia digestion was chosen for further studies.

There is a large amount of data about metal concentrations in spent PCBs in the literature. However, analytical and sampling procedures are often not described (UNEP, 2013). Results greatly depend of the type of WEEE and their origin. Despite this large variability, our data were compared with the literature to be sure that this work was coherent with other studies reported elsewhere. Figure 3b shows the comparison of metal concentrations in spent PCBs reported by the United nations environment programme (UNEP), the United nations university (UNU) and Bizzo et al. in 2013, 2008 and 2014 respectively (Bizzo et al., 2014; UNEP, 2013; UNU, 2008). The study from UNEP does not give information about the type of PCBs and the methodology used for the characterization. The PCBs used in the report published by UNU are from the same category as in the present study, i.e. small WEEE. The study from Bizzo et al. was performed on computers PCBs with aqua regia digestion. These results were also compared with those obtained in the present study (Figure 3b).

292 A generally good agreement was found between the PCBs composition analyzed in the
293 three studies and our present work. There were large amounts of Fe, Cu (>10% in mass)
294 and Al (6-8% in mass) that came from various parts of PCBs such as heat sinks, copper-
295 layer for conduction, coils, *etc*. Sn, Zn and Pb, which were mainly used for soldered joint,
296 represented approximately 1% of the mass of PCBs. A huge difference was observed for
297 Ta since Ta content was approximately 5000 times lower in our study than the value
298 reported in the literature.

299 *3.3. Analysis of solid residues*

300 After the digestion with aqua regia, 40% of solid residues attributed to non-metal
301 elements of PCBs remained in the reactor. In order to evaluate metal concentration in the
302 residues, they were ground to achieve the most efficient metal accessibility of leaching
303 reactive towards potentially remaining metals. Milling was efficient (particle size <100
304 μm) and residues' size reduction was more easily achieved than PCBs' size reduction. No
305 metal was detected through SEM-EDX analysis (see supporting information) which
306 revealed on the other hand the presence of Si, Cl, Ca in the residues; these elements are
307 derived from plastics, ceramics and glasses.

308 The residue remaining after the digestion of the sample n°2 was digested with aqua
309 regia after milling and the residue remaining after the digestion of the sample n°1 was
310 digested using a mixture of HF, HCl and HNO_3. During the second digestion with aqua
311 regia, only 10% of the mass of the residue was dissolved. On the contrary, the digestion
312 with hydrofluoric acid enabled to dissolve 100% (in mass) of the residue. Furthermore,
313 the metal concentrations were much lower in the leachate obtained after the second
314 digestion than after the first digestion. Table 3 gathers (i) the metal concentrations in the

spent PCBs calculated from the data obtained after the first digestion and after both digestions and (ii) the proportion of metal that was leached during the first digestion vs. the total mass, derived from the following equation:

$$\%\ weight\ of\ metal\ leached\ during\ the\ 1^{st}\ digestion = \frac{m_1}{m_1+m_2} \times 100 \qquad [3]$$

where m_1 denotes the mass of metal dissolved by the first digestion and m_2 the mass of metal, dissolved by the 2nd digestion.

The digestion of the residues showed that more than 90% (in mass) of all metals contained in spent PCBs were correctly dissolved by using aqua regia during the first digestion. The digestion was particularly efficient for Cu, Zn, Sn, Pb, Co and Pd, with less than 2% in mass of undissolved metals. In that case, the digestion with $HF/HCl/HNO_3$ enabled to dissolve small quantities of Cu (0.1% in mass), Zn (2.1% in mass), Sn (0.3% in mass), Pb (0.7% in mass), Co (1.1% in mass) and Pd (1.2% in mass). Samples were ground enough so that these metals were efficiently accessible at 750 µm and easily digested with aqua regia. The digestion with aqua regia was efficient for Ni, Ag, Au and Ga, since more than 93% (in mass) of the metal that was digested. Concerning Ta, the digestion with aqua regia was not appropriate at all, since only 0.5% of the mass was digested with aqua regia digestion (see section 3.2).

3.4. Chemical analysis of size fractions

Metals distribution is heterogeneous and initial sizes of the different elements that constitute PCBs can vary a lot from one PCB to another. In addition, when subjected to mechanical constraints, the different types of PCBs components show various behaviors. For example, the materials present in PCBs can exhibit different mechanical properties

that will cause plastic deformations in some cases, while others will rather break. It leads to heterogeneous grinding: some materials can be easily shredded, with homogeneous particle size reductions, while other materials would be only partially reduced. These phenomena may lead to differences of metal distribution in the sample, which may affect the digestion by aqua regia and the representativeness of the sampling protocol. It is therefore important to evaluate this phenomenon. Moreover, it might be interesting to identify a particular size fraction in which valuable metals are present in order to concentrate them for further extraction.

Consequently, chemical analyses of each size fraction with reverse aqua regia were performed. It is important to point out that Ag and Pd concentrations were underestimated by using this method of characterization of spent PCBs, as previously demonstrated (see section 3.2). Metal concentrations in the genuine sample, called "reconstituted sample", were calculated by using the following equation:

$$x_{sample} = \sum_{i=1}^{7} w_{fraction\,i}\, x_{fraction\,i} \qquad [4]$$

where x_{sample}, $w_{fraction\,i}$ and $x_{fraction\,i}$ denote the metal concentration in the genuine sample, the mass fraction of the size fraction *i* and the metal concentration in the size fraction *i*, respectively. Metal concentrations in the genuine sample, as well as in each size fraction, are given in supporting information.

To estimate the heterogeneity resulting from the size reduction, it was required to calculate the ratio of metal contents of a specific size fraction compared to others and compared to the whole sample content. For most metals (Al, Cu, Pb, Sn, Zn, Ni, Ga and

358 Ta), these ratios were not sufficiently high (<5) to have a noteworthy enrichment of a
359 fraction.

360 However, for precious metals (Ag, Au and Pd) and for Fe and Co, a particular size
361 fraction was enriched. The highest concentration of metals was found in the coarser
362 fraction for Ag and Fe (size>1000 µm), in fine particles (size<100 µm) for Au and in
363 middle size fractions (100 µm<size<400 µm) for Pd and Co.

364 The differences of metal contents between 40 g-sample digested by reverse aqua
365 regia and reconstituted sample were calculated and are given in supporting information.
366 For most metals, the relative difference in metal concentrations between both methods
367 was lower or of the same order of magnitude than the intrinsic variability between
368 replicates (See RSD in Table 2).

369 Finally, Figure 4 shows the metal distribution as a function of size fractions. Some
370 fractions were enriched in some metals as previously shown. In the fine fraction (size<63
371 µm), precious metals (Ag and Au) and Ga, which is a strategic metal, were particularly
372 concentrated since it contained 24% Ag, 27% Au and 23% Ga (in mass). Pd and Co were
373 mainly distributed in the fraction -400 µm +200 µm (47% for Pd and 28% for Co in
374 mass). Despite this specific enrichment, all metals were largely distributed in the
375 intermediate size fraction (400 µm < particle size < 800 µm) since this intermediate
376 fraction represented 47% of the total sample mass. In particular, more than 40% of the
377 total mass of Au and Ag were present in this size fraction. This high distribution in the
378 size fraction "-800 µm +400 µm" was also observed for Ga and Cu as it contained at least
379 38% and up to 59% in mass, respectively.

380 **4. Discussion**

381 This work aimed at developing a sampling and characterization procedure for the
382 production of reproducible and well-characterized samples. Concerning the sampling
383 procedure, knife mills and disk mills were tested to reduce the particle size below 750
384 µm. The use of the disk mill increased the particle size, probably because of the
385 formation of clusters observed during this step, due to heat dissipation. Given this result,
386 technologies based on crushing (such as disk mill) were less adapted to reduce PCBs
387 particles' size compared to technologies based on shredding. From the experiments with
388 the knife mill, we can deduce that particles larger than 500 µm were mainly ductile
389 metals and their size cannot be reduced by shredding. The obtained particle sizes may
390 permit a complete accessibility of metals since Yamane et al. (2011) determined that
391 metals are not sufficiently accessible if particles' size is above 1 mm. This accessibility is
392 closely related to the type of insertion and soldered joints of the components in the board.
393 It must be noticed that the samples obtained after the 3rd milling step contain 17% (in
394 mass) of fine particles (size<63 µm). They can be easily lost and potentially hazardous:
395 Zhang and Forssberg (1999) revealed that the fine fraction may be toxic since they
396 contain high Br concentration.

397 Concerning the characterization, digestion with aqua regia was first compared to
398 digestion with reversed aqua regia. High consistency was observed between results
399 obtained by both methods, except for Ag and Pd. More studies would be required to fully
400 understand the associated mechanisms.

401 From our study, metals were classified in three different categories: the ones that met
402 our goals (less than 10% of variation between replicates' metal concentrations and more

than 98% of the metal digested), the ones that partially met them or the ones for which our procedure did not meet the needs.

4.1. Metals for which goals were met

For Cu, Fe, Al, Zn, Pb, and Co, the sampling and characterization procedures were relevant and enabled to obtain reproducible samples: for these metals, RSD and relative differences were lower than 10% for 40-g samples (see Table 2). Moreover, the residues digestion enabled to conclude to an efficient digestion of PCBs samples with aqua regia, since no more than 0.1% to 2% (in mass) of metals remained in the solid residues after digestion.

4.2. Metals for which goals were partially met

For some other metals, the sampling and characterization procedure did not enable to obtain high reproducibility and/or high digestion of metals in the PCBs samples. Concerning reproducibility, despite the low number of replicates, two phenomena could explain the large variation of RSD values: the digestion with aqua regia may depend on metal speciation ; metal is not well-distributed between the different replicates. Concerning digestion, different hypotheses could explain that a part of these metals was not digested during the first digestion : partial accessibility at 750 µm, too short digestion time or metal speciation. The lack of replicates and variability of samples did not enable to confirm or deny these hypotheses.

However, the accuracy obtained with our procedure could be considered satisfactory depending of the aim of the study.

Regarding Ni and Ga, the variation in the content of the different samples was limited (7.2% RSD and 0.9% of relative difference respectively) which enabled to conclude to a high reproducibility. With 94.5% (in mass) of Ni and 93.0% (in mass) of Ga that were digested by aqua regia, the determination of the samples' concentration was under-evaluated but this could be considered acceptable.

Conversely, Pd was highly digested with aqua regia but its reproducibility met only partially our requirement: the relative difference between a duplicate reached 17%.

Finally, concerning Ag, neither reproducibility, nor high digestion were obtained. Part of Ag content was still in the residues after aqua regia digestion (92.6% in mass of Ag digested) and the relative difference between a duplicate reached 19.3%. The precipitation of silver chloride may explain these results (Petter et al., 2014). The use of nitric acid could improve the dissolution of silver and thus its characterization.

For these metals, metal concentration were under-estimated but this could be acceptable depending on the precision needed. The use of hydrofluoric acid did not seem required. It slightly improved the accuracy of metal analysis but was much more complicated to use due to its toxicity compared to aqua regia. Aqua regia is a good compromise between the simplicity of implementation and the accuracy.

4.3. Metals for which goals were not met

For Au, the sampling could not be considered satisfactory, since the relative difference in Au concentration in a duplicate reached 46.9%. This variation could be attributed to the lack of accessibility of fine Au layers in larger particles. 4.8% of the total mass of Au was still present in the residues after the first aqua regia digestion.

For Sn, the sampling and characterization procedure could not be considered satisfactory since the relative difference between the concentrations of a duplicate was 31.3%. The methodology recommended in the standard for the determination of the content in Sn is performed with hydrobromic acid, as Sn is often contained in alloys with Pb and Cd (AFNOR, 2014). Differences in the efficiency of the aqua regia digestion according to the speciation of Sn in the initial PCB could perhaps explain the high relative difference obtained. Moreover, it has been demonstrated that tin slowly precipitates as metastannic acid H_2SnO_3, which could affect its characterization (Mecucci and Scott, 2002).

Finally, aqua regia digestion was absolutely not suitable for the determination of the concentration in Ta: 99.5% (in mass) of the Ta was present in the residues after digestion. The use of fluorhydric acid was needed for this metal. It was likely that Ta comes from the capacitors and is present as metal or oxide (Ta_2O_5), which exhibits low solubility in aqua regia. As an example, Theron et al. (2011) reported that only 3.9% Ta_2O_5 and Ta were dissolved in aqua regia, even under microwave.

4.4. Overall interest of the developed methodology

Table 4 summarizes, for numerous metals, the overall interest of our procedures for the determination of the metal contents of PCBs samples, taking into account the variation of concentrations between different samples and the efficiency of digestion with aqua regia. These methods seemed fully suitable for Cu, Fe, Al, Zn, Pb and Co. They were slightly less suitable for Ni, Ag, Ga and Pd, but could nevertheless be used depending of the aim of the study. Concerning Au and Sn, the relevance of our

procedures was not clearly demonstrated. For Ta, characterization method was undoubtedly not adapted.

After determining the interest of our methodology, each size fraction was analyzed to determine metal distribution. Some enrichments were reported for Ag, Au, Pd, Fe and Co. Several hypotheses can explain this phenomenon: (i) the particle size reduction was heterogeneous for these metals; (ii) they were associated with other elements for which grinding was heterogeneous; (iii) they were included in items of different sizes on PCBs and this impacted the final content of the size fractions of the ground sample. However, the enrichments observed were not large enough to be able to benefit from them. Therefore, the use of sieving to recover enriched fractions would result in the loss of a large part of the metal in other fractions that would not be kept. In addition, the distribution was not homogeneous enough to use only the fine fraction for the development of metallurgical processes, as it is often performed in some studies (Ogunniyi et al., 2009) because the samples would no longer be representative of the initial sample.

5. Conclusion

This study was devoted to the development of a procedure to produce small samples from large amounts of spent PCBs (more than 500 kg) and to determine their metal contents. The objective was to provide a rigorous sampling and characterization procedure to obtain reproducible and well-characterized subsamples of spent printed circuit boards. These materials are complex and heterogeneous, and even if numerous studies have been published about the development of metallurgical processes to recover

491 the metals they contain, very few data about such procedures are currently available in
492 the literature.

493 Our strategy to sample and characterize large samples of spent PCBs combined two
494 main procedures: (i) first, a methodology to reduce the particle size, which enabled to
495 release the elements that constitute the PCBs and to divide the initial samples in
496 homogeneous and reproducible subsamples ; (ii) second, the characterization of the
497 subsamples (40 g). The first procedure relied on the use of a shredder to reduce the
498 particle size under 30 mm and 10 mm, and then on a further milling step with a
499 laboratory knife mill to reach 750 µm. The characterization procedure involved first the
500 digestion of the sub-samples with aqua regia, and then the analysis of leachates with ICP-
501 AES, ICP-MS and FAAS. This approach was completed by additional steps to assess the
502 suitability of the methodology: grinding with other laboratory tools, characterization of
503 the solid residues obtained after aqua regia and sieving and characterization of the size
504 fractions.

505 Regarding the sampling procedure, the use of large shredders followed by a knife
506 milling enabled to reduce particle size to less than 1 mm, threshold below which metals
507 are usually considered to be liberated from polymers, ceramics and glasses, or at least
508 accessible. Material losses were negligible and the measured particle size distribution
509 showed that the d_{80} reached 750 µm, which demonstrated that the shredding methodology
510 was efficient. Additional milling steps did not enable to reduce further the particle size,
511 mainly because of the presence of ductile metals.

512 The digestion of the subsamples with aqua regia enabled the dissolution of more
513 than 98% (in mass) of most metals except for Ta which was only partially dissolved by

aqua regia (95% of the Ta initially present in the sample remained in the solid residue after digestion). This led to substantial underestimation of its content and demonstrated that the methodology developed in this study was not adapted to the determination of Ta concentration in PCBs. Some issues were also encountered with Ni, Ag, Au and Ga that were not completely dissolved during aqua regia digestion (4 to 7% remained in the solid residues), which led to slight underestimations of their contents.

The combination of the sampling and digestion methodologies was suitable for Cu, Fe, Al, Zn, Pb and Co. For Ni, Ag, Ga and Pd, the methodology was less accurate but remained an efficient tool when it is used to estimate the efficiency of metallurgical processes developed to recover these metals in waste PCBs (Hubau et al., 2018). Other analytical methodologies might be established to complete this characterization in the case of a need of accurate determination of metal content (as XRD; Clearfield et al., 2008). For Au and Sn, large variations of their concentration were observed between replicates, while for Ta, the characterization methodology was not adequate.

Finally, the evaluation of the metal composition of each size fraction enabled to conclude that the enrichments observed were not large enough to be able to benefit from them with simple sieving and that the distribution was not homogeneous enough to use only the fine fraction for further studies.

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TABLES

Table 1: Usual methods for the characterization of spent PCBs.

Methods of sample preparation	Analytical methods	Advantages	Drawbacks	Study	Studied element
Dry techniques					
Calcination	X-ray fluorescence (XRF)	Destruction of plastics, which can interfere during analysis	Do not fit with volatile elements (Hg, As, Pb, Sn, Zn…)	Birloaga et al., 2013	Cu, Al, Fe, Sn, Ni, Zn, Pb, Au, Ag
No preparation	XRF	- 10-20% more Cu compared to wet characterization - Easily performed	- Not precise - Need for calibration with particle of similar size and composition, but no existing reference materials	Ernst et al., 2003 Wienold et al., 2011 Morf et al., 2007 Martin et al., 2010 Sun et al, 2015	Ag, Br, Cr, Cu, Fe, Ni, Pb, Pd, Sb Pb, Cd, Hg Al, Sb, Pb, Cd, Cr, Fe,Cu, Ni, Hg, Zn, Sn, Cl, P Cd, Cr, Pb Cu, Sn, Fe, Al, Pb, Zn, Ni, Nd, Ag, SiO_2
Wet techniques					
Aqua regia	Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP AES)	- Large quantities - Less milling - Easily performed - Repeatable - Reproducible	- Digestion not total (40-50% residues) - Not compatible with Ta, Sn - Doubt for Cu	Ernst et al., 2003 Wienold et al., 2011 Ogunniyi et al., 2009	Ag, Au, Be, Cd, Cr, Cu, Ni, Pb, Pd, Sb Pb, Cd, Hg 44 elements
Micro-wave (MW) and aqua regia	ICP-AES	Higher dissolution of Cr and Sb than without MW	- Digestion not total (10% residues) - sample mass <1g	Wienold et al., 2011	Pb, Cd, Hg
Aqua regia followed by calcination and fusion $LiBO_2$	Inductively Coupled Plasma Mass Spectro-metry (ICP-MS)	Digestion almost total (<10% residues)	- Time consuming - Difficult to implement	Holgersson et al., 2017	38 elements
Calcination followed by acid leaching (aqua regia + HF) under micro-wave	Atomic Absorption Spectroscopy (AAS)	Destruction of plastics, which can interfere during analysis	Do not fit with volatile elements (Hg, As, Pb, Sn, Zn…)	Birloaga et al., 2013	Cu, Al, Fe, Sn, Ni, Zn, Pb, Au, Ag
Fusion with sodium peroxide followed by HCl leaching	ICP-AES and ICP-MS	Digestion total	Difficult to implement	Ogunniyi et al., 2009	44 elements
Micro-wave (MW) and HNO_3/HBF_4 $/H_2O_2/H_2O$	ICP-AES	Digestion almost total (2,5% residues)	- sample mass <1g - difficult to implement	Ernst et al., 2003	Ag, Au, Be, Cd, Cr, Cu, Ni, Pb, Pd, Sb
Micro-wave (MW) and HNO_3/HCl $/HF/H_2O_2$	ICP-AES	Digestion almost total	- sample mass <1g - difficult to implement	Xiang et al., 2010	Cu, Pb, Al, Sn, Zn, Fe, Ni, Mg, Sb, Ag, Au, Mn, Co, Pd

641 **Table 2: Metal contents in three samples (mass=40 g). Samples were leached by**

642 **aqua regia at 200 °C at a liquid/solid ratio of 11 mL.g^{-1} (N.A.= not analyzed).**

	Concentrations in %w							**Concentrations in mg.kg^{-1}**					
	Cu	**Fe**	**Al**	**Zn**	**Sn**	**Pb**	**Ni**	**Co**	**Ag**	**Au**	**Pd**	**Ga**	**Ta**
Sample N°1	14.60%	12.20%	6.240%	1.81%	1.89%	1.23%	0.32%	334	198	42.2	22.9	10.6	0.034
Sample N°2	14.32%	12.34%	5.841%	1.51%	1.44%	1.08%	0.32%	374	166	62.0	26.8	10.7	0.038
Sample N°3	14.82%	12.15%	N.A.	1.68%	N.A.	1.21%	0.37%	366	N.A.	N.A.	N.A.	N.A.	N.A.
Average	14.58%	12.23%	6.040%	1.67%	1.67%	1.17%	0.34%	358	182	52.1	24.9	11	0.036
RSD	1.7%	0.8%	-	8.9%	-	7.2%	7.2%	5.9%	-	-	-	-	-
Relative difference	-	-	6.8%	-	31.3%	-	-	-	19.3%	46.9%	17.0%	0.9%	11.8%

643

644 **Table 3: Metal concentrations of the sample n°1 and n°2 after a first digestion with**

645 **aqua regia or after two digestion and ratio (in mass) of metals leached during the 1st**

646 **digestion. Concentrations are given in %w and mg.kg^{-1}.**

		Sample n°1			Sample n°2		
Digestion n°1	**Method**	Aqua regia			Aqua regia		
	% w/w residues	40%			47.5%		
Digestion n°2 on the residues of digestion 1	**Method**	HF/HCl/HNO_3			Aqua regia		
	% w/w residues	0%			90%		
Metal	**Unit**	**Content measured with 1st digestion**	**Content after 2 digestions**	**% recovered from 1st digestion**	**Content measured with 1st digestion**	**Content after 2 digestions**	**% recovered from 1st digestion**
Cu	%w	14.60%	14.61%	99.9%	14.32%	14.34%	99.9%
Fe	%w	-	-	-	12.34%	12.52%	98.5%
Al	%w	-	-	-	5.84%	5.96%	98.0%
Zn	%w	1.81%	1.85%	97.9%	1.52%	1.53%	98.5%
Sn	%w	1.89%	1.90%	99.7%	1.44%	1.45%	99.3%
Pb	%w	1.23%	1.24%	99.3%	1.08%	1.09%	98.8%
Ni	%w	0.32%	0.34%	94.5%	0.32%	0.33%	97.3%
Co	mg.kg^{-1}	334	338	98.9%	374	376	99.5%
Ag	mg.kg^{-1}	198	209	94.6%	166	179	92.6%
Au	mg.kg^{-1}	42.2	44.4	95.2%	62.0	65.9	94.1%
Pd	mg.kg^{-1}	22.9	23.2	98.8%	26.8	27.3	98.4%
Ga	mg.kg^{-1}	10.6	11.4	93.0%	10.7	11.5	93.1%
Ta	mg.kg^{-1}	0.034	7.5	0.5%	0.038	0.045	83.6%

647

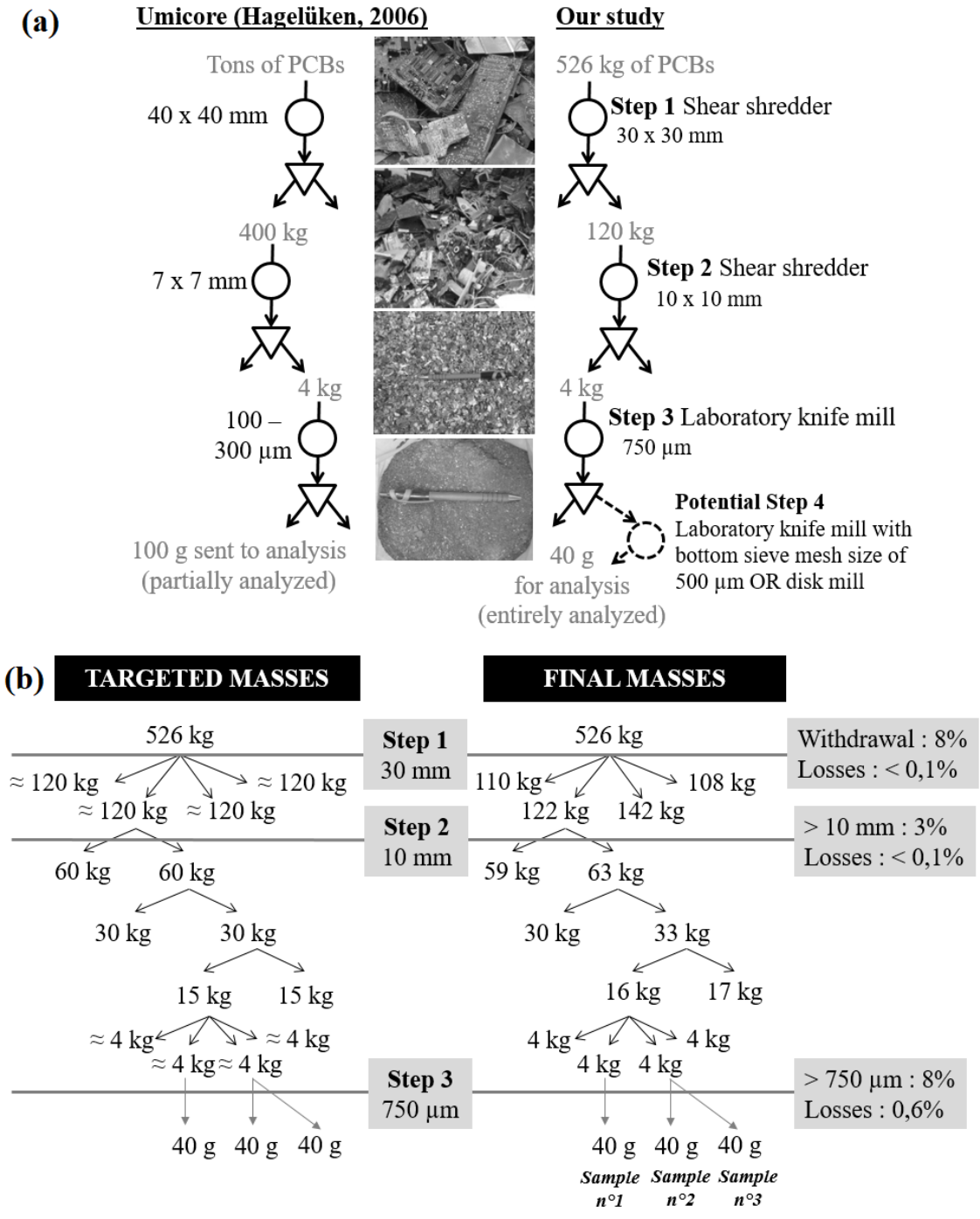
648

649 **Table 4: Overall interest of the methodologies developed for the sampling and**
650 **characterization of PCBs samples, for different metals. The "+" refers to a**
651 **methodology fully adapted for the metal. The "/" refers to a procedure not**
652 **completely suitable which can be used according to the aim of the study and the**
653 **need for accuracy. The "-" refers to a method that is not adjusted for the metal.**
654 **"n.d." refers to "not determined".**

	Cu	**Fe**	**Al**	**Zn**	**Pb**	**Sn**	**Ni**	**Co**	**Ag**	**Au**	**Ga**	**Pd**	**Ta**
Reproducibility of 40 g-samples (RSD <10%)	+	+	+	+	+	-	+	+	/	-	+	/	/
Aqua regia digestion (refers to residues metal contents)	+	n.d.	n.d.	+	+	+	/	+	/	/	/	+	-

655

656 **FIGURES**

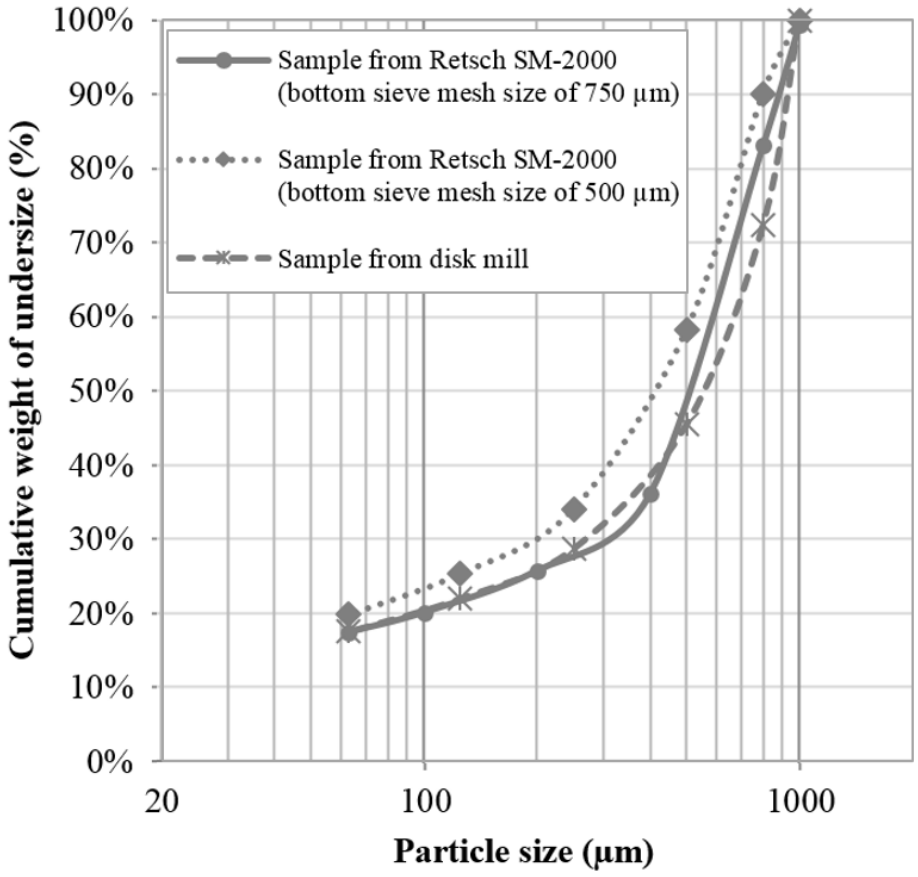


657

658 **Figure 1: Comparison between the grinding procedure used in this paper and by**

659 **Umicore at industrial scale (Hagelüken, 2006) (a) and sampling procedure to**

660 **produce 40 g-replicates from several 4 kg-samples (b).**



661

662 **Figure 2: Particle size distributions of three samples of 290 g milled with a disk mill**

663 **and a laboratory knife Retsch SM-2000 with bottom sieve mesh size of 500 µm and**

664 **750 µm.**

665

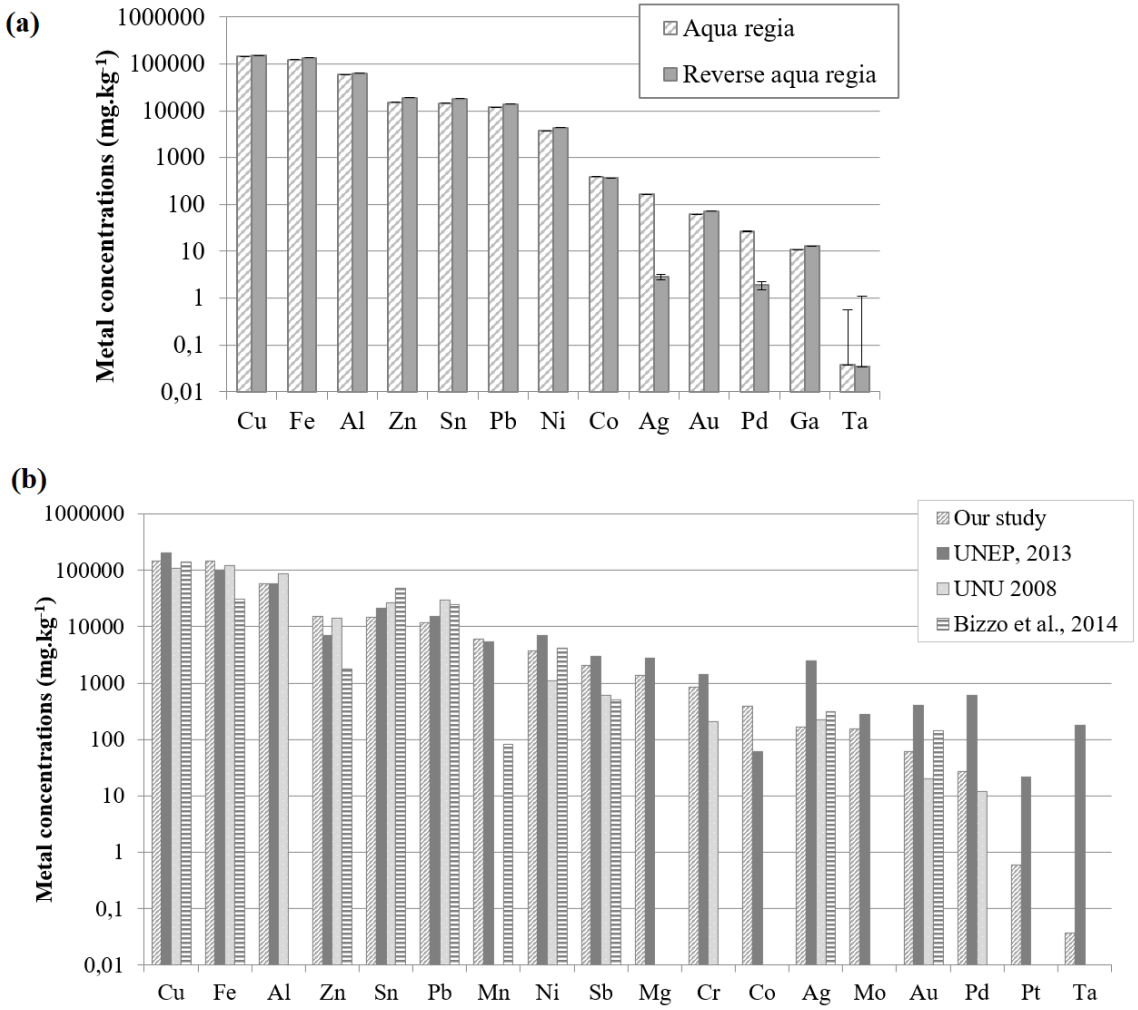
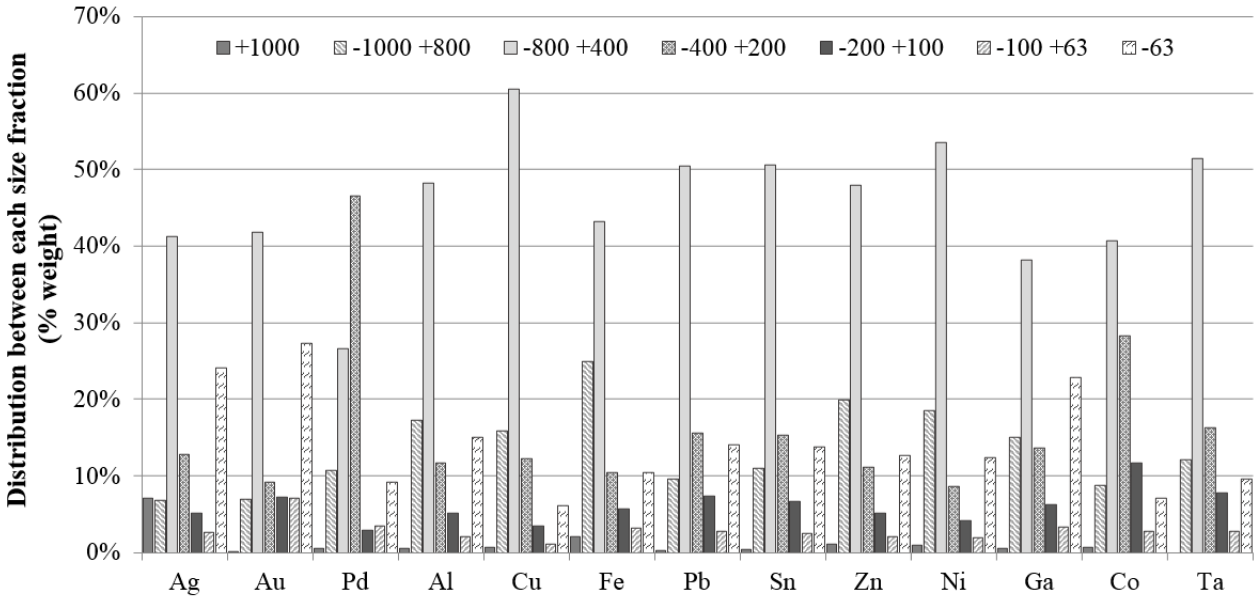


Figure 3: (a) Metal concentrations after leaching 40 g-samples of PCBs by aqua regia or reverse aqua regia (temperature=200 °C, liquid/solid ratio= 11 mL.g^{-1}, analyzed with FAAS for Cu, Fe, Zn, Pb, Ni and Co and with ICP-AES and ICP-MS for others); (b) Comparison of metal concentrations in spent PCBs from the present work, UNEP (UNEP, 2013), UNU (UNU, 2008) and Bizzo (Bizzo et al., 2014).



673

674 **Figure 4: Distribution of metal elements in the different size fractions**