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## **Recycling-oriented methodology to sample and characterize the metal composition of waste Printed Circuit Boards**

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

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

## 26 **1. Introduction**

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

39 Presently, pyrometallurgy is the most common technology implemented to recover  
40 metals from e-waste. In pyrometallurgical processes, spent PCBs are treated with ores in  
41 smelters to recover mainly copper and precious metals. This technology presents several  
42 disadvantages, such as metals losses in the slags (rare earth elements, tantalum), high  
43 energy consumption, toxic emissions, *etc.* (Cayumil et al., 2018; Cui and Zhang, 2008).  
44 Furthermore, only high-grade PCBs, containing high gold concentration ( $> 400 \text{ mg.kg}^{-1}$ ;  
45 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<sub>2</sub> 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

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

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

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

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

## 133 **2. Materials and methods**

### 134 *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<sup>-1</sup> 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  $\mu\text{m}$ ) 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  $\mu\text{m}$  (step 3), (ii) a sample reduced with bottom sieve  
170 mesh size of 500  $\mu\text{m}$  (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  $\mu\text{m}$ , 400  $\mu\text{m}$ , 200  $\mu\text{m}$ , 100  $\mu\text{m}$  and 63  $\mu\text{m}$ . 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 ( $\text{HNO}_3\text{:HCl}$   
179 1:3) prepared by mixing 42 mL of 32%w HCl with 14 mL of 67-69%w  $\text{HNO}_3$ , or reverse

180 aqua regia (HNO<sub>3</sub>:HCl 3:1) (14 mL of 32%w HCl+42 mL of 67-69%w HNO<sub>3</sub>). Nitric  
181 acid (67-69%w, trace metal grade) and hydrochloric acid (32%w, certified for analysis)  
182 were provided by Fisher Chemical. The leaching reactors were heated to 200 °C during 2  
183 hours by means of a Kjeldatherm-Gerhardt digestion system. After cooling, solid/liquid  
184 filtration was performed with cellulose nitrate membrane filters (Sartorius Stedim  
185 Biotech, pore diameter=0.45 µm) in order to separate the leaching solutions and the  
186 residues. The residues were rinsed with water and dried at 40 °C. Metal concentrations in  
187 the filtrate were determined after dilution in 0.5 mol.L<sup>-1</sup> HNO<sub>3</sub> prepared by dilution of  
188 concentrated nitric acid in milliQ water (resistivity= 18.2 MΩ.cm). A Varian SpectrAA-  
189 300 flame atomic absorption spectrometer (FAAS) was used to determine Fe, Cu, Zn, Pb,  
190 Co and Ni concentrations. An ICP-AES Horiba Jobin Yvon Ultima 2 or an ICP-MS  
191 Thermo Scientific X Series were also used to determine other metals concentrations : Ag,  
192 Al, Au, Cr, Ga, Ge, In, Mg, Mn, Mo, Pd, Sb, Sn, Ta, V and W.

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

195 
$$m_{40g}x_{40g} = \sum_{i=1}^8 m_{i5g}x_{i5g} \quad [1]$$

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

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

201 Solid residues resulting from partial leaching by aqua regia were ground for 20 min  
202 at 710 rpm in a planetary mill containing ferro-chromium grinding bowls (Siebtechnik).  
203 After grinding, the solid residues were leached a second time by using two different  
204 methods: (i) 5 g of residues were leached by aqua regia in triplicate in the same  
205 conditions as the first digestion and (ii) 200 mg of residues were leached by a mixture of  
206 1 mL hydrofluoric acid (Merck, 40%w for analysis), 1 mL hydrochloric acid (Fisher,  
207 32%w certified for analysis) and 3 mL nitric acid (Fisher, 67-69%w, trace metal grade) in  
208 duplicate at 150 °C under 125 bars during 20 min and, afterward, at 260 °C under 125  
209 bars during 2 hours. Leachates were analyzed by ICP-MS. Some samples of these  
210 residues were also examined by scanning electron microscopy (SEM HIROX-SH 3000  
211 with integrated EDS Bruker Nano).

### 212 **3. Results**

#### 213 *3.1. Sampling*

214 The initial sample of 526 kg was entirely reduced to 30 mm except 41 kg of large  
215 pieces, mostly corresponding to heat sinks and coils that were removed because it was  
216 not possible to shred them. The ground material was then divided by quartering in 4  
217 samples of respectively 110 kg, 142 kg, 108 kg and 122 kg (see Figure 1b). The  
218 differences obtained between the samples masses might be explained by the formation of  
219 clusters of copper wires that led to changes of incoming flow rate of materials in the  
220 rotary divider. In this step, 3 kg of materials were lost (0.6% of the total mass). Only one  
221 of the four samples (122 kg) was afterward used for this study. In the step 2, this sample  
222 was entirely shredded to 10 mm and divided to obtain sub-samples of 4 kg. Unlike in step  
223 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  $\mu\text{m}$ . 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  $\mu\text{m}$ . 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  $\mu\text{m}$  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  $\mu\text{m}$ ) 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  $\mu\text{m}$  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  $d_{80}$ , 80<sup>th</sup> percentile of the particle size distribution, was equal to  
241 750  $\mu\text{m}$  when using the laboratory knife mill with bottom sieve mesh size of 750  $\mu\text{m}$ ,  
242 equal to 700  $\mu\text{m}$  when using the same device with bottom sieve mesh size of 500  $\mu\text{m}$  and  
243 equal to 850  $\mu\text{m}$  after the 4<sup>th</sup> milling with disk mill. The use of a bottom sieve mesh size  
244 of 500  $\mu\text{m}$  did not enable to reduce the larger particles' size under 700  $\mu\text{m}$ . Even after 2  
245 hours of milling, a large number of particles did not cross the 500  $\mu\text{m}$ -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  $\mu\text{m}$ .

### 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  $\mu\text{m}$ . 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.

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

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

269 the relative difference between the two obtained values was evaluated. For Al, Ga and  
270 Ta, this relative difference was limited (0.9% for Ga, 6.8% for Al, 11.8% for Ta), while  
271 high discrepancies in metal concentrations between samples were obtained for Sn and Au  
272 (31.3% for Sn and 46.9% for Au).

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

279 There is a large amount of data about metal concentrations in spent PCBs in the  
280 literature. However, analytical and sampling procedures are often not described (UNEP,  
281 2013). Results greatly depend of the type of WEEE and their origin. Despite this large  
282 variability, our data were compared with the literature to be sure that this work was  
283 coherent with other studies reported elsewhere. Figure 3b shows the comparison of metal  
284 concentrations in spent PCBs reported by the United nations environment programme  
285 (UNEP), the United nations university (UNU) and Bizzo et al. in 2013, 2008 and 2014  
286 respectively (Bizzo et al., 2014; UNEP, 2013; UNU, 2008). The study from UNEP does  
287 not give information about the type of PCBs and the methodology used for the  
288 characterization. The PCBs used in the report published by UNU are from the same  
289 category as in the present study, i.e. small WEEE. The study from Bizzo et al. was  
290 performed on computers PCBs with aqua regia digestion. These results were also  
291 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  $\mu\text{m}$ ) 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<sub>3</sub>. 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

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

$$318 \quad \% \text{ weight of metal leached during the } 1^{\text{st}} \text{ digestion} = \frac{m_1}{m_1+m_2} \times 100 \quad [3]$$

319 where  $m_1$  denotes the mass of metal dissolved by the first digestion and  $m_2$  the mass of  
320 metal, dissolved by the 2<sup>nd</sup> digestion.

321 The digestion of the residues showed that more than 90% (in mass) of all metals  
322 contained in spent PCBs were correctly dissolved by using aqua regia during the first  
323 digestion. The digestion was particularly efficient for Cu, Zn, Sn, Pb, Co and Pd, with  
324 less than 2% in mass of undissolved metals. In that case, the digestion with  
325 HF/HCl/HNO<sub>3</sub> enabled to dissolve small quantities of Cu (0.1% in mass), Zn (2.1% in  
326 mass), Sn (0.3% in mass), Pb (0.7% in mass), Co (1.1% in mass) and Pd (1.2% in mass).  
327 Samples were ground enough so that these metals were efficiently accessible at 750 μm  
328 and easily digested with aqua regia. The digestion with aqua regia was efficient for Ni,  
329 Ag, Au and Ga, since more than 93% (in mass) of the metal that was digested.  
330 Concerning Ta, the digestion with aqua regia was not appropriate at all, since only 0.5%  
331 of the mass was digested with aqua regia digestion (see section 3.2).

#### 332 *3.4. Chemical analysis of size fractions*

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

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

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

$$350 \quad x_{sample} = \sum_{i=1}^7 w_{fraction i} x_{fraction i} \quad [4]$$

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

355 To estimate the heterogeneity resulting from the size reduction, it was required to  
356 calculate the ratio of metal contents of a specific size fraction compared to others and  
357 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 $>1000\ \mu\text{m}$ ), in fine particles (size $<100\ \mu\text{m}$ ) for Au and in  
363 middle size fractions ( $100\ \mu\text{m}<\text{size}<400\ \mu\text{m}$ ) 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  $\mu\text{m}$ ), 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  $-400\ \mu\text{m} +200\ \mu\text{m}$  (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 ( $400\ \mu\text{m} < \text{particle size} < 800\ \mu\text{m}$ ) 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 “ $-800\ \mu\text{m} +400\ \mu\text{m}$ ” 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  $\mu\text{m}$ . 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  $\mu\text{m}$  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 3<sup>rd</sup> milling step contain 17% (in  
394 mass) of fine particles (size < 63  $\mu\text{m}$ ). 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

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

#### 405 *4.1. Metals for which goals were met*

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

#### 412 *4.2. Metals for which goals were partially met*

413 For some other metals, the sampling and characterization procedure did not enable to  
414 obtain high reproducibility and/or high digestion of metals in the PCBs samples.

415 Concerning reproducibility, despite the low number of replicates, two phenomena could  
416 explain the large variation of RSD values: the digestion with aqua regia may depend on  
417 metal speciation ; metal is not well-distributed between the different replicates.

418 Concerning digestion, different hypotheses could explain that a part of these metals was  
419 not digested during the first digestion : partial accessibility at 750  $\mu\text{m}$ , too short digestion  
420 time or metal speciation. The lack of replicates and variability of samples did not enable  
421 to confirm or deny these hypotheses.

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

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

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

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

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

#### 441           4.3. *Metals for which goals were not met*

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

446 For Sn, the sampling and characterization procedure could not be considered  
447 satisfactory since the relative difference between the concentrations of a duplicate was  
448 31.3%. The methodology recommended in the standard for the determination of the  
449 content in Sn is performed with hydrobromic acid, as Sn is often contained in alloys with  
450 Pb and Cd (AFNOR, 2014). Differences in the efficiency of the aqua regia digestion  
451 according to the speciation of Sn in the initial PCB could perhaps explain the high  
452 relative difference obtained. Moreover, it has been demonstrated that tin slowly  
453 precipitates as metastannic acid  $H_2SnO_3$ , which could affect its characterization (Mecucci  
454 and Scott, 2002).

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

461

#### 462 *4.4. Overall interest of the developed methodology*

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

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

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

## 484 **5. Conclusion**

485 This study was devoted to the development of a procedure to produce small samples  
486 from large amounts of spent PCBs (more than 500 kg) and to determine their metal  
487 contents. The objective was to provide a rigorous sampling and characterization  
488 procedure to obtain reproducible and well-characterized subsamples of spent printed  
489 circuit boards. These materials are complex and heterogeneous, and even if numerous  
490 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  $\mu\text{m}$ . 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  $\mu\text{m}$ , 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

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

520 The combination of the sampling and digestion methodologies was suitable for Cu,  
521 Fe, Al, Zn, Pb and Co. For Ni, Ag, Ga and Pd, the methodology was less accurate but  
522 remained an efficient tool when it is used to estimate the efficiency of metallurgical  
523 processes developed to recover these metals in waste PCBs (Hubau et al., 2018). Other  
524 analytical methodologies might be established to complete this characterization in the  
525 case of a need of accurate determination of metal content (as XRD; Clearfield et al.,  
526 2008). For Au and Sn, large variations of their concentration were observed between  
527 replicates, while for Ta, the characterization methodology was not adequate.

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

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

Methods of sample preparation	Analytical methods	Advantages	Drawbacks	Study	Studied element
<b>Dry techniques</b>					
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	Ag, Br, Cr, Cu, Fe, Ni, Pb, Pd, Sb
				Wienold et al., 2011	Pb, Cd, Hg
				Morf et al., 2007	Al, Sb, Pb, Cd, Cr, Fe, Cu, Ni, Hg, Zn, Sn, Cl, P
				Martin et al., 2010	Cd, Cr, Pb
Sun et al., 2015	Cu, Sn, Fe, Al, Pb, Zn, Ni, Nd, Ag, SiO <sub>2</sub>				
<b>Wet techniques</b>					
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	Ag, Au, Be, Cd, Cr, Cu, Ni, Pb, Pd, Sb
				Wienold et al., 2011	Pb, Cd, Hg
				Ogunniyi et al., 2009	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 <sub>2</sub>	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	Digestion almost total (<10% residues)	- Time consuming - Difficult to implement	Holgerson 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 <sub>3</sub> /HBF <sub>4</sub> /H <sub>2</sub> O <sub>2</sub> /H <sub>2</sub> O	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 <sub>3</sub> /HCl/HF/H <sub>2</sub> O <sub>2</sub>	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<sup>-1</sup> (N.A.= not analyzed).**

	Concentrations in %w							Concentrations in mg.kg <sup>-1</sup>					
	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 1<sup>st</sup>**  
 646 **digestion. Concentrations are given in %w and mg.kg<sup>-1</sup>.**

		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 <sub>3</sub>			Aqua regia		
	% w/w residues	0%			90%		
Metal	Unit	Content measured with 1 <sup>st</sup> digestion	Content after 2 digestions	% recovered from 1 <sup>st</sup> digestion	Content measured with 1 <sup>st</sup> digestion	Content after 2 digestions	% recovered from 1 <sup>st</sup> digestion
<b>Cu</b>	%w	14.60%	14.61%	99.9%	14.32%	14.34%	99.9%
<b>Fe</b>	%w	-	-	-	12.34%	12.52%	98.5%
<b>Al</b>	%w	-	-	-	5.84%	5.96%	98.0%
<b>Zn</b>	%w	1.81%	1.85%	97.9%	1.52%	1.53%	98.5%
<b>Sn</b>	%w	1.89%	1.90%	99.7%	1.44%	1.45%	99.3%
<b>Pb</b>	%w	1.23%	1.24%	99.3%	1.08%	1.09%	98.8%
<b>Ni</b>	%w	0.32%	0.34%	94.5%	0.32%	0.33%	97.3%
<b>Co</b>	mg.kg <sup>-1</sup>	334	338	98.9%	374	376	99.5%
<b>Ag</b>	mg.kg <sup>-1</sup>	198	209	94.6%	166	179	92.6%
<b>Au</b>	mg.kg <sup>-1</sup>	42.2	44.4	95.2%	62.0	65.9	94.1%
<b>Pd</b>	mg.kg <sup>-1</sup>	22.9	23.2	98.8%	26.8	27.3	98.4%
<b>Ga</b>	mg.kg <sup>-1</sup>	10.6	11.4	93.0%	10.7	11.5	93.1%
<b>Ta</b>	mg.kg <sup>-1</sup>	0.034	7.5	0.5%	0.038	0.045	83.6%

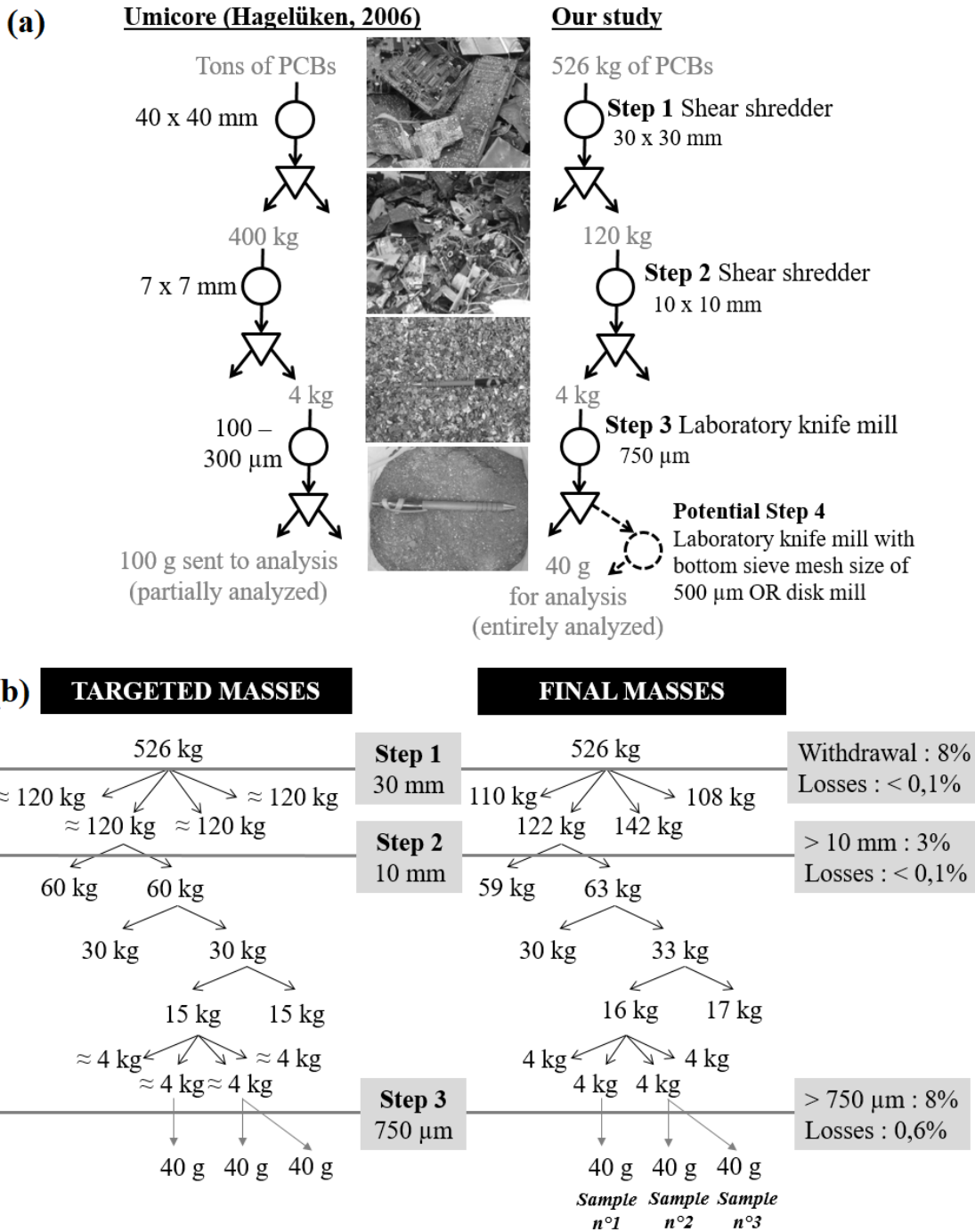
647

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”.**

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

655

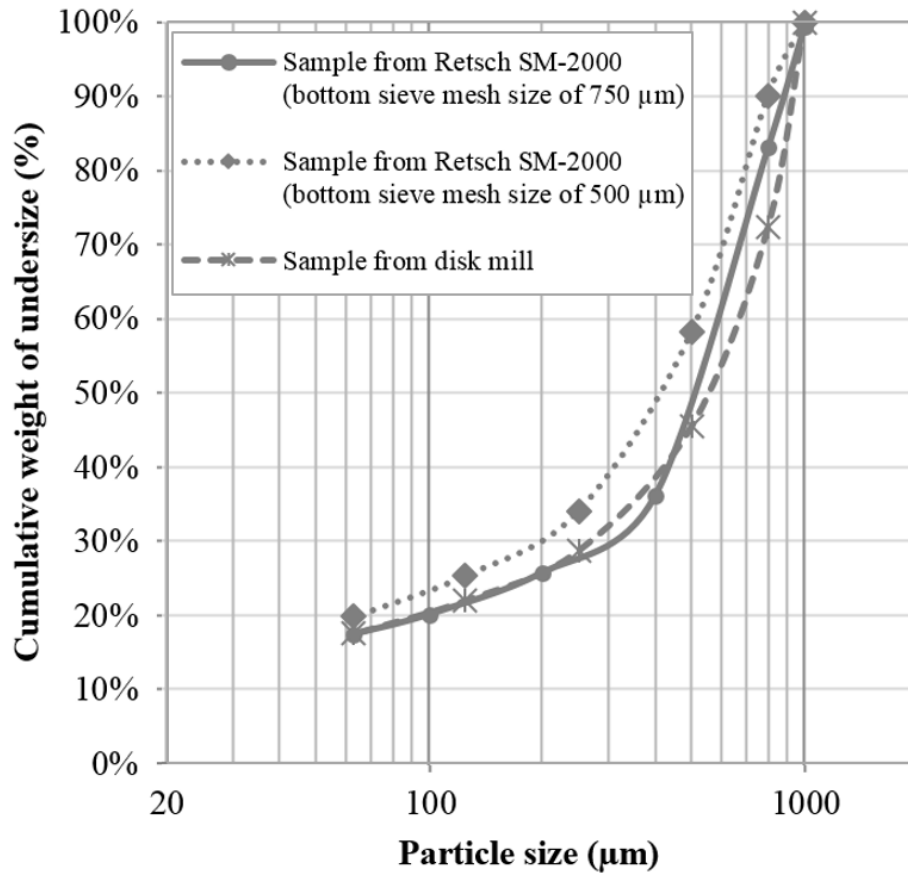


657

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**

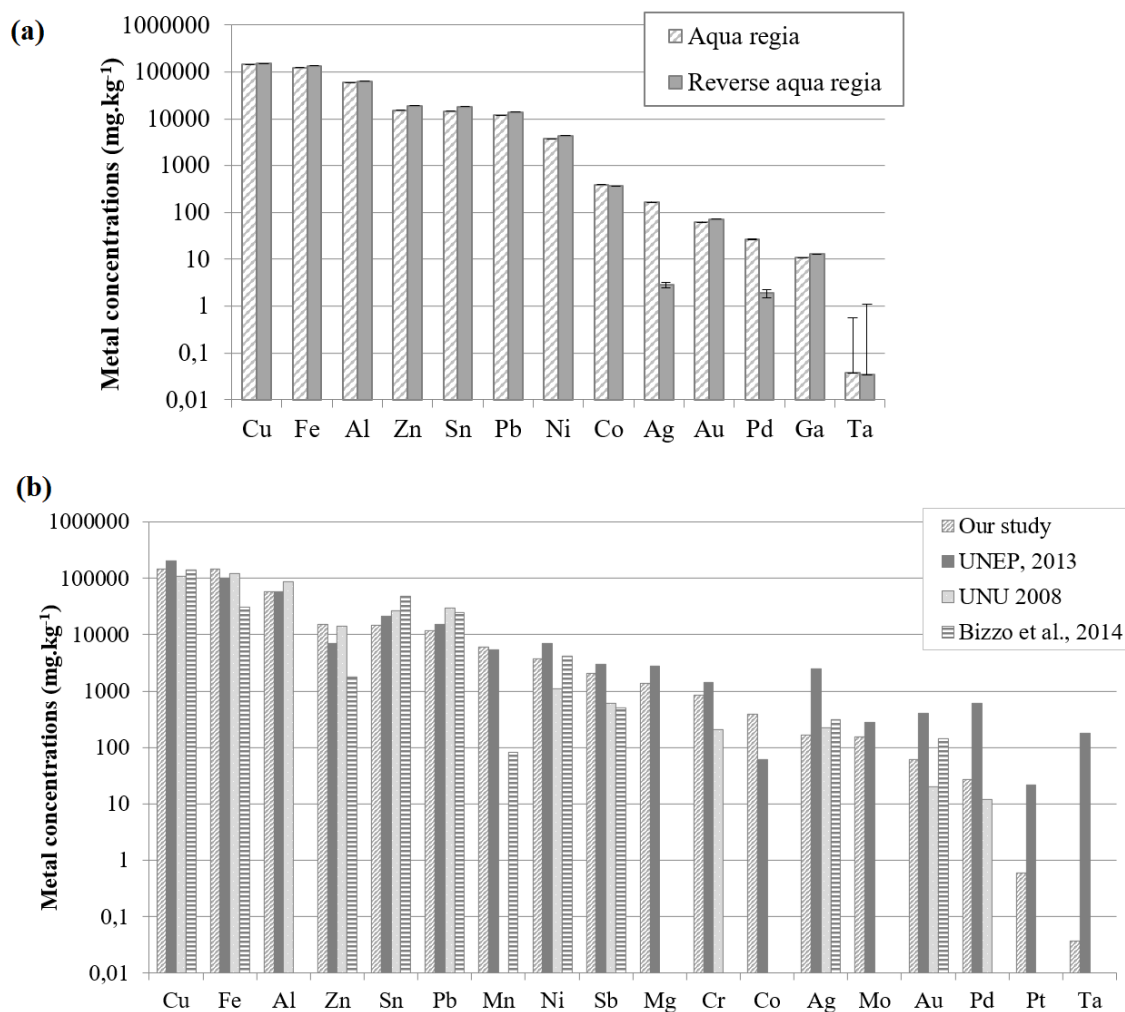
660 **produce 40 g-replicates from several 4 kg-samples (b).**



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



666

667 **Figure 3: (a) Metal concentrations after leaching 40 g-samples of PCBs by aqua**

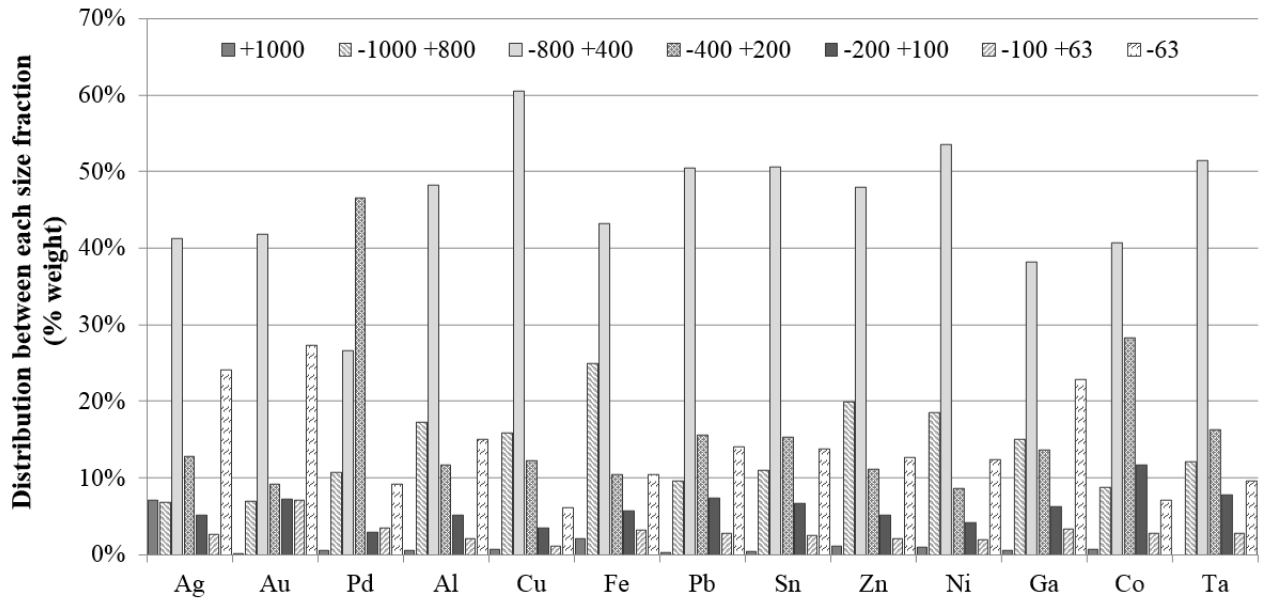
668 **regia or reverse aqua regia (temperature=200 °C, liquid/solid ratio= 11 mL.g<sup>-1</sup>,**

669 **analyzed with FAAS for Cu, Fe, Zn, Pb, Ni and Co and with ICP-AES and ICP-MS**

670 **for others); (b) Comparison of metal concentrations in spent PCBs from the present**

671 **work, UNEP (UNEP, 2013), UNU (UNU, 2008) and Bizzo (Bizzo et al., 2014).**

672



673

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