

Sampling waste printed circuit boards: Achieving the right combination between particle size and sample mass to measure metal content

Solène Touze, Sylvain Guignot, Agathe Hubau, Nicolas Devau, Simon

Chapron

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- 1 <u>Title:</u> Sampling waste printed circuit boards: achieving the right combination between
- 2 particle size and sample mass to measure metal content
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- 4 **<u>Corresponding author</u>**: Solène Touzé s.touze@brgm.fr
- 5 Authors: S. TOUZE¹, S. GUIGNOT¹, A. HUBAU¹, N. DEVAU¹, S. CHAPRON¹
- 6 1-BRGM, 3 av. Claude Guillemin, 45060 Orléans, France
- 7

8 <u>Highlights:</u>

9	•	Ni, Co, Fe, Cu, Pb and Zn content and of associated RSD in waste PCBs were
10		determined
11	•	Effects of sample mass, grain size, and number of replicates were evaluated
12	•	Nugget effect was identified in Ni and Co distributions
13	•	Margins of error in metal content were determined by statistical bootstrap tool
14	•	This study provides a decision-making tool to find the best WPCB preparation
15		method

16 Abstract

The current worldwide expansion of waste PCB (WPCB) deposits represents both a pressing environmental issue and an economic opportunity, fostering the development of numerous recycling processes across the world. An important input for designing such processes is the metallic content of WPCBs, which is assayed by grinding and leaching samples taken from the stack of WPCBs to be recycled. The content values come with substantial uncertainties, arising mainly from the uneven distribution of the metals within the structure of WPCBs.

23 This study aims to quantify the effects on these uncertainties of the particle size, the mass of 24 the sample digested and the number of digestion replicates. It focused on the abundance of 25 six metals in WPCBs: Cu, Fe, Zn, Pb and Ni, and also Co, which is a critical element for the EU. A batch of 485 kg of WPCBs was put through several shredding and splitting steps to 26 27 produce three fractions: one shredded to 2 mm, and two ground to 750 µm and 200 µm. From each sample, 16 samples of 0.5 g, 2 g or 5 g were digested in hot aqua regia. 28 29 Bootstrapping of the results allowed the error around the mean content to be estimated, for each metal and for all the experimental conditions. Considering the largest sample masses 30 31 and three replicated digestions, the uncertainties for Zn (resp. Ni) were reduced from 35 % 32 to 10 % (resp. from 70 % to 10 %) when the particle size was reduced from 2 mm to 200 μ m.

33 1. Introduction

Recycling of Waste Printed Circuit Boards (WPCBs) from Waste Electrical and Electronic 34 Equipment (WEEE) is a major challenge in sustainable resource management. The quantities 35 involved are significant: in 2019, the production of WPCBs amounted to 23 ktons in France 36 and more than 170 ktons in the European Union (EU), according to the European urban mine 37 38 database (WEB 1). Since 2000, numerous recycling chains have been set up to treat this type of waste and to recover some of the metals from WPCBs, and are now well established and 39 40 operational (Ghosh et al., 2015; Rocchetti et al., 2018). In the EU, the state-of-the art technologies mostly involve pre-processing (shredding/physical separation of some 41 elements), and end-processing to extract and refine the metals by pyrometallurgical 42 43 (smelting or pyrolysis) and hydrometallurgical operations (Ning et al, 2017). Smelting operations are conducted in large facilities originally built to produce metals from copper 44 sulphide concentrates, and as such, the design of the pre-processing and refining steps must 45 take into account not only the complexity of the WPCB materials to be processed, but also 46 47 the operational capacities and limitations of the smelters. Consequently, the range of metals that are potentially recoverable by applying current recycling options is still limited, as are 48 49 the rates of recovery. Base metals (such as copper and nickel) and precious metals (gold, platinum and palladium) can be partially recovered, while other elements (such as Sb and 50 51 Ta) are still left as waste. Furthermore, in order to maximize their operating profits, industrial recyclers primarily target so-called rich WPCBs, i.e. those with the highest 52 concentration of precious metals, to the detriment of WPCBs with lower concentrations, so 53 54 that these are largely unaddressed. This context has prompted intense R&D efforts over the 55 last two decades or so (recent reviews in Ning et al., 2017; Awasthi et al., 2018) to develop 56 alternative treatments that are better suited to the diversity of WPCBs and their complex

57 compositions. Obviously, knowledge of the metal composition of WPCBs is crucial 1) to 58 quantify metal flows 2) to quantify losses of metals in recycling chains 3) to explore new 59 processes and markets 4) to adapt recycling processes to changing trends in waste 60 production and 5) to track potentially polluting metals.

To draw a parallel with the design of a metallurgical process for ore beneficiation, the more care is taken in preparing and *sampling* the stack and performing efficient *chemical analyses*, or *assaying*, the more accurate the composition of a given stack of waste PCBs will be.

64 Sampling aims to obtain a sample which is representative of the whole stack, i.e. which contains all the constituents and in exactly the same proportion in which they occur in the 65 stack. This is to reduce the risk of misclassifications of materials, which affects decision-66 making and the cost analysis process. In the ore mining and beneficiation field, the 67 conventional recommendations to enhance the representativeness of samples taken from a 68 pile of materials are to sample fractions of finer particle sizes and to use larger sampling 69 masses, in order to improve the overall homogenization and to limit potential over/under-70 representation of certain elements (Gy, 1979). The larger the mass sizes, the closer the 71 sample will be to the mean composition of the stack. Likewise, the finer the particle sizes, 72 73 the more homogeneous the sample is likely to be. Samples are prepared by applying 74 comminution techniques (including shredding and grinding), and splitting steps. However, 75 WPCBs are characterized by high spatial heterogeneities in their composition and in the physical properties of their constituent materials, which tends to challenge homogenization 76 efforts. In terms of composition, WPCB materials consist of several alternating layers of 77 copper and fibreglass-reinforced polymer resins, with various components (resistors, 78 capacitors, transistors and integrated circuits) soldered onto one of the outermost surfaces. 79

80 In terms of chemical composition, up to 60 different elements go into the manufacture of microprocessors and circuit boards, usually in tiny and dispersive quantities, in combinations 81 that are not found in nature (Bloodworth, 2014), and closely intermingled with phenolic 82 moulding or epoxy resins often reinforced by fibreglass. The multiple applications and 83 84 corresponding equipment embedded in printed circuit boards translate into many different 85 chemical compositions of WPCBs. The current general consensus on composition is approximately 60 (%)wt of non-metallic elements, divided into glass and ceramics (30%) and 86 87 plastics (30%), and 40 (%)_{wt} of metals, which include base metals (Cu, Fe, Al, Sn, Pb, Zn, Ni), precious metals (Pd, Au, Ag), and other valuable metals such as In, Co and Ta (Kaya, 2016). 88 Metals can exist as discrete particles (large or small "nuggets"), as a surface layer and as 89 inclusions (alloy). This complex composition, and especially the fact that there are several 90 91 orders of magnitude between the most and least concentrated metals in a given circuit 92 board is the first major challenge met when trying to obtain representative samples. This is because a highly concentrated metal is likely to be more homogeneously distributed among 93 94 the samples produced after a size reduction and splitting process, so that the variability of 95 the metal content among samples will be low. Conversely, the sub-sample mass and its 96 particle size will have much more influence on the distribution of an element with a low metal content, and the probability of obtaining differences in the analyses of replicates will 97 98 be higher (Gy, 1979).

99 One way to improve homogenization is to work with samples with finer grain sizes, but this 100 brings in a second challenge: the very different mechanical properties of the various parts of 101 the WPCBs, in terms of malleability and ductility, and which react differently to the grinding 102 conditions applied. What is then often observed is stiffer and brittle parts being more easily 103 broken into smaller fragments than ductile ones, as well as limitations on the smallest size

104 that the whole sample can be ground down to. However, this step is often performed only to a partial extent in studies in the literature, in the sense that plastics (Arshadi and Mousavi, 105 106 2015; Hossain et al., 2018) or specific components such as the hard fraction (Li et al, 2012; Priya and Hait, 2018a; Korf et al., 2019; Holgersson et al., 2018) are removed before the size 107 108 reduction steps. In other studies, the sample is not wholly reduced below a target size; 109 instead, undersize sieved fractions are selected, with no further consideration given to the oversize parts (Ogunniyi et al., 2009; Zhao et al., 2017; Korf et al., 2019). This is often 110 111 ascribed to the flexible or ductile parts elongating into flakes larger than the sieve apertures, 112 and therefore remaining in the milling equipment chamber (Hubau et al., 2019; Otsuki et al., 113 2019). One additional point is that grinding WPCBs to fine particles may generate significant losses of valuable elements as dust and through heating (Yamane et al., 2011). In practice, a 114 115 quantitative reduction of a whole WPCB to a size below 250 µm at most seems difficult to 116 achieve by conventional means, i.e., without resorting to cryogenic mills for example (Ernst et al., 2003; Wienold et al., 2011; Zhou et al., 2016). This constitutes a limitation on the 117 118 homogenization of the samples when the aim is to characterize the metal content of the 119 whole WPCB and not only of specific fractions produced from them.

The two challenges, complex composition and the different mechanical properties of 120 constituent WPCB parts, are sometimes intertwined. Owing to some metals being at once in 121 122 the form of surface layers and quite ductile, "nuggets" of very pure metal can be found in every size class in the middlings obtained after preparation by milling. Such cases then 123 compromise the quality of homogenization, and thereby challenge the subsequent sampling 124 125 procedure, in that the samples may not accurately reflect the distribution of these nuggets, resulting for example in wide variations in elements observed in various sub-samples taken 126 from the same sample. 127

128 Sampling procedures that take the above-mentioned specificities of WPCBs into account do not seem to be described in the literature. Besides the specific standards applied to solid 129 fuels (DIN 51701-2) or electro-technical products (IEC 62321-2), which are only partial and 130 rarely accessible, information is available on the "in-house" industrial practices applied by 131 132 the main WPCB recyclers in Europe. Umicore has published its own sampling process in 133 operation for electronic scrap in its Hoboken plant. The chemical analysis is run with samples 134 with particles ranging from 100 μ m to 300 μ m, but there is no information on how the 135 WPCBs are milled to these sizes (Hagelüken, 2006). It is not possible to learn from their procedure because the Hoboken sampling and assaying unit was changed for reasons of 136 efficiency between 2011 and 2013 and no information was published on the new processes 137 (UMICORE, 2012). Other industrial sampling procedures use smelting or calcination before 138 139 the analysis stage (Laubertova et al., 2019).

With regard to *chemical analysis* of ground WPCB samples, several studies recommend the 140 use of aqua regia digestion for metal characterization (Ogunniyi et al., 2009; Mičková et al., 141 142 2018; Andrade et al., 2019). As regards reference material to validate the analysis results, 143 there was no standard reference material available for WEEE and WPCBs at the time of our 144 study (Mičková et al., 2018). Since then, Andrade et al. (2019) have developed a standard 145 WPCB material for metals analysis, but the associated uncertainty remains at a high level for the metals of interest here (14.08 ± 5.67% mass Cu, 3.92 ± 2.05% mass Fe, 0.42 ± 0.15% 146 mass Ni, 1.19 ± 0.20% mass Pb, and 1.36 ± 0.71% mass Zn). BAM has also proposed a 147 reference material from ashed WPCBs that were melted with pyrite (BAM M505a, 148 Bundesanstalt für Materialforschung und prüfung, Berlin), but the final matrix is notably 149 different from shredded WPCBs, due in particular to the absence of plastics. Finally, Priya 150 and Hait (2018b) use a polyethylene reference material in their study but the range of metal 151

concentrations is significantly different to that currently found in WPCBs (100 ppm of Fe in the material vs. around 10% Fe in WPCBs). The characterization of base metal concentrations in WPCBs would benefit from the development of new certified reference materials.

The scientific literature contains some data on the effects of the particle size and sub-sample 156 157 mass, along with the number of digestion replicates, on the accuracy of a given chemical analysis, particularly for WPCB samples with a coarse particle size. Wienold et al. (2011) 158 159 studied the influence of 5 digestion processes, using different sub-sample masses for 160 analysis (0.1 to 5 g) and 4 particle sizes (120 μ m, 250 μ m, 500 μ m and 1500 μ m), on the 161 precision and reproducibility of elemental analysis (Cu, Pb, Cd, Hg) (Wienold et al., 2011). In Wienold's analysis for Cu, Pb and Cd, to achieve a relative standard deviation (RSD) of less 162 than 20%, samples had to be ground to a particle size of < 500 μ m. The influence of the 163 sample mass and the digestion protocol was also investigated by Ernst et al. (2003) using 164 samples with a -250 μ m particle size. The masses were variable (from 0.5 to 10 g) for the hot 165 166 aqua regia digestion protocol in quadruplicate. In Ernst's analysis, the RSD is below 20% for 167 all metals for a sub-sample mass of 0.5 g and below 8% for 10 g(Ernst et al., 2003). Andrade et al. (2019) argue the reverse, with a standard deviation that increases, for most metals, as 168 169 the sample mass increases.

Based on these previous studies, the significance of each of these variables (particle size, mass of the sample used for the digestion protocol, along with the number of digestion replicates) is still difficult to assess. Moreover, none of these studies evaluates the influence of the combination of all these three parameters simultaneously on the uncertainties as to

the metal content, and none of them quantifies the error associated with numerousrepetitions.

176 Given these considerations, the purpose of the present study was therefore to investigate the effects of the three parameters on the data distribution and to calculate the associated 177 margin of error for metal content found in WPCBs. The metals were chosen among those 178 found in the highest concentrations in WPCBs: Cu, with concentrations around 14 (%)_{wt}, Fe 179 3(%)_{wt}, Pb 2.5(%)_{wt}, Ni 0.4(%)_{wt} and Zn 0.2(%)_{wt} (Bizzo et al. 2014). The study also addresses 180 the case of Co, as a sparsely distributed element in WPCBs and a critical material for the EU. 181 182 The sample masses considered are 0.5, 2 and 5 g, and span an order of magnitude that 183 includes most of the masses used in the vast majority of studies dealing with the characterization of WPCBs. Three samples, obtained after initial coarse shredding to 10 mm 184 followed by a careful sampling procedure, were further shredded until they could pass 185 through mill apertures of 2 mm, 750 µm and 200 µm respectively. These sizes correspond to 186 various degrees of liberation of the metal parts, according to the literature (Otsuki et al., 187 188 2020; Bacher et al, 2017, Guo et al., 2011). For a given set of mass and particle size, 16 189 digestions were performed following the same protocol. This substantial number of repetitions is a compromise between technical feasibility and a sufficient number for 190 191 deriving statistics. This number should make it possible to quantify the uncertainties as to metal content and to identify the maximum sources of error (preparation bias and nugget 192 effect for example). Statistical processing of all the data and bootstrapping of the results 193 194 were performed to estimate the uncertainties as to metal concentrations, as depicted by the spread of the confidence interval around the mean content, or margin of error, for each 195 experimental condition and each metal. The aim here was to assess and highlight the 196 importance of the particle size, the sample mass and the number of digestion replicates 197

when considering the development of an efficient WPCB sampling and wet assaying
methodology. Our study also aims to provide information on choosing the right combination
of these three parameters to obtain a given uncertainty as to the metal content.

201 2. Materials and methods

202 2.1. Sample preparation

The WPCBs used for this study were taken from the Small Waste Electrical and Electronic Equipment (sWEEE) category, which comprises audio and video appliances, toys, personal care products and culinary equipment among others. Approximately 500 kg of waste was provided by "Envie 2E Midi-Pyrénées", a waste recovery company operating in France. Materials with harmful environmental impacts, such as batteries, were disassembled, as well as aluminium heat sinks.

The entire sample (485kg) was first shredded with an industrial cutting mill without any 209 210 bottom sieve (Bohmier Maschinen GmbH Material) to a particle size of less than 30 mm. The 211 sample was subsequently quartered with a rotary divider. One quarter of the sample (122kg) was then shredded with the industrial cutting mill with a bottom sieve with 10 mm 212 perforations, to a particle size of less than 10 mm. The < 10 mm sample was divided with a 213 214 riffle splitter to obtain sub-sample masses of 4 kg. Three 4kg samples were used for the 215 tests: i) 2 mm sample: this 4kg sample was shredded in a lab knife mill (Retsch SM2000 with 216 tungsten carbide grinding tools) fitted with a bottom sieve with 2 mm perforations, ii) 750 µm sample: this 4 kg sample was shredded in the same lab knife mill fitted successively with 217 bottom sieves of 2 mm, 1 mm and 750 µm and iii) 200 µm sample: this 4kg sample was 218 219 shredded to 750 µm in the lab knife mill and sent to the Poittemille company (Bethune,

France) to be milled with a Universal grinder (FL1 Poittemille) using 200 μm ring holes.
Sample preparation is detailed in figure 1.

In the further shredding steps, the hammer rotation and the initial feed rates were kept constant. The milling times were not fixed, but correspond to the minimum length of time needed for at least 95% of the feed to pass through the sieve aperture. The unground portion was added to the ground material to produce the same composition as the original WPCB samples. After grinding, a riffle divider was used to obtain sub-samples of 5 g, 2 g and 0.5 g from the 4 kg samples.

The losses of material were less than 1 % in the procedure to obtain the 2 mm and 750 mm samples. The losses associated with the size reduction from 750 μ m to 200 μ m are unknown. The sampling methodology, with the yields and losses associated with each step, is detailed in a previous article by Hubau (Hubau et al., 2019).

To determine the particle size distribution, samples of more than 290 g were suspended in
water and passed through vibrating sieves with square apertures of 4 mm, 2 mm, 1 mm, 800
μm, 400 μm, 200 μm, 100 μm, 63 μm and 20 μm. The size fractions were then dried at 40 °C.

235 2.2. Digestion procedure and analyses

All the WPCB samples were characterised by aqua regia digestion followed by chemical analysis using Flame Atomic Absorption Spectrometry (FAAS). The samples were dissolved in hot aqua regia (HNO₃:HCl 1:3) at reflux, in a vessel equipped with a condenser. The solid /liquid ratio was 1:10 (weight/volume), and the contact time was about 2h. Each leaching fraction was filtered over a 0.45 µm cellulose nitrate filter, and the leachate was diluted with a solution of HNO₃ 0.5 M. The concentrations of Fe, Cu, Zn, Pb, Ni and Co in the resulting solutions were determined by Flame Atomic Absorption Spectrometry FAAS on a Varian

243 SpectrAA-300. Details on the digestion process are given in Hubau et al. (2019). All the 244 chemicals used were of analytical reagent grade.

245 2.3. Experimental programme

246 In order to understand the effects of sub-sample mass and particle size on the accuracy of the metal content determination, 3 samples of different particle sizes (200 µm, 750 µm and 247 2 mm) and 3 different sub-sample masses for digestion (0.5 g, 2 g and 5 g) were studied. 248 Combining these two parameters produced nine different conditions. To be able to perform 249 250 statistical tests, it was decided to repeat each condition at least 16 times; each metal 251 content value represents one measurement of one digestion. The number of independent 252 digestions was respectively: for the 200 µm sample: 5g n=16, 2g n=16, 0.5g n=16; for the 750 µm sample: 5g n=24, 2g n=16, 0.5g n=16 and for the 2 mm sample: 5g n=24, 2g n=16, 0.5g 253 254 n=16. However, for the 0.5 g sample with a 750 µm particle size, one digestion vessel broke 255 during the digestion, so the number of repetitions considered is 15 for this condition.

256 2.4. Statistical analyses

For each metal, statistical analyses were performed to distinguish the gap between the 257 experimental mean value of the metal content from the "true" mean value, which would 258 259 represent the analysis of an infinite number of replicates. The 95% confidence interval was 260 used to quantify this gap. This interval refers to the range of values in which the "true" mean 261 value has a 95% chance of being. It thus depicts the uncertainty over the determination of the metal content. In this study, the 95% confidence interval expressed relatively to the 262 corresponding mean value was called the margin of error (in percentage of the experimental 263 264 mean value).

265 For each metal, the normality and the homoscedasticity of the distribution of the metal concentrations for the nine associated treatments (combination of the 3 different particle 266 sizes and the 3 different sub-sample masses) were tested using the Shapiro test (test to 267 268 determine whether the distribution is normal) and the Bartlett test (test to determine 269 whether the samples were from populations with equal variances), respectively. For some 270 metals (Co, for instance), the measured values associated with some treatments did not 271 follow a normal distribution, according to these tests. These results prevent the use of the 272 classic parametric approach, based on the central limit theorem associated with the Student 273 distribution, to calculate the population variance and draw inferences for the confidence interval. In order to overcome this limitation, an approach based on bootstrapping was used, 274 which is not restricted to a specific type of probability distribution. In the bootstrap 275 276 approach, the hypothesis is made that the measured data for each treatment and for each of the 6 metals are an empirical estimate of the probability distribution. For each treatment 277 performed on the 6 metals, 25 metal content values were randomly selected in succession 278 279 from the set of experimental data. Replacement was performed, i.e. the same experimental 280 value could have been selected an infinite number of times. From these 25 values, a mean 281 value was calculated. These random selections and mean value calculations were performed more than 10 000 times. From these 10 000 mean values, the 95% confidence interval 282 283 around the mean value of the metal content was determined. The margin of error was then calculated, i.e. the confidence interval relatively to the experimental mean value. In order to 284 285 assess the impact of the digestion replicates (n) on the estimation of statistical population 286 properties, several bootstrap sampling sizes were tested (n=2, n=3, n=4, n=5, n=7, n=10, 287 n=15, n=25). All the statistical tests were carried out using R-software 3.5.2 (R Core Team, 288 2019).

289 3. Results and discussion

290 3.1. Particle size distribution

The particle size distributions of the different samples are shown in figure 2. The d80 (i.e. 291 292 80% passing size) of the particle size distribution was equal to 150 μ m, 750 μ m and 1.8 mm 293 for the 200 μm, 750 μm and 2 mm samples respectively. For the 750 μm sample, 20% of the 294 mass was composed of particles larger than 750 µm because shredding was incomplete : for 295 each shredding, some particles did not pass through the bottom sieve of the mill. These 296 particles were added to the milled material to preserve the representativeness of the samples and to ensure that the comparison of the metal content in the three samples would 297 298 not be distorted.

3.2. Estimation of potential biases arising from sample preparation and analysis

300 Despite the fact that no particles were removed during the shredding steps, the additional grinding steps for 750 µm and 200 µm compared to 2 mm were liable to generate some 301 302 interference, including contamination due to the abrasion of mill material or preferential 303 metal losses (dust dispersion for example). One way of highlighting the influence of these 304 different sample preparations is to compare the mean values of the different conditions (table 1). The mean values for metal content remained of the same order of magnitude with 305 306 no erratic points. Wienold et al. (2011) showed a similar trend for Pb content: the Pb content analysis (digested sample mass of 2 g) of coarse samples (scrap and 1.5 mm) remained of the 307 same order of magnitude as for the finest samples (500 μ m, 250 μ m and 120 μ m). If the 308 309 additional grinding steps had generated a bias, this bias would have affected the mean value 310 for each particle size sample differently. For example, if Pb was lost due to dust dissipation during the additional grinding steps, we would systematically have less Pb in 200 µm than in 311 2 mm samples. For all metals, the minimum mean values were not systematically present in 312

one particle size sample, and likewise for the maximum mean values. This observation shows
that there was no evident bias for Ni, Pb, Zn, Fe, Cu and Co mean contents in relation to the
additional shredding step.

316 In order to verify the efficiency of the digestion process, the leaching residues from the 750 µm sample were ground again, digested with an acid mixture containing HF (total digestion) 317 and the leachate was analysed. The analytical procedure for these residues is described in 318 Hubau et al. (2019). The analysis revealed no detectable presence of the six metals 319 considered. Therefore, it may be assumed that Cu, Fe, Pb, Zn, Ni and Co were fully leached 320 321 from the 750 µm sample. Particle size regulates the surface exposed to attack by acid, and 322 may thus significantly affect the kinetics and yield of digestion and hence the apparent metal content. More specifically, for a given mass analysed, a larger grain size will correspond to 323 324 surfaces being less accessible to leaching reagents, which in turn may lead to metal dissolution and therefore a lower apparent metal content. If the 2 mm sample had affected 325 the determination of the metal content, the mean value of the 2 mm sample would have 326 327 been systematically lower than the other mean values, but this was not the case. As seen 328 previously, there was no evident bias for the Ni, Pb, Zn, Fe, Cu and Co mean content, indicating that there is no observable relationship between the efficiency of digestion and 329 330 particle sizes. It is expected that these six metals were also fully leached from the 200 µm and 2 mm sample. 331

332 3.3. Measurement deviation

For the six metals, the Relative Standard Deviation (table 2) showed two trends: i) a decrease in particle size reduces the RSD and ii) for most of the conditions, an increase in the sample mass used for digestion decreases the RSD (5 g < 2 g < 0.5 g). As expected, grinding

particles to obtain the finest sample enhanced the repeatability of the concentration measurements. This is consistent with the Gy theory of sampling (Gy, 1979). The influence of the sample mass on the RSD is also consistent with this theory, despite the results of Andrade et al. (2019), which concluded that for most metals, the RSD was lower with a lower sample mass. The concentration of the element studied also has an indirect effect: the RSD increases when the metallic content decreases (Cu and Fe < Pb and Zn < Ni and Co).

These results are consistent with the results from Wienold et al (2011) and Ernst et al (2003) for copper: the same trends and the same orders of magnitude of RSD are observed in their studies (Wienold et al., 2011; and Ernst et al., 2003). Wienold obtained the same results for the Cu content data set, with RSD < 10% for a 2 g sample mass and a particle size of 120 μm to 1.5 mm, and RSD of around 20% for a 0.1 g sample mass and particle size of 500 μm (n=9).

347 Since it is assumed that there are no biases due to the preparation of materials and the digestion and the analysis procedures, the observed deviation depends only on the residual 348 349 heterogeneity in the sample. As expected, this sensitivity to content level is less visible for 350 the finest particles: the RSD for 200 µm sample are below 8% except for Ni, which indicates 351 low residual heterogeneity in the 200 μ m sample. The RSD for Ni does not follow the same 352 trend because of one erratic point [200 µm; 0.5 g]. For this condition, the erratic point had a value of 0.70 % while the mean value was 0.40% (figure 3). This point may be due to a 353 354 "nugget" effect, i.e., the occurrence of one or several tiny single flakes of pure Ni in the sample that were not reduced even at 200 µm. Finer grinding might be required to ensure a 355 more even distribution of Ni between the samples. This "nugget" effect with Ni is, to our 356 knowledge, not described in the literature. It may be due to the composition of electronic 357 358 components that include Ni as discrete particles.

359 3.4. Distribution discontinuity

Figure 3 gives an overview of the Zn, Ni and Co metal concentrations that were determined
with our replicates: each metal concentration is represented by a black dot, the lines
represent the median values and the crosses represent the mean values. Scatterplots for Cu,
Pb and Fe are shown in the supplementary material since their distribution was similar to
that for Zn, with almost no erratic points (one for Fe at 2 mm; 0.5 g). For the Ni and Co data
sets, some values were erratic: Ni [200 µm; 0.5 g], Ni [2 mm; 2 g] and Co [2 mm; 2 g].

366 Most of these erratic points were observed in replicates from the coarse sample at 2 mm. 367 For Co [2 mm; 2 g], the grades changed abruptly from 311 ppm (mean value) to 1153 ppm, 368 the Ni [2 mm; 2 g] grades changed from 0.45% to 1.45% and the Fe [2 mm; 0.5 g] grades from 14% to 23%, 27% and 28%. The erratic points for Ni and Co came from the same 369 370 digestion sample. The fine particles are more likely to be well disseminated in the shredded sample, and are responsible for a background grade of around 311 ppm for Co, 0.45% for Ni 371 and 14% for Fe. In contrast, the presence or absence of coarse particles mainly made up of 372 373 metal, such as Co, Ni or Fe, can have a strong impact on the analysis. The probability of 374 having coarse particles of metal in a sub-sample is very low. The presence of these erratic points is very similar to the "gold nugget effect" found in assessments of gold deposits 375 376 (Dominy et al., 2018). The Ni anomaly [200 µm; 0.5 g] is more problematic and shows that anomalies can exist even for the finest sample analysed for Ni. Although these erratic points 377 378 do not appear often, once out of sixteen sample analyses is significant and can have a huge 379 impact on analysis results.

380 No erratic points were observed for Cu, Pb and Zn. This does not mean that none can occur381 but that they are likely to be less present.

382 3.5. Modelling the confidence level

Based on the numerous analytical results obtained, a model was developed to calculate the 383 margin of error, i.e. the confidence interval around the mean values. The statistical test was 384 of the bootstrapping type, which relies on random sampling with replacements, as described 385 in the Materials and Methods section. Figure 4 shows the change in the margin of error for 386 387 Zn, Ni and Co content according to the number of analyses performed, the particle size and the sample mass, on a logarithmic scale. "Bootstraps" for other metals were also modelled, 388 389 and are provided in the supplementary material. The aim of this calculation is to create a 390 decision support tool to help choose the appropriate sample mass, particle size and number of repetitions needed to obtain a given margin of error in the value of the metal content. 391

It can be seen in figure 4 that the margins of error tend to drop with the first 4 to 5 392 393 digestions performed, before levelling off over the remaining digestion numbers in the range of 5 to 25, the latter being the upper limit considered in the bootstrapping procedure. It is 394 thus noteworthy that performing only duplicates to determine the metal content will result 395 396 in significant margins of error. Exemplifying this, the 95 % confidence interval for the mean 397 value will represent 10 to 40 % of the mean value itself, considering the case of Zn, with a sample mass of 5 g and the three grain sizes. It is acknowledged that such uncertainties are 398 399 high, and may constitute a serious source of error when calculating the yields and recoveries of metals in a WPCB recycling process. What appears obvious from figure 4 is that the most 400 efficient way of increasing the level of confidence in analytical results is to reduce the 401 particle size. Thus for Zn, with a particle size of 200 µm, the margin of error can drop quickly 402 below 10% with only three measurement repetitions and a sub-sample mass of 2 g. This 403 404 effect is most apparent when considering the case of Co regardless of the sample mass.

For all metals, the best preparation condition to achieve a low margin of error (< 10%) was the finest particle size of 200 μ m and few repetitions (3 or 4) of 2 g sample digestion. However, to avoid the difficulty of shredding WPCBs to 200 μ m, the 750 μ m particle size was found to be acceptable, provided that the sample mass used for digestion was larger than 2 g.

410 Shapiro and Bartlett tests have proven that most of the elements presented do not follow a 411 normal distribution. A non-parametric bootstrap method was therefore used to determine 412 the margin of error for a combination of a particle size, a sample mass and a number of 413 samples analysed. As the margin of error is calculated from an asymmetrical distribution, the 414 mean value is not in the centre of the interval defined by the margin of error (figure 5, black 415 lines): for each metal in all the preparation conditions, there is a larger gap between the 416 mean value and the upper bound than with the lower bound. This specificity means that is not possible to predict the upper and the lower bounds for a new mean value by directly 417 using the margin of error from the bootstrap results. However, it is possible to make the 418 419 calculation from a normal distribution (figure 5, gray dotted lines), which gives half of the 420 margin of error for the upper bound and half for the lower bound. Calculations were made 421 to estimate the error for the lower and upper bounds by applying a normal distribution 422 hypothesis. Table 3 presents the data calculated for a normal distribution ("bound from normal distribution hypothesis") and the comparison with the real bounds obtained with the 423 bootstrap tool ("bootstrap data"), along with the "normal distribution error", which refers to 424 425 the gap between the normal distribution hypothesis and the bootstrap data (see figure 5). Only results for a 0.5 g sample mass are presented here; those for other sample masses can 426 427 be found in supplementary information.

428 Overall, for the upper bound, the difference never exceeds 8% (with triplicates) between the 429 estimate and the actual data. Regarding the lower bound, most of the preparation conditions give a deviation lower than 9% if a triplicate sample is analysed. However, at 2 430 mm, the lower bound presents some significant differences for all metals except Cu. The 431 432 lower bound is mostly underestimated in the case of the normal distribution. With a 0.5 g 433 sample mass, the deviation reaches 17.9% for Fe, 65.4% for Co, 18.2% for Pb 23.3% for Ni 434 and 21.1% for Zn. With 2 and 5 g sample masses, the deviation is greater than 15.5% for Co 435 and Ni at 2 mm. Moreover, for Ni, the deviation of the lower bound is significant even with smaller particle sizes (11.6 and 14.3% for Ni at 750 μ m and 200 μ m respectively). 436

This comparison shows that reducing the particle size gives a better data fit with a normal distribution hypothesis. Thus, the margin of error calculated from bootstrap results can be used as an uncertainty around the mean value, except for the metals that present a nugget effect. Except for Ni, the error given by calculating the upper and lower limits as a normal distribution is less than 2% for 200 µm samples.

442 4. Conclusion

Taking subsamples from a portion of WPCBs could be time-consuming and costly. It is therefore essential to assess the effects of sample preparation on the quality of the results. This assessment allows the appropriate preparation procedure to be established according to data quality objectives.

A series of 9 preparation conditions for WPCB samples was analysed, producing a total of 159 data points per metal (Cu, Pb, Zn, Ni, Fe and Co), from which the effects of particle size, sample mass and digestion repetition were investigated. For some metals, Ni, Co and Fe, small amounts of concentrated nuggets of metal could inflate the total sampling variance.

451 Shredding to fine particles (< 200 μm) helped to reduce this effect for Co and Fe. For Ni,
452 taking additional samples helped to characterize and manage this spatial heterogeneity.

453 This study shows that the uncertainty in the quantitative determination of metals in WPCBs 454 and the dispersion of the values is closely dependent on the preparation of the materials (particle size and sample mass used for analysis) and on their metal content. As expected, 455 the relative standard deviation increases when a larger particle size and a smaller sampling 456 mass are considered, in line with Gy's sampling theory developed for ore sampling. This 457 study quantifies these deviations when i) the particle sizes increase ii) the sample masses 458 459 decrease and iii) indirectly when the content values decrease. Although this appears to be 460 stating the obvious, our study allows the deviations to be quantified. The specific statistical processing of the data through bootstrapping allowed this quantification to be taken further 461 and revealed that large uncertainties remain over metal concentrations if samples are not 462 ground sufficiently finely, and if only a limited number of digestions are performed. These 463 relatively large uncertainties, in comparison with ore, are associated with the highly 464 465 heterogeneous compositions that exist in WPCBs. This study underlines the need to pay 466 specific attention to these heterogeneities.

From statistical analysis of the data, the margin of error was predicted as a function of the sample mass, the particle size and the number of digestion repetitions. Experimenters need to consider the most reasonable balance between these three parameters, according to data quality objectives. The compromise achieved will differ from one metal to another and from one experimenter to the other, depending on their own technical limitations.

472	This article describes features of WPCB characterization data. Our main objective is now to
473	deepen the data analysis. The application of Gy (Gy, 1979) sampling theory to WPCB is in
474	progress and will be detailed in a forthcoming article.

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586 Figures



588 Figure 1: Sampling and shredding procedure.



590 Figure 2: Particle size distributions for the 200 μm, 750 μm and 2 mm samples.



- 592 Figure 3: Scatterplots for Zn, Ni and Co content in WPCB according to particle size and
- 593 sample mass. The lines and crosses represent median and mean values respectively.





598 Figure 4: Margin of error for the mean values for Zn (upper figures), Ni (middle figures) and



—о— 200µm - 0.5g —о— 750µm - 0.5g — 💷 2mm - 0.5g 🛛 --ө- 200µm - 2g --ө- 750µm - 2g -- 🖬 - 2mm - 2g

— 200µm - 5g → 750µm - 5g — 2mm - 5g



Figure 5: Comparison of the 95% confidence interval from a normal distribution and a real

⁶⁰² distribution obtained by bootstrapping.

604 Tables

			0.5 g			2 g		5g				
		200	750	2	200	750	2	200	750	2		
1etal content		μm	μm	mm	μm	μm	mm	μm	μm	mm		
	Cu %	19.6	16.4	17.2	19.1	15.8	17.2	18	15.5	16.6		
	Fe %	12.8	12.2	13.6	12.6	12.2	12.3	11.9	12.2	12.3		
	Pb %	1.21	1.27	1.56	1.23	1.25	1.23	1.09	1.17	1.29		
	Zn %	1.83	1.85	2.01	1.81	1.67	1.79	1.64	1.67	1.62		
	Ni %	0.40	0.45	0.34	0.38	0.45	0.47	0.41	0.38	0.43		
2	Co ppm	342	229	275	326	312	383	315	355	336		

605

Table 1: Mean values from the nine different conditions of WPCB preparation.

			0.5g				2g		5g				
	_		200µm	750µm	2mm	200µm	750µm	2mm	200µm	750µm	2mm		
ve Standard eviation		Cu	5%	9%	24%	3%	11%	11%	3%	6%	7%		
	c	Fe	5%	18%	50%	5%	13%	14%	4%	5%	9%		
	atio	Pb	2%	28%	58%	2%	14%	22%	4%	9%	13%		
	evia	Zn	8%	28%	68%	5%	14%	20%	5%	10%	16%		
lati	Ō	Ni	26%	43%	61%	3%	23%	58%	6%	13%	34%		
Re	_	Со	8%	38%	87%	5%	33%	68%	3%	25%	42%		

609	Table 2:	Relative	Standard	Deviations	(RSD)	for	the	nine	different	conditions	of	WPCB

610 preparation.

				Bounds fro distribution	om normal hypothesis	Bounds fr	om Bootstro	Normal distribution error		
	Particle size	Sample mass (g)	Mean value	Lower bound	Upper bound	Margin of error (%)	Lower bound	Upper bound	Lower bound	Upper bound
7	200 µm		1.83	1.68	1.99	16.9	1.65	1.96	1.5%	1.3%
2n %	750 μm	0.5 g	1.88	1.34	2.43	58.0	1.34	2.43	0.4%	0.2%
70	2 mm		2.00	0.56	3.44	144	0.71	3.59	21.1%	4.2%
A1:	200 µm		0.40	0.31	0.49	45.0	0.35	0.53	11.4%	7.5%
NI %	750 μm	0.5 g	0.45	0.25	0.65	88.9	0.28	0.68	10.7%	4.4%
70	2 mm		0.33	0.12	0.55	130	0.15	0.58	23.3%	6.0%
6.	200 µm		343	315	372	16.6	312	369	0.8%	0.7%
	750 μm	0.5 g	229	133	325	83.8	131	323	1.5%	0.6%
ppin	2 mm		273	24	523	183	68.0	567	65.4%	7.8%
_	200 µm		20	18.7	20.5	9.2	18.6	20.4	0.5%	0.5%
Cu %	750 μm	0.5 g	16.5	14.8	18.2	20.6	14.5	17.9	2.1%	1.7%
70	2 mm		17	12.7	21.4	51.2	12.8	21.5	1.2%	0.7%
F -	200 µm		12.8	12.2	13.4	9.4	12.2	13.4	0.1%	0.1%
Fe %	750 μm	0.5 g	12.2	10.0	14.5	36.9	10.3	14.8	2.9%	2.0%
70	2 mm		13.6	6.8	20.3	99	8.3	21.8	17.9%	6.9%
Dh	200 µm		1.21	1.18	1.23	4.3	1.18	1.23	0.2%	0.2%
PD %	750 μm	0.5 g	1.28	0.86	1.70	65.2	0.88	1.71	1.7%	0.9%
70	2 mm		1.53	0.56	2.49	126.4	0.69	2.62	18.2%	4.8%

Table 3: Comparison between upper and lower bounds from the normal distribution hypothesis and from bootstrap data for triplicates of 0.5 g

sample mass and particle sizes of 200 μ m, 750 μ m and 2 mm.