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► To cite this version:

Solène Touze, Sylvain Guignot, Agathe Hubau, Nicolas Devau, Simon Chapron. Sampling waste printed circuit boards: Achieving the right combination between particle size and sample mass to measure metal content. *Waste Management*, 2020, 118, pp.380-390. 10.1016/j.wasman.2020.08.054 . hal-03027271

HAL Id: hal-03027271

<https://brgm.hal.science/hal-03027271>

Submitted on 21 Sep 2022

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1 **Title:** Sampling waste printed circuit boards: achieving the right combination between
2 particle size and sample mass to measure metal content

3 **Key words:** waste PCB, sampling, characterisation, metals, recycling, urban mining

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7

8 **Highlights:**

- 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**

17 The current worldwide expansion of waste PCB (WPCB) deposits represents both a pressing
18 environmental issue and an economic opportunity, fostering the development of numerous
19 recycling processes across the world. An important input for designing such processes is the
20 metallic content of WPCBs, which is assayed by grinding and leaching samples taken from
21 the stack of WPCBs to be recycled. The content values come with substantial uncertainties,
22 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.
26 A batch of 485 kg of WPCBs was put through several shredding and splitting steps to
27 produce three fractions: one shredded to 2 mm, and two ground to 750 μm and 200 μm .
28 From each sample, 16 samples of 0.5 g, 2 g or 5 g were digested in hot aqua regia.
29 Bootstrapping of the results allowed the error around the mean content to be estimated, for
30 each metal and for all the experimental conditions. Considering the largest sample masses
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 μm .

33 1. Introduction

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

61 To draw a parallel with the design of a metallurgical process for ore beneficiation, the more
62 care is taken in preparing and *sampling* the stack and performing efficient *chemical analyses*,
63 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
65 contains all the constituents and in exactly the same proportion in which they occur in the
66 stack. This is to reduce the risk of misclassifications of materials, which affects decision-
67 making and the cost analysis process. In the ore mining and beneficiation field, the
68 conventional recommendations to enhance the representativeness of samples taken from a
69 pile of materials are to sample fractions of finer particle sizes and to use larger sampling
70 masses, in order to improve the overall homogenization and to limit potential over/under-
71 representation of certain elements (Gy, 1979). The larger the mass sizes, the closer the
72 sample will be to the mean composition of the stack. Likewise, the finer the particle sizes,
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
76 physical properties of their constituent materials, which tends to challenge homogenization
77 efforts. In terms of composition, WPCB materials consist of several alternating layers of
78 copper and fibreglass-reinforced polymer resins, with various components (resistors,
79 capacitors, transistors and integrated circuits) soldered onto one of the outermost surfaces.

80 In terms of chemical composition, up to 60 different elements go into the manufacture of
81 microprocessors and circuit boards, usually in tiny and dispersive quantities, in combinations
82 that are not found in nature (Bloodworth, 2014), and closely intermingled with phenolic
83 moulding or epoxy resins often reinforced by fibreglass. The multiple applications and
84 corresponding equipment embedded in printed circuit boards translate into many different
85 chemical compositions of WPCBs. The current general consensus on composition is
86 approximately 60 (%)_{wt} of non-metallic elements, divided into glass and ceramics (30%) and
87 plastics (30%), and 40 (%)_{wt} of metals, which include base metals (Cu, Fe, Al, Sn, Pb, Zn, Ni),
88 precious metals (Pd, Au, Ag), and other valuable metals such as In, Co and Ta (Kaya, 2016).
89 Metals can exist as discrete particles (large or small “nuggets”), as a surface layer and as
90 inclusions (alloy). This complex composition, and especially the fact that there are several
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
93 because a highly concentrated metal is likely to be more homogeneously distributed among
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
97 metal content, and the probability of obtaining differences in the analyses of replicates will
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
105 a partial extent in studies in the literature, in the sense that plastics (Arshadi and Mousavi,
106 2015; Hossain et al., 2018) or specific components such as the hard fraction (Li et al, 2012;
107 Priya and Hait, 2018a; Korf et al., 2019; Holgersson et al., 2018) are removed before the size
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
110 oversize parts (Ogunniyi et al., 2009; Zhao et al., 2017; Korf et al., 2019). This is often
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
114 losses of valuable elements as dust and through heating (Yamane et al., 2011). In practice, a
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
117 et al., 2003; Wienold et al., 2011; Zhou et al., 2016). This constitutes a limitation on the
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.

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

128 Sampling procedures that take the above-mentioned specificities of WPCBs into account do
129 not seem to be described in the literature. Besides the specific standards applied to solid
130 fuels (DIN 51701-2) or electro-technical products (IEC 62321-2), which are only partial and
131 rarely accessible, information is available on the “in-house” industrial practices applied by
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 μm to 300 μm , 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
136 procedure because the Hoboken sampling and assaying unit was changed for reasons of
137 efficiency between 2011 and 2013 and no information was published on the new processes
138 (UMICORE, 2012). Other industrial sampling procedures use smelting or calcination before
139 the analysis stage (Laubertova et al., 2019).

140 With regard to *chemical analysis* of ground WPCB samples, several studies recommend the
141 use of aqua regia digestion for metal characterization (Ogunniyi et al., 2009; Mičková et al.,
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
146 the metals of interest here ($14.08 \pm 5.67\%$ mass Cu, $3.92 \pm 2.05\%$ mass Fe, $0.42 \pm 0.15\%$
147 mass Ni, $1.19 \pm 0.20\%$ mass Pb, and $1.36 \pm 0.71\%$ mass Zn). BAM has also proposed a
148 reference material from ashed WPCBs that were melted with pyrite (BAM M505a,
149 Bundesanstalt für Materialforschung und prüfung, Berlin), but the final matrix is notably
150 different from shredded WPCBs, due in particular to the absence of plastics. Finally, Priya
151 and Hait (2018b) use a polyethylene reference material in their study but the range of metal

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

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

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

174 the metal content, and none of them quantifies the error associated with numerous
175 repetitions.

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

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

201 2. Materials and methods

202 2.1. Sample preparation

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

209 The entire sample (485kg) was first shredded with an industrial cutting mill without any
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)
212 was then shredded with the industrial cutting mill with a bottom sieve with 10 mm
213 perforations, to a particle size of less than 10 mm. The < 10 mm sample was divided with a
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
217 μm sample: this 4 kg sample was shredded in the same lab knife mill fitted successively with
218 bottom sieves of 2 mm, 1 mm and 750 μm and iii) 200 μm sample: this 4kg sample was
219 shredded to 750 μm in the lab knife mill and sent to the Poitemille company (Bethune,

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

222 In the further shredding steps, the hammer rotation and the initial feed rates were kept
223 constant. The milling times were not fixed, but correspond to the minimum length of time
224 needed for at least 95% of the feed to pass through the sieve aperture. The unground
225 portion was added to the ground material to produce the same composition as the original
226 WPCB samples. After grinding, a riffle divider was used to obtain sub-samples of 5 g, 2 g and
227 0.5 g from the 4 kg samples.

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

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

235 2.2. Digestion procedure and analyses

236 All the WPCB samples were characterised by aqua regia digestion followed by chemical
237 analysis using Flame Atomic Absorption Spectrometry (FAAS). The samples were dissolved in
238 hot aqua regia ($\text{HNO}_3:\text{HCl}$ 1:3) at reflux, in a vessel equipped with a condenser. The solid
239 /liquid ratio was 1:10 (weight/volume), and the contact time was about 2h. Each leaching
240 fraction was filtered over a 0.45 μm cellulose nitrate filter, and the leachate was diluted with
241 a solution of HNO_3 0.5 M. The concentrations of Fe, Cu, Zn, Pb, Ni and Co in the resulting
242 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
247 the metal content determination, 3 samples of different particle sizes (200 μm , 750 μm and
248 2 mm) and 3 different sub-sample masses for digestion (0.5 g, 2 g and 5 g) were studied.
249 Combining these two parameters produced nine different conditions. To be able to perform
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
253 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
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

257 For each metal, statistical analyses were performed to distinguish the gap between the
258 experimental mean value of the metal content from the “true” mean value, which would
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
262 the metal content. In this study, the 95% confidence interval expressed relatively to the
263 corresponding mean value was called the margin of error (in percentage of the experimental
264 mean value).

265 For each metal, the normality and the homoscedasticity of the distribution of the metal
266 concentrations for the nine associated treatments (combination of the 3 different particle
267 sizes and the 3 different sub-sample masses) were tested using the Shapiro test (test to
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
274 interval. In order to overcome this limitation, an approach based on bootstrapping was used,
275 which is not restricted to a specific type of probability distribution. In the bootstrap
276 approach, the hypothesis is made that the measured data for each treatment and for each of
277 the 6 metals are an empirical estimate of the probability distribution. For each treatment
278 performed on the 6 metals, 25 metal content values were randomly selected in succession
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
282 more than 10 000 times. From these 10 000 mean values, the 95% confidence interval
283 around the mean value of the metal content was determined. The margin of error was then
284 calculated, i.e. the confidence interval relatively to the experimental mean value. In order to
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

291 The particle size distributions of the different samples are shown in figure 2. The d80 (i.e.
292 80% passing size) of the particle size distribution was equal to 150 μm , 750 μm 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
297 samples and to ensure that the comparison of the metal content in the three samples would
298 not be distorted.

299 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
301 grinding steps for 750 μm and 200 μm compared to 2 mm were liable to generate some
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
305 (table 1). The mean values for metal content remained of the same order of magnitude with
306 no erratic points. Wienold et al. (2011) showed a similar trend for Pb content: the Pb content
307 analysis (digested sample mass of 2 g) of coarse samples (scrap and 1.5 mm) remained of the
308 same order of magnitude as for the finest samples (500 μm , 250 μm and 120 μm). If the
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
311 during the additional grinding steps, we would systematically have less Pb in 200 μm than in
312 2 mm samples. For all metals, the minimum mean values were not systematically present in

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

316 In order to verify the efficiency of the digestion process, the leaching residues from the 750
317 μm sample were ground again, digested with an acid mixture containing HF (total digestion)
318 and the leachate was analysed. The analytical procedure for these residues is described in
319 Hubau et al. (2019). The analysis revealed no detectable presence of the six metals
320 considered. Therefore, it may be assumed that Cu, Fe, Pb, Zn, Ni and Co were fully leached
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
323 content. More specifically, for a given mass analysed, a larger grain size will correspond to
324 surfaces being less accessible to leaching reagents, which in turn may lead to metal
325 dissolution and therefore a lower apparent metal content. If the 2 mm sample had affected
326 the determination of the metal content, the mean value of the 2 mm sample would have
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,
329 indicating that there is no observable relationship between the efficiency of digestion and
330 particle sizes. It is expected that these six metals were also fully leached from the 200 μm
331 and 2 mm sample.

332 3.3. Measurement deviation

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

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

342 These results are consistent with the results from Wienold et al (2011) and Ernst et al (2003)
343 for copper: the same trends and the same orders of magnitude of RSD are observed in their
344 studies (Wienold et al., 2011; and Ernst et al., 2003). Wienold obtained the same results for
345 the Cu content data set, with RSD < 10% for a 2 g sample mass and a particle size of 120 µm
346 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
348 digestion and the analysis procedures, the observed deviation depends only on the residual
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 µm 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
353 value of 0.70 % while the mean value was 0.40% (figure 3). This point may be due to a
354 “nugget” effect, i.e., the occurrence of one or several tiny single flakes of pure Ni in the
355 sample that were not reduced even at 200 µm. Finer grinding might be required to ensure a
356 more even distribution of Ni between the samples. This “nugget” effect with Ni is, to our
357 knowledge, not described in the literature. It may be due to the composition of electronic
358 components that include Ni as discrete particles.

359 3.4. Distribution discontinuity

360 Figure 3 gives an overview of the Zn, Ni and Co metal concentrations that were determined
361 with our replicates: each metal concentration is represented by a black dot, the lines
362 represent the median values and the crosses represent the mean values. Scatterplots for Cu,
363 Pb and Fe are shown in the supplementary material since their distribution was similar to
364 that for Zn, with almost no erratic points (one for Fe at 2 mm; 0.5 g). For the Ni and Co data
365 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
369 from 14% to 23%, 27% and 28%. The erratic points for Ni and Co came from the same
370 digestion sample. The fine particles are more likely to be well disseminated in the shredded
371 sample, and are responsible for a background grade of around 311 ppm for Co, 0.45% for Ni
372 and 14% for Fe. In contrast, the presence or absence of coarse particles mainly made up of
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
375 points is very similar to the “gold nugget effect” found in assessments of gold deposits
376 (Dominy et al., 2018). The Ni anomaly [200 μm ; 0.5 g] is more problematic and shows that
377 anomalies can exist even for the finest sample analysed for Ni. Although these erratic points
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 occur
381 but that they are likely to be less present.

382 3.5. Modelling the confidence level

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

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

405 For all metals, the best preparation condition to achieve a low margin of error (< 10%) was
406 the finest particle size of 200 μm and few repetitions (3 or 4) of 2 g sample digestion.
407 However, to avoid the difficulty of shredding WPCBs to 200 μm , the 750 μm particle size was
408 found to be acceptable, provided that the sample mass used for digestion was larger than
409 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
417 not possible to predict the upper and the lower bounds for a new mean value by directly
418 using the margin of error from the bootstrap results. However, it is possible to make the
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
423 normal distribution hypothesis”) and the comparison with the real bounds obtained with the
424 bootstrap tool (“bootstrap data”), along with the “normal distribution error”, which refers to
425 the gap between the normal distribution hypothesis and the bootstrap data (see figure 5).
426 Only results for a 0.5 g sample mass are presented here; those for other sample masses can
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
430 conditions give a deviation lower than 9% if a triplicate sample is analysed. However, at 2
431 mm, the lower bound presents some significant differences for all metals except Cu. The
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
436 smaller particle sizes (11.6 and 14.3% for Ni at 750 μm and 200 μm respectively).

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

442 4. Conclusion

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

447 A series of 9 preparation conditions for WPCB samples was analysed, producing a total of
448 159 data points per metal (Cu, Pb, Zn, Ni, Fe and Co), from which the effects of particle size,
449 sample mass and digestion repetition were investigated. For some metals, Ni, Co and Fe,
450 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
455 (particle size and sample mass used for analysis) and on their metal content. As expected,
456 the relative standard deviation increases when a larger particle size and a smaller sampling
457 mass are considered, in line with Gy's sampling theory developed for ore sampling. This
458 study quantifies these deviations when i) the particle sizes increase ii) the sample masses
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
461 processing of the data through bootstrapping allowed this quantification to be taken further
462 and revealed that large uncertainties remain over metal concentrations if samples are not
463 ground sufficiently finely, and if only a limited number of digestions are performed. These
464 relatively large uncertainties, in comparison with ore, are associated with the highly
465 heterogeneous compositions that exist in WPCBs. This study underlines the need to pay
466 specific attention to these heterogeneities.

467 From statistical analysis of the data, the margin of error was predicted as a function of the
468 sample mass, the particle size and the number of digestion repetitions. Experimenters need
469 to consider the most reasonable balance between these three parameters, according to data
470 quality objectives. The compromise achieved will differ from one metal to another and from
471 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.

475

476 Acknowledgments: This study was carried out under the French FOAMEX research project,
477 funded by the French National Research Agency (ANR).

478

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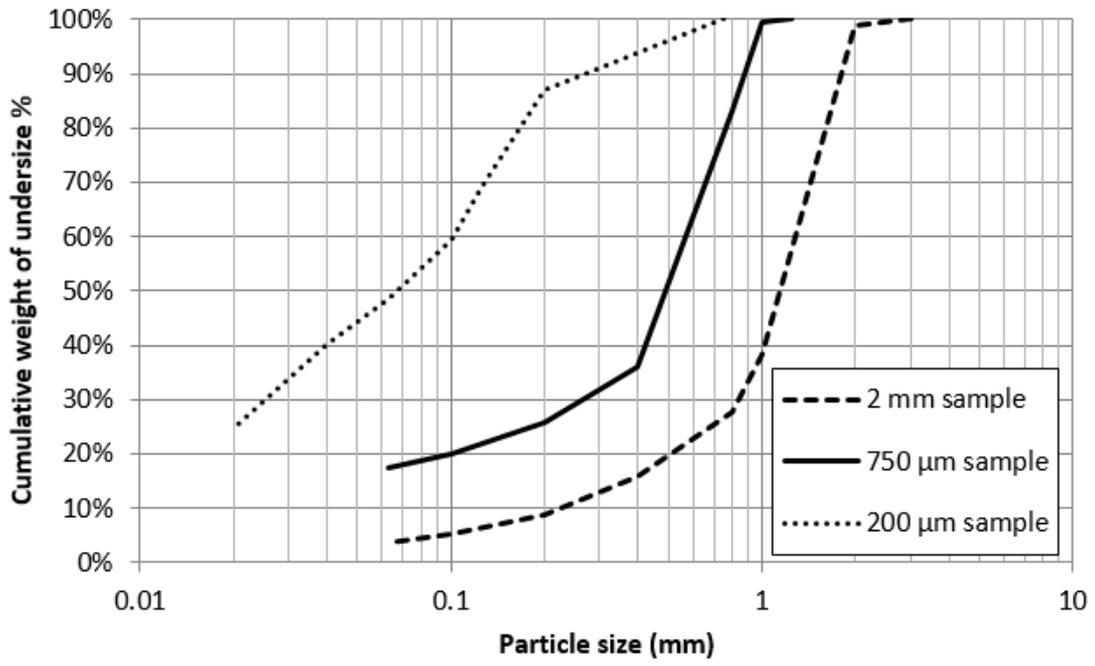
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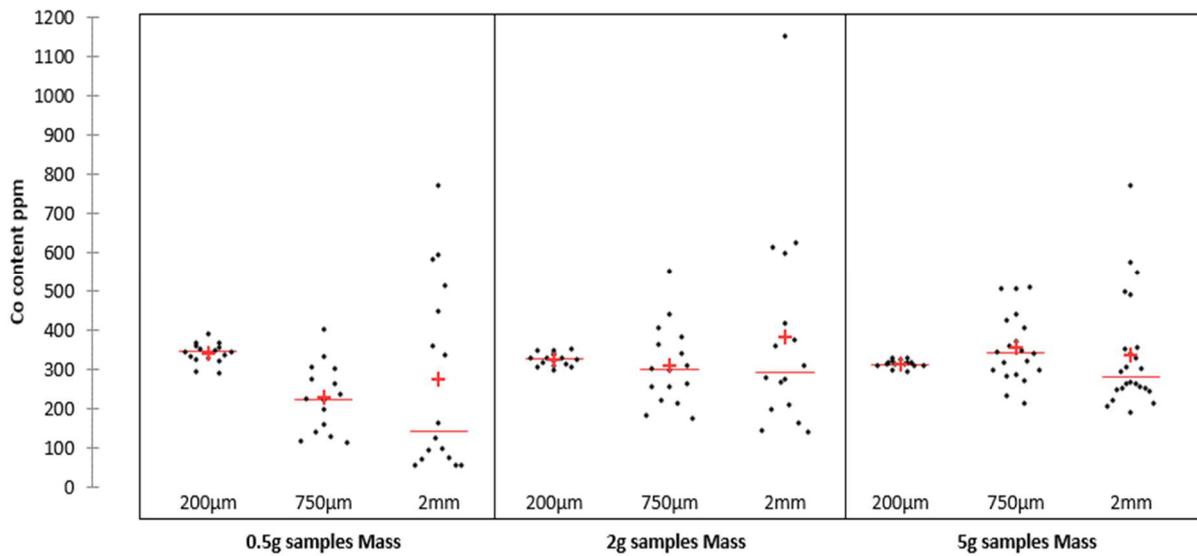
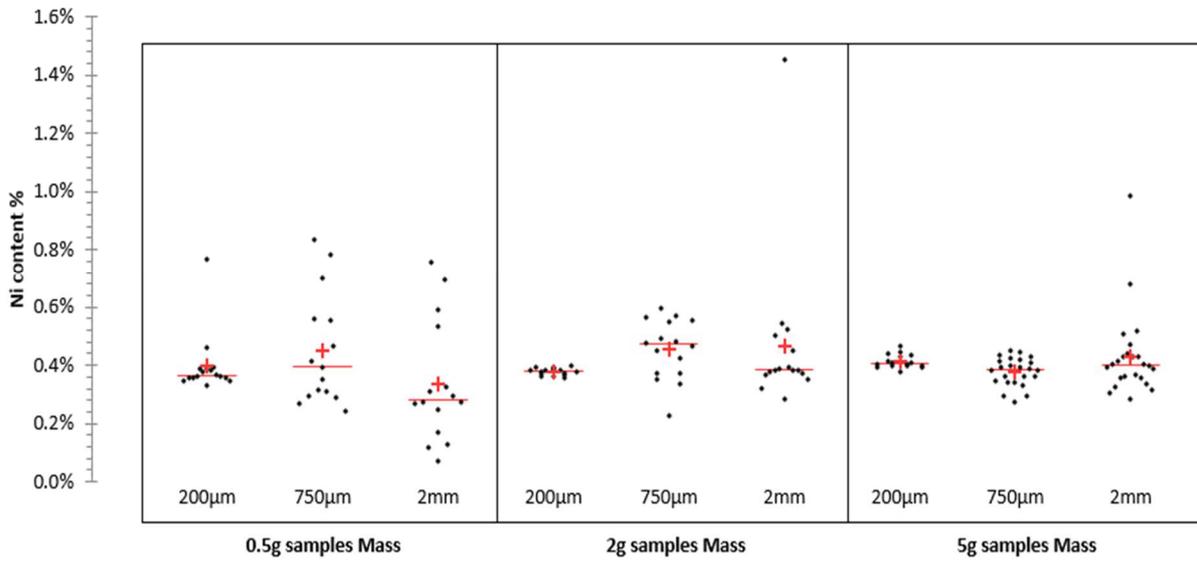
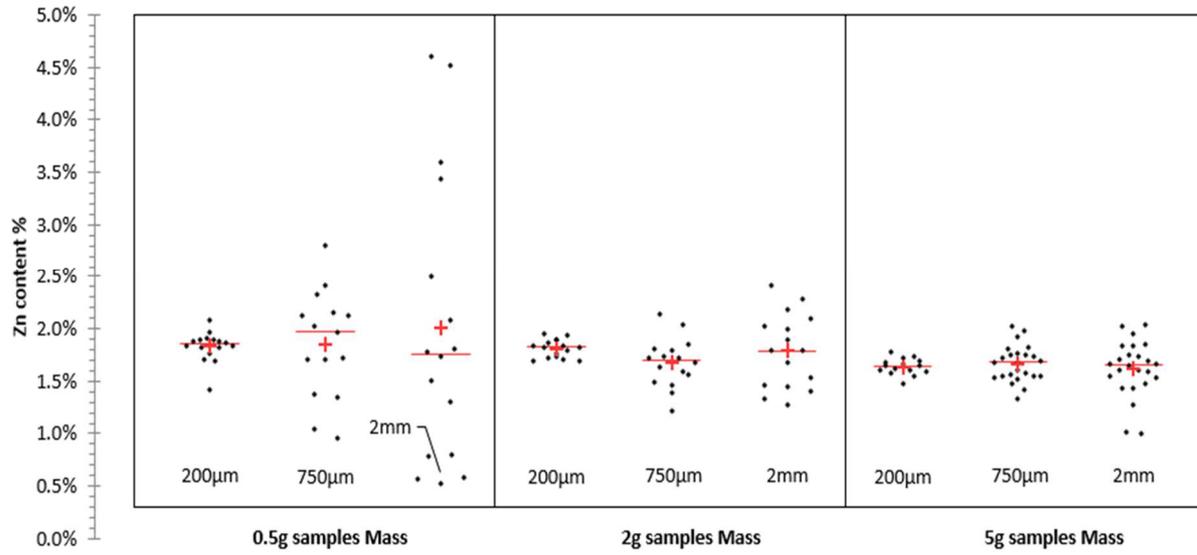
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588 Figure 1: Sampling and shredding procedure.



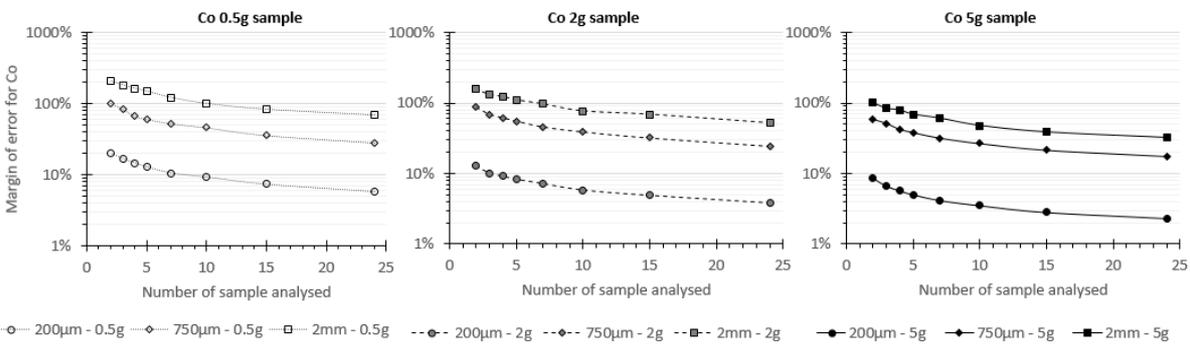
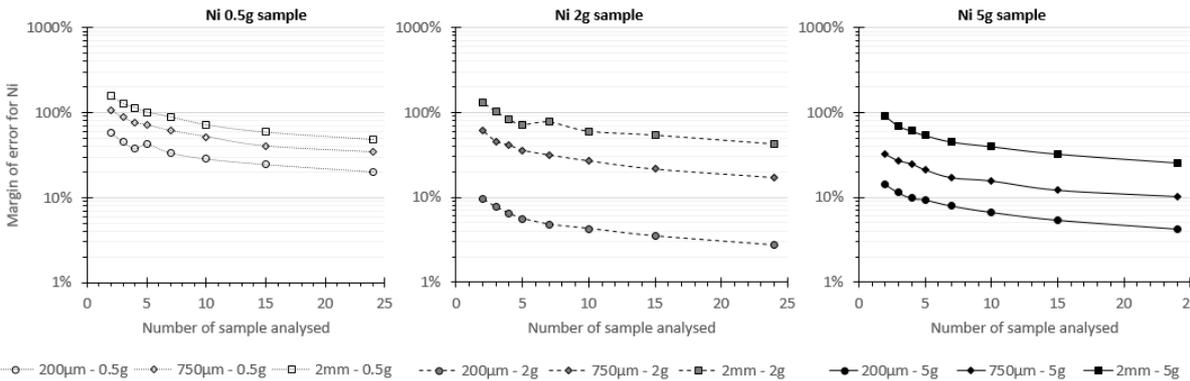
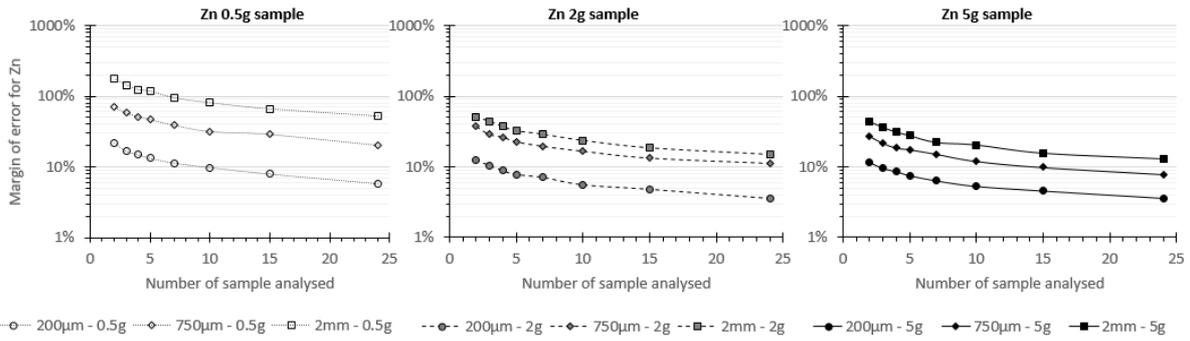
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590 Figure 2: Particle size distributions for the 200 μm, 750 μm and 2 mm samples.

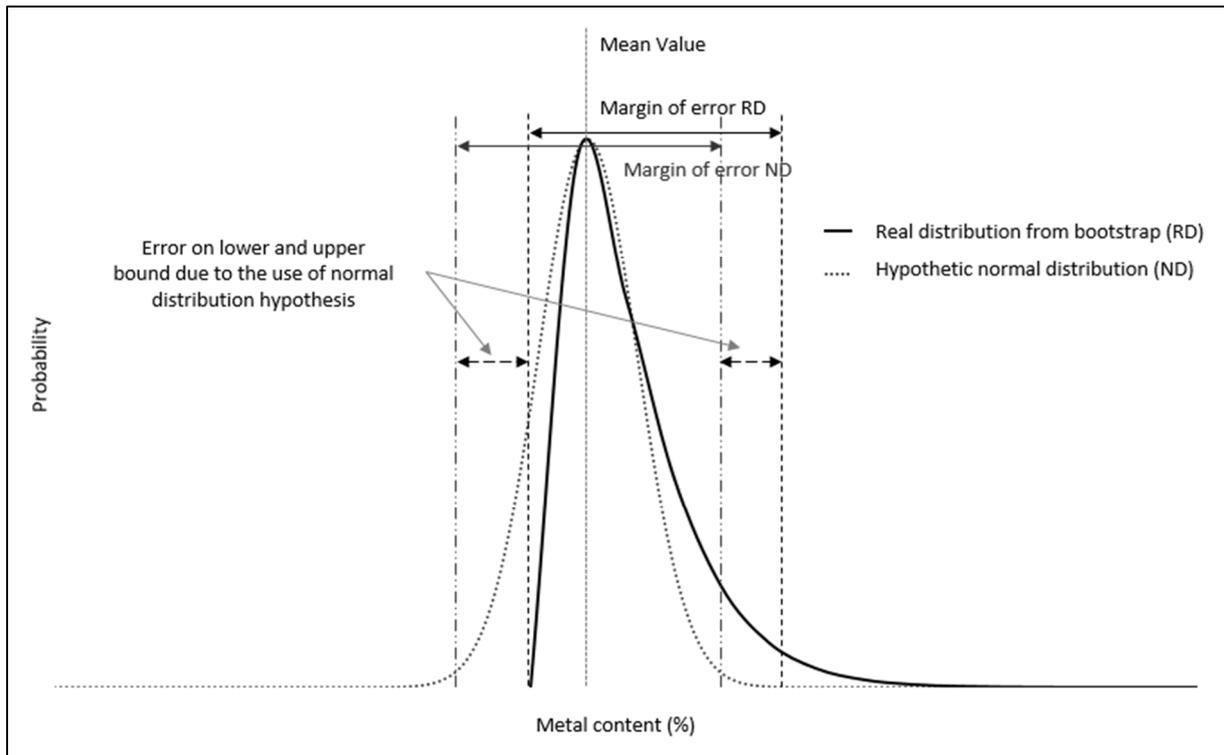


592 Figure 3: Scatterplots for Zn, Ni and Co content in WPCB according to particle size and
593 sample mass. The lines and crosses represent median and mean values respectively.

594



598 Figure 4: Margin of error for the mean values for Zn (upper figures), Ni (middle figures) and
 599 Co (lower figures) with samples of 0.5 g (left), 2 g (middle) and 5 g (right).



600

601 Figure 5: Comparison of the 95% confidence interval from a normal distribution and a real
 602 distribution obtained by bootstrapping.

603

604 Tables

Metal content	0.5 g			2 g			5g		
	200	750	2	200	750	2	200	750	2
	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
Co ppm	342	229	275	326	312	383	315	355	336

605

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

607

Relative Standard Deviation	0.5g			2g			5g		
	200µm	750µm	2mm	200µm	750µm	2mm	200µm	750µm	2mm
Cu	5%	9%	24%	3%	11%	11%	3%	6%	7%
Fe	5%	18%	50%	5%	13%	14%	4%	5%	9%
Pb	2%	28%	58%	2%	14%	22%	4%	9%	13%
Zn	8%	28%	68%	5%	14%	20%	5%	10%	16%
Ni	26%	43%	61%	3%	23%	58%	6%	13%	34%
Co	8%	38%	87%	5%	33%	68%	3%	25%	42%

608

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

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

611 Table 3: Comparison between upper and lower bounds from the normal distribution hypothesis and from bootstrap data for triplicates of 0.5 g
612 sample mass and particle sizes of 200 µm, 750 µm and 2 mm.

613