

Estimation of uncertainty for measuring metals content in waste printed circuit boards

A. Hubau^a, S. Touzé^b, S. Brochot^c and P. Wavrer^d

^aBRGM – 3 avenue Claude Guillemin BP36009 – 45060 Orléans - France. E-mail: a.hubau@brgm.fr

^bBRGM – 3 avenue Claude Guillemin BP36009 – 45060 Orléans - France. E-mail: s.touze@brgm.fr

^cCASPEO – 3 avenue Claude Guillemin BP36009 – 45060 Orléans - France. E-mail: s.brochot@caspeo.net

^dCASPEO – 3 avenue Claude Guillemin BP36009 – 45060 Orléans - France. E-mail: p.wavrer@caspeo.net

The amount of waste printed circuit boards (WPCBs) currently represent a fast-growing issue that must be properly managed to limit their impact on the environment and human health. Due to their metal content, they can also be considered as a resource. Their characterization is a key point for evaluating different valorisation processes. The conventional methodologies to characterize wastes and/or metal resources are hardly applicable to such waste, as they are highly heterogeneous, difficult to micronize, and their individual components (plastics, glass, ceramics, and metals) are hard to liberate. Thus, in parallel to developing analytical tools that allow their accurate characterization, a sampling strategy suitable for WPCBs must also be established. In this study, an empirical approach was developed that aims at estimating the uncertainty arising from sampling WPCBs. To do so, the duplicate method of uncertainty estimation was followed, to compare the metal content in different sub-samples and to determine confidence intervals.

Introduction

Waste printed circuit boards (WPCBs) are gaining increasing importance due to their high metal content (around 30 to 40 wt%) and the increase of volumes that are produced. They are thus considered as a secondary resource, but also as potentially harmful wastes requiring to be handled with caution. While many studies deal with the development of new processes to valorise these wastes, there is very few studies dealing with the establishment of a sampling strategy enabling to obtain representative and reproducible samples. Three challenges are arising when developing a WPCBs sampling strategy. First, it is difficult to decrease the particle size of WPCBs. This issue is mainly linked to the presence of ductile metals, preventing the use of most of the conventional shredding and grinding equipment. The wet grinding processes produce wastewater that must be treated, while dry grinding processes produce dust, causing a potential loss of precious metals, as well as an increase of temperature that probably leads to the partial degradation of resins and plastics¹. Secondly, these wastes are very heterogeneous, with a composition that changes over time. Some of the constituting materials (plastics, resins, glass, ceramics and metals) are embedded or diluted (as alloys) in other materials, preventing their complete liberation. There is also a large range of metal content, with metals that are highly concentrated (as Cu, with a content reaching up to 20 %w/w) or that are only present in PCBs as trace elements (as Pt, with less than 10 mg.kg⁻¹). Finally, the last point concerns the lack of reference material, preventing to assess analytical uncertainty.

To the authors' knowledge, as of date, there is no adjustment of the Theory of Sampling (TOS) for WPCBs. The sampling strategies that are available in the literature on this material are mainly based on very small samples (around ten kilograms of WPCBs from a single batch at most) and are evaluating the quality of the last sampling step (production of the test portion used for the analysis). They are also based on pyrometallurgical approaches to reduce grinding issues and sample mass. However, this last strategy is not applicable when aiming at obtaining representative samples of WPCBs containing intact non-metal fractions (plastics and resins). Moreover, the quality of sampling is not evaluated in most of these studies. Due to the high heterogeneity of this material and the difficulty to obtain a complete liberation of constituting elements, the modelling approach to quantify the uncertainty, such as the one developed by Pierre Gy, is not applicable to the best of current knowledge, as there are no data available in the literature on the liberation factor, shape factor or constitution factor.

In this study, an empirical approach was chosen to estimate the uncertainty arising from sampling WPCBs. To do so, the duplicate method was applied to a unique batch of around 500 kg of WPCBs. As recommended in the Eurachem guide on measurement uncertainty², the measurements of metal contents in WPCBs samples were replicated after successive shredding and subsampling steps (see Figure 1) and uncertainties were estimated at different levels of the sampling plan. To do so, the content of six metals (Cu, Fe, Ni, Zn, Pb and Co) was determined for two laboratory samples (LS) of 4 kg of -10 mm WPCBs. These two laboratory samples were ground to minus 750 µm and two 40 g test samples (TS) were taken for each. Each duplicate test sample was divided into 8 test portions (TP) which were analysed (Figure 1).

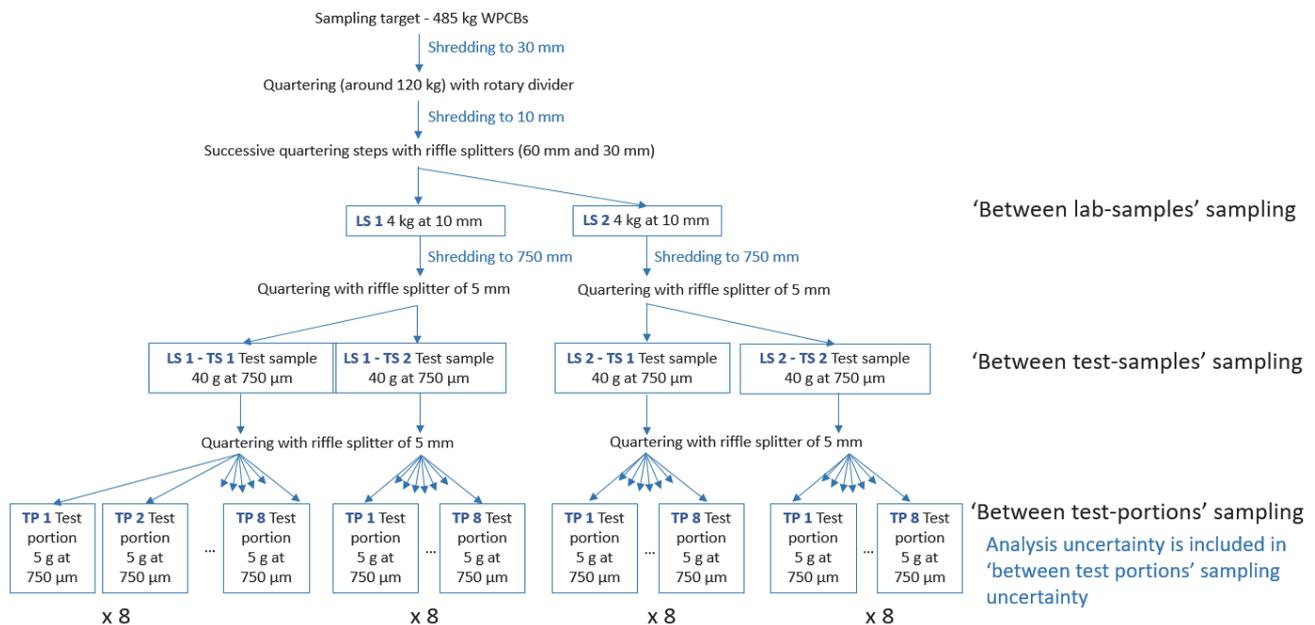


Figure 1. Sampling plan used in this study.

The sampling quality of “between laboratory samples (LS)”, “between test samples (TS)” and “between test portions (TP)” was evaluated. Some statistical tools were used to determine if the mean values of the test samples were significantly different. Variances and standard deviations were calculated and the contributions of “between test portions” sampling, “between test samples” sampling and “between laboratory samples” sampling to the total uncertainty were determined for each metal. Finally, intervals for the metal content values at 95 % confidence level were determined. The goal was to provide insights in the quality of sampling and to assess the reproducibility of the composition of sub-samples for further work on the development of WPCBs recycling technologies. From this study, a new sampling plan for extra batches of WPCBs could be designed.

Materials and methods

WPCBs sample, sampling and characterization

WPCBs used in this study were provided by a French recycling company, from the small waste electrical and electronic equipment category (mix of appliances such as computer, audio and video equipment, toys, personal care products, small kitchen appliances, etc.). The whole methodology used for sampling the 526 kg batch of WPCBs was previously detailed in Hubau *et al.* (2019)³ and is given in Figure 1. Photographs of samples are given in Figure 2.



Figure 2. WPCBs samples (raw material, -30 mm, -10 mm, -2 mm and -750 µm, from left to right).

To determine metal contents, each test portion was digested with aqua regia (HNO₃:HCl 1:3) with a solid to liquid ratio of 1:11 w/v. The digestions were performed using a Kjeldatherm-Gerhardt digestion system, maintaining the aqua regia at reflux for 2 hours. After solid-liquid separation, leachates were analysed by flame atomic absorption spectrometer (Varian SpectrAA-300). The efficiency of aqua regia digestion for such wastes has been previously demonstrated^{3,4} (less than 2 wt.% of Cu, Zn, Sn, Pb, Co and Pd are undissolved, and less than 7 wt.% for other metals, except for Ta). The same operator performed all the grinding, quartering, digestion and analysis operations for all of the 32 test portions. In this study, the observed variability both includes the uncertainty arising from the sampling steps (TSE) as well as the total analytical error (TAE estimation is described elsewhere⁵).

Statistical tools

After determining the standard deviation on the 32 measurements for each metal, it appears that the relative standard deviation is very large for Co (22.3 %) (Table 4). It is thus better to consider the natural logarithm of metal content values for the calculation of the uncertainty factors and for the application of statistic tests, as recommended by Eurachem guide². Shapiro-Wilk tests were performed on these values to ensure that the hypothesis of log-normal distribution for metal contents cannot be rejected. For this study, the significance level for the p-value was fixed to 0.05. As demonstrated in Table 1,

hypothesis of log-normal distribution for metal contents in all the 32 test portions cannot be rejected. The hypothesis of normal distribution cannot be rejected too, while it is more difficult to conclude for Fe. These tests were also performed within each test sample (n = 8, data not shown) and similar results were obtained.

Table 1. p-values obtained with normal and log-normal distributions of metal contents when considering the 32 test portions.

Distribution	Cu	Fe	Zn	Pb	Ni	Co
Normal	0.657	0.067	0.884	0.200	0.489	0.204
Log-normal	0.662	0.172	0.802	0.614	0.210	0.766

Shapiro-Wilk tests were also performed on the residuals (difference between measured values and their estimates with the log-normal distribution), for which the hypothesis of normal distributions cannot be rejected, allowing to use ANOVA tool (Excel Stat 2019.3.2). Tukey tests of pairwise comparison were used to compare the mean values of each test sample. The significance level for Tukey test was fixed to 0.05.

Variance, standard deviation and uncertainty factor calculations

The calculation of variance was performed following the Eurachem guide methodology². Variance can be calculated when a reasonable number of values are studied. However, as a misuse of language, Eurachem guide uses the term of variance for low number of samples (even 2) and this terminology was thus used in our study.

The formulas used to estimate the variance arising from “between test portions” sampling, from “between test samples” sampling and from “between laboratory samples” sampling are given in Table 2, with $x_{i,j,k}$ referring to the natural logarithm of the metal content in the test portion k, from test sample j, from laboratory sample i.

Table 2. Formula used to calculate the sum of squares, degree of freedom and variance for TP, TS and LS sampling stages.

Formula	“Between test portions” sampling	“Between test samples” sampling	“Between laboratory samples” sampling
Mean value	$\bar{x}_{ij} = \frac{1}{N_{TP}} \sum_{k=1}^{N_{TP}} x_{ijk}$	$\bar{x}_i = \frac{1}{N_{TS}} \sum_{j=1}^{N_{TS}} \bar{x}_{ij}$	$\bar{x} = \frac{1}{N_{LS}} \sum_{i=1}^{N_{LS}} \bar{x}_i$
Sum of squares SS	$SS_{TP} = \sum_{i=1}^{N_{LS}} \sum_{j=1}^{N_{TS}} \sum_{k=1}^{N_{LS}} (x_{ijk} - \bar{x}_{ij})^2$	$SS_{TS} = \sum_{i=1}^{N_{LS}} \sum_{j=1}^{N_{TS}} \sum_{k=1}^{N_{LS}} (\bar{x}_{ij} - \bar{x}_i)^2$	$SS_{LS} = \sum_{i=1}^{N_{LS}} \sum_{j=1}^{N_{TS}} \sum_{k=1}^{N_{LS}} (\bar{x}_i - \bar{x})^2$
Degree of freedom df	$df_{TP} = N_{LS}N_{TS}(N_{TP} - 1)$	$df_{TS} = N_{LS}(N_{TS} - 1)$	$df_{LS} = N_{LS} - 1$
Variance Var	$Var_{TP} = \frac{SS_{TP}}{df_{TP}}$	$Var_{TS} = \frac{1}{N_{TP}} \left(\frac{SS_{TS}}{df_{TS}} - \frac{SS_{TP}}{df_{TP}} \right)$	$Var_{LS} = \frac{1}{N_{TP}N_{TS}} \left(\frac{SS_{LS}}{df_{LS}} - \frac{SS_{TS}}{df_{TS}} \right)$

For this study, N_{TP} , N_{TS} and N_{LS} refers to the number of test portions (8), test samples (2) and laboratory samples (2) respectively, with the indices k, j and i respectively, x_{ijk} being the logarithm of content in the TP k of TS j of LS i.

From this, the standard deviation (SD), the relative standard deviation (RSD), the expanded uncertainty factor (F_U) and the limits for confidence interval for each contribution were calculated as follow (example given for TP sampling):

$$SD_{TP} = \sqrt{Var_{TP}}$$

$$RSD_{TP} = \frac{SD_{TP}}{\bar{x}}$$

$$F_{U_{TP}} = e^{2SD_{TP}}$$

$$\text{Lower confidence interval limit} = \frac{\bar{x}}{F_U} \text{ and Upper confidence interval limit} = F_U \cdot \bar{x}$$

For the expanded uncertainty factor, the coverage factor of 2 enables approximately a 95 % confidence on the calculated interval. When the calculated variance estimator is negative, it is supposed to be null.

Results

Pairwise comparison of mean values

The pairwise comparison of mean values was used to compare the metal contents of the test samples and determine if significant differences exist between mean values that could reveal a bias during the “between laboratory samples” sampling. To express the results of this Tukey test, mean values are associated to a group: two values are not in the same group if their mean values are significantly different (see Table 3). For example, Cu, Ni and Co mean values are all in the same group, meaning that there is no significant difference between mean values for the 4 test samples.

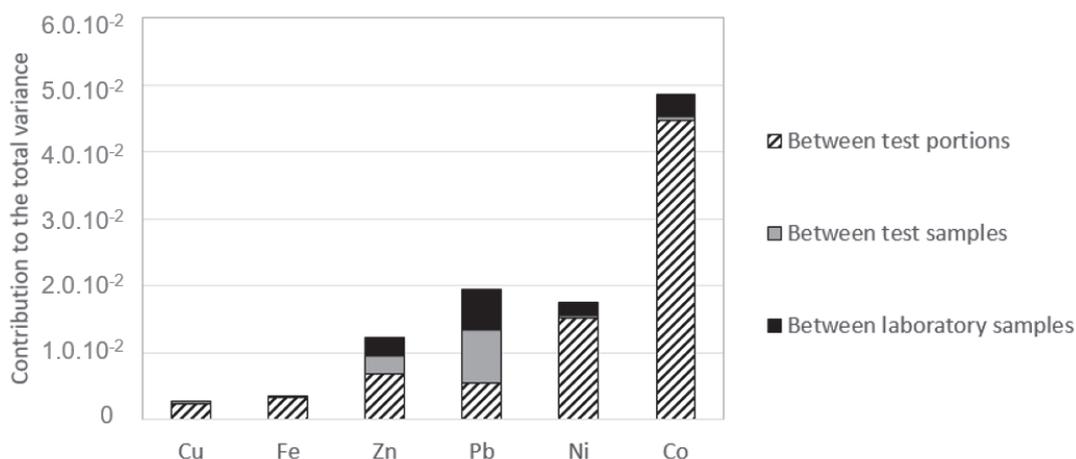
Table 3. Mean value of metal content and results of the pairwise comparison of mean values from test portions with Tukey test.

Metal	Cu	Fe	Zn	Pb	Ni	Co
Mean value (n=32)	15.4 %	12.5 %	1.68 %	1.23 %	3800 mg.kg ⁻¹	350 mg.kg ⁻¹
Test sample	Groups					
LS1-TS1 (n=8)	1	1-2	1	1	1	1
LS1-TS2(n=8)	1	1	1-2	2	1	1
LS2-TS1 (n=8)	1	1	2	2	1	1
LS2-TS2 (n=8)	1	2	1-2	3	1	1

For Fe and Zn, two different groups are observed, which means that there are some significant variations between mean values of some samples. However, the distribution between groups is not the same for both metals and some mean values are belonging to both groups. For Pb, there is a significant difference of mean values for all samples, except for LS1-TS2 and LS2-TS1 mean values. This distribution between groups is not linked to the laboratory sample from which they are originated, thus enabling to conclude that there is a sufficient degree of reproducibility between the laboratory samples (4 kg samples with particle size less than 10 mm). The variations observed between test samples are not caused by a bias during “between laboratory samples” sampling.

Variance calculations

Following the duplicate methodology, it was possible to partition the total variance, to determine the contribution of all the studied sampling steps to the total variance. The total variance, given in Table 4, increases with decreasing metal content: Cu total variance is 0.00281 while its mean content is around 15.4 % (w/w), while it reaches 0.0485 for Co, which is much less concentrated in WPCBs (mean content around 350 mg.kg⁻¹). The contribution of each sampling step variance to the total variance is given in Figure 3. Three classes of metals can be distinguished, correlated to their contents in WPCBs.

**Figure 3. Components of the variance of the logarithm of content for LS, TS and TP sampling stages contributions for the six metals.**

For Cu and Fe, the uncertainty arising from “between laboratory samples” sampling is calculated as zero, meaning that it is negligible compared to other contributions. This may be due to their high content in WPCBs and that for each piece of board, thus enabling a good distribution between the 4 kg samples at 10 mm. On the contrary, the “between test portions” sampling mainly contributes to the total variance. Two main hypotheses can explain this result: (i) first, this variance both includes the variance from analysis and from the “between test portions” sampling (this hypothesis is valid for all metals). This hypothesis and the corresponding uncertainty analysis is investigated and presented in another paper of WCSB10 proceeding⁵. (ii) Secondly, Fe and Cu are mainly present as coarse particles, with very high content, which are not easy to grind and are thus largely distributed in the -800 + 400 μm size fraction of the samples⁶. With these large particle sizes highly liberated, their distribution between the 5 g samples (test portions) may not be homogeneous, thus leading to the high contribution of the “between test portions” sampling step into the total variance.

For Zn and Pb, with mean contents reaching around 1.5 % (w/w), the contribution of the three sampling steps to the total variance are of the same magnitude. As previously observed with pairwise comparison of mean values, their distribution between the 4 kg sub-samples (laboratory samples) may already differ.

For Co and Ni, it appears that the “between test samples” sampling does not largely contribute to the total variance. The “between test portions” sampling is the main contributor of the variance, while there is also a contribution from the “between laboratory samples” sampling. Ni and Co are used as small batteries in WPCBs, which are supposed to be removed during the depollution of WPCBs (however not the case in this study). Ni may also be originated from stainless steel. In the -10 mm laboratory samples, there might be intact small batteries that are not equally distributed between samples, creating some variations due to nugget effect. That could cause the high values of “between laboratory samples” variances observed for Ni and Co compared to other metals. In the 5 g test portions, previous study⁴ showed that erratic points might be observed for Ni and Co, maybe also due to the “nugget” effect, i.e., the occurrence of one or several tiny single flakes of concentrated metal in one test portion (however not observed at 750 μm in their study). These erratic points, which were not observed for Zn, Cu and Pb, might explain the large variance arising from “between test portions” sampling for Ni and Co.

These results show that the uncertainty is mainly due to the last sampling step (TP), except for Pb. It is therefore necessary to work on this step to reduce significantly the total uncertainty. Besides working on analysis uncertainties, it is possible to increase the mass of TP and/or decrease its particle size.

As observed by other authors⁷, the use of less than eight duplicates may increase the uncertainty on variance estimates. In this study, it could be very useful to supplement the data with other laboratory and test samples characterization. It is nevertheless interesting to see that for most metals that are studied, the highest uncertainty contribution originates from the sampling step with the larger number of replicates.

Uncertainty factor and 95 % confidence interval limits

From the total variance, the expanded uncertainty factor was calculated, then enabling to calculate the limits of the interval in which 95 % of the values of metal contents should be comprised. Results are given in Table 4. These intervals are not centred on the mean value as a log-normal distribution was used. As the objective of this study is to characterize the reproducibility of samples to use them for further developments of metal recovery processes, the knowledge of metal contents intervals helps to better characterize the initial content and thus the efficiency of the processes that are developed.

Table 4. Mean content, relative standard deviation (RSD), total variance, total uncertainty factor and 95 % confidence interval limits for the six metals.

	Metal content in %(w/w)				Metal content in mg.kg ⁻¹	
	Cu	Fe	Zn	Pb	Ni	Co
Mean value of metal content	15.4	12.5	1.68	1.23	3752	350
RSD (%)	5.8	6.9	10.3	12.5	13.3	22.3
Total variance*	2.81.10 ⁻³	3.55.10 ⁻³	1.22.10 ⁻²	1.94.10 ⁻²	1.75.10 ⁻²	4.85.10 ⁻²
Total uncertainty factor	1.11	1.13	1.25	1.32	1.30	1.55
95 % confidence interval limits	13.8 - 17.1	11.1 - 14.1	1.34 - 2.08	0.93 - 1.62	2850 - 4850	220 - 530

* The total variance is calculated with the natural logarithm of metal content values, as explained in the Material and Methods section.

The width of these intervals is limited for Cu, Fe and Zn. However, for Pb, Ni and Co, these intervals are quite large. Two options emerge. For valuable metals that are in the scope of the process development, mass balances based on fine characterization of the outputs of the developed process are required to obtain accurate efficiency yields of the process. For other elements that are not targeted in the process but that may affect its efficiency, the knowledge of these intervals may be sufficient.

Conclusion

This study gives an overview of the application of variance analysis to the sampling of WPCBs which are highly heterogeneous materials. From the pairwise comparison of the mean values, the calculation of variances and the determination of 95% confidence interval limits, this study assessed the quality of the WPCBs sampling plan that was used.

It appears that the “between laboratory samples” sampling (4 kg with particle size lower than 10 mm) partially contributes to the uncertainty. However, the distribution of metals in the two different laboratory samples that are studied was not highly affected by this sampling step. It would be of interest to increase the number of replicates at this step to confirm this result.

For most metals, the sampling of the test samples (40 g with particle size lower than 750 µm) does not highly contribute to the uncertainty on the metal content compared to the sampling of the test portions (5 g with particle size lower than 750 µm) as expected. The uncertainty calculated both arose from sampling and analysis. Based on a bootstrap strategy, previous work based on this last step evaluated the interest of replicating the test portions to reduce the uncertainty on metal content determination⁴. To do so, three test portion masses were used (0.5 g, 2 g, and 5 g) as well as three top particle sizes (200 µm, 750 µm and 2 mm). It concluded that for 5 g test portions, a 200 µm fineness drastically reduces the width of intervals in which metal content values are comprised, while a 750 µm fineness is a good compromise (when considering the time and energy consumption of the pulverizing step from 750 to 200 µm). That is consistent with the fundamentals of TOS: particle size, or diameter of the largest particles, must be reduced before reducing the sample mass if one do not want to increase the Fundamental Sampling Error (FSE). Nevertheless, the observed differences in variability cannot be only explained with this FSE approach⁵.

To go further, it could be interesting to consider trace elements that are valuable in WPCBs (critical metals such as Ga, Ta, Nd, La, Au, Pt, Pd). This will be in the scope of the MetroCycleEU project⁸ funded by EMPIR EURAMET initiative, in which a similar sampling strategy will be developed and evaluated.

ORCID iDs

A. Hubau: <https://orcid.org/0000-0002-3896-7220>

S. Touzé: <https://orcid.org/0000-0002-0840-4494>

S. Brochet: <https://orcid.org/0000-0002-9015-9693>

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