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Research Paper

Estimation of the uncertainty of metal content in a batch of waste printed circuit boards from computer motherboards

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ABSTRACT

Electronic wastes are a valuable resource due to their critical and precious metal content. To include these wastes in recycling or recovery chains, it is necessary to precisely determine their metal content. Because analysing the whole sample of a batch of electronic waste is not practical, different preparation and sampling or subsampling steps are necessary. Sampling induces an error in the composition of the final sample compared to that of the initial batch, which finally leads to uncertainty in the final metal content measurement as compared to the “actual” batch metal content. The aim was to characterize the uncertainty in metal content of a batch of 372 kg of WPCB. Thirty-nine metals were analysed and thirty-two were considered: base, precious, rare-earths and critical metals. An empirical method (i.e. replicated measurement tests) was thus applied, based on statistical calculations according to Eurachem Guidelines. Uncertainty arising during the 3 different stages of the preparation process (primary, secondly and tertiary sampling steps) was calculated. For the analysed given weight (0.5 g), the shredding efficiency, which directly affects metal particle size distribution, was found to be the most important factor influencing the uncertainty. Uncertainties in base metal content, which is often concentrated in the coarsest particles, arose mainly from the last preparation step (tertiary sampling). Conversely, precious metals and rare-earths were finely ground during the 3 preparation steps, which led to low uncertainties, despite their low concentration in the waste (<337 mg/t for precious and < 35 mg/t for rare-earths).

1. Introduction

1.1. Printed circuit boards

Metals from Waste Electrical and Electronic Equipment (WEEE) are a new source of raw material. In the current context of depletion of natural resources and the need to save them, it is essential to exploit these “urban mines”. In WEEE, Waste Printed Circuit Boards (WPCB) concentrate the non-ferrous metals and are thus of interest. Over the last few years, the increasing volume of WPCB from electronic waste has made recycling financially viable. The French environmental agency (ADEME) published a report in 2022 on the collection and treatment of WEEE (ADEME 2022). In this document, agency indicated that 9581 t of WPCB from household WEEE were declared as specific waste in 2021 in France. The agency indicated that these figures are likely underestimated due to incorrect reporting and the existence of an illegal market. The market for “high-grade WPCB” (WPCB with an amount of

gold > 100 ppm) was driven by gold and copper content while the “low-grade WPCB” market was driven by copper content. The majority of WPCB is processed in copper smelters (D’Adamo et al., 2019). In Europe, the main operators are Glencore, Umicore, Aurubis and Boliden. They recover numerous metals such as copper, lead, nickel, gold, silver, platinum, etc. from their mixture of waste (electronic scrap (e-scrap), industrial scraps, spent rechargeable batteries, catalytic converters, etc.).

1.2. Knowledge on WPCB composition

To assess the proportion of recoverable metal, it is essential to have information on the metal content of these materials at different stages in the industrial processes (i.e. waste financial value, process adjustments, loss quantification, etc.). Reliable chemical characterization of WPCB is thus necessary. As the whole batch (also called sampling target) cannot be analysed, most of the time, the process generally starts with a primary

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subsampling, i.e. the taking of a primary sample that is supposed to represent the sampling target (Ramsey and Ellison, 2019). This primary subsample undergoes processing steps which include different physical preparation steps which lead finally to the laboratory sample and more precisely to the analytical portion that will be digested.

The analysis of metals, whether highly or poorly concentrated, is a first challenge with respect to WPCB, since they are highly-heterogeneous composite materials. The complete digestion of such complex mixtures of elements or materials is a major challenge. In previous years, some studies focused on the development of analytical protocols for determining the composition of WPCB samples: Wienold et al. (2011) and Andrade et al. (2019) tested several solvents in the leaching step and they stated that the aqua regia digestion method (connected to inductively coupled plasma optical emission spectrometry, ICP-OES) exhibited superior leaching efficiency and yielded optimal outcomes for numerous metals elements for the examination of WEEE.

To fulfill the basic requirements for decision-making processes, a reliable method for determining the uncertainty in estimates of the metal content of these wastes is necessary. This uncertainty calculation has to take into account the heterogeneity of the material, since heterogeneity cannot be eliminated, only limited. Sampling uncertainty at the different steps of the measurement process is therefore a key issue. As a reminder, uncertainty does not represent the difference between the measured and the unknown true value, but it is an interval that includes all the possible results of the measurement at a chosen confidence level.

Even if sampling rules are fully complied with, it is not possible to produce a perfectly representative sample; a sub-sample is never exactly the same as the target. This fact gives rise to a measurement variation between the sample and the target, which creates uncertainty due to sampling. Determining the sampling uncertainty associated with the measurement of the metal content of a batch of WPCB is currently a challenge.

As part of the EU project MetroCycleEU, metrological institutes throughout Europe are working to find ways of meeting the two challenges (i.e. analytical developments and uncertainty evaluation). The project focuses in particular on technology-critical elements (Co, Ga, Ge, In, Ta, Nd, Pr, Dy, Gd, La, Au, Pt, Pd, Rh) in different urban mine wastes (WPCB, light-emitting diodes and batteries) (MetroCycleEU project, 2020). The objectives are to compare the analytical methodologies, as well as to determine a sampling strategy for WPCB, to help stakeholders obtain accurate information on urban mine contents.

1.3. Sampling and sampling uncertainty

1.3.1. Current WPCB sampling strategies

After being thrown away, WEEE are collected and sorted. WPCB are separated from other materials. Afterwards, they may be manually sorted according to their grade (content in precious metals). Once a sufficient number of WPCB has been collected (the minimum recommended volume is from a few tonnes to 10 tonnes according to Umicore and Mitsubishi Materials Metal Recycling (MMMR) websites – 2024), most WPCB batches are sold to smelter companies for metal recovery. Their prices are determined by the extent to which they contain copper and/or precious metals. Each WPCB batch should thus be considered as a sampling target for which an accurate knowledge of their precious metals and Cu content is required. To do so, smelter companies most of the time first prepare sub-samples (primary sampling) of a few kilograms with a particle size reduced to a few millimetres; it is the primary sampling. The samples are then sent to laboratories to determine their metal content. The samples for assay (a few kg with particles a few mm in size) are routinely melted by means of a melting agent (fire assay). This method volatilizes metals which have a boiling temperature lower than the melting temperature (this could be the case for Zn, Sn, Pb, Cd, Mg alloys, As, Hg, Se and Rb). Two companies detailed publicly their sampling plan. They used mass reductions of the order of 1:1000 to

1:10,000 (Umicore, see Pauels, 2022, and MMMR website, 2024), their sampling plan are summarised in Fig. 2. However there is little information in the literature about their methodologies for determining metal content and there is no information on the corresponding sampling uncertainty. This method was developed for the analysis of copper and precious metals and its effectiveness on TCE metals is unknown. The fire assay was not used in this study, as it cannot be used for all metals.

In recent years, some scientific studies proposed a methodology for sampling and analysing WPCB. In particular, Hubau et al. (2019) and Touzé et al. (2020) detailed a sample preparation strategy based on the alternation of grinding and division steps. These preparations started from an original sample of approximately 500 kg of whole WPCB up to particle sizes of 750 µm for Hubau and 2 mm, 750 µm 200 µm for Touzé. The uncertainty related to the metal content of a batch of 485 kg of WPCB was then evaluated (Hubau et al., 2022). This methodology was however proposed for a limited number of metals (Cu, Fe, Zn, Ni, Co and Pb). For the 6 analysed metal, the uncertainty factor vary from 1.11 (Cu) to 1.55 (Co). Those first studies need to be confirmed on other batches and for a wider range of metals.

1.3.2. Methodologies to evaluate sampling uncertainty

There are two ways of estimating the uncertainty inherent in a sampling plan. The first scheme involves “*a priori*” sampling using Pierre Gy’s theory and formula (a bottom-up approach; Gy, 1979; Gy, 1992). This probabilistic approach is based on estimating all the contributions of all the steps of the measurement method to the uncertainty. Both the constitution and the distribution heterogeneities are considered. This method may be difficult to implement because scientists have to know all the sources of uncertainties beforehand. In particular, the nature of the material should be modelled. As WPCB compositions are complex, it is difficult to build a realistic material model.

The second strategy is based on “*a posteriori*” distribution (a top-down approach). From a set of data from a trial, uncertainties are calculated, without necessarily knowing any of the sources individually. The following sources of error are included: random errors from the sampling and analysis (i.e. precision), together with systematic errors (i.e. bias). The Eurachem/Citac guide (Ramsey and Ellison, 2019) contains methodologies that have been developed to assess the uncertainties arising from the random errors. In particular, it describes the duplicate method as one of the simplest and probably most cost-effective method for estimating uncertainty arising from sampling and analysis. The duplicate samples are obtained using a single sampling protocol carried out by a single person (sampler). Both duplicate samples are subject to physical preparation resulting in two separate samples. Duplicate portions are drawn from both samples and analysed in duplicate (i.e. duplicate chemical analysis). This system of duplicated sampling and chemical analysis on both samples is known as a ‘balanced design’. Note that the duplicate method does not include any contribution from sampling bias, which must be either assumed to be negligible, or estimated separately. Multiple samplers, multiple protocols and/or inter-organisational sampling trials can be used to estimate this bias.

1.4. Objectives of this article

This study first aimed to describe a new and efficient sampling and preparation methodology designed especially for WPCB. The sampling methodology was adjusted to the analysis constraints of permissible mass and particle size. Aqua regia digestion followed by ICP was applied to determine metal contents. The main objective was then to estimate the confidence interval on the concentration of around thirty-two metals in a whole batch sample of 372 kg of WPCB. An uncertainty factor was estimated according to the empirical approach using a replicate experiment. This experimental plan was used to estimate the relative contribution of each sampling step to the overall uncertainty. An experimental design with replicate data was set up.

2. Materials and methods

2.1. Sample

The WPCB used in this study were provided by a French recycling company (Valordis). They came from computer mother boards produced before 1994. The computers were collected in an industrial sorting chain where they were dismantled manually to extract the mother board WPCB. The batch taken (372 kg) was a part of a commercial batch produced by the recycler business; the mass ratio is around 1:50 (sample target mass was 372 kg while the batch sold by the recycler was around 20 t). The batch was prepared by the recycler. These WPCB are considered by recyclers to be rich in gold with content of 100 mg/kg.

2.2. Preparation

The whole sample (372 kg) was first shredded with an industrial shredder (a slow rotating Mecarocanne shredder with stainless steel shears) to a particle size smaller than 20 mm.

This step was followed by primary sampling (division 1 – Fig. 1) that was done by incremental sampling on a moving material flow after homogenization. The sampling bench included a feed hopper supplying a conveyor belt (flowrate: 12 kg/min). The incremental samples were taken manually at the discharge end of the belt to simulate a belt-end, cross-cut sampler, for which one cutter operation (=1 increment) takes 14 s. The procedure was systematic; ten elementary samples of approximately 3 kg were taken to produce 3 composite samples of approximately 30 kg. The 3 samples of 30 kg (particle size < 20 mm) were named primary samples (PS1, PS2 and PS3).

Each primary sample was shredded successively with 8 mm, 6 mm, 4 mm and 2 mm sieves in a lab knife mill (Fritsch, Pulverisette 19 with tungsten carbide knives). Each primary sample (30 kg ground to 2 mm) was divided by riffle splitters (chute widths of 60 mm and 30 mm) to obtain 3 samples of 2.6 kg each (division 2 – Fig. 1) (with the rest of the material being stored). The 3, 2.6 kg samples (particle size < 2 mm) were named secondary samples (for example, the three secondary samples from PS1 were named PS1-SS1, PS1-SS2 and PS1-SS3).

Each secondary sample was ground twice in a vibratory mill (ESM236-1bs Siebtechnik in ST52-3 steel) loaded with 50 kg of steel grinding balls and 1.3 kg of sample (operating time 4 h). After this step, each sample was sieved to 200 µm. Particles with a size larger than 200 µm were shredded one by one in a lab knife mill (Fritsch, Pulverisette 19) with a 500 µm perforated sieve. To further reduce the particle

size, a shredding test was carried out with the 250 µm perforated sieve (Fritsch Pulverisette 19) but this proved to be inconclusive. The large particles were mixed with the rest of the sample (particles < 200 µm) to keep the representativeness of the sample. It resulted that some particles in the prepared samples were still larger than 200 µm. The 9 samples were divided by riffle splitter (chute widths = 5 mm) into three sub-samples to obtain 27 samples of 0.5 g (division 3 – Fig. 1). These 27 final samples of 0.5 g (particle size 200 µm) were named tertiary samples (TS1, TS2 and TS3). Photos of the target sample as well as, PS, SS and TS samples are shown in the [Supplementary Material Fig. S1](#).

After this process, 27 samples were thus produced, called PSI-SSj-TSk, with i, j and k between 1 and 3.

The mass losses associated with size reduction steps were 4.3 % for the first step (shredding to 20 mm), 1.4 % (average of 3 SS procedures) for the second step (shredding to 2 mm) and 3 % (average of 9 TS procedures) for the milling step (milling to 200 µm). Material loss comes from dust sucked up by the dust collector, particles lost in the nooks and corners of the shredders and particles projected outside the shredders during the loading and unloading steps.

The sampling plan design was based on existing procedures from the literature (Fig. 2). Umicore published in 2022 its own sampling process in operation for electronic scrap in its Hoboken plant (Pauels, 2022). Mitsubishi, a Japanese smelter, created in 2017 a joint venture facility in the Netherlands (MMMR), which was specialized in sampling, weighing and preparing e-scrap materials (MMMR website, 2024). The sampling process of Umicore and MMMR plants has two division steps and two particle reduction steps, they are reported in Fig. 2. In the two sampling plans, the sample for assay weighs a few kilograms and the mass reductions are of the order of 1:1000 to 1:10,000. The samples for assay are sent to laboratories for analysis (1.5 to 4 kg at 7 mm for Umicore and a few kg at 5 mm for MMMR). For Umicore and MMMR, Fig. 2 is incomplete and it only details the sampling steps done in the treatment plant (2 steps) but not the sampling/preparation steps done in the laboratory. Hubau et al. (2019) proposed a 3-step plan.

2.3. Particle size distribution

Particle size distributions were determined after each shredding step (20 mm; 2 mm and 200 µm). Particle size distributions were determined on one PS and one SS sample (i.e. 30 kg at 20 mm and 2.6 kg at 2 mm). For the TS sample, the mass taken was greater than the TS mass (244 g instead of 0.5 g) because it was not possible to perform sieving on a 0.5 g sample. The distributions were obtained by dry sieving for 30 mm,

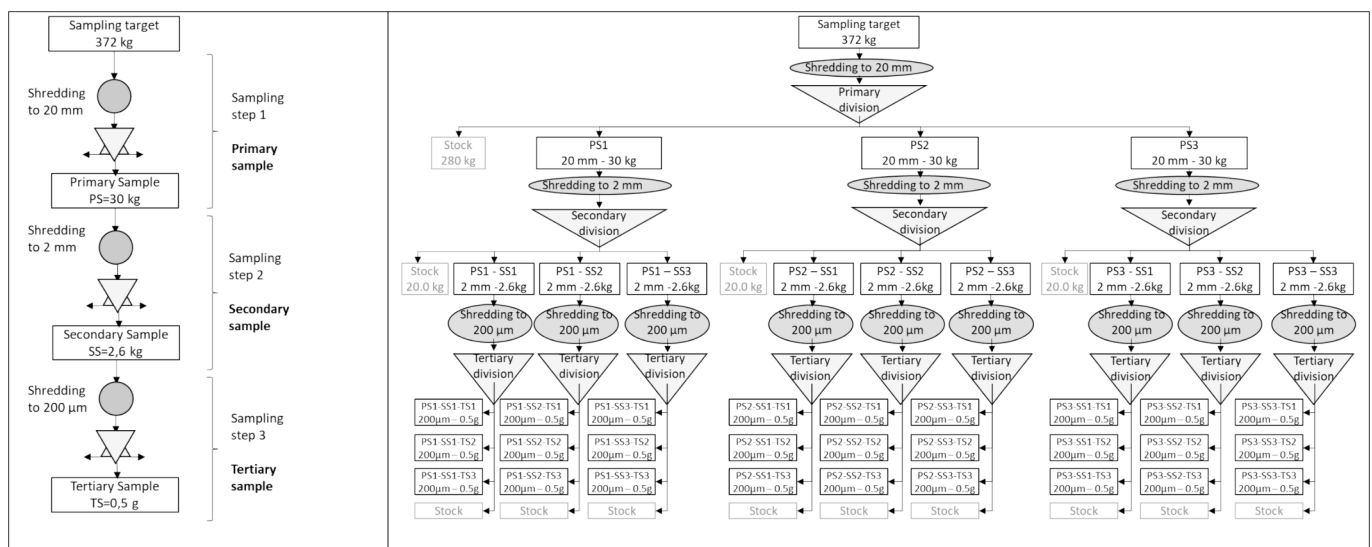


Fig. 1. Sampling and shredding procedure.

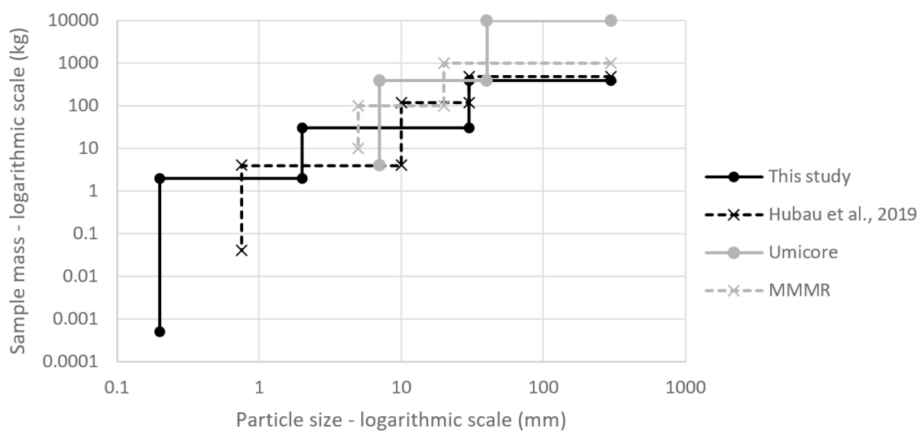


Fig. 2. Sampling plans described in the literature (combination of particle size reduction steps and sample divisions, reading from top-right to bottom-left).

10 mm and 5 mm sieves and wet sieving for smaller sieves (2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm, 0.063 mm, 0.04 mm and 0.02 mm). Each size fraction was dried at 40 °C before weighing.

2.4. Particle size content

The distribution of metals through the size fractions was determined on TS sieved samples. As a reminder, even though the preparation of the TS samples was performed with the objective of reaching 200 μm . It does not mean that all the particles of the sample has a size lower than 200 μm . In this respect, the TS samples were sieved at 250 and 500 μm (as described in section 2.3) to determine the composition of the coarsest particles. The 8 particle size fractions obtained by wet sieving (in section 2.3) were combined to obtain only 3 particle size fractions: > 500 μm , 250–500 μm and < 250 μm . The particle size distribution was: 14.0 %wt for particles > 500 μm , 3.7 % for 250–500 μm and 82.3 % for < 250 μm . The metal contents of the 3 fractions were measured following the methodology described in section 2.5 below. Two replicates of digestion were made for each of the 3 fractions and the results reported are the mean of the two values ($n = 2$). A ratio of metal content of fraction > 500 μm versus fraction < 250 μm was calculated (metal content in > 500 μm divided by metal content in < 250 μm), as an indicator of the enrichment of the coarsest particles versus the finest.

2.5. Metal content determination

Metal content determination was performed with aqua regia leaching. The following metal contents were analysed: Ag, Al, As, Au, Ba, Ce, Cd, Co, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Ho, La, Lu, Mn, Mo, Nd, Ni, Pb, Pd, Pr, Pt, Rh, Sb, Sm, Sn, Ta, Tb, Tm, Y, Yb, Zn and Zr. This method yielded reliable results on WPCB, in comparison with other conventional analytical methodologies (i.e. alkaline fusion or acid leaching with HF or HClO_4). The only exception is Ta for which an HF acid blend or alkaline fusion are required (Korf et al., 2019; Mährlitz et al., 2019). It was thus not considered in this study.

The analyses were carried out in BRGM's laboratories (Loiret-France). The BRGM, like most analysis laboratories, is equipped with an automated digester upstream of the ICP; the capacity of this digester requires taking a sample mass of around 0.5 g. This type of digester (capacity 0.5 g) is the most common in analysis laboratories; this is why this study selected this mass. Samples were digested by microwave aqua regia (Anton Paar Mutiwave GO) and 0.5 g of each Psi-SSj-TSk sample was mixed with 8 mL of aqua regia (HNO_3 : HCl 1:3). The nitric acid (67–70 %w, trace metal grade) and hydrochloric acid (32 %w, certified AR for analysis) were provided by Fisher Chemical. Samples were heated to 175 °C for 30 min. Analyses were then performed by TQ ICPMS (Agilent 8900) with external calibration. Depending on the elements and

interferences, different gas modes were used: gas-free, helium or oxygen (with or without mass transition). Solution blanks were run in each series. In order to avoid the impact of analytical drift on the estimation of statistical data from the sampling plan, the analyses were carried out in random order. Quality controls were also added to control instrumental drift.

2.6. Sampling uncertainty evaluation

Sampling uncertainty (U) is evaluated by the statistical estimate of variance s^2 with $U=s$. The variance tracks the average degree to which each point differs from the mean. The variance was calculated following the Eurachem guide methodology (Ramsey and Ellison, 2019).

The first step of this methodology involves verifying that the distribution of the effect is approximately normal (i.e. Gaussian). In our study, Shapiro-Wilk tests were performed on a data set to evaluate the normality of distribution with Excel Stat (version XLSTAT 2023.1.3.1407). The significance level for the p-value was set to 0.05. In case the normality could not be confirmed, natural logarithms of the metal content values were calculated according to the Eurachem guidelines. Shapiro-Wilk tests were performed on these values to ensure that the hypothesis of log-normal distribution for metal contents cannot be rejected.

The formulas used to estimate the variance arising from tertiary, secondary and primary sampling are given in Table 1, with $x_{i,j,k}$ referring to the metal content in the tertiary sample “k”, in the secondary sample “j”, and in the primary sample “i”. The metal content could be transformed into a natural logarithm of metal content if necessary. N_{TS} , N_{SS} and N_{PS} refers to the number of tertiary samples (3), secondary samples (3) and primary samples (3) respectively. Intermediate variances (Var_{SS} and Var_{PS}) were calculated by subtracting variances ($\text{var1} - \text{var2}$). In some cases, subtraction resulted in a negative value. This indicated that the subtracted variance (var1) is negligible compared to its predecessor (var2). In this case, the Eurachem guide suggests setting the value to zero (example A4 of the Eurachem guide; Ramsey and Ellison, 2019).

The total variance was calculated as the sum of the TS, SS and PS variances:

$$\text{Var} = \text{Var}_{TS} + \text{Var}_{SS} + \text{Var}_{PS} \quad (13)$$

The standard deviation SD is calculated as the root square of the total variance, while the relative standard deviation RSD equals the ratio of SD and \bar{x} . To obtain a 95 % confidence on the calculated value of uncertainty, a coverage factor of 2 is taken into account to obtain the expanded uncertainty U :

$$U = 2SD \quad (14)$$

Table 1

Formula used to calculate the sum of squares, degree of freedom and variance for TS, SS and PS sampling stages (Ramsey et al., 2019).

Formula	Sampling “between tertiary samples”	Sampling “between secondary samples”	Sampling “between primary samples”
Mean value	$\bar{x}_{ij} = \frac{1}{N_{TS}} \sum_{k=1}^{N_{TS}} x_{ijk}$ [1]	$\bar{x}_i = \frac{1}{N_{SS}} \sum_{j=1}^{N_{SS}} \bar{x}_{ij}$ [2]	$\bar{x} = \frac{1}{N_{PS}} \sum_{i=1}^{N_{PS}} \bar{x}_i$ [3]
Sum of squares SS	$SS_{TS} = \sum_{i=1}^{N_{PS}} \sum_{j=1}^{N_{SS}} \sum_{k=1}^{N_{TS}} (x_{ijk} - \bar{x}_{ij})^2$ [4]	$SS_{SS} = \sum_{i=1}^{N_{PS}} \sum_{j=1}^{N_{SS}} \sum_{k=1}^{N_{TS}} (\bar{x}_{ij} - \bar{x}_i)^2$ [5]	$SS_{PS} = \sum_{i=1}^{N_{PS}} \sum_{j=1}^{N_{SS}} \sum_{k=1}^{N_{TS}} (\bar{x}_i - \bar{x})^2$ [6]
Degree of freedom df	$df_{TS} = N_{PS} N_{SS} (N_{TS} - 1)$ [7]	$df_{SS} = N_{PS} (N_{SS} - 1)$ [8]	$df_{PS} = N_{PS} - 1$ [9]
Variance Var	$Var_{TS} = \frac{SS_{TS}}{df_{TS}}$ [10]	$Var_{SS} = \frac{1}{N_{TS}} \left(\frac{SS_{SS}}{df_{SS}} - \frac{SS_{TS}}{df_{TS}} \right)$ [11]	$Var_{PS} = \frac{1}{N_{TS} N_{SS}} \left(\frac{SS_{PS}}{df_{PS}} - \frac{SS_{SS}}{df_{SS}} \right)$ [12]

Metal contents are thus expressed as $\bar{x} \pm U$ (15)

When log-transformation is performed, results are not expressed in the original units of the metal content (i.e. mg/kg). An expanded uncertainty factor is then calculated:

$${}^F U = e^{2SD} \tag{16}$$

The interval of confidence is not symmetrical around the mean value. It is defined with upper and lower confidence interval limits calculated as:

$$\text{Lower confidence interval limit} = \frac{\bar{x}}{F U} \tag{17}$$

$$\text{Upper confidence interval limit} = {}^F U \cdot \bar{x} \tag{18}$$

A single sampler and a single sampling protocol were used in the whole study in order to determine sampling precision. This method did not enable us to estimate sampling bias, nor analytical bias. In our study, the variance calculated is the sum of two independent contributions: the variance due to the sampling and the variance due to analytical process. Analytical variances were thus included in the tertiary sampling uncertainty. In the case of WPCBs, a previous study (Brochet et al., 2022) showed that, due to the high heterogeneity of the material, the analytical variances are negligible with respect to sampling variance. Even if the WPCB and the sampling plan were different, there is enough similarity between these two studies (similar study object and same analysis methodology) to deduce that the analysis variances are negligible in respect to the sampling variances in our study.

The Eurachem guide (Ramsey and Ellison, 2019), recommends considering eight primary samples. Lyn et al. (2007) demonstrated that the methodology can be applied to less primary samples without modifying the uncertainty estimate. However, they demonstrated that it influences the uncertainty on the uncertainty value. In this study, the preparation of the samples from the 20 kg (primary sample) was a tedious and complex task. We decided to limit replication of the primary samples to only 3 replicates.

3. Results

3.1. Particle size distribution

The particle size distribution of PS, SS and TS are given in Fig. 3. The d_{80} and d_{90} (i.e. 80 % mass and 90 % mass passing size) of the particle size distributions were: for PS, $d_{80} = 22 \mu\text{m}$ and $d_{90} = 26 \mu\text{m}$, for SS, $d_{80} = 1.8 \text{ mm}$ and $d_{90} = 2.5 \text{ mm}$ and for TS, $d_{80} = 207 \mu\text{m}$ and $d_{90} = 738 \mu\text{m}$. The differences between the d_{80} and d_{90} are limited for primary and secondary samples. However, they are very high for the tertiary sample. This means that the majority of particles in this sample are fine ($< 200 \mu\text{m}$) but some very coarse ($> 1000 \mu\text{m}$) particles remain. This is probably due to the ductility of metals that are hardly shredded to achieve small sizes (Hubau et al., 2019).

3.2. Metal contents

Ge, Pt and Rh content mean values were close to or lower than the

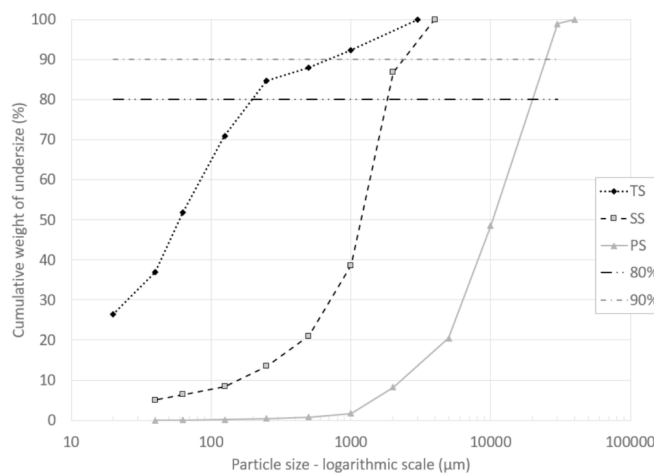


Fig. 3. Particle size distributions of PS, SS and TS samples.

limit of quantification (0.05 mg/kg for Pt and Rh and 0.4 mg/kg for Ge). This may arise both from a low content in WPCB from computer motherboards (as for Rh) or from their low dissolution with aqua regia (as for Ta, see Hubau et al., 2019). Consequently, these metals were not considered for the study.

The hypothesis of normality from the Shapiro-Wilk test was rejected for Zn, Sn, Ba, Sb, Mn, Zr and Co. It was decided to perform log-transformation for all metals. On log-data the hypothesis of normality was rejected for Cd, Zr and Ba. These three elements were excluded from the statistical processing.

For the other metals, the mean metal content, expanded uncertainty factor and confidence interval limits are given in Table 2.

The total amount of “metals” in the WPCB (sum of metals) is 42.6 % wt. Base metals (Al, Cu, Fe, Ni, Pb, Sn and Zn) represent 97.4 %wt of WPCB metals, while Au content reaches 65 mg/kg. The Au content is 35 % lower than expected, as the WPCB batch was supposed to be rich (grade around 100 mg/kg). The content in rare earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb) is quite limited (lower or equal to 10 mg/kg each), except for Nd. The concentration of these elements may vary greatly from one waste type to another. For example, unlike in our study, Baez et al. (2022) reported values higher than 100 mg/kg for at least one REE in their WPCB sourced from information technology and telecommunication equipment (e.g., computers, tablet computer, mobile phones, etc.).

The expanded uncertainty factor is small for Ag, Al, Au, Cu and Ga (${}^F U < 1.2$) showing good reproducibility between the 27 values. The factor is high for As, Co, Eu, Gd, Mn, Ni and Sn (${}^F U > 1.5$) and very high for Cr and Mo (${}^F U > 2$). These high values of expanded uncertainty factor lead to large confidence intervals and poor estimation of the total metal content. As an example, for chromium the content is between 0.13 and 1.5 %, at the opposite; for Cu and Au the distribution is more narrowly spread (between 19.5 and 26.3 % for Cu and between 54 and 77 mg/kg for Au.).

As previously explained, metal content values followed a normal distribution for most of the metals, but not for all of them. To facilitate

Table 2

Metal contents in %wt. or mg.kg-1 (mean value for the 27 PSI-SSj-Tsk), expanded uncertainty factor and lower and upper confidence interval limits.

	Al	Cu	Fe	Zn	Ag	As	Au	Ce	Co	Cr	Dy	Er	Eu	Ga	Gd	Ho
Unit	%wt	%wt	%wt	%wt	mg/ kg	mg/ kg	mg/ kg	mg/ kg	mg/ kg	mg/ kg	mg/ kg	mg/ kg	mg/ kg	mg/ kg	mg/ kg	mg/ kg
Limit of quantification	2.5.10 ⁻⁴	5.10 ⁻⁵	2.0.10 ⁻³	5.10 ⁻⁴	0.05	0.25	0.05	0.05	0.25	0.5	0.005	0.005	0.005	0.5	0.005	0.005
Mean value	5.31	22.6	9.55	2.52	367	8.22	65	9.28	55	4	9.20	0.23	0.15	8.30	3.15	5.11
^F U (without unity)	1.14	1.16	1.46	1.39	1.16	1.51	1.19	1.24	1.87	3.38	1.21	1.21	1.55	1.19	1.51	1.21
Lower confidence interval	4.66	19.5	6.53	1.81	316	5.45	54	7.46	29	1	7.58	0.19	0.10	7.0	2.09	4.24
Upper confidence interval	6.06	26.3	13.9	3.50	426	12.4	77	11.5	102	14	11.2	0.28	0.24	9.9	4.75	6.16
										370						
										290						
										800						
Unit	La mg/kg	Lu mg/ kg	Mn mg/kg	Mo mg/ kg	Nd mg/ kg	Ni mg/ kg	Pb mg/ kg	Pd mg/ kg	Pr mg/ kg	Sb mg/ kg	Sm mg/ kg	Sn mg/ kg	Tb mg/ kg	Tm mg/ kg	Y mg/ kg	Yb mg/ kg
Limit of quantification	0.05	0.005	0.5	0.5	0.005	0.5	0.05	0.05	0.005	0.05	0.005	0.25	0.005	0.005	0.05	0.005
Mean value	6.31	0.03	1 043	27	35.0	5	4	3.57	2.11	2	3.96	4 830	0.06	0.03	10.5	0.24
^F U (without unity)	1.28	1.36	1.51	3.26	1.38	1.59	1.43	1.33	1.31	1.33	1.38	1.74	1.37	1.27	1.24	1.29
Lower confidence interval	4.93	0.02	688	8	25.3	3	3	2.68	1.61	1	2.86	2 780	0.05	0.02	8.5	0.19
Upper confidence interval	8.07	0.04	1 579	88	48.5	8	6	4.75	2.78	2	5.47	8 370	0.09	0.03	13.0	0.31
						190	860			130						
						270	400			600						
						250	950			840						

the comparison of results between metals, they were all treated with the same methodology (log-transformation). However, the two approaches (treatment of original values and log-transformed values) were compared according to the confidence interval limits. The results are shown in Table S2 (see Supplementary Material). The use of the log-transformation approach is more inclusive of the few very high values and is therefore more representative of the scatter of the original measurements.

3.3. Particle size distribution versus content

The materials of which the WPCB are composed, have different mechanical properties, which affect the grinding of the particles. Under the pressure of shredding, some materials will deform, while others will tend to form pellets, or even break. This leads to heterogeneous grinding and variability in the particle size distribution of the crushed metals. This phenomenon may affect the representativeness of the samples for certain metals. To evaluate this occurrence, the final samples issued from tertiary samples (TS) were analysed to determine the potential enrichment of the coarser fraction (10 % of the particles were found to be larger than 700 µm) and to evaluate the distribution of metals through the size fractions.

Analysis per particle size fraction was carried out in duplicate, since it is not enough to limit the metal content uncertainty. Then, the metal particle size distribution in TS was considered from a qualitative and not a quantitative viewpoint. As a reminder, TS was prepared by using a 200 µm sieve in the shredder; however, it should be noted that not all particles in the sample are smaller than 200 µm.

There is a strong enrichment in the coarse fraction (>500 µm) for some metals (Co, Cr, Cu, Fe, Mn, Mo, Ni, Sn and Zn) (Table 3). For these metals, the content ratio “>500 µm/ < 250 µm” is between 1.9 (Sn) to 17.8 (Cr). As a reminder, the particle size was reduced using a shredder. The shredder uses a shear mode to cut the materials: two perpendicular forces (that are equal and opposite in direction) are applied to the material. The effectiveness of the shear depends on the yield stress of the material to be cut. The difference in mechanical property between metals leads to differential shredding but it is difficult to predict their individual behaviour as their form in WPCB (alloys, pure metals etc.) is unknown. However, for base metals with mean content > 1 % (Cu, Fe, Ni and Zn), we have observed visually that Cu, Zn, Fe and Ni particles tend

Table 3

Metal contents in each size fraction, ratio > 500 µm / < 250 µm and comparison between reconstituted and analysed values.

	Metal content (mg/kg)			Ratio > 500/<250 µm
	< 250 µm	250–500 µm	> 500 µm	
%wt	82.3	3.7	14.0	–
Ag	429	308	63.5	0.15
Al	60 400	30 200	3 120	0.05
As	13.5	12.9	17.6	1.30
Au	67.9	37.0	16.7	0.25
Ce	12.8	6.9	0.2	0.01
Co	43.3	70.2	207	4.79
Cr	1 450	5 350	25 800	17.76
Cu	145 000	376 000	487 000	3.36
Dy	11.1	5.72	0.11	0.01
Er	0.29	0.16	< LOD (0,005)	
Eu	0.22	0.11	< LOD (0,005)	
Fe	61 500	95 700	258 000	4.19
Ga	9.61	6.50	6.47	0.67
Gd	3.76	2.01	0.04	0.01
Ho	6.12	3.17	0.06	0.01
La	8.18	4.19	0.11	0.01
Lu	0.04	0.02	0.00	0.00
Mn	836	839	2 790	3.33
Mo	19	36	144	7.64
Nd	43	22	0.6	0.01
Ni	3 470	7 190	14 800	4.28
Pb	4 050	3 550	827	0.20
Pd	4.5	0.9	0.3	0.07
Pr	2.8	1.4	0.1	0.03
Sb	2 520	2 310	60	0.02
Sm	4.8	2.5	0.1	0.01
Sn	5 900	9 010	11 200	1.91
Tb	0.10	0.05	0.002	0.02
Tm	0.04	0.02	< LOD (0,005)	
Y	14	7.0	0.2	0.01
Yb	0.33	0.14	< LOD (0,005)	
Zn	8 400	60 000	104 000	12.40

to form pellets in the shredding chamber. For less concentrated metals (Co, Cr, Mn, Mo and Sn), there is not enough information about their distribution in the WPCB to explain this behaviour. Cr could be integrated in stainless steel components, an alloy which is very difficult to shred (high yield stress; Cambridge University Engineering Department,

Materials Data Book, 2003).

For others metals (Ag, Al, Au, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pb, Pd, Pr, Sb, Sm, Tb, Tm, Y and Yb), there is an enrichment in the fine fraction (<250 μm) with the mass ratio “>500 μm/ < 250 μm” being lower than 0.25 (value obtained for Au). For base metals with a concentration > 1 % (Al and Pb), their low contents in the coarse fraction show that they were easy to shred. This is consistent with the mechanical properties of some aluminium alloys which have low yield stress. Pb, commonly used as a pad, has a very low yield stress. Au is present as a very thin layer on connectors, the shred step probably caused particle-on-particle scrubbing of these parts and also freed Au fine particles. Hino et al. (2009) showed that the greater the milling impact forces in a ball mill, the more gold is found in < 250 μm fraction. For all the rare earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y and Yb) and less concentrated metals (Ag and Sb), there is not enough information about their distribution in the WPCB to explain this behaviour.

As and Ga are equally distributed between the size fractions, with no special enrichment of one fraction versus another.

3.4. Contribution to the variance

Following the duplicate methodology, it was possible to determine the contribution of the 3 sampling steps to the total variance (Fig. 4).

Various behaviour of metals can be distinguished: 1) the variance is mainly due to tertiary sampling step (58 to 100 %). This concerns 11 metals: Au, Co, Cr, Cu, Fe, Ga, Mn, Mo, Ni, Pd, Yb and Zn, 2) the variance is mainly due to secondary sampling step (61 to 96 %), this concerns 10 metals: Ag, Ce, Er, Eu, Lu, Pb, Sb, Sn, Tb and Tm, 3) the variance is mainly due to primary sampling step (62 to 76 %), this concerns 6 metals (Gd, La, Nd, Pr, Sm and Y), 4) all the sampling steps contribute equally to the variance, this concerns 4 metals (Al, As, Dy and Ho) and 5) the variance is not affected by primary sampling for 19 metals (Ag, Ce, Co, Cr, Cu, Er, Eu, Fe, Ga, Mn, Mo, Ni, Pb, Sb, Sn, Tb, Tm, Y and Zn).

4. Discussion

A schematic diagram was proposed to compare the different results. The comparison between enrichment of some particle size fractions and the uncertainty factor is given in Fig. 5. It makes it possible to highlight 4 categories of metals with distinct behaviours.

4.1. Precious metals

The fine particles of the tertiary sample were enriched with the three precious metals (Ag, Au and Pd) compared to the other size fractions. The metals were thus finely ground during the preparation stage. Ag and Au uncertainty factors (equal to 1.16 and 1.19 respectively) were in the “Top 5” of the lowest uncertainty factors while Pd had an intermediate but still limited uncertainty factor ($F^U=1.33$). Their ability to be finely ground probably made it possible to limit the sampling error for Ag and

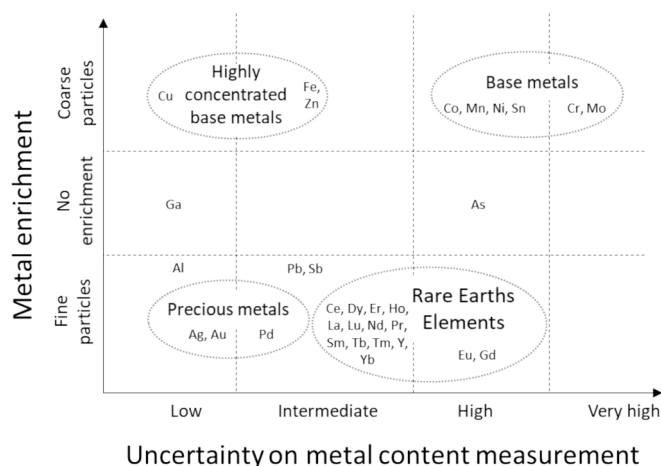


Fig. 5. Schematic diagram for the comparison of metal enrichment and metal content uncertainty. The thresholds for uncertainty on metal content measurement are: Low $F_u < 1.2$, Intermediate $1.2 \leq F_u < 1.5$, High $1.5 \leq F_u < 2$, very high $F_u \geq 2$. The thresholds for metal enrichment are: Fine particles size ratio < 1, no enrichment $1 \leq$ size ratio < 1.3 and coarse particles size ratio ≥ 1.4 .

Au.

For these three metals, the tertiary sampling provided the major contribution of the total sampling variance (between 39 and 61 %). The secondary sampling step also contributed to the uncertainty for all three metals. The primary sampling step contributed to the variance in the case of Pd and Au, but not for Ag. As the uncertainty factor was quite low for all these metals, it was not easy to interpret the contribution of each sampling step to the total variance.

4.2. Rare earth elements

Among the rare earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y and Yb), similar behaviour between the different elements was noted. First, it was shown that they were finely ground in the tertiary sample, as for precious metals. For all of them, except Eu and Gd ($F^U=1.5$), a low expanded uncertainty factor was estimated ($F^U < 1.2$), which is consistent with a good homogeneous repartition of the metals in the samples, even if their content is quite low (<10 mg/kg for most of them).

4.3. Base metals group

In this group, the following metals were considered: Al, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Sn and Zn. Most of them (Co, Cr, Cu, Fe, Mn, Mo, Ni, Sn, Zn) were particularly concentrated in the coarsest particles of the tertiary sample.

For Co, Cr, Mn, Mo and Ni, the enrichment in coarse particles was

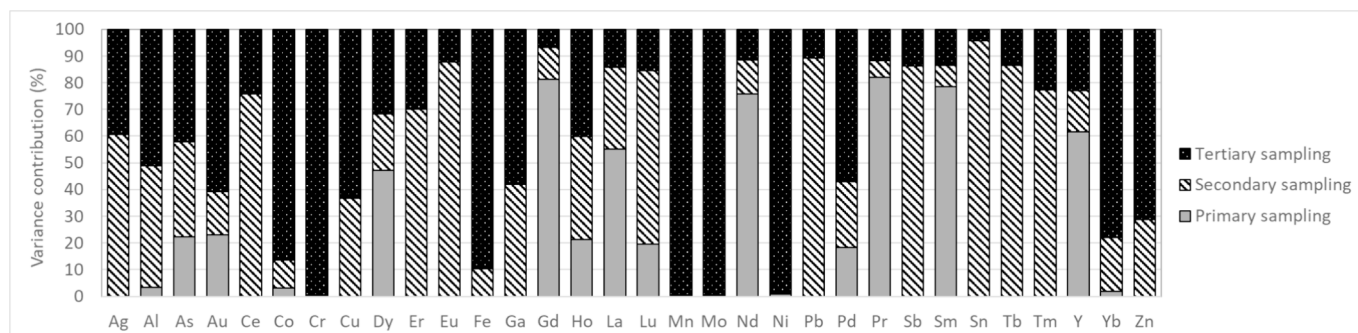


Fig. 4. Variance contributions for PS, SS and TS sampling steps.

correlated with a high uncertainty factor ($FU > 1.5$ in Table 1) arising almost exclusively from the tertiary sampling (see variance contribution in Fig. 4). The presence of large particles that were particularly enriched with these metals created heterogeneity that affected the representativeness of the tertiary sampling step. According to Gy's theory (1979), the fundamental sampling error is based on the random draw of a certain number of particles. Consequently, the larger the fragments, the fewer there are in the sample and the more the relative variance increases; this is what happened for this group of metals. The analysed given mass (0.5 g) was not sufficient to obtain representative samples.

For Cu, Fe and Zn, the tertiary sampling step also mainly contributed to the uncertainty of the sampling, but this uncertainty was quite limited ($1.1 < FU < 1.5$). Their presence in the coarsest particles created heterogeneity during the tertiary sampling step but it was counterbalanced by their high content. These are 3 of the 4 most concentrated metals of the samples (with a content of 22.63 % for Cu, 9.55 % for Fe and 2.52 % for Zn). The high contents implied a significant number of coarse particles of these 3 metals in TS samples which reduced the variance compared to the metals mentioned above (Co, Cr, Mn, Mo and Ni).

Conversely to other base metals, Al, the last of the four most concentrated metals in the sample, was concentrated in fine particles. The ability to finely grind aluminium made it possible to considerably limit the issue of representativeness, which was correlated with a low uncertainty factor ($FU = 1.1$). Moreover, as for Cu, its high content limited any potential influence of particle size distribution. The main contributions to the uncertainty were the primary and secondary sampling steps.

Sn was more weakly concentrated in the coarse particles than the previous base metals (Co, Cr, Cu, Fe, Mn, Mo, Ni, Zn): the ratio of Sn content between coarse and fine particles was 1.91 while the other base metals' ratios were > 3.3 . The concentration in coarse particles was not correlated with a predominance of tertiary sampling step contribution in the variance as previously seen, but rather with the secondary sampling step. It is possible that the enrichment of coarse particles in Sn was not sufficient to affect the tertiary sampling. The uncertainty factor was quite high ($FU = 1.73$).

Pb and Sb content mean values (0.49 wt% and 0.21 wt% respectively) were similar to the ones for Ni and Cr. However, their uncertainty factors were lower ($FU = 1.43$ and 1.33 respectively, compared to 1.59 and 3.38 for Ni and Cr respectively). This may arise from a different behaviour during shredding: coarse particles were enriched in Ni and Cr but not in Pb and Sb. Pb was not particularly concentrated in one size fraction. Conversely, Sb was finely ground, which is coherent with its use as flame retardant in organic phases (epoxy resins, which are easy to grind). This probably explains why Pb and Sb had limited uncertainty factors. For both of them, the secondary sampling step was the main contributor to the sampling variance.

4.4. Other metals

As and Ga are the only metals which were quasi equally distributed in all the particle size fractions; no clearly metal enrichment in coarse or fine particles was observed. Gallium in printed circuit cards (PCB) is mainly used as wafer semiconductors and it is mainly used as GaAs form (U.S. Geological Survey, 2023). The results on these 2 metals agree with this information: the contents of these two metals were very close $As = 8.22$ mg/kg and $Ga = 8.30$ mg/kg (respective molar masses of 74 and 69 g/mol) and they behaved the same during the grinding stage. On the other hand, this does not explain the difference in FU between the two metals; As uncertainty factor was high (1.51), while it was much more limited for Ga (1.19).

4.5. Comparison with a previous study

Such a methodology was already applied in Hubau et al. (2022) on a

limited range of metals (Co, Cu, Fe, Ni, Pb and Zn). It is not possible to directly compare the variance estimates between the previous study and this one, as it was neither the same WPCB batch (WPCB from small waste electrical and electronic equipment category versus WPCB from computer motherboards) nor the same sampling plan. In particular, the final shredding step was performed with a perforated sieve of 750 μm , which was much larger than the one used in this study (200 μm). The particle size distribution in the "750 μm sample" from Hubau et al, 2019 was re-analysed in order to evaluate the consistency between metal distribution through the size fractions and FU factors (data are shown in Table S3 in Supplementary Material). The results are highly consistent between both studies: 1) Fe Cu Ni and Zn are mainly distributed in the coarsest particles 2) Fe and Cu have limited uncertainty far lower than Ni and Zn and 3) Co and Pb are quite equally distributed in the particles independently from their particle sizes.

5. Conclusion

This study focuses on the sampling uncertainty associated with metal content in Waste Printed Circuit Board samples. The main objective was to estimate the confidence interval on the concentration of around thirty-two metals in a whole batch sample of 372 kg of WPCB. The uncertainty factor was estimated according to the empirical approach using a replicate experiment (Eurachem methodology). The sampling uncertainty resulting from each preparation step was evaluated and correlated, when possible, to metal particle size distribution in the analysed sample.

It demonstrated that precious metals were particularly concentrated in fine particles. The particle fineness implied a significant number of particles of these metals in the analysed samples which limit the uncertainty linked to the sampling, even though their contents were not high. The same was observed for rare earth elements.

Conversely, most of the base metals were difficult to grind. This resulted in an enrichment of the coarse particles in base metals. Thus, the last preparation step, which consists in going from a sample of 2.6 kg at 2 mm to a sample of 0.5 g at 200 μm for analysis, was the step which contributed the most uncertainty in sampling. It could be of interest to add an intermediate grinding and division step, in order to reduce the sampling uncertainty or to take a larger analysis mass, 5 g for example. The current uncertainty was often quite significant for these base metals. This was, however, counterbalanced for Cu, Fe and Zn, by their high contents. The study demonstrated that the ability of each material to be ground largely influenced its distribution in the samples during preparation and thus the sampling uncertainty.

The sampling and analysis methodology developed in this study was carried out on one category of WPCB; it can now be deployed on others categories of boards. Even if WPCB have very variable metal contents depending on their uses, years of manufacturing and brands, they have strong similarities: 1) they are composed of a printed board, solder and components 2) the metals used in the WPCB have often the same use (gold in coating, copper as basic conductor, aluminium as thermal dissipaters, etc.) and are therefore dispersed, deposited in an equivalent manner. This observation suggests that many metals will behave identically in the shredder (e.g. gold enriches in the fines, copper in very large quantities in the coarse particles). The orders of magnitude of the uncertainty on certain metals may therefore be extrapolated to other categories of WPCB. This hypothesis could in the future be confirmed by experimental tests on new WPCB batches and the creation of a variogram.

CRediT authorship contribution statement

Solène Touzé: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Conceptualization. **Agathe Hubau:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Conceptualization. **Jean-Philippe**

Ghestem: Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Methodology, Investigation, Conceptualization. **Pauline Moreau:** Writing – review & editing. **Nicolas Lafaurie:** Writing – original draft, Formal analysis. **Johanna Noireaux:** Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2024.08.010>.

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