

## Experimental determination of the constitutional heterogeneity for sampling of Waste Printed Circuit Boards

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**Sampling and analysis of Waste Printed Circuit Boards (WPCBs) become of high importance because of the strong increase in the annual production of such waste and equally because of the value and criticality of the contained metals. As a result of human production, we could expect to know exactly the heterogeneity of constitution of WPCBs, but this is still far away from reality, and there is no effective data available due to lack of documentation and rapid obsolescence of such equipment, the lot composition itself being highly variable over time.**

**In the frame of a project focused on the WPCBs recycling, BRGM has conducted a set of experiments with the double objective to define an appropriate sampling and analytical procedure and to estimate the variability of such procedures for the determination of the content of six metals. Different operating conditions have been tested: three grinding sizes and three sample masses. For each case, the procedure has been repeated several times sufficient to consider statistics. A theoretical study has then been performed to deconvolute sampling and analytical errors from these statistics. The paper presents this approach and the techniques used to go back to the heterogeneity of such material. The analytical error is calculated for the different protocols allowing the experimental identification of the last stage total sampling error. Discussion is made about the possibility to estimate the intrinsic heterogeneity parameter at the different stages of the sampling procedure.**

### Introduction

Due to the increasing consumption of electronic devices such as computers, smartphones, screens, toys, but also all embedded processors and Internet of Things (IoT) devices, the Waste Printed Circuit Boards (WPCB) will also continue to increase rapidly, without considering the huge stock of such waste lying dormant in households, offices, and industrial stock rooms. As a non-negligible secondary source of critical and precious metals, the WPCB are the focus of increasing interest for recycling and recovery. But this resource is eminently variable in space, depending on the concentration of specific kinds of devices during collection, but also with time due to the rapid evolution of the technologies and the resulting short lifetime of such devices. Continuous monitoring of this resource and estimation of its potential value through recovery processing necessitate to regularly analyse it by taking and processing samples.

But the WPCB are very heterogenous objects made of similar electronic components but in a wide range of proportions (Figure 1). The composition of these components in terms of metals is also very variable. Consequently, there is a large intrinsic heterogeneity whatever the stage in the sampling process: entire PCBs after dismantlement, pieces of PCB after shedding, individual components, fractions of components after grinding, liberated fractions of metals from components and printed boards after pulverisation. In addition, the metals as analytes are present in different forms: as pure metal or alloy in individual pieces or in composite materials, as component of minerals, or in electrolytes. The notion of liberation is then not evident and its description very complex with different liberation scales.

Consequently, it is necessary to return to the basis of the theory of sampling hopping to understand the behaviour of such material during sampling. A fine description of the heterogeneity of constitution is then necessary. Unfortunately, it appears very difficult to obtain it because of the wide variety of WPCB, the lack of initial goods documentation and the difficulty to identify the origin after waste collection. The other way is to observe the variability appearing during the sampling stages and use statistical tools to analyse it in conjunction with the theory of sampling. For that, several experiments have been performed and detailed in previous papers<sup>1,2</sup>. Different kinds of interpretation of results have been done<sup>1,2,4</sup>, the current study trying to differentiate the variability due to sampling and the variability due to analytical protocols.

The first part of this paper shortly presents the experiment and discusses the observed variability. The tentative to look for the reason of the extent of this observed variability into the size (the mass) of the sample and its fineness partially fails, as expected. One of the causes of this failure is coming from the importance of the analytical error, the calculation of which being subject of the second part. The last part tries to isolate the sampling error from the observed variability by deducting the variance of the analytical error from the experimental variance to have the pure sampling variance. The contribution of the different components of the overall sampling error is then discussed.



**Figure 1. A lot of WPCB illustrating the high heterogeneity of the material to be sampled.**

### Variability assessment study

As a human production, the constitution of the printed circuit board (PCB) in terms of electronic components and chemical composition of these components may be a priori known. In the real world, not only the documentation about identified types of PCB is difficult to obtain, but it is generally impossible to identify the type of PCB. It is why the heterogeneity of these pieces of equipment cannot be described by this way. In addition, after shredding, the heterogeneity of produced particles is very difficult to predict from the knowledge of PCB heterogeneity. Only an empirical statistical approach seems possible.

In this experiment, the objective is to obtain an estimate of the variability of the material composition when taking a sample from a lot of WPCB for chemical analysis. The variability assessment is performed for different sample preparation protocols, the analytical procedure for each metal content being the same for all sampling types. A great number of samples are drawn from the same lot for each protocol type with the objective to obtain the main parameters of the variability distribution. The variability in the content measurement results is mainly due to sampling error, but also to analytical error.

### Sample taking and preparation

Only one 526 kg lot of WPCB has been used for this experiment to reduce the risk of inter-lot variability (Figure 1). It has been ground to -30 mm (Figure 2 left). Due to components which are difficult to break (such as coils, transformers, or coolers), only 481 kg are passing 30 mm control sieve. Only this fraction is considered as the lot from which samples are taken. This lot is then homogenized and divided using a rotary splitter, one fourth of 122 kg being randomly selected for grinding to -10 mm with more than 96 % passing (Figure 2 right). After homogenization, the 122 kg are divided to obtain approximately 16 kg in three stages using a 60 mm riffle splitter, then divided to obtain four samples of approximately 4 kg in two stages using a 30 mm riffle splitter. Three of these samples have been ground to -2 mm using a Retsch SM 2000 laboratory shredder (Figure 3 left). Two of them have then been ground to -750  $\mu\text{m}$  (Figure 3 right). One of the -750  $\mu\text{m}$  samples has been divided and 2 kg have been ground to -200  $\mu\text{m}$  using a Poitemill knife mill. After homogenization, each ground sample of WPCB has been divided using a 15 mm riffle splitter, the obtained 2 kg being divided using a 5 mm riffle splitter to obtain numerous samples of 5 g, 2 g and 0.5 g as detailed in the Table 1. The 0.5 g samples have been obtained by scooping from 2 g splitting fractions. This procedure (Figure 4) has been described in detail by Hubau et al<sup>1</sup> and Touz  et al<sup>2</sup>.

**Table 1. List of generated samples.**

Sample name	Number of samples	Fineness	Mass
2 mm 5 g	24	2 mm	5 g
2 mm 2 g	16	2 mm	2 g
2 mm 0.5 g	16	2 mm	0.5 g
750 $\mu\text{m}$ 5 g	24	750 $\mu\text{m}$	5 g
750 $\mu\text{m}$ 2 g	16	750 $\mu\text{m}$	2 g
750 $\mu\text{m}$ 0.5 g	15	750 $\mu\text{m}$	0.5 g
200 $\mu\text{m}$ 5 g	16	200 $\mu\text{m}$	5 g
200 $\mu\text{m}$ 2 g	16	200 $\mu\text{m}$	2 g
200 $\mu\text{m}$ 0.5 g	16	200 $\mu\text{m}$	0.5 g

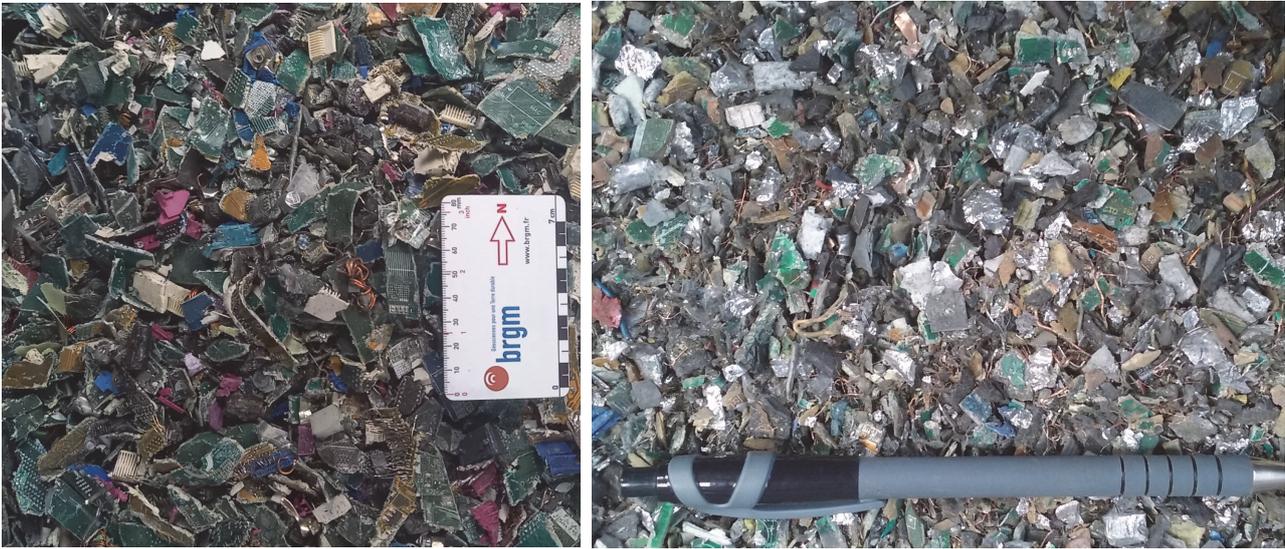


Figure 2. The lot of WPCB after shredding to -30 mm (left) and a quarter of that lot after shredding to -10 mm (right).



Figure 3. 4 kg sample of WPCB shredded to -2 mm (left) and another 4 kg sample shredded to -750 µm (right).

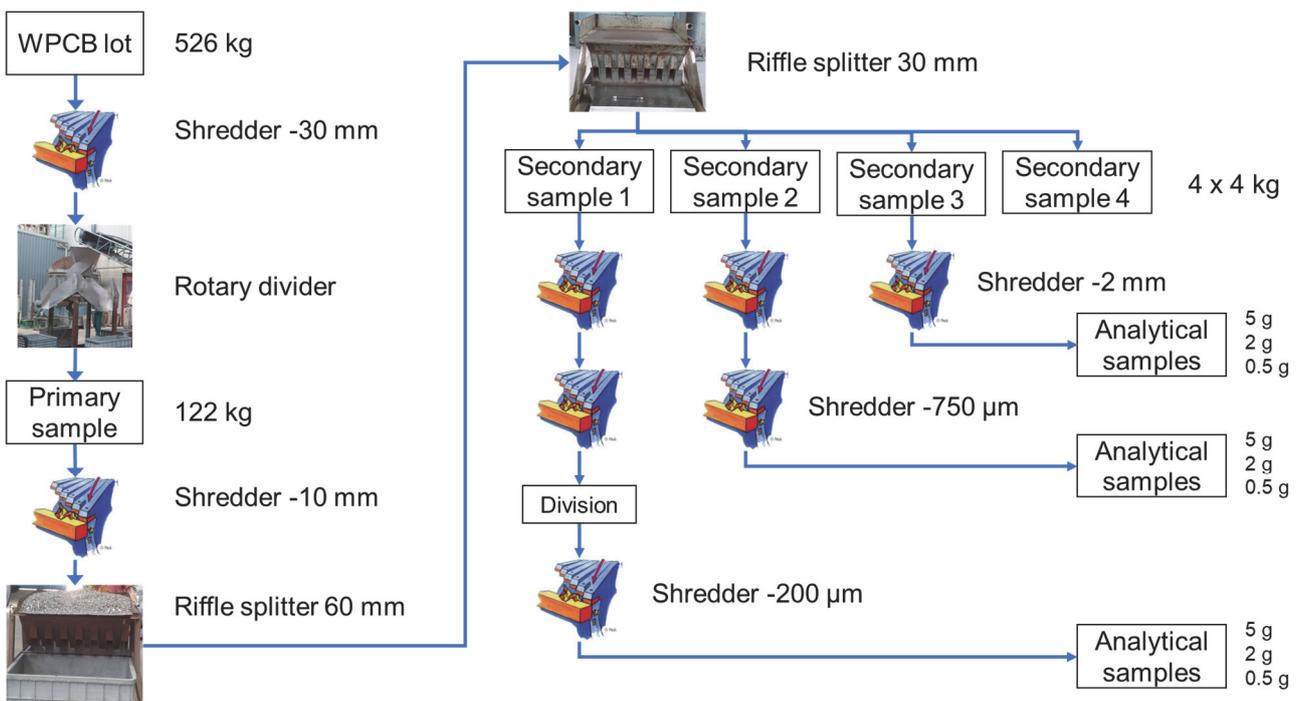


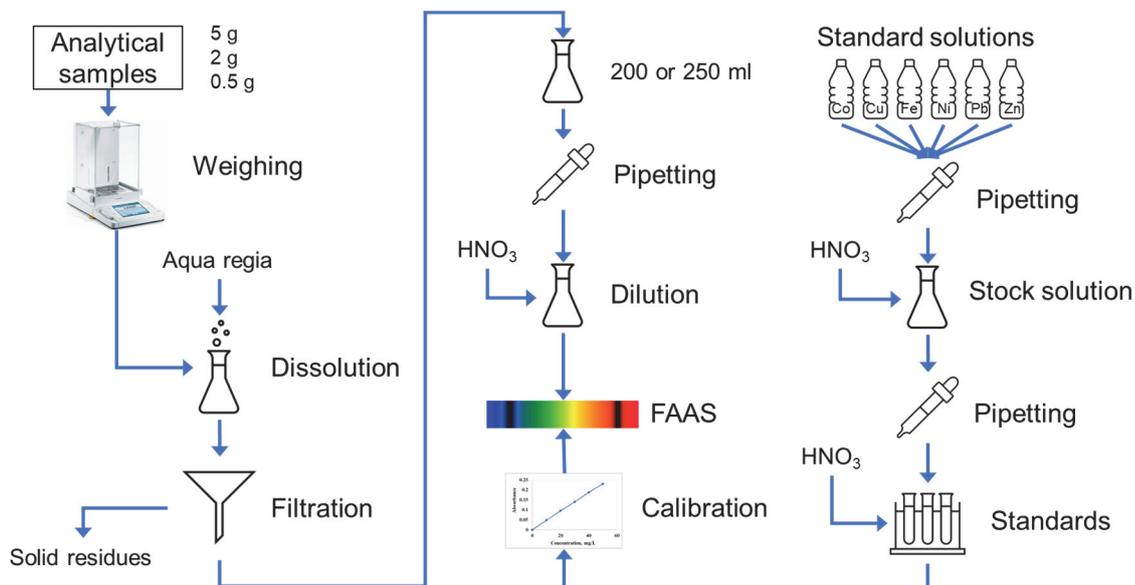
Figure 4. WPCB sampling procedure resulting in several kinds of samples for analysis.

Sample analysis for metal contents

These 159 samples have been analysed for Cu, Fe, Ni, Pb, Zn and Co contents following approximately the same procedure (Figure 5). Each sample of ground WPCB has been precisely weighed using a Sartorius MSU225P scales. The samples were dissolved in hot aqua regia (HNO<sub>3</sub>:HCl 1:3) at reflux, in a vessel equipped with a condenser. The solid/liquid ratio was

1/10 (weight/volume), and the contact time was about 2 h. Each leaching fraction was filtered over a 0.45 mm cellulose nitrate filter, and the leachate was diluted with a solution of  $\text{HNO}_3$  0.5 M. Details on the digestion process are given in Hubau et al<sup>1</sup>, including the control of remaining solid residues.

The concentrations of Cu, Fe, Ni, Pb, Zn and Co in the resulting solutions were determined by Flame Atomic Absorption Spectrometry FAAS on a Varian SpectraAA-300. The volume of these resulting solutions is 250 ml gauged with class A measuring flask, except for most of 750  $\mu\text{m}$  5 g samples for which a 200 ml flask has been used. Samples of these solutions have been taken for FAAS analysis after dilution depending on the analysed metal. Samples for analysis of Cu, Fe, Ni, Pb and Zn have been diluted by 200 except for 750  $\mu\text{m}$  5 g samples for which they have been diluted by 100 only. Dilution was manually performed by taking 100  $\mu\text{l}$  using a class A 10-100  $\mu\text{l}$  pipette which are diluted with  $\text{HNO}_3$  0.5 mol/l in a 20 ml class A measuring flask (10 ml in case of dilution by 100). Samples for analysis of Co have been diluted by 5 or 10 except for 750  $\mu\text{m}$  5 g samples for which they have not been diluted. Dilution by 5 and 10 was manually performed by respectively taking a volume of 2 or 1 ml using a class A pipette which is diluted in a 10 ml class A measuring flask. During FAAS measurement, an automatic dilution can be performed to adjust the content to the calibration curve range.



**Figure 5. Analysis and FAAS calibration procedures.**

**Calibration curve determination.** The FAAS calibration curve is obtained by analysis of a set of four standards obtained by dilution with various dilution factors of a stock solution with a known composition in terms of Cu, Fe, Ni, Pb, Zn and Co contents (Figure 5). To consider the matrix effect, the ratios between the contents in the stock solution are close to the expected ones in the analysed solutions. A blank solution (named zero) is also used for the 0 mg/l calibration.

The stock solution composition is 20 mg/l of Cu and Fe, 5 mg/l of Pb, 2 mg/l of Ni and Co, and 1 mg/l of Zn. It is obtained by respectively diluting 4000  $\mu\text{l}$ , 1000  $\mu\text{l}$ , 400  $\mu\text{l}$  and 200  $\mu\text{l}$  of 1000 mg/l standard solutions of corresponding metals into a 200 ml measuring flask completed with a solution of  $\text{HNO}_3$  0.5 mol/l.

Four standards, numbered 1, 2, 3 and 4, are obtained by dilution of this stock solution. The standard 4 correspond to the stock solution itself. The standards 1, 2 and 3 are obtained by respectively pipetting 5 ml, 10 ml and 15 ml of stock solution completed by  $\text{HNO}_3$  solution in a 20 ml measuring flask. The Table 2 summarizes the constitution of the standards for calibration from the stock solution.

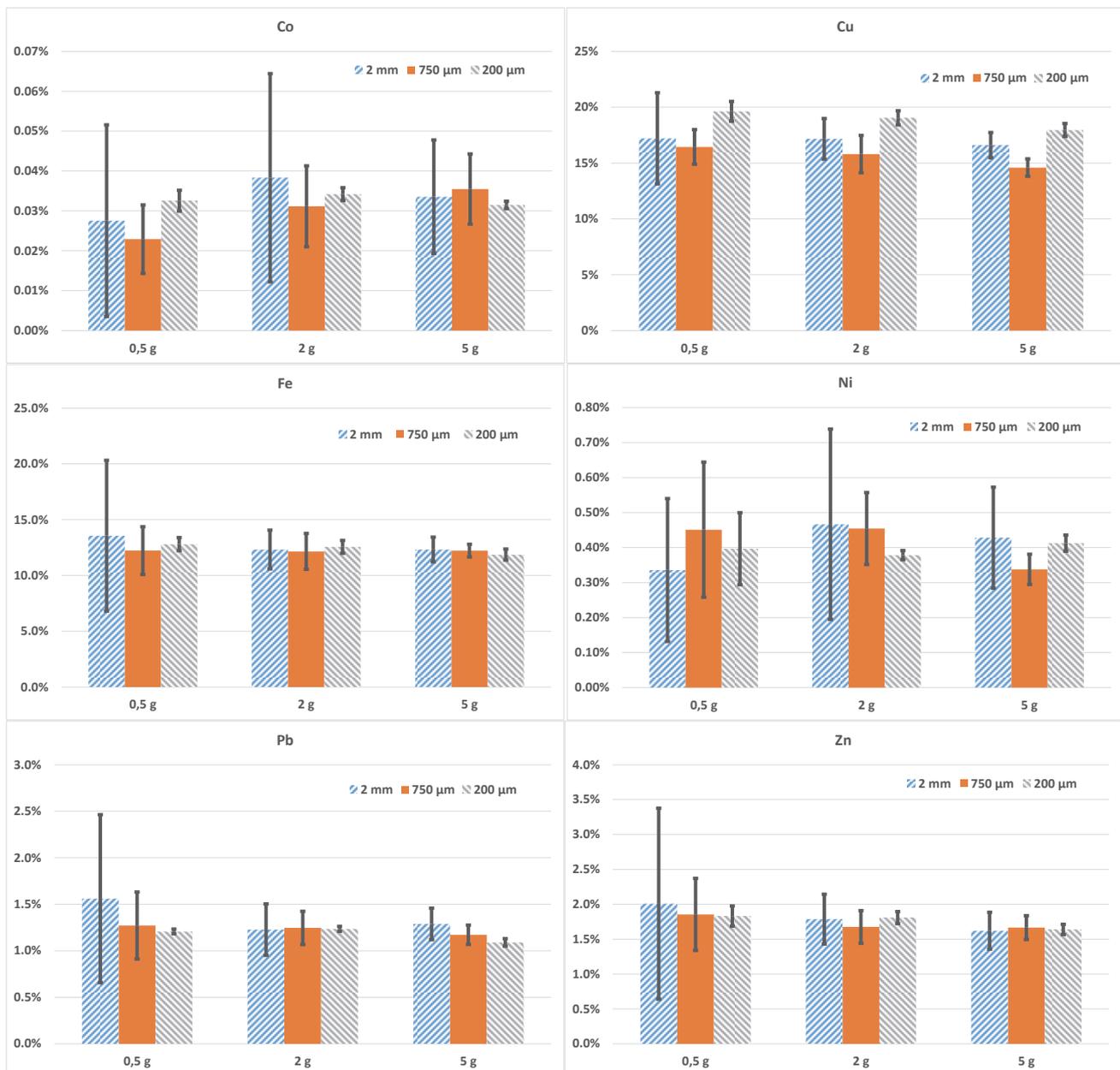
**Table 2. Stock solution and calibration standards constitution.**

	Co	Cu	Fe	Ni	Pb	Zn
Standard solution contents (mg/l)	1000	1000	1000	1000	1000	1000
Pipetting volume ( $\mu\text{l}$ )	400	4000	4000	400	1000	200
Stock solution contents (mg/l)	2	20	20	2	5	1
Calibration standard 1 contents (mg/l)	0.5	5	5	0.5	1.25	0.25
Calibration standard 2 contents (mg/l)	1	10	10	1	2.5	0.5
Calibration standard 3 contents (mg/l)	1.5	15	15	1.5	3.75	0.75
Calibration standard 4 contents (mg/l)	2	20	20	2	5	1

The calibration curve for each metal is obtained by measuring the absorbance of the zero solution and the four standards with fitting of the obtained points with a linear function for Co, Fe and Ni, or a quadratic function for Cu, Pb and Zn. These functions are used to obtain the metal contents in the leachate solution from the measurements of the absorbance.

#### Observed variability

The Figure 6 gives the average values of the metal contents for each sample type for which the error bars indicate the plus and minus one standard deviation considered as the observed variability.



**Figure 6.** Average content (%w/w) per sample mass and sample fineness for Co, Cu, Fe, Ni, Pb and Zn. The error bars indicate the  $\pm$  one standard deviation of the variability.

As expected, the general trend is a decreasing variability with decreasing maximum particle size of the sample. Despite some exceptions, the general trend is a decreasing variability with increasing sample mass. In some cases (Co 0.5 g, Cu all masses and Ni 5 g), the difference between average values of the different fineness seems larger than the internal variability. This is because all the samples of a given fineness, whatever the sample mass, are coming from the same 4 kg sample taken from the initial 122 kg sample ground to -10 mm. It appears there is important heterogeneity between the 10 mm pieces of WPCB with certainly some ones generating a nugget effect, hence this larger difference. After grinding, this effect disappears.

#### Sources of variability

Observing the Figure 1, it clearly appears the main parameters influencing the variability are the mass and the fineness of the analytical sample. As the relative variance of the sampling error depends on the mass of sample and on its intrinsic heterogeneity, itself depending on the fineness of the material, it seems reasonable to consider the sampling error as main source of variability. But, as it is shown in the following sections, the other component of the overall measurement error, the analytical error, is also depending on the mass of sample.

Even though the Pierre Gy's simplified formula cannot be applied in this case (the particle density distribution depends on their size), a similar formula can be used to estimate the impact of the analytical error:

$$\sigma^2 = \frac{IH}{M_s} = \frac{Kd^3}{M_s}$$

Assuming the observed variance  $\sigma^2$  is inversely proportional to the mass of sample  $M_s$  (the lot mass, 4 kg, being large compared to the sample mass) with the intrinsic heterogeneity  $IH$  as proportionality factor, and proportional to the volume of largest particles  $d^3$ , the parameter  $K$  can be calculated for each sample type (Table 3). The large difference between the  $K$  values for a given analyte suggests:

- The analytical error plays a non-negligible role in the overall measurement error.
- The simplified formula cannot be applied in this case.

**Table 3. Values of the K parameter in g/cm<sup>3</sup>.**

Sample type	Co	Cu	Fe	Ni	Pb	Zn
2 mm 5 g	112	3	5	71	11	17
2 mm 2 g	116	3	5	85	13	10
2 mm 0.5 g	48	4	15	23	21	29
750 μm 5 g	731	34	25	194	92	124
750 μm 2 g	503	53	82	243	98	93
750 μm 0.5 g	167	10	36	216	95	92
200 μm 5 g	534	652	1094	1936	867	1279
200 μm 2 g	602	279	528	300	121	561
200 μm 0.5 g	363	127	130	4207	27	393

To estimate the relative contribution of these two hypotheses, it is necessary to estimate the analytical error, subject of the next section.

### Calculation of the analytical error

In our case, the analysis part of the global experiment starts with the last WPCB sample weighing just before digestion. The analytical error is coming from the imperfection of the analysis protocol, of the devices used to perform intermediate measurement and of the operator. To calculate the analytical error, it is necessary to decompose the procedure in its different stages, identify and classify all the sources of uncertainty at each stage, calculate the first moments of the distribution of these uncertainties when possible, or at least estimate their magnitude, then calculate the full analytical error using error propagation rules.

The metal content  $C_{sol}$  in the solid WPCB sample is given by the formula:

$$C_{sol} = \frac{V_{dig}V_{dil}\mathcal{F}(A; \mathcal{E})}{M_sV_pR_{FAAS}}$$

Where:

- $M_s$  is the mass of solid sample before digestion.
- $V_{dig}$  is the volume of solution after digestion and completion in the measuring flask.
- $V_p$  is the volume of solution pipetting for dilution.
- $V_{dil}$  is the volume after dilution.
- $R_{FAAS}$  is the automatic dilution factor of FAAS (= 1 if there is no automatic dilution).
- $\mathcal{F}(A; \mathcal{E})$  is the metal content in the diluted solution calculated as a function of the measured absorbance  $A$ . This function is fitting the calibration curve with a set of parameters  $\mathcal{E}$  which have been obtained during calibration stage.

The more evident sources of uncertainty are coming from the measurement of the above parameters. But some other sources must be considered:

- After digestion, the solid residues can contain remaining metals which have not been subject to digestion. The coarser are the particles, the larger is the risk of such remaining metals, due to non-liberation or to longer leaching time. The residue analysis did not detect any remaining metals or at very low quantity compared to total amount for the 750 μm fineness<sup>1</sup>.
- The matrix effect during FAAS has been partially considered by using a stock solution, then standards, with a composition close to the one of the analysed solutions. However, many other elements (as Al, Mn, organics) were not considered in the standards.

### Sample mass measurement

The mass of sample is measured using precision scales. The main sources of uncertainty are coming from the imperfection of the device which are the readability, the repeatability, the linearity, the off-centre, the temperature sensitivity and the calibration test weight. The sample is put in the digestion flask for weighing. The mass of the flask constitutes the tare (approximately 150 g), the measurement of which is also source of uncertainty.

The scales being regularly calibrated and controlled, the risk of bias is low and negligible compared to the standard deviation. The variance of the relative measurement error for the mass  $M$  is given by the formula:

$$\sigma^2(M) = \sigma_R^2 + \frac{\sigma_A^2}{M^2}$$

Where:

- $\sigma_R^2$  is the relative component coming from the off-centre, the temperature sensitivity and the calibration test weight.
- $\sigma_A^2$  is the absolute component coming from the readability, the repeatability and the linearity.

The mass of sample  $M_s$  being the difference between the total mass  $M_T$  and the tare mass  $M_t$ , the relative variance of the sample mass measurement is:

$$\sigma^2(M_s) = \frac{M_T^2\sigma^2(M_T) + M_t^2\sigma^2(M_t)}{M_s^2}$$

The measurement error (with 95 % confidence level) for the three masses are then 0.022 % for 5 g, 0.054 % for 2 g and 0.22 % for 0.5 g.

### Digestion volume measurement

The volume of solution after digestion and completion with  $\text{HNO}_3$ ,  $V_{dig}$ , is measured using a 200 ml or 250 ml class A measuring flask. The main sources of uncertainty are coming from the tolerance of the flask ( $\pm 0.15$  ml), the operator sensitivity for reaching the mark, which can be estimated to two drops of liquid ( $\pm 0.1$  ml), the temperature variation ( $\pm 3^\circ\text{C}$ ) causing liquid dilatation (supposed the same as water).

The calculated measurement error is 0.18 % for the 250 ml flask and 0.19 % for the 200 ml one.

### Pipetting volume measurement

The volume of solution pipetted from the previous flask for dilution,  $V_p$ , is measured using a 10-100  $\mu\text{l}$  pipette for dilutions by 200 and 100, a 100-1000  $\mu\text{l}$  pipette for dilution by 10 and a 500-5000  $\mu\text{l}$  pipette for the dilution by 5. The main sources of uncertainty are coming from the tolerance of the pipette, the graduation linearity, the repeatability, the temperature variation ( $\pm 3^\circ\text{C}$ ) causing liquid dilatation (supposed the same as water).

The calculated measurement error is 1.1 % for the pipetting of 100  $\mu\text{l}$  or 1 ml, and 2.2 % for the pipetting of 2 ml.

### Dilution volume measurement

The previous pipetted volume is poured in a 10 ml or 20 ml class A measuring flask and completed with  $\text{HNO}_3$  to reach the dilution volume,  $V_{dil}$ . The main sources of uncertainty are coming from the tolerance of the flask ( $\pm 0.025$  ml and  $\pm 0.03$  ml respectively), the operator sensitivity for reaching the mark, which can be estimated to one drop of liquid ( $\pm 0.05$  ml), the temperature variation ( $\pm 3^\circ\text{C}$ ) causing liquid dilatation (supposed the same as water).

The calculated measurement error is 0.66 % for the 10 ml flask and 0.37 % for the 20 ml one. The error associated to the dilution factor is given in Table 4.

**Table 4. Measurement error associated to the dilution factor (95 % confidence level).**

Dilution factor	5	10	100	200
Pipetting volume (ml)	2	1	0.1	0.1
Dilution volume (ml)	10	10	10	20
Measurement error	2.26 %	1.27 %	1.27 %	1.15 %

### Automatic dilution error

Despite the manual dilution, it may be necessary to have an additional dilution performed automatically by the FAAS system. This automatic dilution being done using peristaltic pumps, the error on the expected dilution factor,  $R_{FAAS}$ , is estimated to 2 % by the manufacturer.

For low dilution factor, this error is comparable to the one we can have by manual dilution. But for higher dilution factors, it is more accurate to perform manual dilution. Especially as this automatic dilution arises after a manual dilution, the total dilution error being the sum of both. It is preferable to directly reach the range of contents of the calibration curve by manual dilution, avoiding the risk to have an automatic dilution.

### Uncertainty of the stock solution composition

The stock solution being used to produce standards, the uncertainty about its composition takes part in the error associated to the parameters of the function fitting the calibration curve. The concentration  $C_M$  of the metal M in the stock solution is given by:

$$C_M = \frac{C_{sM} V_{pM}}{V_f}$$

Where:

- $C_{sM}$  is the concentration of metal M in the standard solution: 1000 mg/l with a tolerance of  $\pm 10$  mg/l.
- $V_{pM}$  is the volume of pipetted standard solution: 4 ml for Cu and Fe, two times 200  $\mu\text{l}$  for Co and Ni, 1 ml for Pb and 200  $\mu\text{l}$  for Zn.
- $V_f$  is the volume after dilution in the 200 ml class A measuring flask.

The errors with 95 % confidence level for the estimation of the stock solution composition are 1.49 % for Co and Ni contents, 1.35 % for Cu and Fe contents, 2.70 % for Pb content and 1.50 % for Zn content.

### Uncertainty of the calibration standards composition

The standards 1, 2 and 3 are obtained by manual dilution of 5 ml, 10 ml and 15 ml of stock solution respectively into a 20 ml class A measuring flask. The pipetted volume is done using the same 5 ml pipette. The standard 4 is the stock solution itself. The Table 5 gives the error with 95 % confidence level associated to the expected composition of the standards.

**Table 5. Composition error (95 % confidence level) of the calibration standards.**

Calibration standard	Co	Cu	Fe	Ni	Pb	Zn
1	1.64 %	1.52 %	1.52 %	1.64 %	2.78 %	1.65 %
2	1.62 %	1.50 %	1.50 %	1.62 %	2.77 %	1.63 %
3	1.62 %	1.49 %	1.49 %	1.62 %	2.77 %	1.63 %
4	1.50 %	1.35 %	1.35 %	1.50 %	2.70 %	1.51 %

### Absorbance measurement error

The absorbance is given in units of absorbance (UA) and varies from small negative value (corresponding to a null concentration) to 0.55 UA. The sources of uncertainty can be divided in three main groups according to their origin: the flame, the light source and the optics<sup>3</sup>. Three uncertainty components are then assumed: stability with  $\pm 0.0003$  UA, base line with  $\pm 0.0003$  UA and repeatability with  $\pm 0.0002$  UA.

### Linear regression parameters error

If the calibration curve is supposed to be a linear function of type  $y = ax$ , the parameter  $a$  is obtained by regression on a set of four standard measurements  $(x_i; y_i)$ ,  $x_i$  being the metal content in the standard and  $y_i$  the measured absorbance. Its value is given by:

$$a = \frac{\overline{xy}}{\overline{x^2}}$$

Where:

$$\overline{xy} = \frac{\sum_i w_i x_i y_i}{\sum_i w_i}$$

$$\overline{x^2} = \frac{\sum_i w_i x_i^2}{\sum_i w_i}$$

$$w_i = \frac{1}{\sigma^2(y_i) + a^2 \sigma^2(x_i)}$$

The absolute variances of the error associated to the absorbance measurement ( $\sigma^2(y_i)$ ) and to the standard composition estimate ( $\sigma^2(x_i)$ ) have been defined above. Consequently, the uncertainty about the value of the regression parameter is given by its relative variance:

$$\sigma^2(a) = \frac{1}{a^2 \sum_i w_i x_i^2}$$

The error (95 % confidence level) associated to the regression parameter for Co, Fe and Ni analysis is then 1.07 %, 0.99 % and 1.07 % respectively. The variance of the measurement error associated to the content in the solution,  $\mathcal{F}(A; a)$ , for the measured absorbance  $A$  is given by:

$$\sigma^2(\mathcal{F}(A; a)) = \sigma^2(a) + \frac{\sigma^2(A)}{A^2}$$

Where  $\sigma^2(A)$  is the absolute variance of the absorbance measurement error.

### Overall analytical error

When combining the components of all these sources of errors, the relative variance of the overall analytical error is given by the sum of the individual relative variances:

$$\sigma^2(C_{sol}) = \sigma^2(M_s) + \sigma^2(V_{dil}) + \sigma^2(V_{dil}) + \sigma^2(V_p) + \sigma^2(R_{FAAS}) + \sigma^2(\mathcal{F}(A; a))$$

As some of these components depends on the content of the analyte, the relative analytical variance and, consequently, the width of the 95 % confidence interval, must be calculated for each analysed sample. The Table 6 gives the range of calculated errors, coming from the range of measured contents, for each sample type.

The ranges of errors clearly show that the average value depends on the mass of analytical sample while the width of this range depends on the fineness of that sample. The second point can be easily explained as it is linked to the sampling error which is expected to decrease when the particle size decreases for a given sample mass, resulting in a narrower range of contents. The first point is more linked to the dilution process which uses the same factor whatever the initial sample mass, except for Co. Consequently, the concentration in the analysed solution is proportional to the mass of initial analysed sample resulting in a lower measured absorbance for small samples. As the main dependence of the relative variance with the content is coming from the absorbance measurement error which has a constant absolute variance, too low absorbance results in a large measurement error.

In fact, the dilution factor must be adapted to the expected content. If a factor of 200 seems adapted for the 5 g samples, it must be reduced to 80 and 20 for the 2 g and 0.5 g respectively.

**Table 6. Minimum and maximum analytical errors\* observed per sample type for Co, Fe and Ni contents.**

Sample type	Co analytical error		Fe analytical error		Ni analytical error	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
2 mm 5 g	1.8 %	2.7 %	3.3 %	4.1 %	1.7 %	2.3 %
2 mm 2 g	1.8 %	4.7 %	1.7 %	1.8 %	1.8 %	4.5 %
2 mm 0.5 g	3.1 %	23.9 %	1.6 %	2.6 %	7.6 %	77 %
750 $\mu$ m 5 g	2.3 %	2.3 %	2.6 %	2.6 %	1.8 %	2.1 %
750 $\mu$ m 2 g	2.6 %	3.1 %	1.7 %	1.8 %	2.4 %	4.2 %
750 $\mu$ m 0.5 g	4.3 %	12.2 %	3.0 %	4.8 %	6.7 %	21.8 %
200 $\mu$ m 5 g	2.6 %	2.6 %	1.6 %	1.6 %	1.9 %	2.0 %
200 $\mu$ m 2 g	2.7 %	2.8 %	1.7 %	1.8 %	3.4 %	4.2 %
200 $\mu$ m 0.5 g	4.1 %	5.4 %	3.4 %	4.1 %	7.2 %	16.4 %

\* The term "error" is used here as the width of the 95 % confidence interval calculated as 1.96 times the standard deviation. Calculated errors with value larger than 20 % are displayed just to indicate they are large, but their value is not in accordance with some assumptions which have been done for their estimation, such as the error propagation rule and the distribution normality.

## Discussion about sampling error

As all samples of a given fineness have been drawn from the same 4 kg lot, the observed variability includes this last sampling stage (laboratory sample taking) and the analysis. Consequently, by subtracting the average variance of the analytical error from the variance of the observed variability, it remains the variance of the last stage sampling error.

The Table 7 gives the obtained sampling error (95 % confidence level) and the associated intrinsic heterogeneity *IH* for the measurement of the Co, Fe and Ni contents per sample type.

**Table 7. Observed sampling error\* and associated intrinsic error per sample type for Co, Fe and Ni contents.**

Sample type	Sampling error (95 %)			Intrinsic heterogeneity** (g)		
	Co	Fe	Ni	Co	Fe	Ni
2 mm 5 g	84 %	18 %	67 %	1.165	0.05168	0.7389
2 mm 2 g	134 %	28 %	115 %	1.144	0.04843	0.8369
2 mm 0.5 g	171 %	98 %	116 %	0.4036	0.1321	0.1849
750 $\mu$ m 5 g	49 %	8.7 %	25 %	0.2928	0.009353	0.07750
750 $\mu$ m 2 g	64 %	26 %	45 %	0.2736	0.04477	0.1317
750 $\mu$ m 0.5 g	74 %	35 %	83 %	0.07519	0.01632	0.09532
200 $\mu$ m 5 g	5.2 %	8.1 %	10.8 %	0.004228	0.01037	0.01844
200 $\mu$ m 2 g	9.3 %	8.9 %	5.7 %	0.005117	0.004689	0.001933
200 $\mu$ m 0.5 g	15 %	8.2 %	49 %	0.002777	0.000925	0.03278

\* The term "error" is used here as the width of the 95 % confidence interval calculated as 1.96 times the standard deviation. Calculated errors with value larger than 20 % are displayed just to indicate they are large, but their value is not in accordance with some assumptions which have been done for their estimation.

\*\* The term "intrinsic heterogeneity" is abusive in this case as this parameter is defined for the fundamental sampling error (FSE) while it is used here for the overall sampling error which includes FSE and other non-negligible components. It is named "pseudo intrinsic heterogeneity" in the following discussion.

All the samples of a given fineness have been drawn from one lot of approximately 4 kg ground to the target, except for the -200  $\mu$ m lot which is of 2 kg. Consequently, the obtained sampling error only concerns the last stage of sampling when taking 5 g, 2 g or 0.5 g of sample from a lot of 4 kg or 2 kg. In all cases, the mass of lot can be considered as large compared to the mass of sample and its influence on the sampling error is negligible. As expected, it is well observed the obtained sampling error is decreasing when the mass of sample increases, and that for all fineness and analytes (except for 200  $\mu$ m 2 g samples for which the variance of the observed variability was particularly small for Ni content and high for Fe content). But the values of the intrinsic heterogeneity indicate the variance of the total sampling error is not inversely proportional to the mass of sample.

As the 4 kg (or 2 kg) lots have been obtained by division of one 122 kg lot which had been previously ground to -10 mm, it is possible to compare the effect of fineness: the samples of the same mass have an observed sampling error decreasing when the size of the largest particles decreases, as expected. But the intrinsic heterogeneity is not proportional to the third power (or a smaller power) of that maximum size indicating the simplified formula of Pierre Gy cannot be used.

The main sampling error components which must be considering in this case are:

- The fundamental sampling error (FSE), the variance of which is clearly inversely proportional to the mass of sample. The intrinsic heterogeneity associated to the FSE is certainly not proportional to the unit mass of the largest particles due to the nature of the components bearing the followed metals which have different behaviours during grinding and have a wide range of densities. Being theoretically defined as the minimum sampling error when the sample drawing follows a strict and ideal equiprobability rule, this component is independent of the sampling conditions, the other components being in charge to consider the gap between ideal and reality.
- The grouping and segregation error (GSE), the variance of which is proportional to the one of FSE with both grouping and segregation factors, following the Pierre Gy's approach<sup>5</sup>. But these factors are not constant regarding the mass of sample and are very difficult to estimate (even though their product is frequently assumed to be one). In the present case, the use of riffle splitters by experimented operators from the lot to the analytical sample let think a limited effect of grouping and segregation against the equiprobability rule. There is an infringement of rules for the 0.5 g sample drawing which has been done by scooping. Fortunately, scooping was performed from a 2 g intermediate sample obtained by riffle splitting and four samples was taken for each 2 g, preventing unacceptable bias on the determination of the mean value. The counterpart is a risk of larger observed variability for these kinds of 0.5 g samples, due to GSE, but, in opposition to any expectation, the contrary is observed with a lower pseudo intrinsic heterogeneity for two thirds of sample types (Table 7).
- The increment delimitation error (IDE) and increment extraction error (IEE) are mainly linked to the increment taking device, its design, its size, and its use. The riffle splitter has been mainly used for this experiment. It is not the best system for sample division, but it can be very efficient if it is well used with a size well adapted to the maximum particle size and the sample mass, which seems the case here. These components are due to side effect generating a relative variance which is constant versus the sample mass. This variance can be neglected when the volume in which the side effect occurs is small compared to the total volume of the sample. This is the case for this experiment.

To summarize, it appears the calculated variance of the sampling error is only partially inversely proportional to the sample

mass and the obtained pseudo intrinsic heterogeneity is decreasing as the sample mass reaches 0.5 g, quite unexpectedly. The reasons of that can be:

- The analytical error is wrongly estimated due to some mistakes in parameter estimations. Consequently, the sampling error is wrongly estimated.
- The observed variability does not reflect the true variability because of insufficient number of samples or because of conditional probability due to the successive division process.
- In the grouping and segregation error (GSE), the segregation and grouping factors are higher for larger samples due to interaction between particles (electrostatic effects, entanglement) which can be more frequent when there is more material to divide. This effect can also generate IDE and IEE.

Deeper investigation and additional experiments must be conducted to try to answer these questions.

## Conclusion

This approach trying to separate analytical error and sampling error from the experimentally observed variability in sample analysis had as objective to better understand the behaviour of the material during the sampling stages and propose a sampling protocol well adapted to the WPCB. If part of this questioning has been answered, other part remains, and additional questions arose.

The analytical error has been calculated by considering the full process of analysis from the weighing of the WPCB sample for analysis to the results delivered by the FAAS device. If some values of analytical process parameters remain uncertain, the general error calculation method constitutes a base line for this kind of procedures. In this case, it is very difficult to verify this error estimate using standards as such standards do not exist in the market and cannot be easily produced with sufficient level of accuracy. Only the last stage of FAAS of solution can be controlled by liquid standards and subject to statistical analysis.

The procedure to estimate the sampling variability has also been questioning during this study and further investigations will necessitate more attention in the general protocol, in the choice of devices, and in the practice. The division process is mainly concerned by this point, but also the grinding stages as this kind of WPCB material is very difficult to grind, specifically for fine grinding. This difficulty calls the opportunity to use fine grinding for sampling in mind. Other sample preparation techniques may be easier without reducing the representativeness of the sample.

In any case, further investigations are necessary, not limited to the six metals studied here, to define a sampling and analytical procedure which is technically and scientifically accurate enough and industrially acceptable. Indeed, if major recycling consumer companies, mainly metal producers, have their own sampling and analytical procedures, a lot of smaller companies involved in WEEE recycling are looking for methods of waste value estimation which are accurate and relatively simple to carry out. In such a way, accuracy and transparency for material valuation in commercial transactions between the different stakeholders of the recycling can be a leverage for the growth of the circular economy.

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## References

1. A. Hubau, A. Chagnes, M. Minier, S. Touzé, S. Chapron and A.-G. Guezennec, "Recycling-oriented methodology to sample and characterize the metal composition of waste Printed Circuit Boards", *Waste Management*. **91**, 62–71 (2019). <https://doi.org/10.1016/j.wasman.2019.04.041>
2. S. Touzé, S. Guignot, A. Hubau, N. Devau and S. Chapron, "Sampling waste printed circuit boards: Achieving the right combination between particle size and sample mass to measure metal content", *Waste Management*. **118**, 380–390 (2020). <https://doi.org/10.1016/j.wasman.2020.08.054>
3. A. Petrov, G. Gentsheva, I. Havezov and E. Ivanova, "Determination of the Uncertainty of the Flame Atomic Absorption Spectrometer for Copper, Cobalt, Cadmium, and Nickel", *Analytical Letters*. **42**, 2509–2519 (2009). <https://doi.org/10.1080/00032710903243513>
4. A. Hubau, S. Touzé, S. Brochot and P. Wavrer, "Estimation of uncertainty for measuring metals content in waste printed circuit boards", in *Proceedings 10th World Conference on Sampling and Blending (WCSB10)*, TOS forum (2022).
5. P. Gy, *Hétérogénéité, Echantillonnage, Homogénéisation, Ensemble cohérent de théories*, Masson, Paris (1988).