# A novel method to calculate the size of representative waste samples based on particles size

#### SUPPLEMENTARY MATERIAL

Giovanni Beggio<sup>1</sup>, Pierre Hennebert<sup>2</sup>

<sup>1</sup> Department of Civil, Environmental and Architectural Engineering, University of Padova, Via Marzolo 9, 35131, Padova, Italy

<sup>2</sup> Ineris (French National Institute for Industrial Environment and Risks), BP 2, F-60550 Verneuil-en-Halatte, France.

Corresponding author: giovanni.beggio@unipd.it

#### **Table of Contents**

<u>1.</u>	Further in-depth discussion of the approach proposed in this work	2
<u>2.</u>	Some methods for the assessment of p	.7
	2.1. Calculation of p from concentration limit in waste and functional concentration of a substant in the product that became waste	ce . 7
	2.2. Tentative calculation of p from population data	8
<u>3.</u>	Analytical and intra-laboratory variability from repeated analysis on a set of test portions prepare according to the approach by number of particles	ed I 1
<u>4.</u>	Further discussion on incorrect sampling and sample preparation1	13

#### 1. Further in-depth discussion of the approach proposed in this work

The logical development behind the approach presented in the paper for the calculation of the size of representative sample of wastes is summarized in Table 1S. The formulas presented in the paper and deepened in the next paragraphs are resumed in Table 2S.

Observation	Consequence for representative sampling
Waste batches are commonly characterized by positively skewed distributions of characteristics of interests and particles sizes.	→ The rare fractions of particles increase significantly the mean of the measurand; → there could be size-concentration relationships that influence the mean concentration; → Rare particles in concentration and in size must be included in the sample with a reliably similar proportion $p$ as they occur in the population.
Recalling the binomial probability distribution, it is possible to calculate the number of particles $n$ that should be present in samples	$n \ge \frac{(1-p)}{CV_p^2 p}$
Minimal observable variability $CV_p$ can be estimated as the analytical variability obtained with the smallest possible ("homogeneous") test portion under "repeatability" conditions (Hennebert and Beggio, 2021).	$\rightarrow CV_p = CV_r = CV = 0.1$
The minimum number of "rare" particles (both in concentration and in size) in a sample should be 100 (Hennebert and Beggio, 2021).	$\rightarrow np \ge \frac{(1-p)}{cV_p^2} \approx \frac{1}{cV^2} \approx 100 \text{ (with } p \ll 1)$
The number of particles n in a representative sample depends on $p$	$\rightarrow n = \frac{100}{p}$

Table 1S. Logical development of the approach presented in the paper

Table 2S. Summary of the formulas proposed in the paper for the calculation size of a representative sample in terms of the number of particles. All terms are defined in the paper. \* These formulas are described in the

	$\frac{\text{Distribution}  \text{of}}{\text{the measurand}}$ $\rightarrow$	<u>Normal</u> <u>(</u> <i>CV</i> <sub>pop</sub> <u>≤ 0.5)</u>	$\frac{\text{Not normal}}{(CV_{pop} > 0.5)}$	$\frac{\text{Not normal}}{(CV_{pop} > 0.5)}$	<u>Not known</u>	-
	$\begin{array}{c} \underline{Particles} & \underline{size} \\ \underline{distribution} \\ \rightarrow \end{array}$	<u>Homogeneous</u>	-	-	-	Heterogeneous
Requirements for representative sampling L	To be known or assumed ↓	Ļ	Ļ	Ļ	Ļ	Ļ
1. Number of rare particles	Fractions of rare particles	<i>p<sub>c</sub></i> = 0.1	<i>p<sub>c</sub></i> = 0.01	<i>p<sub>c</sub></i> = 0.001	$p_c = \text{conc}$ limit/functional concentration (Hennebert and Beggio, 2021)	p <sub>s</sub>
	Number of particles <i>n</i>	$n = 10^3$	$n = 10^4$	$n = 10^5$	<i>n</i> = 100/ <i>p<sub>c</sub></i>	$n = 100/p_s$
	Mass of sample by number of particles <i>M<sub>sam,c</sub></i>	$n * \overline{M_p} = \frac{(1 - p_c)}{CV^2 p_c} * \frac{\pi}{6} (D_{95})^3 * \rho_p * g * f$ (Eq. 2)			100 * s/S (Eq. 4)	
2. Probabilistic performance of sampling	Number of increments $n_{inc}$	20	50	50	50	50
	Mass of sample by increments* <i>M<sub>sam,inc</sub></i>	$20 * (3D_{95})^3 * \rho_b$	$50 * 4 * (3D_{95})^3 * \rho_b$	$50 * 40 * (3D_{95})^3 * \rho_b$	$50 * (n/2700 * f * g) * \frac{\rho_p}{\rho_b}$	$\frac{f}{27S}\frac{\rho_p}{\rho_b} * (3D_{rs})^3$ $* \rho_b$
3. Mass for analyses and reserves	Mass for analyses and reserve	Sum of test portions, repetitions and reserve for all analyses and tests				

#### 1.1. Equalizing $M_{sam,c}$ and $M_{sam,inc}$

The size of a sample  $M_{sam,c}$ , considered representative of the population's characteristics of interest, is calculated multiplying a number of particles in the sample (calculated based on binomial distribution) by their average mass, as indicated in European sampling standards and recalled in Eq. 2 of this paper.

On the other hand, composite samples made up of a number of increments must be produced to ensure probabilistic performance of sampling and to provide results representative of the average value of the measurand in the waste lot, i.e., considering possible spatial/temporal variability among particles. This requirement is laid down in the European standard and recalled in Eq. 6 of this paper. In particular, Eq. 6 ensures that large particles will not be segregated during sampling, by imposing the dimensions of the sampling instrument to be at least 3 times the size of the largest particle. Therefore, an increment is made of that corresponding volume, or a multiple  $I_{inc} \geq 1$  of it. Therefore, Eq. 6 can be rewritten as follows:

$$M_{sam,inc} = n_{inc} * I_{inc} * (3D_{95})^3 * \rho_h$$
(Eq. 1S)

To satisfy all requirements, the size of a sample must be the maximum values calculated between Eq. 2 and Eq.6. This can be done by introducing Eq. 1S, equalizing  $M_{sam,c}$  with  $M_{sam,inc}$  and adjusting  $n_{inc}$  and  $I_{inc}$ .

An empirical number of  $n_{inc} = 20$  increments is generally recommended in standards to consider variability in the composite sample from the waste lot. The number of increments is determined empirically and should be as large as possible. For instance, the authors calculated the variability of total Br concentration in a composite sample as a function of number of increments from individual plastic scraps characterized by a distribution of Br content rightly skewed by just some highly concentrated particles, showing that 50 increments of  $(3D_{95})^3$  size reduces the CV of measured total Br within repeated samples to < 0.1 (results not shown).

Therefore, as n (the number of particles in the sample) and  $n_{inc}$  (the number of increments) are fixed according to the population characteristics, by equalizing  $M_{sam,c}$  with  $M_{sam,inc}$ , we get:

$$I_{inc,c} = \frac{1}{n_{inc}} * n * \frac{\pi}{6} * \frac{1}{27} * f * g * \frac{\rho_p}{\rho_b}$$
(Eq. 2S)

For normal distribution of the measurand among particles, the frequency of particle of interest can be set to  $p_c = 0.1$ , as suggested for major constituents in European sampling standards. Since it was demonstrated that  $n * p_c = 100$  (Eq. 1 of the paper), in this case  $n \approx 1,000$ . Further, by assuming  $n_{inc} = 20$ , f = g = 1, and  $\rho_p = \rho_b$ , Eq.2S delivers  $I_{inc,c} \approx 1,031/n$ . As  $n \approx 1,000$ ,  $I_{inc} \approx 1$ . The volume of an increment can be limited to one time the volume of the sampling instrument: one uptake is enough for one increment. Also, the volume of a representative sample is the volume of 20 increments of  $3D_{95}$ -size cube, representing the volume of 540 (i.e.,  $20*3^3$ ) spheres having a diameter of  $D_{95}$ , divided by their cubic equivalent factor  $\frac{\pi}{6}$  (V cube  $= D_{95}^3$ , V sphere  $= \frac{\pi}{6} D_{95}^3 \approx 0.5 * D_{95}^3$ ). These results are presented in the 3<sup>rd</sup> column of Table 2S.

For more heterogeneous distributions,  $p_c$  is lower, and  $n_{inc}$  should be increased. Three cases are presented in 4<sup>th</sup>, 5<sup>th</sup> and 6<sup>th</sup> column of Table 2S.  $I_{inc}$  increases according to n and  $n_{inc}$ , corresponding to larger and larger samples to capture rarer and rarer particles.

The amount of material necessary for the analyses must also be considered (Eq. 7 of the paper). A duplicate sample or at least some reserve of material should also be considered. The mass to sample is the maximum of the masses required by concentration, by increments, or by analyses.

#### 1.2. Equalizing $M_{sam,s}$ and $M_{sam,inc}$

The size of a sample  $M_{sam,s}$ , considered representative of the population particles size distribution, is that containing 100 particles rare in size, i.e., belonging to the less numerous size class, as recalled in Eq. 4 of the paper.

Here also, the two conditions laid down in Eq. 4 and Eq. 1S must be satisfied simultaneously: the largest sample size among the two is taken. To do so,  $M_{sam,s}$  and  $M_{sam,inc}$  can be equalized and solved in terms of  $I_{inc}$ . These results are presented in the 7<sup>th</sup> column of Table 2S.

To simplify the process, we must suppose, by similarity with the approach used in the European sampling standards, that the mass of a particle "rare in size" s can be estimated by:

$$s = \frac{\pi}{6} * f * D_{rs}{}^3 * \rho_p$$
 (Eq. 3S)

Where  $D_{rs}$  is the biggest dimension measured within the particles rare in size.

The shape factor f can be calculated as indicated in the European standard for sampling of solid recovered fuels (CEN, 2021). The shape factor f should be used for non-spherical particles. In particular, it is the ratio of the maximum volume of a particle (a mass fraction of 95% of particles are smaller) divided by the volume of a cube whose size is the maximum length of a particle (a mass fraction of 95% of particles are smaller) of particles is less than this maximum length), namely  $f = [(length * width * depth)/(D_{95}^{-3})]$ . As the shape factor is based on cube, it seems logical to remove from Eq. 3S the  $\pi/6$  factor (i.e., coming from volume of sphere). However, for the sake of continuity of the equations, it is kept here, in tribute to the difficulty of evaluating the average mass of a particle in a mixture of different particle size. It must be kept in mind that the formulas above are only approximations.

Therefore,  $M_{sam,s}$  and  $M_{sam,inc}$  are equalized with:

$$I_{inc,s} = (100 * f * \frac{\pi}{6} * D_{rs}^{3} \frac{\rho_{p}}{s}) / (n_{inc} * D_{95}^{3} * \rho_{b})$$
(Eq. 4S)

Assuming  $n_{inc} = 50$ , to tackle broad particle size distributions, and  $D_{rs} \approx D_{95}$ , Eq. 4S becomes:

$$I_{inc,s} = \frac{f}{27S} \frac{\rho_p}{\rho_b} \ge 1 \tag{Eq. 5S}$$

Each of the 50 increments must have a volume of  $I_{inc,s} * D_{rs}^{3}$ . This number  $I_{inc,s}$  increases when the form factor f increases (i.e., the particles are more cubic), when S decreases (i.e., the particles rare in size are rarer in the lot), and when the bulk density  $\rho_b$  of the waste decreases relatively to the particle density  $\rho_p$ .

To be practical, if we suppose that the densities are equal (typically the bulk density is 2 to 10 times lower than the particle density), to have  $I_{inc,s} = 1$ ,  $M_{sam,s}$  and  $M_{sam,inc}$  are equal only if f = 27 S. Not taking into account the  $\pi/6$  factor (see above), f = 14 S. In this case, the equality of mass of sample is only possible for rare particles with a relative high f factor (more cubic). For instance, if S = 0.01, f = 0.14, and if S = 0.05, f = 0.70 (i.e., the particles are more cubes than spheres), and S = 0.07 for f = 1 (the particles are cubes). Calculation of  $I_{inc,s}$  for different cases are presented in Figure S1. Calculated  $I_{inc,s}$  is <1 for flat, frequent, low-density particles (e.g., cardboard) and must then be set to 1.



Figure S1: Calculated Isize (the multiplying factor of the volume of 50 increments in case of representative sampling in terms of number of particles) as a function of the shape factor f, the mass fraction of rare particle in size S, and the ratio of density of particles and bulk density of the waste  $\rho$ part /  $\rho$ bulk (noted  $\rho/\rho$ ). When Isize is < 1, (flatter, more frequent and low-density particles – in red), Isize must be set to 1.

In all other cases (i.e., flat particles),  $M_{sam,s}$  and  $M_{sam,inc}$  are equal when  $I_{inc,s}$  will be increased. This demonstrates the importance to use the shape factor f, the mass fraction of rare size particles S, the density of the particles, and the bulk density of the waste to calculate the size of a representative sample.

Also in this case, the amount of matter necessary for the analyses must also be considered. It is the sum of the aliquot of each analysis. A duplicate sample or at least some reserve of material should also be considered (last row of Table 4).

#### References

CEN, 2021. EN ISO 21645. Solid recovered fuels — Methods for sampling.

Hennebert, P., Beggio, G., 2021. Sampling and sub-sampling of granular waste: size of a representative sample in terms of number of particles. Detritus 17, 30–41. https://doi.org/https://doi.org/10.31025/2611-4135/2021.15139

#### 2. Some methods for the assessment of p

### 2.1. Calculation of p from concentration limit in waste and functional concentration of a substance in the product that became waste

The fraction of 'rich' particles (p) that must not be exceeded in waste to not trespass a concentration limit (CL) in mean in all particles can be calculated from the functional concentration of the analyte in the products that became waste. The 'rich' particles are the particles with the recommended functional concentration (FC). That concentration can be found in producer's catalogue and in technical literature or safety data sheets. If the other particles of the lot have a null concentration, if all the particles have the same weight, the mean concentration of the lot of particles is equal to p.FC + (1-p).0 = p.FC. That concentration must be lower or equal to the CL. From that, we have p.FC  $\leq$  CL or p  $\leq$  CL/FC. The fraction of particle of interest is simply lower or equal to the ratio of the concentration limit in waste and the functional concentration in products.

This approach is illustrated for brominated flame retardants (European Commission 2021) and for mercury in household waste (Table S3).

For brominated flame retardants, the fraction of particle of interest is the ratio of the Low Pop Concentration Limit (LPCL) of the flame retardant in waste and the functional concentration (FC) of that flame retardant in products. The result for polybromodiphenylethers (PBDEs), hexabromocyclododecane (HBCDD) and short-chain chlorinated paraffins (SCCPs) are presented in the following table:

Substance	Considered Low POP Concentration Limit LPCL (mg/kg)	Polymer	Functional co range (mg/kg	oncentration (FC) ;) (in products)	p = LPCL/FC (expressed as a fraction of 1)	
			Min FC	Max FC	With Min FC	With Max FC
PBDEs	200	High-impact polystyrene*	110 000	150 000	0.0018	0.0013
		Polyamide*	130 000	160 000	0.0015	0.0013
		Polyolefins*	50 000	80 000	0.0040	0.0025
		Polyurethanes*	100 000	180 000	0.0020	0.0011
		Styrene copolymers*	120 000	150 000	0.0017	0.0013
HBCDD	100	Polystyrene foam*	8 000	40 000	0.0125	0.0025
		XPS**	5 000	30 000	0.0200	0.0033
		EPS***	1 000	9 000	0.1000	0.0111
		XPS***	6 000	14 000	0.0167	0.0071
SCCPs	420	Rubber****	1 500	30 000	0.2800	0.0140

Table S3. Examples of the size of a representative sample (p and n) for PBDEs, HBCDD and SCCPs based on LPCL options and functional concentrations (FC) (European Commission 2021).

For mixed waste, rounded maximal 'p' is 0.001 for PBDEs, 0.003 for HBCDD and 0.015 for SCCPs. The number of particles that a representative sample should contain is n = 100/p = about 100,000 for PBDEs, 40,000 for HBCDD and 7,000 for SCCPs for the LPCL options considered in the table above.

For mercury in household waste, a hypothetical example is the presence of dental amalgam waste in household waste. The functional concentration of mercury in dental amalgam is 50%. The concentration limit of mercury that renders a waste hazardous (Hennebert 2019b, using M-factors of 100) is 25 mg/kg. The particle fraction of dental amalgam for household waste not being hazardous, if all the particles have the same weight, should not be larger than p = CL/FC = 25 mg/kg / 500 000 mg/kg = 0.00005 = 5 10-5. The number of particles in household waste sample should be  $n = 100/p = 2 10^6$ . If the mean mass of one particle in household waste is 10 grams, the mass of a representative sample is 20 tons. This is not unrealistic, since in household characterization campaigns, some tons are sampled (Wavrer et al. 2010). The "true" concentration of mercury in municipal waste can only be known by such large samples. That

extreme example of « nugget » effect can explain the sudden peak emission of mercury in flue gas of municipal solid waste incinerators (revealed only by continuous Hg monitoring in flue gas). To reduce 20 tons to a laboratory sample of 20 kg, keeping 2 million of particles in the laboratory sample, the particle size should be reduced to about 4 mm before mixing and subsampling...

#### 2.2. Tentative calculation of p from population data

For sampling for resource evaluation, for instance for the assessment of concentration of valuable elements or substances to recover, if no better assessment of p is available, a simple approach can be developed from the minimal, mean and maximal observed concentrations in different individual composite samples of a population. These synthetic data are frequently published or available. If the measured values are not normally distributed, it means that every individual sample is too small to capture the variability of the whole population. The concentration of these individual samples is the mean concentration of the particles they are made of and does not allow to know the composition of individual particles, which is more variable. It could nevertheless be used in a first approach. The population of individual samples can be conceptually divided in a group of low value, and a group of high value with a p frequency. The mean concentration of the population is equal to (1-p).low value + p.high value. In a conservatory approach, it is proposed to take the minimal observed value or the LOQ for "low value", and the maximal observed value for "high value". The mean concentration is roughly approximated by [(1-p).Cmin + p.Cmax]. If p is "low", (1-p) is close to 1. It comes that

$$p \approx (mean \text{ concentration} - minimal \text{ concentration})/(maximal \text{ concentration})$$
 (Eq. 6S)

The minimal concentration can be the one observed in the population or can be the limit of quantification by the measurement method. The limit of quantification is the minimal concentration that can be measured with an acceptable variability. It can be conventionally assessed for each analytical method as being 10 times the standard deviation of repeated measurements of a sample with a null concentration (blank).

This approach is illustrated for element concentration in printed circuit boards (Korf et al. 2019) and digestates (Beggio et al. 2019).

Literature data of elemental composition of printed circuit boards (PCB) has been compiled by Korf et al. (2019) from 37 authors with 103 samples of up to 52 elements, and in total 1 to 92 element concentration (Figure S2). Keeping here only the 33 elements with at least 10 data (up to 92 data), 32 elements have a CV > 0.5 (Figure S2). In this data set, the maximum reported concentration is > 2.5 times the mean concentration for 31 elements out of 33 (mean ratio max/mean = 6, maximum ratio = 21).

"p" can be estimated for 33 elements (Figure S3). The estimated ps are clearly "high", starting from 0.05. The 'rare composite samples' are quite frequent or even common with that method. Not all elements have been measured in all samples. The observed variability used to assess p is smoothed using composite samples. This method can help as a first preliminary assessment. Alternatively, the result could be used to increase the size of the composite samples to be representative of the whole population.



Figure S2: CVs (blue bars) and mean concentrations of 25 elements (orange line) in printed circuit boards (calculated from data of Korf et al. 2019)



Figure S3: Approximation of p for 33 elements in printed circuit boards by the min/mean/max concentrations of the population (calculated from data of Korf et al. 2019)

Another case, presented in Table S4, is composition of digestates from national characterization data in Italy (Beggio et al. 2019).

Table S4. Approximation of p for 7 elements in agro-industrial and municipal digestates in Italy (data of Beggio et al. 2019)

Waste	Agro-industrial digestate ( $n = 919$ )			= 919)	Organic fraction of municipal solid waste digestate ( $n = 1397$ )			
Parameter				p = (mean-				p = (mean-
(mg/kg)	mean	min	max	min)/max	mean	min	max	min)/max
Hg	0.05	0.05	0.05	-	0.08	0.03	0.1	0.50
Zn	280	31.7	1780	0.14	233	37.4	427	0.46
Cu	62.2	2.78	219	0.27	53.2	19.4	111	0.30
Cd	0.4	0.1	5	0.06	0.58	0.14	1.58	0.28
Ni	8.2	1	65	0.11	11.03	4.9	24.5	0.25
Cr	8.74	5.41	12.51	0.27	12.74	6.81	26.6	0.22
Pb	4.66	0.62	11.3	0.36	18.6	2	123.6	0.13
Mean p				0.20				0.31

There is no relationship between the mean concentration and the estimated p. In this case, all the elements are measured and found, excepted for mercury in agro-industrial digestates. These parameters are ubiquitous. At national level, p estimated from population data is between 0.06 (Cd, mean concentration 0.4 mg/kg) and 0.46 (Zn, mean concentration of 233 mg/kg) – 0.50 (Hg, mean concentration of 0.08 mg/kg).

As a conclusion, the estimated p by population data are in these two cases always  $\ge 0.05$ . With p = 0.05, the number of particle in a sample should be n =  $100/p = 2\ 000$ . Rare particles of eventual "nuggets" will not always be captured with that number of particles.

From population, when detailed data are available, the assessment of p by the distribution of the concentrations should be done.

#### References

- Beggio G, Schievano A, Bonato T, Hennebert P, Pivato A. 2019. Statistical analysis for quality assessment of digestates derived from separately collected organic fraction of municipal solid waste (OFMSW) and agro-industrial feedstocks. Should the input feedstock to anaerobic digestion determine the legal status of digestate? Waste Management, 87 (2019) 546-558.
- Korf, N., Løvik, A.N., Figi, R., Schreiner, C., Kuntz, C., Mählitz, P.M., Rösslein, M., Wäger, P., Rotter, V.S., 2019. Multi-element chemical analysis of printed circuit boards – challenges and pitfalls. Waste Manag. 92, 124–136. https://doi.org/10.1016/j.wasman.2019.04.061
- European Commission (Directorate general for Environment), Bio Innovation, INERIS, RPA 2021. Study to support the assessment of impacts associated with the review of limit values in waste for POPs listed in Annexes IV and V of Regulation (EU) 2019/1021. April 2021. KH-06-21-119-EN-N. 596 p. doi:10.2779/63162 . https://op.europa.eu/en/publication-detail/-/publication/c7c70b73-3798-11ec-8daf-01aa75ed71a1/language-en

## 3. Analytical and intra-laboratory variability from repeated analysis on a set of test portions prepared according to the approach by number of particles

The following graphs are built with validation data of EN 15413 "Solid recovered fuels - Methods for the preparation of the test sample from the laboratory sample". The size of the representative samples and the test portions of heterogeneous waste were calculated for municipal solid waste (MSW) plus pieces of shredded tyres, and demolition wood, using the sampling in number of particles and the form factor f. A p value of 0.001 is assumed in the standard for calculations in the standard.

Analytical variability of 1 g test portions prepared according to EN 15413 (p=0.001)

The variability achieved by analytical repetitions is depicted in Figure S4.



Figure S4: Analytical variability of test portions of municipal solid waste mixed with shredded tyres (a) and demolition wood (b)

Most elements have CV < 0.10 and all parameters but copper have CV < 0.20: the size of a representative sample by the number of particles is effective to control the variability of test sample and test portion. Metallic copper is a malleable element present at least partly in wires or parts that does not break into particles, unlike the rest of the waste or the material. Iron is to a lower extent similar. Particle creation before size reduction is not effective with classical laboratory devices (here two steps; cutting mill to 2 mm and centrifugal mill to 0.5 mm). This behaviour has been observed in other waste like incinerator bottom ashes.

Sub-sampling and analytical variability of 50 g test portions prepared according to EN 15413 (p=0.001)

In Figure S5 the variability is presented from the results of repeated preparation of test sample (an intermediate subsample of 50 g between the laboratory sample and the test portion of 1 g) and analysis of MSW plus pieces of shredded tyres:



(b)

Figure S5: (a) intra-laboratory variability of analysis of test samples (an intermediate subsample of 50 g between the laboratory sample and the test portion of 1 g) of municipal solid waste mixed with shredded tyres. Elements with CV > 0.2 are labelled in red. (b) Same data as a function of mean concentration of elements.

#### Interpretation:

As analytical CVs are all < 0.20 (excepted for Cu – Figure S4), it can be concluded that

- 11 elements with sub-sampling and analytical CV < 0.20:

9 major (high concentration) constituents have a sub-sampling and analytical CV < 0.13 (mean = 0.08): Mg, Na, K, Al, Si, Ca, Moisture, Ash and Carbon. The elements are not in metallic form in MSW, excepted Al, that is crushable. The sample pre-treatments for subsampling does not create a high additional variability to the analytical variability (Figure S4);

2 minor (low concentration) constituents have low CVr (mean 0.05): Mn, Sr. It can be concluded that they are uniformly distributed in the different particles of the MSW (p is probably > 0.001);

- 8 elements with sub-sampling and analytical CV > 0.20: W, Ni, Cr, Ba, Zn, Cu, Ti and Fe.

Some metallic constituents are difficult to reduce in fine size with laboratory material: Fe Cr Ni of stainless steel, Zn plated steel pieces of shredded tyres. Copper is again a special case (sub-sampling and analytical CV = 1.02): this malleable element is not crushable and generates few particles when shredded. There is no explanation for the higher variability of Ti, Ba and W. It can be concluded that they are not uniformly distributed in the different particles of the MSW (p is probably < 0.001).

From an experimental sub-sampling CV of 0.40 and to have a CV of 0.10, the size of the sample should be increased by  $n2/n1 = CV_1^2/CV_2^2 = 0.40^2/0.10^2 = 16$ .

The conclusion is that these 50 g samples are too small in number of particles to generate a narrow Normal distribution of repetitions with CVr < 0.20 for W, Ni, Cr, Ba, Zn, Cu, Ti and Fe. If these elements are of concern, the size of the sub-samples should be increased, and their subsequent comminution up to the test portion of 1 g improved, which is not an easy task...

#### 4. Further discussion on incorrect sampling and sample preparation

An example of low-quality sampling by the QUOVADIS project is presented in EN 15442. Four solid recovered fuels have been sampled by 5 samplers from 5 EU countries and analysed in 5 different laboratories. The concentration data are not published, but only the mean CVs per parameter, presented as reproducibility (inter-laboratory) and repeatability (intra-laboratory) results. The results are summarized in **Errore. L'origine riferimento non è stata trovata.**S6. Excepted the "global" parameters that are moisture and calorific value, all the elements have CV > 0.20.

The  $CV_{analyses}$  are high, indicating, if we understand well the data, probably an incorrect sample preparation in the laboratory. From one laboratory sample, every laboratory should be able to repeat analyses with lower CV. As for all parameters the  $CV_{sampling and analysis}$  is similar to the  $CV_{analysis}$ , the variability clearly stems from the analyses: the sampling does not create a significant additional variability. The size reduction in the laboratory should have been ruled by the approach in number of particles. These works have been used to write the EN 15442. Note that copper is again the most variable element.



Figure S6 : CV of sampling and analyses (orange) and CV analysis (blue) of different solid recovered fuel (data from QUOVADIS project presented in EN 15442) (Moi = moisture, Cal = calorific value).