

A NOVEL METHOD TO CALCULATE THE SIZE OF REPRESENTATIVE WASTE SAMPLES BASED ON PARTICLES SIZE

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ABSTRACT

A novel approach to determine the size of samples of granular wastes is proposed, forwarding the concept of the “number of particles”, as previously introduced by the authors. To be representative with a minimum error, it was demonstrated that at least 100 particles showing the presence of the characteristic of interest, shall be collected in the sample. Waste particles are usually characterized by size-concentration relationships. However, in waste sampling standards they are not explicitly considered when estimating the size of the sample. In this context, this paper extends this requirement to the number of particles “rare is size”, belonging to the less represented size fraction in the waste to be characterized. The number of particles is then transformed into a mass by a formulation that avoids using unrealistic assumptions on particles features. Results derived from the application of the two formulations on 5 different types of waste show that their equivalency relies on how similar are, the proportions of particles rare in concentration and rare in size in the batch to analyse. Here, preliminary knowledge on particles physical features and distribution of the measurand is key to derive coherent values for mass of samples. Finally, the need to perform on-site size reduction is discussed for cases where the application of both the conventional and novel approaches could have led to unpractical management of too large-sized waste samples.


1. INTRODUCTION

In the European standards, the formulas proposed for the calculation of the size of a waste sample are grounded on the “binomial jar” approach (CEN, 2006). In particular, the degree of representativeness depends on the number of particles of interest within all particles caught from the lot during sampling. Here, “particles of interest” only refers to those particles showing the presence of the characteristic to be measured in the waste lot, such as chemical content or material composition. Their number in the sample strongly influences the resulting analytical value (i.e., the mean value of the searched characteristic between all particles making up the sample). The more the proportion resembles that occurring in the waste lot, the more the samples are representative, the nearer is the measured value to the real one. As proposed by the authors in a previous publication, a minimum number of particles of interest in the sample can be calculated, which, if satisfied, could lead to a controlled degree of variability of this proportion within a set of repeated samples (Hennebert and Beggio, 2021). From that number, the mass of a sample can be calculated according to some approximations.

However, the composition and material of coarse waste particles are usually different from fines (Haynes et al., 2015; Hennebert, 2020; Priya and Hait, 2021; Viczek et al., 2021b). This is due to the fact that the relationship between size and composition is not controlled in waste production processes, thus remaining in practice unknown. In waste sampling standards the particle size and the concentration are not simultaneously and explicitly considered when estimating the size of the sample. In this context, neither appealing to the so-called Theory of Sampling (ToS) as proposed by Gy, (2004) would likely help to fill this gap. About this latter, even in its narrow application in the waste field, dedicated only to material composition analysis, this issue is acknowledged but no practical solution is proposed (Wavrer, 2018).

This said, the current size-calculation approach misses to put a requirement on the granulometric distribution of the sample, which could not reliably resemble that occurring in the waste lot and thus possibly leading to an unexpected degree of variability of the measurements.

This question is not much addressed either in the scientific literature. To the authors knowledge, only two recent and well-documented publications investigate such issue,

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by discussing the results of a so-called Replication Experiment (RE) (Danish Standards, 2013), performed to assess the variability, within a set of 10 equivalent samples (i.e., collected following the same instructions), of the material composition (Khodier et al., 2020) and chemical-physical features of Mixed Commercial Waste (MCW) (Viczek et al., 2021a). For the RE, the sampling procedure was based on the Austrian Standard ÖNORM S 2127, which indicates an “empirical” formula for the calculation of the sample size, based on a minimum number of 10 increments per 200 t of waste, whose mass (in kg) is determined by multiplying 0.06 times the 95th percentile of the particle size (in mm). The two papers present data on materials and elements distribution per size class. Khodier et al., (2020) reports that the variability in material composition is greater for class sizes occurring in smaller mass fractions. These latter are represented by coarser particles, i.e., 80-100 mm, 100-200 mm and 200-400 mm, which led to high levels of Relative Sampling Variability (RSV), i.e., $RSV > 50\%$, for most of the materials categories investigated (up to 230% for wood particles sized 200-400 mm). Consistently, Viczek et al., (2021) showed that the values of RSV of repeated elemental analysis are significantly (but moderately) correlated with particle size. In particular, positive correlation is noted, with the highest RSV ($> 80\%$) reported for the 80-100 mm size class. Further, the RSV of elements concentrations calculated for the single particle size fractions decreases with increasing value of the mass fractions of that particles size class. Since very few parameters were measured with a low level of RSV, the results derived from the analysis of the samples collected according to the Austrian Standard risk to be not usable for testing programmes requiring high reliability (e.g., in case a parameter is usually measured in a range including a compliance limit). In practice, this situation arises when the samples do not contain “enough” particles in these size classes to reliably resemble the heterogeneity of the population in a reproducible manner (i.e., ensuring the proportion of the rare particles, which is critical for the measurement of a reliable mean value between the particles).

In this context, the authors of the two studies discuss the obtained variability referring to the theoretical framework proposed by the ToS. In particular, in Khodier et al., (2020) the variability in material composition throughout the different size classes is explained by the high degree of distributional heterogeneity occurring in MCW, i.e., influenced by the tendency of scraps to segregate spatially in a waste lot; while, in Viczek et al., (2021), the high degree of RSV linked to analytical results is discussed assuming an high value of constitutional heterogeneity shown by MCW, which is determined by the differences of chemical contents between individual fragments and prevent from the possibility to collect samples characterized by an identical composition of the lot. To tackle this unacceptable variability, both studies concluded that higher number of increments and larger samples are needed to decrease the two contributions: however, no solutions are proposed on how to determine these larger values.

To fill this gap, a practical approach is proposed here starting from the calculation of the size of a representative

sample by ensuring that at least 100 particles of interest are present in it, as suggested originally by the authors in a previous paper (Hennebert and Beggio, 2021). The novelty of this contribution stands from introducing the need to also include 100 particles rare in size within the number of particles of interest that should be present in the sample. A reconciling formulation is then presented to add the requirement laid down in this work and to those previously proposed in Hennebert and Beggio, (2021). Finally, results were discussed from the application of the two proposed formulations to calculate the size of representative samples for 5 different waste types.

2. THEORETICAL DEVELOPMENT

2.1 Requirement I: minimum number of particles of interest (connection to Hennebert and Beggio, 2021)

This approach underlies the formulas included in the European standards on sampling CEN/TR 15310-1 and EN 15002 for the estimation of the minimum size of laboratory samples and test portions (CEN, 2015, 2006). Its statistical basis (i.e., the binomial probability distribution) is fully described in a previous work by the authors (Hennebert and Beggio, 2021). Briefly, assuming the minimum achievable value for the variability between a set of repeated samples of $CV = 0.1$, it is demonstrated that a sample must contain a number n of particles:

$$n \geq \frac{(1-p_c)}{CV^2 p_c} \approx 100/p_c \quad (1)$$

to be representative of the waste lot (i.e., the population), this latter characterized by a number fraction of “particles of interest” $p_c \ll 1$. Here, particles of interest are defined as the elements of the population showing the occurrence of the researched characteristic, e.g., a physical constituent, a substance or an element. When discussing waste materials, these could be thought also as particles “rare in composition”. Therefore, Equation 1 simply states that the number of particles of interest $n \cdot p_c$ that must be collected in a representative sample (and sub-samples up to the test portions) is at least 100.

The fraction p_c of particles “rare in composition” is most of the time not known but can be assumed, as suggested in the European standards, ranging from 10^{-1} to 10^{-4} according to the distribution of the particles of interest in the population (i.e., normal or rightly skewed), or even to 10^{-6} for the so-called “nugget” effect. Previous knowledge of the waste is therefore key to provide reliable estimation of p_c . This could be achieved by data derived from basic characterization campaigns of the waste material. An alternative method based on regulatory limits for compliance testing of products is proposed in Hennebert and Beggio, (2021). A further procedure useful when a lot of single particles data are available is described in the Supplementary Material.

For practical reasons, the next step is to transform the number of particles in the sample into a volume and a mass of sample. As elucidated in Hennebert and Beggio, (2021), the current approach underlying the formula in the European standards EN 15002 and CEN/TR 15310-1 is to multiply n (as introduced in Equation 1) by the aver-

age mass of particles in the population \overline{M}_p (kg), this latter roughly estimated assuming an average spherical volume of particles corrected for particles size distribution and deviation from the spherical configuration:

$$M_{sam,c} = n * M_p = \frac{(1-p_c)}{CV^2 p_c} * \frac{\pi}{6} (D_{95})^3 * \rho_p * g * f \quad (2)$$

Where $M_{sam,c}$ is the mass of the representative sample (g), D_{95} (cm) is defined as the 95th percentile of particles diameters, g is a correction factor for particle size distribution (ranging from $g=1$ for uniform distribution, to $g=0.25$ for broad distribution), f is a form factor considering deviation from a spherical configuration (ranging from 1 for perfectly spherical scraps to $<< 1$ for sheet-like particles) and ρ_p ($g\text{ cm}^{-3}$) is the specific mass of the particles (assumed averaged for multi-materials waste batches).

In practice, this step represents the largest practical difficulty, due to the heterogeneous distribution of shape and size of particles in waste materials. How can one estimate reliably the mean size or mass of particles in a waste lot when the relative particle mass can vary of many orders of magnitude? This issue is currently acknowledged by the European standards, which suggest to take the results from Equation 2 just as a “rough” estimate, however enough precise to know the order of magnitude of the sample size (CEN, 2006).

2.2 Requirement II: Minimum numbers of particles “rare in size” and “rare in composition”

When size-composition relationships are not known for the particles making up the lot (as it is frequently common in the waste field), the same approach can be expanded also to those particles “rare in size”. These latter can be defined as those belonging to the less numerous size-class within the whole number of particles making up the population. Their number fraction within the waste lot can therefore be quantified with p_s . Consistently with the assumptions underlying Equation 1, it should be required that also at least 100 particles rare in size should be present in the sample, or equivalently, that a sample must contain a number n_s of particles of (Equation 3):

$$n_s \geq 100/p_s \quad (3)$$

However, in most of the cases, n_s cannot be calculated due to the difficult quantification of p_s . For instance, fines are frequently so numerous that it is in practice out of the resource of the sampler to count them. These numbers could be roughly estimated for each size class by converting the mass (easily measurable during granulometric analysis) into a number of particles with hypotheses of geometry and particle density. Anyway, for size classes characterized by just several particles, this number can be easily counted during granulometric analysis. In the waste field, one can expect that these fractions are most of the times the large ones.

At this point, a novel formulation is proposed to derive a consistent mass of the sample $M_{sam,s}$ (kg) while avoiding strong assumptions on the average geometry and density of particles:

$$M_{sam,s} = 100 * s/S \quad (4)$$

which considers only the mass fraction of particles rare in size S (-) and the average mass of particles rare in size s (kg). Practically, s and S should be quantified during preliminary characterization through conventional granulometry and particle sizes distribution analysis, taking care to count at least the number of particles resulting on the three top sieves characterized by decreasing mesh size. According to their practical experience, the authors suggest assessing at least five mesh sizes, to be chosen so that the number of particles in the class size with the lower number of particles approaches 100 (i.e., to be representative). After having identified the size class characterized by the lowest number of particles, s and S can be calculated as the ratio between the mass of size class of particles rare in size and the counted number of particles or the mass of the sample used for granulometric analysis, respectively.

Likewise, an equivalent approach could be proposed to calculate $M_{sam,c}$ (kg), thus substituting the formulation of Equation 3:

$$M_{sam,c} = 100 * c/C \quad (5)$$

Where c (kg) is the average mass of particles of interest and C is their mass fraction (-). However, c and C cannot be routinely measured today. With the development of combined optical measurements of the composition and size of individual particles and machine learning techniques, also this approach considering the of mass fraction of particles of interest could be feasible in the future (Bonifazi et al., 2021; Kroell et al., 2021).

2.3 Further requirements

As discussed in Hennebert and Beggio, (2021), the use of the binomial distribution for the calculation of the number of particles included in a representative sample strictly requires that each sampling action shall be carried on as a casual/probabilistic event, where each particle has an uniform non-zero possibility to be collected during sampling.

In this context, the European sampling standard introduces a further requirement to avoid negative segregation of large particles during sampling, i.e., the size of the three dimensions (length, height and width) of the sampling instruments shall measure at least 3 times D_{95} (cm). Consequently, the volume of the sampling instrument should be at least $(3 * D_{95})^3$ (cm^3). This corresponds to the minimum volume of the materials picked up with a sampling action, i.e., an increment.

When the results shall be representative of the average composition of the waste lot (as it is typical for waste compliance testing), and thus consider possible heterogeneous distribution (spatial and/or temporal) of the material’s features (i.e, size and composition), the laboratory samples must be composed of a number of increments collected randomly throughout the lot. This number of increments should be estimated according to the actual variability of the population, as indicated in the European sampling standard (CEN, 2006).

Based on this, the mass of the laboratory sample shall be:

$$M_{sam,inc} = n_{inc} * (3 * D_{95})^3 * \rho_b \quad (6)$$

Where $M_{sam,inc}$ (g) is the mass of the sample, ρ_b ($g\ cm^{-3}$) is the bulk density of the material and n_{inc} is the planned number of increments.

The theoretical development of the formulas equalizing $M_{sam,c}$, $M_{sam,s}$ and $M_{sam,inc}$ is presented in the Supplementary Material.

Furthermore, the mass of the sample should be large enough to satisfy the requirements laid down by the set of planned analytical protocols in terms of test portions, repetitions and reserves:

$$M_{sam,a} \geq \sum \text{analytical requirements} \quad (7)$$

Finally, by reconciliation, the mass of the sample satisfying all the conditions proposed to achieve representativeness is the following:

$$M_{sam} = \max(M_{sam,c}; M_{sam,s}; M_{sam,inc}; M_{sam,a}) \quad (8)$$

With $M_{sam,c}$, $M_{sam,s}$, $M_{sam,inc}$ and $M_{sam,a}$ as calculated according to see Equation 2, 4, 6 and 7, respectively.

2.4 The number of particles in the Theory of Sampling

In this context, it is worthwhile noting how ToS implies the statistical concept of number of particles in its most known formulation, virtually building a bridge with the approach proposed in this paper. In particular, ToS statistical development is clearly grounded in the binomial probability distribution (Gy, 2004).

The original formula proposed by Gy, (2004) to quantify the minimum relative variability, in terms of variance, achieved by the act of sampling (i.e., called the Fundamental Sampling Error) is the following:

$$\sigma^2 = \left(\frac{1}{M_{sam}} - \frac{1}{M_l} \right) \sum_{i=1}^n t_i m_i \left(\frac{a_i - a_l}{a_l} \right) \quad (9)$$

where M_{sam} and M_l are the masses of the sample and the lot, respectively, t_i is the mass fraction of the i -th group of particles, each one characterized by a mean mass of m_i , a_i is the value of the measurand as measured in the i -th group of particles and a_l is the true value of the measurand in the entire lot (which is the value a sample should represent). In Equation 9, the variability is calculated as a function of the ratio between the mass of one particle (i.e., $\sum_{i=1}^n t_i m_i$ - estimated as the weighted average among each family), divided by the mass of the sample M_{sam} , which is nothing else than the inverse of a number of particles.

To be practical, Equation 9 needs the introduction of strong assumptions to build the heterogeneity model of the material to be analysed. Accordingly, an alternative formulation was proposed Gy, (2004):

$$\sigma^2 = \left(\frac{1}{M_{sam}} - \frac{1}{M_l} \right) HI_l = \left(\frac{1}{M_{sam}} - \frac{1}{M_l} \right) c f l g d_{95}^3 \quad (10)$$

where HI_l , the so-called Heterogeneity Invariant, can be estimated by assuming material-specific values for d_{95} (95th percentile particle size), f and g (shape granulometric factors, respectively, equivalent to those introduced for Eq. 2), the liberation factor l , measuring the degree of liberation of a substance within a matrix and originally developed in the ores field (ranging 0 to 1 from complete segregation to complete liberation) and the constitutional parameter

c , which can vary from 0 to several orders of magnitude. Methods to estimate empirically these latter parameters are described in Gy, (2004), especially for ores. However, no waste-specific references are found in the literature to estimate l and c . As no "liberation" of elements should be considered when measuring total elemental content, $l = 1$ can be considered a realistic assumption for waste materials. Conversely, a simplified expression for c is usually introduced for simple particles (i.e., consisting either of 100% or 0% of the measurand to be analyzed):

$$c = \rho_p \frac{1 - a_l}{a_l} \quad (11)$$

where, ρ_p is the particles density and a_l is the value of the measurand to be analyzed in the lot. This latter, when expressed as a fraction, can be considered equivalent to p_c as defined in Equation 1. With $\sigma^2 = CV^2$ and by considering that usually $M_l \gg M_{sam}$, Equation 10 becomes:

$$CV^2 = \left(\frac{1}{M_{sam}} \right) c f l g d_{95}^3 = \left(\frac{1}{M_{sam}} \right) \rho_p f g d_{95}^3 \left(\frac{1 - p_c}{p_c} \right) \quad (12)$$

where, if rearranged, M_{sam} is calculated equivalently as stated by Equation 2. In other words, in a simplified version of the ToS, it can be shown that the variance is a function of the number of particles as described by the binomial probability distribution.

3. MATERIALS AND METHODS

3.1 Wastes characterization data

Physical characterization data were collected for 5 types of wastes. In particular, D_{95} (mm), D_{05} (mm), ρ_b and ρ_p ($kg\ m^{-3}$), S (% w/w), s (kg), shape and granulometric factor f and g were determined. Both experimental data and information collected from the literature were considered.

First, data from mixed commercial waste (MCW) generated in Austria were derived from those presented in Khodier et al., (2020). Besides presenting a detailed in-depth discussion on sampling issues on this waste type, this paper was chosen because it provides mass shares of the particle-size classes. These values were used to determine the D_{95} and the D_{05} by linear interpolation. Being direct measurement not available, the number of particles in each size-class was determined by dividing the resulting mass of each size class by the average mass of particles belonging to that class. This latter was estimated by assuming spherical-shaped particles (i.e., $f = 1$) and a value for particle density estimated based on weighted average of densities of the materials constituting that size class. In this way, both s and S could be finally determined.

Further, the particle and bulk density together with granulometry were determined in lab by the authors on 4 additional waste samples: plastic shreds from waste of electric and electronic equipment (WEEE) generated at a treatment facility located in France (Hennebert, 2020); automotive shredder residue (ASR) produced by a private plant treating end-of-life vehicles for metal recovery located in central Italy and previously analysed (Pivato et al., 2019); 50mm undersieve bottom ashes (BA), collected after metal separation at the output from an incinerator located in France

recovering heat from the thermal treatment of municipal solid waste; recovered aggregate (RA), derived from the treatment of a mix of bottom ash from incinerated municipal waste, construction and demolition waste and foundry slags from a treatment plant located in the north-east part of Italy.

In particular, particle size distributions were derived by granulometric analysis, conducted on each investigated material through sieving and weighing the resulting sieved fractions. The adopted mesh-size series was 1-2-5-10-20-50-100-200 mm. For each waste type, size-class mass shares were used to determine D_{95} and D_{05} by linear interpolation. Particles number and weight were measured on the resulting fractions characterized by the 3 bigger size-classes to determine S and s . In particular, mean mass of particles for each of the coarser size-classes was estimated as the average weight between the counted and weighted particles. For each of the finer size classes (i.e., stopping at smaller mesh sizes) the number of particles was estimated by dividing the measured mass with the mean mass of particles, these latter assumed spherical and characterized by ρ_p .

3.2 Calculation of size of representative samples

Waste characterization data have been used as input values to compare the resulting values for $M_{sam,c}$ and $M_{sam,s}$ calculated according to the proposed formulations (Equation 2 and 4, respectively). In particular, when using Equation 2 different p_c values were used, according to the specific waste types and to the possible objectives of the dedicated testing programmes:

- For MCW, the primary objective of the characterization campaign was to estimate the materials composition of the waste lot in terms of mass fractions, focusing on the largest mass shares, apart from peculiar hazardous materials (e.g., batteries, toners, chemicals, etc.). In Khodier et al., (2020), the values (expressed as mass fractions) observed in the whole samples (i.e., not referring to the size classes) were 0.039 for textiles, 0.041 for inert material, 0.043 for paper, 0.044 for metals, 0.055 for 2D plastics, 0.071 for wood, for plastics 3D (0.122), for cardboard (0.128), and for the residual fraction (0.458). The observed p for the materials per size class are of course much lower, 26 out of 57 being < 0.01. Therefore, two cases are presented here, with $p_c = 0.01$ (considered as a safety approach) and with $p_c = 0.04$ (representing the rounded frequency of textile fraction with $p_c = 0.039$);
- For WEEE, assuming the quantification of Flame Retardants (i.e., PBDEs) as a possible aim of a dedicated testing programme, a value of 0.001 for p_c was set by using the ratio between the concentration limit of the specific POP additive and their functional concentration, as suggested in Hennebert and Beggio, (2021);
- Similarly, for ASR, BA and RA a p_c value of 0.001 was used as suggested from EN 15310-1 to take into account the effect of few concentrated particles within heterogeneous waste lots (CEN, 2006).

4. RESULTS AND DISCUSSION

4.1 Comparison between $M_{sam,c}$ and $M_{sam,s}$

Besides the requirement on minimum mass of the increment, the novelty of the approach of this work lies on the proposition of two formulas enabling the sampler to calculate as many masses of sample that should include 100 particles considered rare in terms of both presence of measurands and size, respectively. The mass of the sample that should be used will be therefore the maximum between the calculated values. Here, several waste characterization data were collected by the authors and used to calculate the mass of laboratory sample for five types of wastes, according to the approach proposed by this work, to compare and discuss the obtained values. Results are presented in Table 1.

Investigated samples are characterized by a ratio D_{95}/D_{05} covering a wide range of values. Lower values for D_{95}/D_{05} mean broader, i.e., more heterogenous, particles size distribution (in mass). Therefore, investigated materials can be ordered on a scale of increasing size distribution heterogeneity starting from WEEE samples, characterized by $D_{95}/D_{05} \approx 2.5$, MCW with $D_{95}/D_{05} \approx 49$, BA and RA by $D_{95}/D_{05} \approx 800$, and ASR samples by $D_{95}/D_{05} \approx 2.400$. These results indicate much higher degree of particle size heterogeneity for samples showing “fines” (i.e., $D_{05} < 1$ mm). Also, the range of calculated values does not seem coherent with the one used to calculate g , used in Equation 2 to take into account broad particles size distribution when deriving the average mass of particles, which can therefore result in overestimated values.

The value for $M_{sam,s}$ is maximum for municipal commercial waste MCW, with the largest D_{95} , which is characterized by a large mass fraction of rare particles in size S (0.21 kg/kg). These are large particles (i.e., 0.1 – 0.2 m) and heavy (i.e., estimated $s = 1.8$ kg/particle). The weight of 100 of these particles is 180 kg and as they represent 0.21 kg/kg, the weight of waste containing these 180 kg is 841 kg, higher than the 240 kg that have been sampled by Khodier et al., (2020). Here, the estimated particles mass is remarkably higher than that found empirically by Weissenbach and Sarc, (2022), reporting for pre-shredded MCW with sizes from 80-500 mm a mean and maximum particle weight of 36.3 g and 882.5 g, respectively. This discrepancy is likely due to the calculation assumptions which considered spherical-shaped particles characterized by an averaged density, although the coarser particles of MCW are typically 2D-shaped plastic foils or textiles, while 3D particles are often foams with a much lower density (e.g., hollow materials wood particles).

The next $M_{sam,s}$ is the one of automotive shredder residue ASR, with very low mass fraction of rare particles in size S (0.003 kg/kg), mainly consisting of relatively light ($s = 0.005$ kg/particle) coarse hollow foam pieces (i.e., 0.05 – 0.1 m). The resulting $M_{sam,s}$ is 167 kg. The bottom ash BA and recovered aggregates RA (being characterized by a calculated D_{95} of about 2 cm) have intermediate values of S and s , resulting in samples of 45 and 27 kg, respectively. These samples are larger than the usual ones of about 10 kg which are suggested in published sampling plans (Hen-

TABLE 1: Characterization data measured for five waste types and used to calculate masses of samples containing 100 particles “rare in concentration” ($M_{sam,c}$, Equation 2) and “rare in size” ($M_{sam,s}$, Equation 4). Data on Municipal Commercial Waste (MCW) were collected from Khodier et al., (2020), while values for waste of electric and electronic equipment (WEEE), automotive shredder residue (ASR), bottom ashes (BA) and recovered aggregates (RA) were measured by the authors.

		MCW	WEEE	ASR	BA	RA
Characterization Data						
ρ_b	kg m ⁻³	350	150	300	1,250	1,520
ρ_p	kg m ⁻³	1,022	670	877	2,500	2,100
D_{95}	mm	165	95	72	16	16
D_{05}	mm	3.38	38.00	0.03	0.02	0.02
f	-	1	0.06	0.18	1	1
g	-	0.25	0.5	0.25	0.25	0.25
S	(kg/kg)	0.214	0.026	0.003	0.02	0.086
s	kg	1.800	0.004	0.005	0.009	0.023
s/S	kg	8.41	0.15	1.67	0.45	0.27
Calculations of the mass of the representative sample						
$M_{sam,c}$	kg	6,009 ($p_c=0.01$) 1,502 ($p_c=0.04$)	902	771	134	113
$M_{sam,s}$	kg	841	15	167	45	27

nebert and Beggio, 2021). The waste of electrical and electronic equipment WEEE shreds have a rare small fraction with a low mass fraction S (0.026 kg/kg) and a low mass of particle s (0.004 kg/particle). This results in a sample of 15 kg (or a volume of about 100 L), significantly higher than what is recommended in the CENELEC CLC/TS 50625-3-1 (CENELEC, 2015).

The estimated total number of particles in the $M_{sam,s}$ for the different wastes was variable (results not shown). Samples of BA and RA, which were characterized by the presence of “fines” (assumed here as particles < 1 mm), have number of particles in the order of magnitude of billions. Further, samples of MCW and ASR residue have particles in the range of millions. Instead, WEEE sample contain just thousands of particles, as a results from the more “homogeneous” granulometry if compared to the size distributions characterizing the other analysed materials (Figure 1).

$M_{sam,s}$ is always lower than $M_{sam,c}$ (Table 1). Two groups can be identified: $M_{sam,c}$ for WEEE is 61 times higher than the corresponding $M_{sam,s}$ while a ratio 2 – 7 can be calculated for the four other materials. Note that this depends on the value of assumed p_c . The two calculated masses could be equal if p_c is increased by the factor $M_{sam,c} / M_{sam,s}$. Excepted for WEEE (as discussed below), the resulting p_c (i.e., multiplied by a 2 – 7 factor) is $p_c = 0.08$ for MCW and $p_c = 0.003 - 0.005$ for the other wastes. Where the objective of the analysis is material characterization (as in Khodier et al., 2020), a p_c value of 0.08 means that every material fraction present at a lower percentage (in number of particles) than 0.08 in the lot will occur with a variability greater than 10% in a set of equivalent samples, which could be convenient for a rough characterisation. A p_c value of 0.003 – 0.005 has the same meaning for much rarer fractions, leading then a much more precise characterisation.

The $M_{sam,c} / M_{sam,s}$ ratio's range of 2-7 seems very realistic since the calculated mass of $M_{sam,s}$ has the same

order of magnitude than the calculated $M_{sam,c}$. When looking at the number of particles in the samples, the $M_{sam,c}$ contain about 100 to 10,000 more particles than the targeted 100,000 particles (i.e., by assuming a p_c of 0.001 in Equation 1). This could suggest that the conversion of the target number of particles into a mass by using the size of the largest particles D_{95} (Equation 2), even if optimized by the parameters f and g, results in a conservative approach, which is probably unavoidable. In practice, Equation 2 seems to overestimate the mean mass of particles, and this is more evident considering the presence of fines in all tested materials excepted for WEEE. For this latter, characterized by the absence of fines, the two approaches are complementary: 2,000 particles in $M_{sam,s}$ and 100,000 particles for concentration (assuming a p_c of 0.001), because the particles rare in size are in practice not “rare” (i.e., $S = 0.214$). To equalize the two masses, p_c should be 0.05 that is 50 times higher. That frequency of 0.05 is meaningful in unsorted shreds (for polymers, for metals, for additives), but could result in too high variability for quality assessment and impurity quantification of secondary raw material for the circular economy (Hennebert, 2020).

4.2 Decreasing the mass of the laboratory sample: particles size reduction and sub-sampling

It should be noted that the values for $M_{sam,c}$ in Table 1 are larger than what is recommended in usual sampling plans (Hennebert and Beggio, 2021). Consequently, considering the costs related with collecting and transporting such samples to the laboratory, the values in Table 1 could be estimated as unpracticable by the actors involved in the waste characterization. These calculated samples are large because the value of p_c used for the calculations are assumed conservatively low, as suggested by the European standards on sampling (CEN, 2015, 2006). Again, the method performed to better assess p_c is a key factor in optimizing the mass of a sample: ideally, this could be done

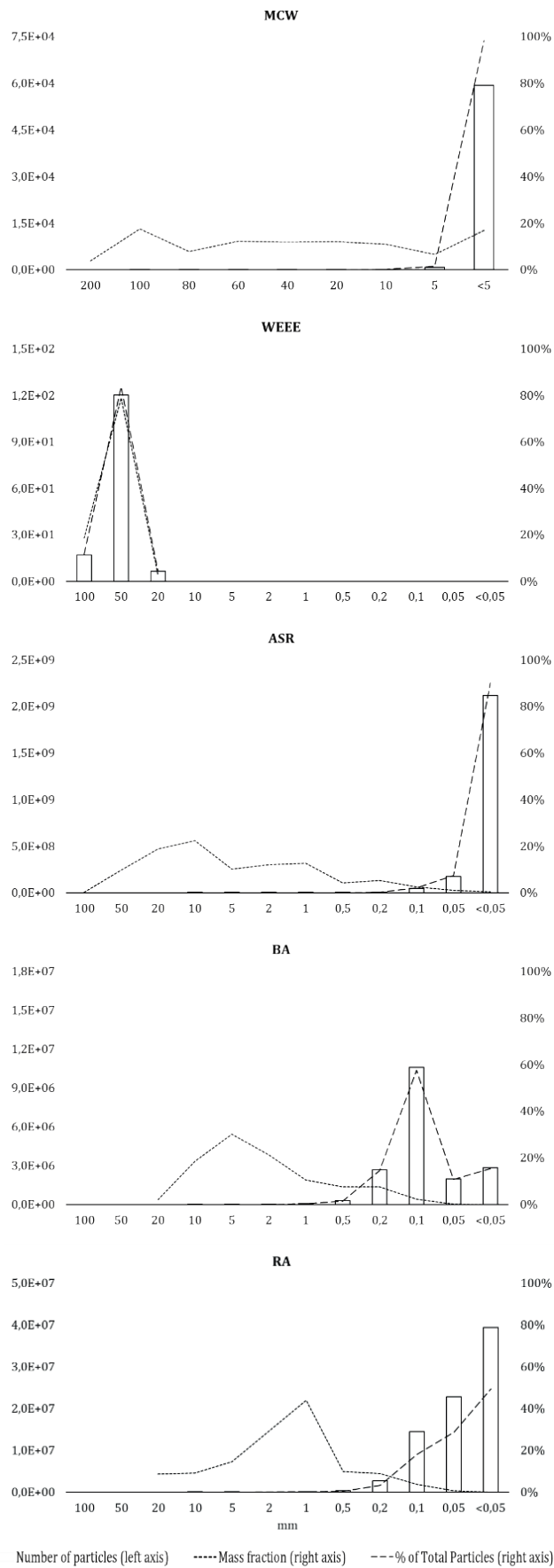


FIGURE 1: Particle sizes distribution for five types of waste, expressed as number of particles per size-class (left axis) and fraction of particles in the size-class on total number of particles (right axis), and in mass (right axis).

by checking the occurrence of the property of interest particle per particle, manually or by automated analyser. However, whether p_c values cannot be estimated more reliably, the solution to reduce the mass of the laboratory sample is on-site particles size reduction and further sub-sampling of the “primary samples” indicated in Table 1.

In practice, the sample masses calculated in Table 1 should be assumed as the minimum values allowing the samples to contain the minimum number of particles as calculated by Equation 1. Smaller samples would be characterized by lower number of particles thus leading to higher variability of repeated analyses on a set of identical samples. In this context, to maintain this variability within the required threshold, smaller samples must contain the same minimum number of particles as the primary samples. This could be done by increasing the number of particles in the primary samples by particles size reduction (i.e., shredding, grinding, cutting or milling according to the physical features of the materials) and sub-sampling (e.g., by riffle splitters or quartering and coning). Ideally, this process allows to achieve a sample size suitable for a laboratory sample characterized by the same p_c of the primary sample (Figure 2). Equivalently, particles size reduction allows to decrease D_{95} together with the mean mass of particles as estimated in Equation 2.

Considering the features of the 5 materials analyzed in this study (Table 1), Table 2 presents the values of particles size $D_{95,r}$ calculated rearranging Equation 2, needed to decrease the $M_{sam,c}$ to 20 kg while maintaining the same values of p_c . Here, $D_{95,r}$ can be reached by applying size reduction to the whole mass of the primary sample. By decreasing the size of particles, the values of g could also vary, as visible in Table 2 for WEEE, where $D_{95,r}$ was calculated assuming $g = 1$, derived by the fact that $D_{95,r}$ results lower than D_{05} (see Table 1). Furthermore, the smaller particles could be more spherical than their parent particles. Therefore, as the size decreases, f also increases towards 1 as elongated and flat particles are reduced to more compact shapes (cuboids, spheroids).

A typical argument is that reduction of the entire mass of the primary sample can be very expensive and time consuming. However, according to confidential information collected by the authors, frequently waste characterization campaigns must be redone because of the achieved ex-

cessive variability between equivalent samples (i.e., “outliers”) due to too small laboratory samples and incorrect laboratory preparation. These additional costs would be much higher than those dedicated to the on-site reduction of some hundreds kgs of waste.

Further, one can observe that the large particles are those that will be mostly reduced (USEPA 2002), thus increasing the frequency of particles “rare in concentration”. However, taking a sample with the same number of particles, this increase in p_c in the primary sample would just reduce the variability between multiple equivalent samples (Hennebert and Beggio, 2021). A reverse case is observed for malleable and ductile metals (mainly copper and lead particles), which do not fragment under the force of compression, as in a jaw crusher in the case of mineral wastes, or cutting/tearing as in shredder used for mixed wastes (Bunge, 2019). The relative frequency of un-shredded particles will thus decrease together with the increase of the variability. Here, the only solution is to melt in a metallurgical furnace a large quantity of waste (with a melting additive), achieve optimal mixing, then cast a homogeneous ingot, which should be finally drilled or sawed for analysis (Bunge, 2019). This unusual method is used to assess for instance precious metals concentration in waste, with p_c of about 1 per million and consequent nugget effects.

5. CONCLUSIONS

A novel formulation was described to integrate the conventional approach for calculating the size of a waste sample as indicated in the European waste sampling standards. This latter does not consider possible size-content relationships in waste particles making up the lot, which however frequently occurs in waste materials. This gap is easily filled starting from the concept of a minimum number of particles that should be present in a sample to be representative of a waste lot with a controlled variability within repeated samples. As elucidated in a previous paper by the authors, it depends on the proportion of particles “rare in concentration”, showing the characteristics to be quantified in the waste lot (the approach of the current European standard) and of those “rare in size”, the less represented size-class (the approach proposed by this work). The final number of particles in a sample fulfilling both

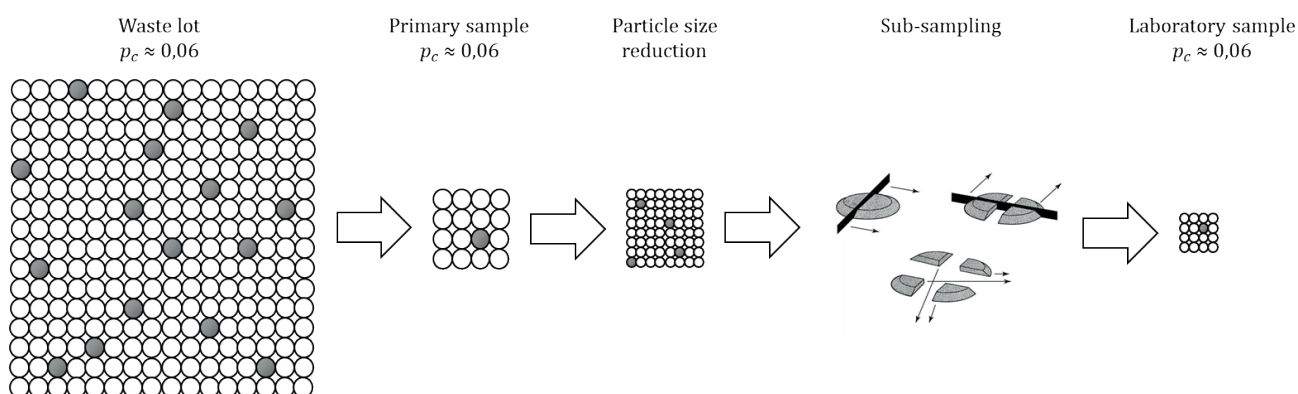


FIGURE 2: Graphical representation of the ideal process for decreasing the size of samples.

TABLE 2: Size of particles to derive a sub-sample of 20 kg from the laboratory (or primary) samples as calculated in Table 1. For each waste type, $D_{95,r}$ are calculated according to Equation 2 by assuming the same p_c of the primary sample in Table 1 and setting $M_{sam,c}$ to 20 kg.

		MCW	WEEE	ASR	BA	RA
$D_{95,r}$	mm	25 ($p_c=0.01$) 40 ($p_c=0.04$)	21.00	1.20	0.85	0.90

requirements depends on the rarity of the measurand and size chosen by the sampler to be reliably represented in the sample itself. The conversion of that number of particles in a mass relies on hypothesis on averaged geometry, shape and density of particles, whose estimation could be problematic in heterogeneous waste. To avoid unrealistic assumptions, this paper proposes an alternative approach based on values easily measurable during particle size distribution analysis.

Both formulations were applied on 5 different waste types to derive the mass of the sample to be indicated in dedicated sampling plans. Results showed that the conventional approach agrees well with the new proposition, leading to masses of sample characterized by the same order of magnitude, at least for heterogeneous particle size distributions showing presence of fines (i.e., < 1mm). For more homogeneous particle size distributions (e.g., WEEE), the sample calculated according to the conventional approach resulted one order of magnitude higher, being the proportion of rare particles in concentration far lower than those considered rare in size. The correct assessment of the frequency of particle with the property of interest is therefore critical. A refined quantification of its value could come from particle per particle analysis. Here, optical on-line element analysers (eventually coupled to a sorting machine) or material fraction separator on conveyor belt are recommended to quantify a large number of particles and assess it correctly when it is expected to be low (e.g., < 0.01).

When samples masses are calculated and thought as unpractical for management, a representative sample can only be achieved after size reduction in the waste processing facilities. It is easily calculated that a laboratory sample of 20 kg should have a maximum particle size of 10-20 mm to contain 100 000 particles of this size (without considering the fines).

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