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THE SORTING OF WASTE FOR A CIRCULAR ECONOMY: SAMPLING WHEN (VERY) FEW PARTICLES HAVE (VERY) HIGH CONCENTRATIONS OF CONTAMINANT OR VALUABLE ELEMENT

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ABSTRACT: The measurement of elements in numerous individual particles ($\geq 1 \text{ cm}^2$) by a portable X-ray fluorimeter is used to review a part of the sampling theory of granular solid waste for environmental studies and the circular economy. The paper addresses the case when the concentration of element or substance is not related to the grain size. The key concept (from the binomial law) is the number of particles that must be present in a portion of matter to be representative of a larger portion of matter. This number depends on the frequency of particles having the studied property, and on the desired variability of this property. In all cases, the lowest achievable variability is the analytical variability with the smallest possible test portion (results cannot be less variable). The studied property can either be the presence of an element or a substance, or the presence of an element or a substance at a given concentration. Those concepts are the basis of the existing sampling standards but are not presented as such. As a result, the equations of these standards are not easy to understand and, to our knowledge, rarely used to calculate the mass of a representative sample. When the distributions of concentrations are skewed by (very) large values, the last centiles of concentration tremendously increase the observed mean concentration of a waste heap or flow, and a representative sample must include these last centiles of particles for a proper characterizing and sorting of waste and secondary raw material for the circular economy.

Data of centiles of concentrations per particle and laboratory analytical variability are presented. The resulting recommended number of particles that should be present in a sample at any scale from the waste stream (thousands of tons) to the test portion (frequently less than one gram) is estimated at 100 000. Some published sampling plans (from the waste stream to the laboratory sample) and analytical standards (from the laboratory sample to the test portion) are then reviewed for the number of particles. It is crucial to measure the mean mass of the particles to sample, from the granulometric distribution of the particles, and the bulk density, to determine the weight and volume of 100 000 particles.

If there is a fine fraction ($< 63 \mu\text{m}$ or even $< 1 \text{ mm}$), the recommended mass or volume complies with the requirement of $n \geq 100\,000$. When there is no fine fraction, like for some WEEE plastic scraps, the volume recommended in technical specification and standard for laboratory sample can't have enough particles for $p = 0.001$, but well for $p = 0.1$ for plastics from small household appliances or higher p for plastics from fluorescent lamps. These p values must be verified for these plastics but are probably not unrealistic for the unsorted fraction. On the other hand, using the equation of the sampling standards

overestimates the mean mass of particle when fines are present. Another application is the evaluation of the number of particles to measure individually, in order to calculate the fraction of particles trespassing a given concentration of an element, and the confidence interval of that fraction.

Keywords: binomial law, analytical (fundamental) variability, sampling plan, test portion

1. INTRODUCTION

Some granular waste streams have many particles with a low concentration of contaminants and few particles with a high to very high concentration of contaminants. The same distribution can be observed for valuable elements. Some typical examples are synthetic materials containing one or more families of hazardous substances: plastics of certain categories of waste of electrical and electronic equipment or end-of-life vehicles ($\pm 90\%$ of the particles/scrap leaving the shredder contain few or no total bromine, indicator of brominated flame retardants), plastics of empty packaging of plant protection products (each empty package of 400 g contains one or two "active ingredients" among the about three hundred approved in the EU), shredded untreated wood from packaging with some pieces of woods with preservative (due to imperfect sorting). A consequence of these skewed distributions is that the last percentiles tremendously influence in these observed cases the mean constituent concentration of the sample (as measured in the laboratory).

The correct testing of waste allows informed decisions to be made on the appropriate way in which they should be treated (or not), recovered or disposed of. Sampling plans address the heterogeneity at the scale of a population (for instance annual production or daily stream of waste) with a potential identification and consideration for factors that influence ("stratify") the constituents in the population (EN 14899: 2016). "Homogeneous" populations or sub-populations are then sampled. Several mono- or composite- (made of increments) representative samples are taken and analyzed. This paper addresses the rationale for representative sampling from a population or sub-population of solid waste, as well as the test portion for extraction and analysis, based on properties of individual particles. The paper deals with "small" variability (particle variability or smallest analyzable matter portion variability). Particle refers here to the physically distinct portion of solid matter not bound to the other portions at the time of sampling. It is equivalent to part, piece or scrap. Sampling is like drawings of white or black balls from a set of balls, which is statistically described by the binomial law. The final equations presented in sampling standards are revisited here starting from that distribution. **The key concept is the number of particles that should be part of a representative sample, for a given analytical variability, and a given percentile of particles with a given property (presence or absence of an element or substance, or presence above or below a given concentration).** This number lies between 1000 and 100 000. With non-destructive physical methods for measurement (X-Ray fluorescence or in some cases hyperspectral NIR imaging), some individual particle characteristics are available. The measurement of the particles fraction having for instance, a concentration higher than a concentration limit, with its uncertainty, can be done.

This paper first illustrates that skewed distributions can be encountered at a particle scale in waste. The influence of the last quantiles on the mean concentration of the sample (the concentration of the sample that is measured in the laboratory) is presented. Such skewed distributions also occur between samples at larger scales (national scale, characterization campaign scale) and this variability must be handled by sampling plans, which is not the issue of this paper.

Parameters for the calculation of the number of particles are suggested from experimental data: the analytical variability (intra- and inter-laboratory) from the analysis of reference material, of laboratory samples and of validation trials of standards is presented. These values of state-of-the-art practices can be used for sampling.

The size of the laboratory samples from an Extended Producer Responsibility organization, a Professional Union, and waste of electrical and electronic equipment (WEEE) standard are then

critically assessed for the number of particles. From the laboratory sample, the test portions obtained by sample laboratory preparation in analytical standards (laboratory work from the laboratory sample to the test portion for extraction and measurement) are also assessed. Some laboratory samples could contain not “enough” particles, which is not the case with the analytical test portions.

Finally, when a particle-per-particle analysis is available, a method for the assessment of the particle fraction complying or not with a given concentration, and its confidence interval, is proposed.

2. MATERIAL AND METHODS

2.1 Theory of representative sampling of particles (without relationship between size and concentration)

2.1.1 The binomial distribution: the number of particles to have in a sample (n)

If there is a connection between the size of the particles and their concentration of measurand, the Pierre Gy's equations (ISO 11648-2) should be used: each class of size has its own frequency of presence or concentration of measurand, which must be taken into account for the sampling. This is the case, for instance, when a mineral of interest is present as a separated mineralogical phase of a given size range (particularly when the ore is ground). A full presentation of the theory of sampling (TOS) is available (Gy 1982, Gy 2004 a to d).

In all other cases, the binomial distribution describes the probability, for n individual drawings of lot from a heap or a flow having binary characteristic (white or black balls) with a **known p frequency**, to have x positive drawings. The binomial function $B(n, p)$ is mathematically described in statistic text books or in statistical software tutorials. It can be demonstrated from the repetition of drawings of lot that the estimator of the particles fraction with a given characteristic follows a normal (gaussian) distribution, and that:

- the estimator of the number of positive drawings is $\hat{x} = n.p$;
- the estimator of the variance of the binomial distribution is $s^2 = n.p.(1-p)$;
- the square of the coefficient of variation of \hat{x} or p is $CV^2 = s^2/\hat{x}^2 = n.p.(1-p) / n^2.p^2 = (1-p) / n.p$.

From that, n , the number of balls to draw to assess p with a given CV is:

$$n = (1-p) / (CV^2 \cdot p) \text{ (Eq. 1)}$$

Where

n = number of drawings

p = probability of success

CV = coefficient of variation of n or p (= standard deviation of the number of positive in repeated drawings divided by the mean number of positive drawings).

For the sampling, “ n ” is the number of particles (drawings) taken. In the standards (historically NVN 7302:1997, then CEN/TR 15310-1:2001 and EN 15002: first version 2006, last version 2015), it is not presented as such but incorporated in the equation giving the mass of the laboratory sample or of the test portion. This paper shows that n is the basis for a sound sampling. For the following, only CEN/TR 15310:2001 will be mainly cited, but the theory refers to the three mentioned standards.

The significance of p is documented in the standards as the “fraction of particles with a given characteristic”. In practice, it is known only by its estimator noted \hat{p} in this document. Typically, in waste, the concentration of constituents in a particle is seldom 100%. However, it can happen, for instance, in nearly pure molten metal droplets in municipal solid waste incinerator bottom ash. The concentration of constituents in a particle is rather a continuous function from the limit of quantification to the maximum, depending on the genesis of the particle (from solid fractionation, multi-mineral solid fraction, massive precipitation, surface precipitation, surface complexation, particles aggregation...). The objective here is

to include in the sample the particles that cover the full range of the concentration of constituents in the population. If all those particles contain the same individual concentration of measurand ($p=1$), sampling and analyzing one single particle will be enough, as it is the case for homogeneous industrial products. The signification of p for waste sampling is the (unknown) fraction of particles of the population having a characteristic that is wanted to be present in the n drawings from that population with the same frequency (considering the minimal variability of measurement of that characteristic). Two identical (operational) definitions of “ p ” are:

- to obtain a representative sample: p = the quantile (percentile) of rare particles that is necessary to have in the sample to obtain a mean concentration close to the mean concentration of the population (typically to be determined by laboratory analysis). In this case, typically p and CV are fixed, and n is calculated;
- to control the conformity of individual particles of a population to a given concentration limit: p = the quantile (percentile) of particles having a concentration higher than a given fixed (a priori or a posteriori) concentration (to be determined by measurement of n individual particle). In this case, p and its CV are calculated from the n individual measurements.

CV is the coefficient of variation of the observed frequency \hat{p} when n drawings are done. If more drawings are done (n increases), CV will decrease. In all cases, the lowest achievable variability is the analytical variability with the smallest possible (“homogeneous”) test portion? The results cannot be less variable. To calculate n , CV can be fixed to that value, because if a larger n is used and hence a lower CV is obtained, the analytical technique will not be able to show this reduced variability. The CV is fixed to the “fundamental error”, the inherent variability shown by a material and its analysis at the smallest scale of measurement. In other words, it is the lowest variability that can be achieved, only due to material heterogeneity and analysis variability at the lowest scale of measuring. The CV of analytical methods is also called relative standard deviation (RSD). In EN 15002:2015, it is suggested to use CV = 0.1, $p = 0.1$ for major elements of the matrix, and CV = 0.1, $p = 0.001$ for minor constituents. The corresponding n are (Eq. 1) 900 and 99900, respectively.

2.1.2 From the number of particles (n) to the mass of the representative sample (M_{sample})

The mass of a representative sample is n (the number of particles) times the mean mass of the particles. It comes that:

						Note
M_{sample}	=	n	·	Mean $M_{particle}$		
	=	$(1-p) / (CV^2 \cdot p)$	·	Mean $V_{particle}$	·	ρ_{solid}
	=	$(1-p) / (CV^2 \cdot p)$	·	V_{95}	·	g_v · ρ_{solid}
	=	$(1-p) / (CV^2 \cdot p)$	·	L_{95}^3	·	g_c · ρ_{solid} Cubic particle
	=	$(1-p) / (CV^2 \cdot p)$	·	$Lx_{95} \cdot Ly_{95} \cdot Lz_{95}$	·	g_p · ρ_{solid} Plate particle
	=	$(1-p) / (CV^2 \cdot p)$	·	$\pi/6 \cdot D_{95}^3$	·	g_s · ρ_{solid} (Eq. 2) Spherical particle
 V_{sample}	=	 M_{sample}				 ρ_{bulk}

g_s = correction factor for particle size distribution (CEN/TR 15310-1):

Grain size distribution	D ₉₅ /D ₀₅	g _s
Uniform	D ₉₅ /D ₀₅ ≤ 1	1
Narrow	1 < D ₉₅ /D ₀₅ ≤ 2	0.75
Medium	2 < D ₉₅ /D ₀₅ ≤ 4	0.5
Broad	4 < D ₉₅ /D ₀₅	0.25

With

$\rho_{solid}, \rho_{bulk}$ = solid, bulk density

V_{95} = 95th percentile of volume of particles

L_{95} = 95th percentile of side of cubic particles

Lx_{95} , Ly_{95} , Lz_{95} = 95th percentile of sides of plate or cuboid particles

D_{95} = 95th percentile of diameter of spherical of particles

D_{05} = 5th percentile of diameter of spherical of particles

Equation 2 is equal to those of the standards (Annex C of NVN 7302, Equation D1 of CEN/TR 15310-1, Equation B1 of EN 15002). When there are “fine” particles in the sample, the approximation of the mean volume of particle as the volume of the 95th centile in diameter multiplied by the bulk density and by g overestimate the mean mass of particle (g should take a lower value to consider larger grain size distributions - see section Results). It must be kept in mind that the formulas above are only approximations.

Particle size reduction operations (particle creation by shredding, grinding, cutting, milling, ... of the sample) make it possible to obtain subsamples that are characterized by the same p and CV than the initial sample. In case of spheres or cubes, the size reduction ratio of particle is the cubic root of the mass reduction ratio (for instance, 2.2 times smaller for a 10 times reduction of the mass, 4.6 times smaller for a reduction of mass of 100, and 10 times smaller for a reduction of mass of 1000). For plate-like particles, sheets or flat scraps, it must be calculated on a case-by-case basis. The whole (laboratory) sample must be shredded or ground or milled before mixing and reducing the mass.

2.2 Data

Different data sets were used. For the distributions of concentration at the particle scale, original data of particle analysis in different WEEE plastic individual particles were measured by portable X-ray fluorimeter calibrated with reference material for Br and Sb. For the observed variability at the analytical scale, the original repeated XRF analysis of (certified) reference plastic material, the data of one characterization campaign (personal communication), and the triplicate analysis of laboratory sample of small household appliances and screens plastics for elements and brominated flame retardants (Hennebert and Filella 2018) were used. The validation data from leaching tests and biotests standards (references in Table 2) were also used. For the assessment of the number of particles in laboratory samples from published sampling plans, a technical report on sampling of shredded wood from Extended Producer Responsibility companies (Valdelia and Ecomobilier 2018) and a document of sampling of municipal solid waste incinerator bottom ashes in France (SVDU 1995) were exploited. For the sampling of plastics of small household appliances, screens and lamps, the sampling plans recommended in technical specification and standard were used (CENELEC TS 50625-3-1 and EN 50625-3-2, respectively).

3. RESULTS AND DISCUSSION

On one hand, **the estimation of n** capturing the p^{th} percentile of the constituent distribution, with a given coefficient of variation CV (that cannot be lower than the analytical variation) is presented. The number of particles in laboratory samples of in published sampling plan (from waste stream to laboratory sample) and in test portions of analytical standards (from laboratory sample to analyzed test portion) will then be compared with the recommended n .

On the other hand, when the measurand can be measured in each particle (typically with non-destructive physical methods), **the estimation of p** (the fraction of particles having a concentration higher than a given concentration limit) and its coefficient of variation CV from n individual measurements are presented (with fewer details). This approach is necessary to assess, for instance, the fraction of scraps that must be sorted out after a shredded, or the quality of sorted fractions.

3.1 Observed particle scale distribution

Two examples of particle analyses of plastics particles of WEEE are presented in Figure 1. In this type of composition, the last percentiles tremendously influence the mean concentration (Table 1). The median and the mean are very different. The normal distribution does not fit with the data (Figure 1, Table 1).

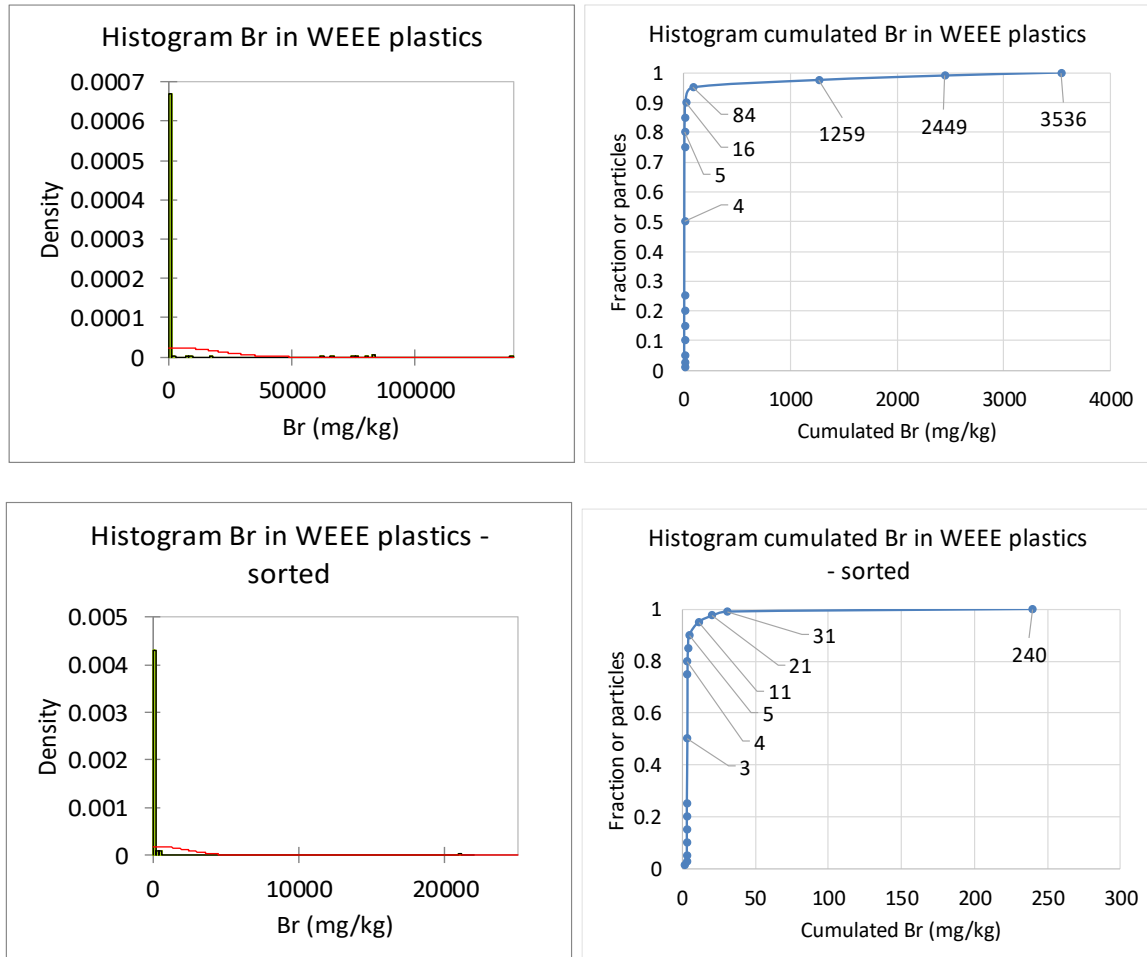


Figure 1: Particle concentration of bromine in WEEE plastic scraps (left), mean concentration of bromine in the cumulated fraction of particles (right) with the mean cumulated concentrations of the 50th, 75th, 90th, 95th, 97.5th, 99th and 100th percentiles of the particles. The normal distribution with same mean and s is indicated (red line). Upper figures: plastics after shredder (n = 200, median = 5 mg/kg, mean = 3 536 mg/kg, max = 139 300 mg/kg, s = 16 968 mg/kg, CV = 4.80). Lower figures: plastic after density sorting (n = 200, median = 4 mg/kg, mean = 240 mg/kg, max = 21 000 mg/kg, s = 2 094 mg/kg, CV = 8.72).

Table 1: Distribution of Br in individual particles of plastics of WEEE – comparison with concentrations calculated with a normal distribution with same mean and standard deviation

Observed distribution ($\bar{x} = 3\,536$ mg/kg, $s = 16\,968$ mg/kg)						Normal distribution with same \bar{x} and s		
n particle (sorted by increasing concentration)	Corresponding centile	Br concentration in the centile (mg/kg)	Br mean concentration in cumulated centile (mg/kg)	Ratio (Br concentration in the centile / mean)	Ratio (Br concentration in the centile / median)	Cumulated probability ($t_{1-\alpha/2}$)	Corresponding probability coefficient $t_{1-\alpha/2}$ (concentration $n = \bar{x} + t_{1-\alpha/2} \cdot s$, standard deviation)	Br calculated concentration in the centile (mg/kg)
100	0.50	5 (median)	4	0.0007	1	0.50	0	3 536
190	0.95	7 601	84	11	232	0.95	1.64	31 364
195	0.975	74 538	1 259	14	533	0.975	1.96	36 793
198	0.99	82 604	2 449	17	748	0.99	2.33	43 071
200	1	139 300	3 536	18	903	0.999	3.09	55 967

The normal distribution underestimates the contribution of the last centiles to the mean. For instance, the two more concentrated particles of 200 (rank 199 and 200) increase the mean concentration of 1000 mg/kg and represent about $\frac{1}{4}$ of the total bromine present in the batch of particles. A trivial hypothetical case (999 particles without 0 mg/kg and 1 particle with 100 000 mg/kg, mean concentration 100 mg/kg) and measured data indicate that these few particles must absolutely be “captured” (be present) in a representative laboratory sample. If they are not (if there are not “enough” particles in the sample), different laboratory samples will give highly variable mean concentration per sample (as measured in the laboratory). The concentration of individual particles cannot be predicted with mean and standard deviation, as usual, with the normal distribution (Table 1).

Sometimes the distribution is trimodal, as exemplified in the bromine concentration of sorted dense plastic scrap of cathode ray tubes (Figure 2). There are three groups of concentration: < 1 000 mg Br/kg (no bromine, but probably other additives that densify the plastic), 15 000 – 45 000 mg Br/kg (insufficient concentration for fire protection, probably the result of improper recycling), and 50 000 – 150 000 mg Br/kg (fire protected plastics).

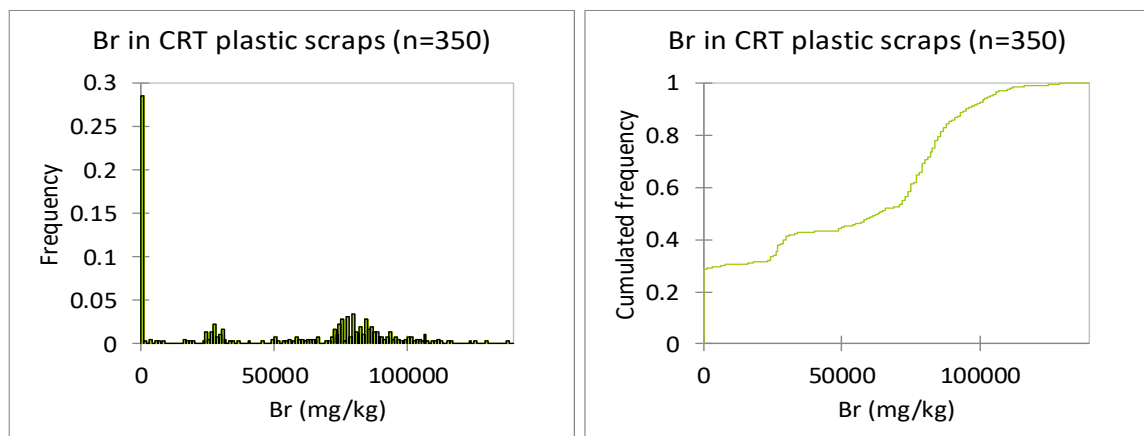


Figure 2: Tri-modal distribution of total bromine in density-sorted plastic scraps of cathode ray tubes (CRT) ($n = 350$, median = 63 850 mg/kg, mean = 53 261 mg/kg, max = 137 100 mg/kg, $s = 39\,577$ mg/kg, CV = 0.78).

It should be noted that such skewed distributions are also observed at population scales. This point is briefly mentioned here because it is not the topic of this paper. In national multi-annual sampling campaigns of sediments by Water Agencies in France (Padox and Hennebert 2010a, b), heavy metals, PAH, PCB, and matrix parameters have all their CVs greater than 0.5 and no distributions are normal or log-normal ($n = 551$ to 11966). The distributions of the total Hg in composts, fluvial and marine sediments, and agricultural soils in France are not normal either ($n = 379$ to 8798) (Hennebert 2019). In composts from organic fraction of municipal waste (separately collected or mechanically sorted) of 30

sites in France (n = 390), most of the parameters were not normally distributed (Zdanevitch 2012). Beggio et al. (2019) have studied the data available on digestates from agricultural residues and organic fraction of municipal solid waste in Italy. Digestates are sludge-like materials where a minor solid fraction coexists with a larger liquid fraction (both in mass and volume). Half of the parameters have CV > 0.5 and the only normally distributed parameters are: volatile fatty acids, biogas potential (n = 39 to 133) and Cu, total Cr, Zn (n = 256 to 465). In a large sampling campaign of shredded wood from furniture and construction and demolition (C&D) in France (Ecomobilier and Valdelia 2018), no parameters had a normal distribution (n = 81). The parameters K, N, Cl, B, Br, PCB, HCH and benzo(a)pyrene presented less variation (CV < 0.50). The parameters As, Cd, Cr, Cu, F, Hg, Pb, S, Zn, PCP, PAH (16), phenol index and formaldehyde had CVs > 0.50. **Error! Reference source not found.** The CVs for C&D wood are in the range of 1 – 3.5, and for furniture wood in the range of 0.3 – 1.6. It can be concluded that the distribution of many constituents in different samples of waste -or more generally in mixed materials handled by men- is frequently skewed by some large values. A consequence can be a high and unexplained variability in the laboratory results of different samples (typically CV > 0.50). The samples with high concentrations shouldn't be discarded as "outliers", but should be considered as the signature of the humankind spreading elements and substances in the environment...

3.2 Observed variability at the analytical scale

"CV" in Equation 1 stands for the variability of the measurement at the smallest analytical scale (on the smallest test portion that can be analyzed). In order to assess this parameter, this paragraph gathers experimental results on analytical CVs of granular solid waste.

Two cases are distinguished: the analysis without extraction (direct analysis like XRF or analysis of liquid extracts), and extraction followed by the analysis (typical solid analysis). The analytical variability of homogeneous liquid samples or liquid extracts of solid waste is well known as "low" (typically CV ≈ 0.03). The variability of analysis of solids is higher. Many solid analyses consist of two steps: a solid/liquid extraction, and the analysis of the liquid extract. For the measurement of the total content (of element or substance), the extraction is done under extreme conditions (fine powder, acids or base, solvent, high temperature, etc.), potentially until the total dissolution of the solid matrix, which can be easily verified by the analyst. These strong conditions guarantee that total extraction occurs. But regarding the measurement of partial content of element or substance (like leaching tests, percolation tests, (bio)available concentrations...), the extraction is done under milder conditions (coarser particles or aggregates, deionized water or mild extractant like EDTA or sodium dithionite, room temperature, mild solid/liquid separation at the end of the extraction, etc.). The extraction must follow exactly the protocol, and the protocol itself shouldn't have variants; otherwise the extraction ratio could be higher or lower. Due to this two-step-procedure, and since partial extraction is more variable, the analytical variability of solid samples is typically higher than the one of liquids.

The CVs of different cases are presented in Table 2.

Table 2: Observed variability at analytical scale

Sample	Parameters	Methods	Analysis (without extraction)						Extraction and analysis of the extract					
			Intra-laboratory			Inter-laboratory			Intra-laboratory			Inter-laboratory		
			n	CV mean	CV max	n	CV mean	CV max	n	CV mean	CV max	n	CV mean	CV max
Plastic reference material (original data)	Br	XRF	25	0.01										
	Sb	XRF	25	0.03										
Plastic reference material (pers. com.)	Elements and Brominated flame retardants (BFR)	Combustion, IC and EN 62321-6										n.k.*	0.06*	0.13*
												12	0.20	0.36
Laboratory samples of WEEE Plastic scraps (Hennebert and Filella 2018)	Br	Combustion, IC						33 t	0.10	0.27				
	Sb	Combustion, ICP						33 t	0.10	0.25				
	BFR	EN 62321-6						178 t	0.16	0.64				
	All							244 t	0.14	0.64				
Leaching tests: Prepared solutions and solid samples validation data	Elements, anions	EN 12457-2 Solutions analyses: ICP, IC; Solid samples: leaching, leachate analyses	38	0.04	0.24			38	0.17	0.77	38	0.37	1.1	
Biotests: Reference solution (liquid) or spiked media (solids) of the standards	EC50	Biotests: Vibrio ISO 11348-3, Pseudokirchneriella EN ISO 8692, Arthrobacter ISO 18187 Eisenia ISO 17512-1	8 (1 test)	0.20	0.38	17 (3 tests)	0.25	0.39						

*n.k. = not known, data of certificate of reference material; t = triplicate

For the analysis without extraction, the intra-laboratory variability is low (mean CV = 0.01 – 0.03) (light green cells), with clearly higher values for biotests (CV = 0.20 for intra-laboratory repetitions, CV = 0.25 for inter-laboratory repetitions, yellow cells).

For extraction and analysis, with laboratory samples, the intra-laboratory variability is moderate: mean CV = 0.10 – 0.17 for intra-laboratory repetitions, on plastics (a difficult matrix) and leaching tests (mid-green cells). For inter-laboratory variability, the CV is low for inter-laboratory repetitions on plastic reference material according to their certificate (CV = 0.06), higher for routine laboratories (CV = 0.20) (dark green cell), and still higher for leaching tests (CV = 0.37) (orange cell).

The biotests used in Table 2 are the ones of a test battery suggested to assess the hazard property HP 14 Ecotoxic in waste (Pandard and Roembke 2013, Hennebert 2018), and for which the data is available in the standards. The CVs are calculated from the intra-laboratory variability on one reference substance (1 spiked solid media), and the inter-laboratory variability on prepared matrices (2 liquid solutions and 1 spiked solid media). There are not enough data of inter-laboratory trials on true waste samples in the standards, including sample preparation and leaching for the aquatic tests, to calculate a representative CV. The inter-laboratory analytical CVs are high (mean 0.25).

For leaching tests (EN 12457-2), the variability of inter-laboratory tests of prepared solid samples is clearly higher. The data for the different tests are presented in Figure 3. According to some experts from standardization committees, the inter-laboratory variability originates from the different options available in the standard for liquid-solid contact (rolling, tumbling) and liquid-solid separation (decantation, filtration, centrifugation), that should be fixed in the standard to reduce the inter-laboratory variability. The influence of all these parameters was discussed in an inter-laboratory test (Van der Sloot et al. 2000).

From these observations, a table can be suggested, with as an input observed CVs in different cases and as an output the possible cause(s) if high values of CVs are observed (Table 3):

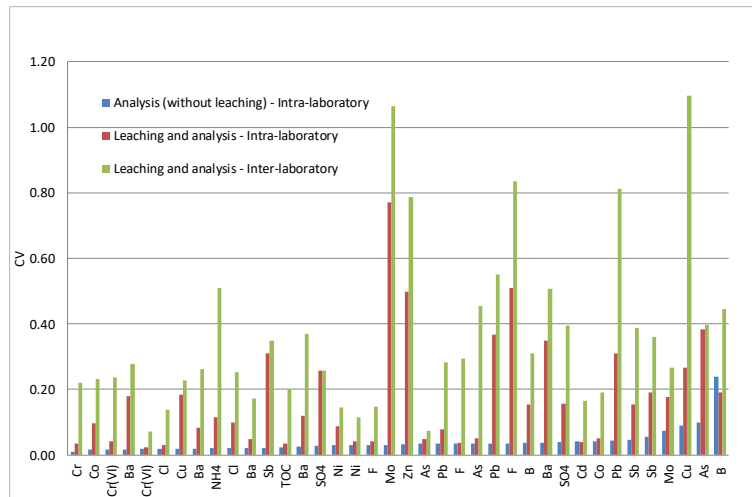


Figure 3: Analytical variability of leaching test (data from EN 12457-2)

Table 3: State-of-the-art analytical CVs and possible causes of higher CVs in intra- and inter-laboratory measurements

Scale	Sample	CV of analysis (without extraction)	CV of extraction and analysis	Possible cause and action
Intra-laboratory	Liquid sample or liquid extract	High > 0.10	-	Improve the analysis methods in the laboratory
	Pre-treated test portion (n ≥ 100 000) from the same laboratory sample	Low < 0.10	High > 0.20	Improve the extraction methods in the laboratory
	Different laboratory samples from the same population	Low < 0.10	High > 0.20	Check if the laboratory samples contain “enough” particles
Inter-laboratory	Different laboratory samples from the same population	Low < 0.10	High > 0.20	Check if the laboratory samples contain “enough” particles
	Pre-treated test portion from the same laboratory sample	Low < 0.10	High > 0.20	Check if the standard enables too many variations, which must be avoided between laboratories

3.3 Calculating the number of particles (n) from assumed p and analytical CVs

Nowadays, in most cases, the information on particle composition and variability is not available . When the distribution of the measurand in the different particles is abnormal (indices: CV of different “small” samples > 0.50), or when a heterogeneous distribution is foreseen, it is recommended to calculate the size of the laboratory sample with $p = 0.001$, as shown in paragraph “Observed distribution at particle scale”. Major or matrix parameters are typically less variable, and a lower p can be used for them. Nevertheless, most of the time there only will be one sampling for all the parameters, and then the most stringent conditions will apply. EN 15002 recommends $p = 0.001$ for minor contaminant parameters, and $p = 0.1$ for major or matrix parameters.

The CV that must be considered to determine “n” corresponds to the “fundamental error” (CEN TR 15310-1). It is the lowest variability that can be achieved on the smallest analyzable test portion, in a laboratory. It seems appropriate to calculate the size of the laboratory sample with $CV = 0.10$, as shown in paragraph “Variability at analytical scale”. One advantage of $CV = 0.10$ is that it makes it possible to highlight the analytical variability larger than $CV = 0.10$. Larger CVs can also be used.

Different ‘n’ can be calculated with Equation 1 (Table 4). For $CV = 0.10$, $n = 99\ 900$ for $p = 0.001$, and $n = 900$ for $p = 0.1$ (light green cells). For $CV = 0.15$, ‘n’ is reduced by a factor 2.25 and for $CV = 0.20$ is reduced by a factor 4.

Table 4: n as a function of p and analytical CV

$n = (1-p) / (CV^2 \cdot p)$ (Eq. 1)	Minor constituents – suggested in EN 15002 p = 0.001	p = 0.005	p = 0.01	p = 0.025	p = 0.05	Major constituents – suggested in EN 15002 p = 0.1	p = 0.2	p = 0.5
CV = 0.10 (intra-laboratory on samples – suggested in EN 15002)	99900	19900	9900	3900	1900	900	400	100
CV = 0.15 (intra-laboratory on samples)	44400	8844	4400	1733	844	400	178	44
CV = 0.2 (inter-laboratory on samples)	24975	4975	2475	975	475	225	100	25

3.4 Assessment of ‘n’ in laboratory sample of sampling plans and in test portions of analytical methods

3.4.1 Sampling plans (from population to laboratory sample)

Four cases of sampling plan from technical reports or standards are compared with the optimal size of a representative sample, expressed as n, from the largest to the smallest (Table 5):

- (i) Wood from furniture protocol for sampling from Ecomobilier and Valdelia (2018) is done in two steps. Increments of 5 m³ are taken. Their number is 20 + 0.06 times the mass of the batch (in tons). This composite sample is shredded on site and sieved in two fractions (80 – 15 mm, and < 15 mm). Each fraction is sampled in order to make a laboratory sample of 2 kgs;
- (ii) Sampling of municipal solid waste incinerator bottom ashes is done mainly in France according to the protocol from SVDU (1995). Six to one hundred increments of 10 liters are taken, mixed and quartered until a laboratory sample of 2 to 8 kg is obtained.
- (iii) The sampling of plastics from waste of electrical and electronic equipment (WEEE) after shredding is described for plastics of small household appliances (SHA) and screens in CENELEC TS 50625-3-1. One-day representative production is sampled all day long to end with laboratory samples of 7.5 to 25 liters for SHA;
- (iv) The same standard applies to lamps plastics in EN 50625-3-2, ending to a laboratory sample of 1 liter for lamps.

For the first two cases, the mean mass of particle is hypothesized (from data of CEDEN, the consulting company of Valdelia and Ecomobilier, and SVDU, using unbound mixtures for roadwork platforms granulometry), and calculated with Eq 2. For the third and fourth cases, it is estimated from original laboratory data.

For wood coming from construction and demolition waste and furniture, the estimated corresponding number of particles in the laboratory sample using a mean particle mass is large, according to the authors of the study (200 000 and 40 000 for the two size fractions). However, using Eq. 2, that number is calculated as insufficient (33 for the 80 – 15 mm fraction).

For municipal solid waste incinerator bottom ashes, using a granulometric distribution (fines are present), the calculated number of particles in the laboratory sample is large as well (greater than 100 million). However, using Eq. 2, that number is calculated as insufficient (165). Nevertheless, some (non-ferrous) metals are more concentrated in fractions of 1 to some millimeters, according to the literature (Chimenos et al 1999, Holm and Simon 2017) and to recovery practices that become widespread.

Table 5: Assessment of sampling plans (from population to laboratory sample) by calculated n (color of cells - pink: $10\ 000 \leq n < 100\ 000$; orange: $1000 \leq n < 10\ 000$; red: $n < 1000$)

Waste, Source	Steps, Remark	Size of 95 th percentil e = D ₉₅	M	n _{inc}	V _{inc} (M _{inc}) L (kg)	V _{sam} l	Bulk densit y kg/l	Solid densit y kg/l	M _{sa} m kg	Mean mass of particle (estimated) kg	n particles - calculated	Hypothesis # for calculation of n
C&D and furniture wood in 2 steps (CEDEN)	Step 1 Sampling, few fines	2	100 tons	26	5 000	130 000	0.200		26 000	20	Intermediate 1300	4
		2	1000 tons	80	5 000	400 000	0.200		80 000	20	Intermediate 4000	4
	Step 2 Shredding, sieving, resampling	<0.015							2	0.000010	200 000	2
		0.080 < <0.015							2	0.000050	40 000	2
		0.080 < <0.015						0.9	2	6.0E-02	33	1
MSWI bottom ash (SVDU)	fresh	0.050, 1%<63µ m		6	10 l (or 10 kg)				2	2.00E-08	1.00E+08	2
		0.050, 1%<63µ m		30	10 l (or 10 kg)				8	2.00E-08	4.00E+08	2
	matured	0.050, 1%<63µ m	2000 to 20000 tons	10 to 100	10 kg (< 0.1m)				6.75	2.00E-08	3.38E+08	2
		0.050, hyp. No fines	2000 to 20000 tons	10 to 100	10 kg (< 0.1m)			2.5	6.75	4.1E-02	165	1
Plastics of shredded WEEE Small Household Appliances (CENELEC TS 50625-3-1)	No fines (< 1 mm)	<0.020	1 d production	10	3	7.5	0.288		2.2	0.002	1080	3
		0.020 < <0.050	1 d production	10	5	12	0.288		3.5	0.004	864	3
		0.050 < <0.100	1 d production	10	10	25	0.288		7.2	0.008	900	3
		0.050 < <0.100	1 d production	10	10	25	0.288		7.2	0.008	900	3
Plastics of shredded WEEE Lamps (EN 50625-3-2)	No fines (< 1 mm)	<0.005	1 d production	10	1	0.300		0.3	0.001	300	3	
		0.005 < <0.020	1 d production	10	1	0.300		0.3	0.002	150	3	
		0.020 < <0.050	1 d production	10	1	0.300		0.3	0.004	75	3	
		0.050 < <0.100	1 d production	10	1	0.300		0.3	0.008	38	3	

M = mass or fraction of the production that is sampled

n_{inc} = number of increments (individual takings) that constitutes the laboratory sample

V_{inc}, M_{inc} = volume or mass of one increment

V_{sam}, M_{sam} = volume or mass of the laboratory sample

The hypotheses of Table 5 for the mean mass of particle are the following:

1: $M_{particle} = \pi/6 \cdot D_{95}^3 \cdot g \cdot \rho_{solid}$ ($g = 0.25$) (Eq. 2)

2: calculation from estimated granulometric distribution with a large granulometric range according to contacted authors or professional unions

3: estimated from laboratory measurements of sets of scraps for SHA and screens (no fine fraction, narrow distribution), estimated for scraps of lamps

4: estimated by the authors after contact for this study

For plastics scraps of waste of electrical and electronic equipment, according to technical specifications or standards or CEN, the size of the laboratory sample is 7.5 to 25 liters for small household appliances, and 1 liter for fluorescent lamps. The weight of individual particles and bulk densities has been measured, and realistic rounded values are used in Table 5. The number of particles present in the laboratory samples of 1 liter to 25 liters (depending on the size of the plastic scraps) is

calculated as insufficient for $p = 0.001$, but corresponds to $p = 0.1$ for small household appliances (Eq. 1 used as $p = 1 / ((n, CV^2) + 1)$ or Table 4) and $p = 0.25$ to 0.73 for shredded fluorescent plastics. These p values must be verified for these plastics but are probably not unrealistic for the unsorted fraction. Plastics from small household appliances are largely brominated (Hennebert and Filella 2018) and plastic waste from fluorescent lamps are most often brominated (personal communication from the French organization of extended producer responsibility), indicating that most or all of those waste are brominated (p approaches 1).

3.4.2 Analytical methods (from the laboratory sample to the test portion)

Different cases are presented, from large to small test portions: laboratory percolation tests and leaching tests, aliquots for laboratory mineral digestion or organic extraction (Table 6). The maximum grain size and the mass of the test portions are given in the standards.

For test portions from laboratory sample, the mean mass of the particle is calculated using Equation 2 as the volume of a sphere with a diameter of the maximum size multiplied by g (set to 0.25) and a hypothetical solid density of 2 kg/l. For percolation and leaching tests, cases with the presence of a fine fraction ($10\% < 1$ mm) were also used.

Table 6: Assessment of analytical methods (from laboratory sample to test portions) by calculated n (color of cells - pink: $10\ 000 \leq n < 100\ 000$; orange: $1000 \leq n < 10\ 000$; red: $n < 1000$)

Source	Size 95th percentile	Vsam	Bulk density	Solid density	Msam	Mean mass of particle	n	Hypothesis
	m	l	kg/l	kg/l	kg	kg	particles	
Percolation test EN 14405	0.010 Column 0.1 m i.d.	2.36	1.6	2	3.8	3.0E-04	14 400	1
	Idem with 10%<1 mm				3.8	5.2E-06	730 769	2
	0.004 Column 0.05 m i.d.	0.59	1.6	2	0.9	1.7E-05	56 250	1
	idem with 10%<1 mm				0.9	4.6E-06	195 652	2
Leaching test EN 12457-4	0.010			2	0.090	3.0E-04	344	1
	idem with 10%<1 mm			2	0.090	5.2E-06	17 308	2
Leaching test EN 12457-1, -2	0.004			2	0.090	2.0E-05	5 371	1
	idem with 10%<1 mm			2	0.090	4.6E-06	19 565	2
Leaching test EN 12457-3	0.004			2	0.175	2.0E-05	10 445	1
Elements XRF analysis EN 15309	0.000150			2	0.010	8.8E-10	11 317 685	1
	0.000080			2	0.005	1.3E-10	33 571 746	1
Elements Digestion EN 13656	0.000250			2	0.0002	4.1E-09	48 892	1
	0.000250			2	0.0004	4.1E-09	97 785	1
PCB analysis EN 15308	0.000500			2	0.010	3.3E-08	305 577	1
	0.000500			2	0.025	3.3E-08	763 944	1
PBDE products EN 62321-6	0.000500			1.1	0.0001	1.8E-08	5 556	1
PBDE waste EN 16377	0.002000			1.1	0.0030	1.2E-06	2 604	1

PCB = polychlorobiphenyls, PBDE = polybromodiphenylethers

The hypotheses for the mean mass of particles are the following:

1: $M_{\text{particle}} = \pi/6 \cdot D_{95}^3 \cdot g \cdot \rho_{\text{solid}}$ ($g = 0.25$) (Eq. 2 – from the standards)

2: calculation from estimated granulometric distribution, large granulometric distribution according to some authors or professional unions

No firm conclusion can be drawn from the table since the results with the method of the standard (Hypothesis 1 in the table) do not match with the results from the granulometric distribution. This point is further discussed in section “3.5 Importance of assessing the mean mass of particles” below.

For percolation and leaching tests, the number of particles calculated by the formula of the standard

(Eq. 2) never reaches 100 000 and is even around 300 in the leaching test with the 10 mm grain size. This number of particles is also always lower than the number calculated with a hypothesis of 10% of particles < 1 mm, which is a realistic assumption after the size reduction.

For analytical measurements (direct such as X-ray fluorimetry) or after digestion / extraction, the test portion calculated with Equation 2 is greater than or equal to 100,000, with the exception of the PBDE analysis. As the size reduction occurs, it is likely that the real number of particles in the test portions will be higher.

3.5 Importance of assessing the mean mass of particles ($M_{\text{sample}} = n \cdot \text{mean } M_{\text{particle}}$)

The best approach in order to estimate the mass or the volume of the laboratory sample is to measure the mean mass of the particles and to multiply it by n (preferably 100 000). The volume is obtained by conversion of this mass with the bulk density. If $D_{95}/D_{05} > 4$, the mean mass of the particle is reduced by a factor $g_s = 0.25$ (4 times reduction). In waste, if "fines" are present, the ratio D_{95}/D_{05} will be much larger (one to several order of magnitude), and Eq. 2 (from the standards) will overestimate very largely the mean particle mass. It is therefore very important for heterogeneous grain size material to have information on the granulometry of the waste in order to be able to estimate the mean mass of particle with some precision. The granulometric distribution should be measured (specially the fines, at least the fraction < 1 mm, and better the fractions < 63 μm or < 50 μm) without aggregates dissociation. The agronomic sand/silt/clay fractions after aggregates destruction does not correspond to what is sampled... and should not be used as such. Solid density (to convert particle size into particle mass) and bulk density (to convert sampled volume into sampled mass) should also be measured. If these data are not available, Equation 2 can be used as a first approximation, in sieved fraction of construction and demolition waste or bottom ash, for instance, or in some scraps from shredder (materials that don't "burst" under compression: metal droplets, metal pieces, plastics).

It is easy to calculate that there is at least 100 000 particles in 0.01 g of particles with $D_{95} = 0.063$ mm, or 0.03 g of particles with $D_{95} = 0.1$ mm, or 0.4 g of particles with $D_{95} = 0.25$ mm, or 3 g of particles with $D_{95} = 0.5$ mm, or 26 g of particles with $D_{95} = \leq 1$ mm (Eq. 2, hypothesis of density of solid of 2 kg/l, $g_s=0.25$).

3.6 Assessment of p and its CV from measurements of individual particles

It can be necessary to assess p, the fraction of particles with a given characteristic (for instance with constituent concentration > z mg/kg), for the quality control of secondary material, for example.

Individual particle measurements must be available. In order to estimate the number of particles to be measured to assess p with a given confidence interval, one could proceed as follows:

- Measure the constituent concentration in n particles (for instance 100);
- Calculate x (number of particles \geq a given value), the estimator of p ($\hat{p} = x / n$), the standard deviation of x ($s = \text{square root of } [n \cdot \hat{p} \cdot (1 - \hat{p})]$) (see 0), the CV of x ($= s / x$) and the CV of \hat{p} ($= s / x$);
- If CV is deemed too high, continue the measurements (increase n) and recalculate \hat{p} and CV until you obtain the desired CV.

An example with plastics of WEEE is given in Table 7. Total bromine has been measured particle by particle over four batches of particles. The estimates of $p \geq 2000$ mg Br / kg (in fractions) and its variance are $\hat{p} = 0.72$ (0.01), 0.06 (0.01) and 0.01 (0.007), respectively. The number of particles that should be measured in order to obtain a CV of 0.10 are 39 particles for the most brominated batch (350 were measured), to 9 900 particles for the least brominated lot (200 were measured). This method is therefrom useful to produce a result (here the fraction of particles that have a concentration < 2000 mg/kg) with a given confidence.

Table 7: Assessment of p and CV from n individual particles measurements - examples

Assessment of p (number of particles > 2000 mg/kg and CV of p)	Plastics scraps CRT > 2000 mg Br/kg	Mixed plastic scraps - input	Mixed plastic scraps – sorted, low density
n	350	200	200
x = n particules ≥ 2000 mg Br/kg	252	12	2
Estimator of p = $\hat{p} = x/n$	0.72	0.06	0.01
Standard deviation of x	8.4	3.4	1.4
CV of \hat{p}	0.03	0.28	0.70
Standard deviation of \hat{p}	7.6	3.4	1.4
Ex-post calculation of n for CV=0.10			
$n = (1 - \hat{p}) / (CV^2 \hat{p})$	39	1567	9900
INFO			
Mean Br concentration of particles mg/kg	53 261	3 536	2 407
Median mg/kg	63 850	5	4
Standard deviation mg/kg	39 577	16 968	2 094
CV	0.78	4.80	8.72

4. CONCLUSIONS

If the concentration is not dependent of the particle size, the key concept for representativity (a smaller portion has the same composition than a larger portion) is the number of particles, from the binomial law, using the lowest variability achievable in analysis (result cannot be less variable), and the fraction of particles with the property of interest (named “p”). Analytical coefficient of variations (CVs) from validation data of standards or characterization campaigns showed that a CV of 0.10 can be achieved for solid matrices. With portable X-ray fluorescence, elemental concentration of individual particle is available. Data on individual particle distribution of element in some waste demonstrate the importance to capture the rarest concentrated particles (p = the 999th particle of 1000) that may tremendously influence the mean concentration. To be sure to “capture” these particles, p can be set to the 999th particle of 1000. With these CV and p, “n”, the number of particles in a representative sample with a skewed distribution of element or substances by particle can be calculated to be typically 100 000 particles. This result is in accordance with the general recommendation of EN 15002 for minor constituents. The number will be lower for major constituents with less skewed distribution. Simple physical characteristics of the particles (granulometric distribution, mean mass or mean volume, bulk density - frequently not measured) are then used to calculate the mass and volume of the “n” particles constituting a representative laboratory sample or test portion. With these findings, the recommended mass of the laboratory samples (from sampling plans of professional unions or standards) and test portions for laboratory analysis (from standards) can be revisited. If there is a fine fraction (< 63 µm or even < 1 mm), the recommended mass or volume of the sampling plans will comply with the requirement of $n \geq 100\ 000$. When there is no fine fraction, like for some WEEE plastic scraps, the volume recommended in technical specification and standard for laboratory sample can’t have “enough” particles for $p = 0.001$, but well for $p = 0.1$ for plastics from small household appliances or higher p for plastics from fluorescent lamps. These p values must be verified for these plastics but are probably not unrealistic for the unsorted fraction. On the other hand, when there is a fine fraction, the equation of the standards overestimates the mean mass of particle, and hence the mass needed for the laboratory sample. An original method for the assessment of p (with its CV) from measurements of n individual particles has been tested on some plastic samples.

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