THE INHERENT VARIABILITY OF SOME ENVIRONMENTAL ANALYTICAL METHODS HAMPERS THE CIRCULAR ECONOMY OF MATERIALS

Pierre Hennebert [1,*], Anne-Françoise Stoffel [2], Mathieu Hubner [2], Daniel Fortmann [2], Patricia Merdy [3] and Giovanni Beggio [4]

[1] Ineris (French National Institute for Industrial Environment and Risks), BP 2, F-60550 Verneuil-en-Halatte, France.
[2] Eurofins Analyses pour l'Environnement France, Direction Technique et Développement, 5 rue d'Otterswiller, 67701 Saverne, France
[3] IM2NP Institute of Materials Microelectronics Nanosciences of Provence, UMR CNRS 7334, Aix-Marseille Université, University of Toulon, France
[4] Department of Civil, Environmental and Architectural Engineering, University of Padova, Via Marzolo 9, 35131, Padova, Italy

ABSTRACT
This paper is the third part of three papers on sampling by the number of particles, focusing on analytical variability. The objective is to propose a target variability of waste and contaminated soil analyses (extraction and quantification), that can be used for calculation of the size of a representative sample. Data of intra- and inter-laboratory variability are presented. As the variability of the quantification step (after extraction) is limited in waste and soil analyses to about 0.01, the analytical variability stems from three main sources: (i) non-homogeneous test portions; (ii) for partial extraction methods, variable extraction rate, due to presence of options in the method or insufficient time for equilibrium (leaching or percolation test, biotests); and (iii) ill-defined solid/liquid separation (leaching or percolation tests), critical since there are colloids and nanoparticles in the leachates, representing from 0 to 100% of the element fraction in the leachate. Counter-intuitively, the centrifugation (annex E of EN 12457) series before the 450 nm-filtration delivers leachates more concentrated in particles (median size 150 nm, 1 sample) and statistically more concentrated in elements (+13%, 27 samples, 287 paired data). Without centrifugation, the filter cake that builds up on the membrane is an additional filter. A target intra-laboratory variability of CVr = 0.10 (10%) and inter-laboratory variability of CVR = 0.20 (20%) is proposed for all analytical methods. The methods with higher CVr and CVR should be revisited to not jeopardise the sampling and characterisation efforts of waste and soil, particularly for valorisation in the circular economy.

1. INTRODUCTION

The sampling operations produce from a large population (1-1 000+ t) a representative laboratory sample (1-100 kg), that is further pretreated with intermediary steps in the laboratory up to a test portion (0.1-1-100 g) that is analysed most frequently by liquid extraction and quantification. At each step the material must contain "enough" particles so that every particle has the same probability to be present in a smaller material portion. To have an acceptable variability of the characterization of the waste, the variability of sampling and the variability of laboratory analyses must be controlled. A validated standardized analytical method must have a limited variability when analyzing test portions homogeneous at their scale, to ensure consistency of results and comparability of data. The variability is conven-iently expressed as the relative standard deviation (RSD – the standard deviation divided by the mean) also called coefficient of variation (CV). This ratio is unitless or can be expressed in percentage. It allows immediate comparison of variability of methods. Environmental analysis frequently occurs in two steps: extraction or digestion (from a solid or a liquid to a liquid, eventually purified) and quantification (measurement of the analyte in the extract). These two steps are analysed separately here when the data are available. "Analysis" in this paper refers to the extraction and the quantification steps.

The distribution of characteristics of populations are very frequently positively skewed by some large values and is not normal (gaussian). They must not be confounded with the analytical variability on homogenized test portions,

which is normally distributed if the analyses are repeated on correctly prepared test portions. The art of characterization is to sample representatively that population, to subsample identically up to a representative test portion, and to analyse test(s) portion(s) with a controlled variability.

Sampling specialist Pierre Gy, author of The Theory of Sampling of Granular Materials for the Mineral and Mining Industry, now used worldwide, noted that for inorganic, metallic and physico- chemicals on which he worked, "the biases that we have actually observed can reach 1000% in primary sampling and 50% in secondary sampling, while the analysis biases hardly exceed 0.1 to 1% (a little more for traces)" (Gy 1996).Given this background, what is a reasonable and achievable variability of analysis of heterogeneous waste and contaminated soil ? For the difficult case of lead (a malleable element) in very heterogeneous mixed solid waste, Viczek et al. (2022) report a CV=1.80 for sampling + analyses, a CV=0.32 for analyses (extraction and quantification) and a CV=0.15 for quantification. The latter value (of repeated quantification of extract) can be considered as high in comparison with the other date presented in this paper. For solid recovered fuel, Gerassimidou et al. (2020) have measured, with fully "nested" experiments (with repetitions of each step of sampling and analysis), for the last stage of subsampling (6.5 g in their case) to the test portion and the analysis of the test portion a CVs of: 0.007 for moisture content, 0.014 for calorific value, 0.016 for ash content and 0.050 for total chlorine. These "macro" parameters are more uniformly distributed in the particles of the waste than lead and their variability is known to be lower.

These two examples suggest that analytical variability must be under control and that a reasonable value for waste assessment can be achieved even in heterogeneous waste. Gerassimidou et al. (2020) note that a suggested value for a reasonable sub-sampling (test portion) and analysis uncertainty could be considered < 0.15 (< 15%), citing Gerlach and Nocerino (2003).

The different steps to calculate the size of a representative sample by the number of particles (as in waste standards) rely on a targeted variability of (sampling + analysis). It is hence necessary to have analytical methods with a controlled variability.

This study has arisen from practical cases. A quasi-systematic difference in leaching concentration of waste and contaminated soil has emerged between French service laboratories (higher concentrations) and some of their Dutch and German homologues. Another case is the unfortunate extreme variability of ecotox test of municipal solid waste incinerator bottom ashes during a characterization campaign in France, increased in case of neutralization of the leachate, probably by uncontrolled solid/liquid separation, that hampered in practice to make a decision on the ecotoxicity.

This paper is the third part of three papers on sampling by the number of particles. It is focused on analytical variability. To well understand the subject, according to our experience of communication on sampling, some more general notions are illustrated in the Supplementary Information. In the Part 1 of the SI, some skewed distributions of populations are graphically presented: weight of objects and civic amenity site, size, mass and density of particles of solid recovered fuel, contaminants in sediments, brominated flame retardants in plastic scraps. These data indicate that the last centile(s) determines the mean concentration. The different steps necessary to determine the size of a representative laboratory sample and subsample up to the test portion that is the part analysed is the recalled in the Part 2 of the SI. An example of reduction of the variability of concentration in individual analytical samples that come from the same composite sample without sample pre-treatment from a non-normal to a normal distribution is presented in Part 3 of SI.

Some data on analytical variability (Hennebert and Beggio 2021) showed that an intra-laboratory variability of 0.10 (10%) is achievable for total analysis of waste with extraction, and an inter-laboratory variability of 0.24, but not for partial analysis like leaching tests and ecotoxicological tests. The objective of this paper is to propose a target variability of waste and contaminated soil analyses (total concentration with extraction) from more data, that can be used for calculation of the size of a representative sample. A target variability is requested by sampling specialists (for instance Esbensen and Ramsey 2015). A second objective is to identify for the leaching tests the causes that make them less precise for the characterization of waste that is more and more requested in circular economy, when wastes become products that must fulfil precise specifications. A third objective is to present variability of ecotoxicological tests to encourage further refinements of these tests.

2. MATERIAL AND METHODS

2.1 Validation data and quality assurance data from analytical standards

The mean concentration, the number of laboratories, the number of outliers, the mean concentration (without outliers) and its coefficient of variation (CV, also called relative standard deviation – RSD) of repeated analyses in every laboratory (intra-laboratory repeatability CVr) and repeated analyses of all the laboratories (inter-laboratory reproducibility CVR) were collected from the annexes of the CEN standards (cited in their respective sections) and discussed.

For the case of the accelerated percolation of construction material prEN 16637-3:2021 (proposed to waste as prEN 17516), more detailed data from report (Garcia-Ruiz et al. 2020) have been used to assess the influence of parameters, of concentration, of percolation fraction and of sample on repeatability and reproducibility. For intra-laboratory variability of homogeneous test portions, the data of repeated analyses of homogenized soil or sludge used as internal reference for quality control system and reference solutions from a large agro-environmental laboratory of INRAE (France), have been used. For intra-laboratory of potentially heterogeneous test portions, the composition data of mixed commercial waste have been recalculated from (Viczek et al. 2021), and their CVr obtained (Details in Hennebert and Beggio 2021). The data from quality assur-

ance round robin national tests in France of 2019 and 2020 of two aquatic ecotoxicological tests, with pure reference solutions (dissolved chemicals of analytical grade) and two samples of homogenised liquid waste were also used.

2.2 Characterisation of particles and element concentrations in waste leachates (EN 12457-2)

An experiment conducted at University of Toulon (France) assessed the influence of the centrifugation step on the number and the size of particles passing through the filtration membrane. The sample was an excavated contaminated sediment dredged from a canal in the north of France. The sample was air dried. The sample has been leached according to EN 12457-2: sieving < 4 mm, 24 h rotary tumbler, L/S = 10 L of deionised water / kg dry matter. The sample was decanted for 15 minutes. The supernatant was separated, homogenised, and divided in two subsamples. One subsample was frontally filtrated with 0.45 μm membrane with a vacuum device. The other sub sample was centrifuged during 30 min with 2000 g, and then filtered. The number and size of particles of the two leachates were assessed by a Nanoparticle Track Analyzer immediately after filtration of 50 and 100 ml. The mass of the filter before filtration and the mass of the filter and the filter cake after filtration and drying were recorded.

Another experiment was conducted at Eurofins service laboratory in Saverne (France). The protocol was the same as described above, except that centrifugation was 4 min at 3500 g, and that frontal filtration was done with an automated high-pressure filter and stopped after 300 mL of leachate. Not all the volume of the leachate has been filtered, as it is the common practice. Twenty-seven samples (4 wastes, 2 sludges, 6 sediments, 15 soils) underwent leaching test and analysed for turbidity and physico-chemical parameters (electrochemistry and titration analyzers), dry residue (gravimetry), anions (TOC-meter, spectrophotometry), and inorganic elements (12 heavy metals by ICP-MS). The values lower than the limit of quantification for centrifugated or non-centrifugated fraction or both were not used, as done for the assessment of validation trials.

2.3 Protocol of the column test prEN 16637-3

An accelerated percolation test has been proposed to evaluate the release of dangerous substances from construction material (project of standard prEN 16637-3 of CEN/TC 351). Starting from the waste upward column percolation test EN 14405, (< 4 or < 10 mm, column of 30 cm height, water velocity equivalent to the half of the column per day), the size of the grain was increased to 22 and 44 mm with a broader column, and the water velocity was increased by a factor 3 or 4. Depending on the porosity of the packed material in the column, the residence time is 24 h in the waste percolation test, and 6-8 hours in the accelerated percolation test. Seven fractions from cumulated L/S = 0.1 to 10 l/kg were collected and analysed separately. The waste test lasts typically one month, while the accelerated test lasts for one week. Since the first fractions after equilibrium and after 0.1 L/kg are obtained after 3 days.

3. RESULTS AND DISCUSSION

3.1 Theoretical discussion: how high can be the variability of a standardized analytical method?

By the virtue of the repetition of random independent measurements in the same conditions, the distribution of the means from repeated measurements tends to a normal distribution, if the number of repetitions increases. When the characterisation campaign of population (i.e., repetition of the same measurements on a set of equivalent samples from the same population) shows many low values and some high values, producing a non-normal distribution, it is likely that the samples and subsamples are too small to capture in all cases the rare particles that "make" the mean. In these cases, these high values should not be considered as "outliers". The samples are not representative of the whole population but only of a part of it. If the resulting CV of the characterization campaign is > 0.50, the approximation by a normal distribution is not relevant for environmental samples. The calculated confidence interval of the mean is not representative of the real distribution of the data. The results should be described as a distribution and its centiles. A confidence interval of the median can be calculated by a ranking method (Environmental Agency et al, 2021). A second characterization campaign with larger samples (calculated with the information from the first campaign) is recommended.

To set limit to the variability of analytical methods, it should be considered that:

- repeated analyses of homogeneous test portions (homogeneous at the scale of the test portion) are normally distributed;
- in a normal distribution, 95.4% of the population has a value between the mean (x) ± 2*standard deviation (s), 2.3% have values lower than (x − 2 s) and 2.3% have values higher than (x + 2 s);
- If CV is < 0.5, the first values up to the 2.3th centile are < (x − 2 CV x) = < (x − x) = < 0 : they are negative;
- In the case of physical, chemical or biological measurements, no results are negative. The lowest value of a normal distribution should be close to zero, approximated with the limit of quantification of the method.

As a consequence, the maximum CV of any repeated correct measurements of samples of waste and soils should be 0.5. The normal distributions with different CVs are graphically illustrated in Part 4 of the Supplementary Informations. An ISO document proposes a maximum of inter-laboratory CVR = 0.40 with additional condition on number of laboratories, number of outliers and limit to extraction rate for water analyses (ISO 2016). That value is also accepted for instance for the difficult extraction and analysis of polybromodiphenylethers in plastics (USEPA 2010). Sampling specialists like Kim Esbensen propose for the sampling and the analysis CVR in all the case lower than 0.35 and better lower than 0.20: "When the GEE (Global Estimation Error = CV of sampling and analysis) has exceeded 35%, the empirical distribution has departed significantly from normality. The larger the GEE, the larger this departure and the greater the error that is introduced

in the estimation. The international sampling community recommendation is that RSV should in general not be allowed to exceed 20% without investigative consequences » (Esbensen and Ramsey 2015).

Based on observed analytical variability, it is proposed and discussed in this paper for standardized analysis with extraction and quantification a maximum intra-laboratory variability of 0.10 (10%) and a maximum inter-laboratory variability of 0.2 (20%), that can be used to calculate the size of a representative sample. A higher analytical variability jeopardises the efforts of sampling. Calculated normal distributions with CV of 0.2, 0.4 and 0.25 are presented in the Part 4 of the SI.

It should be noted that the variability of standardized analytical methods for compliance with specifications of products or raw material is 0.01 (1%) or less (Gy 1996).

3.2 Observed variability of standardized analytical methods of waste

The variability of the analyses at different steps of the procedure from the laboratory sample to the test portion is presented, with original data and literature data. Analyses with total extraction to measure total concentration are less variable than the analyses with partial extraction and are presented first. A first approach on the variability of 14 parameters can be found in Hennebert and Beggio (2021). The variability of non-extractive method like X-ray fluorescence is around 0.01. The next paragraphs present some data on methods with total and partial extraction followed by quantification.

3.2.1 Total concentration or total extraction and concentration

Intra-laboratory analysis of test portions of an internal reference material or a control solution (control quality)

An example of distribution of repetition of total organic carbon in soil from homogeneous test portions for the first 17 weeks of 2022 from a home-made reference material is given in Figure 1 (courtesy of INRAE, unpublished data).

The distribution is normal (gaussian) and the CVr is 0.016. For the same first 6 months of 2022, the same laboratory had the following CVrs: major element, total nitrogen soils 0.028 (n=92), sludges 0.011 (n=306), trace elements, Hg 0.083 (n=15), Pb 0.086 (n=25). For organic micropollutants, for a large time span, the control solution of benzo a pyrene (polycyclic aromatic hydrocarbon) has a CVr of 0.072 (n=456, 2013-2022), and the congener PCB 52 has a CVr of 0.079 (n=466, 2009-2022).

Intra-laboratory analyses of laboratory samples from extremely heterogenous waste in size of particles, material and composition (mixed commercial waste)

The composition data of this maybe most heterogeneous waste (with household waste) and the CVr of 31 parameters (30 elements and the lower heating value) recalculated - Viczek et al. 2021 - are presented in Figure 2). Four elements have CVr > 0.40. 87% of the CVrs are lower than 0.40 and 55% of the CVrs are lower than 0.20. The CVrs do not significantly depends on concentration, from 1 to 100 000 mg/kg.

The comparison with the case of test portions (Figure 1, para above) indicates that the variability originates from the laboratory samples. The authors conclude that the composite laboratory samples should be larger than 240 kg to reduce the variability. In practice an additional shredding and mixing step on field should be performed to keep the size of the laboratory sample practical and to reduce the variability of the laboratory sample. This case illustrates the heterogeneity of laboratory samples.

Intra- and inter-laboratory analyses of homogeneous laboratory samples (validation data of standards)

The data of 20 parameters of 15 methods of total content of elements and substances (PAH, PCB, PBDE, PCDD/F) were compiled and are synthetised in Table 1. The mean CVr is 0.07 and the mean CVR is 0.27 (with one method > 0.40). Additional detailed data can be found in Hennebert and Beggio (2021).
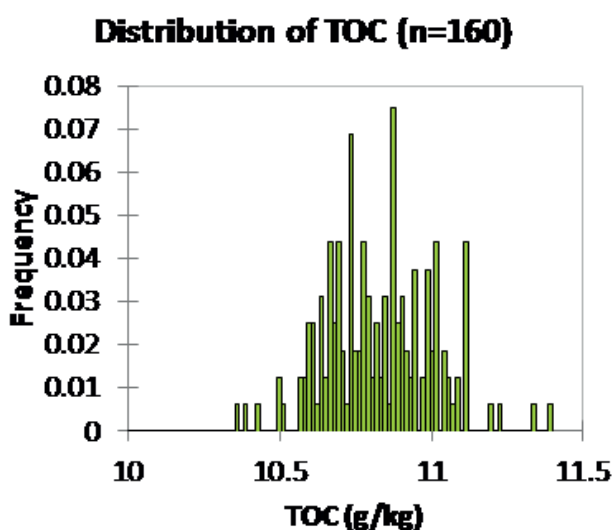

Distribution of TOC (n=160)

FIGURE 1: Analytical variability of test portions: Total Organic Carbon of laboratory reference soil during quality control of the first 17 weeks of 2022 (courtesy of INRAE, France) - mean = 10.8 mg/kg, s = 0.178 mg/kg, CVr = 0.016 = 1.6%, normally distributed.
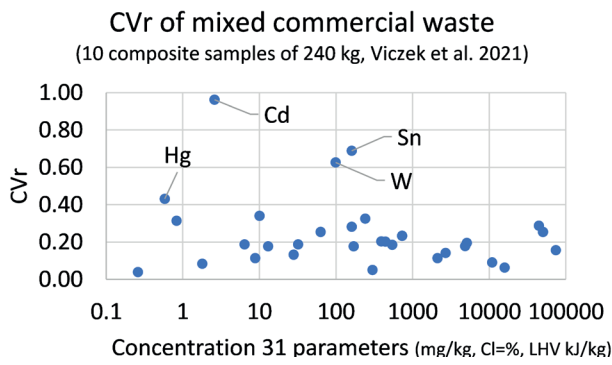
CVr of mixed commercial waste
(10 composite samples of 240 kg, Viczek et al. 2021)

FIGURE 2: CVr of mixed commercial waste (pretreatment, extraction, quantification), an extremely heterogeneous material (calculated from Viczek et al 2021). 55% of CVr < 0.20, 87% of CVr < 0.40 (max CVR recommended ISO) (Cl = total chlorine, LHV = lower heating value).

Discussion on total analyses

Strong conditions of size of particles, temperature and chemical energy are used to guarantee the complete extraction of the most recalcitrant samples. In case of homogeneous test portions (at the scale of the test portion) used in internal quality control, the distribution is normal, and the intra-laboratory variability is in the range 0.02 – 0.08 (INRAE data). For 19 standards, the mean intra-laboratory variability of validation trials with prepared samples is 0.07. For extremely heterogeneous waste like mixed commercial waste, the intra-laboratory variability in Viczek et al., (2021) is higher, indicating that in that work the already large laboratory samples are too small to always have the same composition. In that extreme case, the variability stems from the laboratory samples.

For 20 standards, the inter-laboratory variability of validation trials is 0.27, an acceptable performance, lower than the maximum of 0.40 recommended in ISO (2016) and indicating a normal distribution of the results of the different laboratories.

3.2.2 Partial extraction: batch leaching tests EN 12457-2

The variability of partial extraction and quantification results are presented and discussed. In case of partial extraction, mild conditions of size of particles, temperature and chemical energy are used to mimic the environmental conditions that could prevail when the waste is in contact with the environment. These tests are used for landfill acceptance in Europe (EC 2003). Experimental data obtained

TABLE 1: Variability of validation data of 20 EN and ISO standards and methods of total analyses of elements and substances of waste, biowaste, soil and sludge.

	CVr	CVR
n	19	20
min	0.010	0.060
median	0.074	0.276
mean	0.074	0.268
max	0.170	0.580

for this paper on the presence of colloids and particles < 450 nm in the leachates are presented and can explain, together with the agitation conditions (according to the literature) and the use of a centrifugation or not (original 287 paired data), the variability of the method.

The variability of analyses, repeatability (CVr) and reproducibility (CVR) of the validation data detailed in the annexes of the batch leaching test EN 12457-2 are presented in Figure 3 as a function of parameter concentration (data
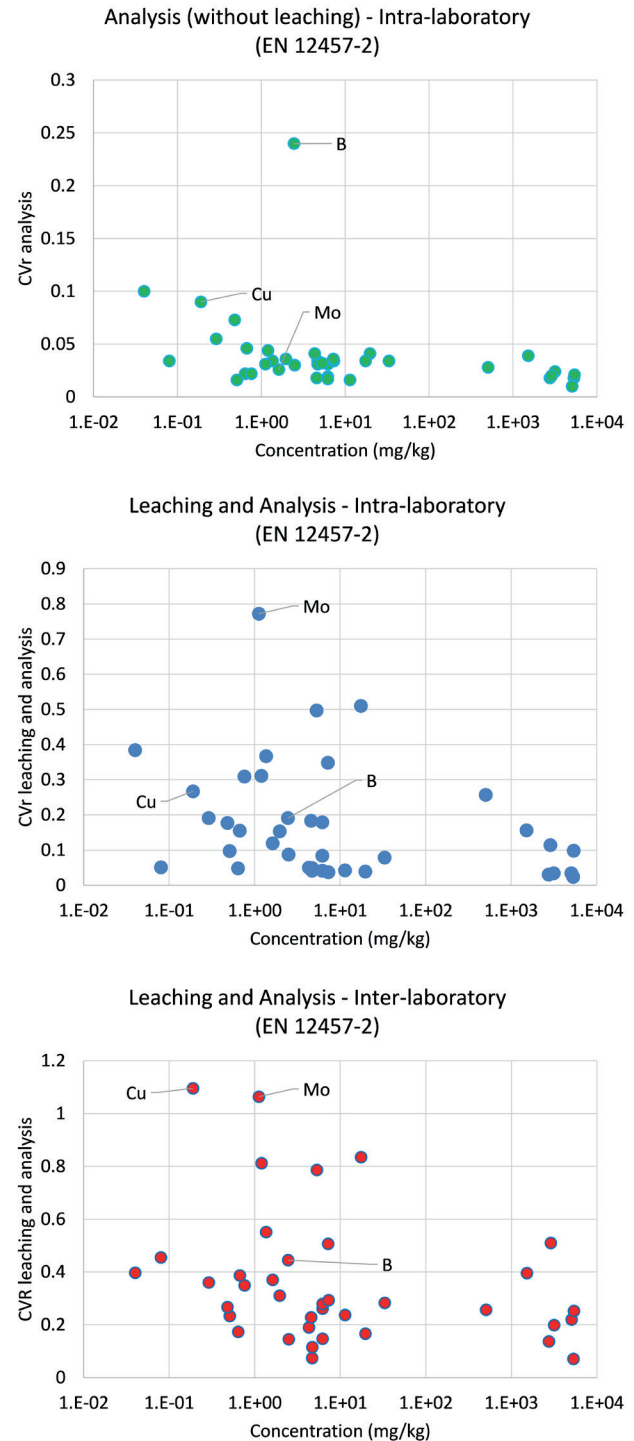
Analysis (without leaching) - Intra-laboratory
(EN 12457-2)

Leaching and Analysis - Intra-laboratory
(EN 12457-2)

Leaching and Analysis - Inter-laboratory
(EN 12457-2)

FIGURE 3: CVr of analysis of leachate, CVr and CVR of (leaching and analysis of leachate - validation data of EN-12457-2).

> LOQ).

The 24-hour batch leaching tests are mainly used for landfill acceptance or allocation of inert waste in the EU. The average intra-laboratory CVr is 0.17 (n=38, different waste, element concentration > LQ) and the average inter-laboratory CVR is 0.36 (idem).

The analyses of leachates (Figure 3 first part) have 33 intra-laboratory CVrs < 0.05, 4 CVrs in the 0.05 − 0.10 range. Boron is an exception with a CVr = 0.24 for a mean concentration of 2.45 mg/kg, which results probably of a well-known interference with glassware, that probably some laboratories haven't taken into account (the individual data of concentrations are not available).

The variability increases from intra-laboratory analysis (Figure 3 second part) to inter-laboratory leaching tests (Figure 3 third part) as illustrated for three labeled elements B, Cu and Mo (the scales of the Y axis are different). The analysis of boron is variable probably due to its adsorption on glass. The analyses of molybdenum and copper have CVr < 0.10. With intra-laboratory leaching and analysis, the CVrs triple. Molybdenum is the less repeatable, probably due to its sensitivity to pH, with the possible influence of atmospheric carbon dioxide during the test.. Boron has a CVr of 0.19, like the one of the analyses of 0.24. With inter-laboratory leaching and analysis, the CVRs are about the double of the CVrs. Molybdenum and copper are the less reproducible : the variability of molybdenum is present already in the intra-laboratory tests (hypothesis of sensitivity to pH), and copper increases very largely its variability probably due to the random presence of malleable metallic copper wires that don't crush into particles when subsamples and test portions are prepared. The CVs are here again not dependent of the concentrations, which covers a 5 log-range (0.1 − 10 000 mg/kg).

To identify and reduce the variability of the EN-12457-2 series, which causes practical problems of equal level playing field in Europe among service laboratories (some laboratories have systematically lower leaching concentrations), a literature survey and experimental results with their statistical interpretation have been produced and are detailed in Part 6 of the SI.

The literature shows that despite filtration with 450 nm membrane filter, there are always particles in leachates, and that these particles can contain 0 to 100% of an element in the leachate. These results are presented in Part 6 of the SI. For instance, the leachate of a sediment has about 108 colloids and nanoparticles per milliliter filtered leachates, with a median size of 150 nm and a 90th centile size of 200 nm. The experimental evidence of the presence of particles and their elemental concentration (up to 100% of the concentration of the leachate) is confirmed by numerous publications. The Part 5 of the Supplementary Information presents an illustrated review of 6 publications among many establishing that evidence. For instance, colloids or nanoparticles were found in all the 134 tested leachates (Hennebert et al. 2014, 2017).

The presence of these particles is influenced by two parameters: the energy of agitation (Yasutaka et al. 2017) and the solid/liquid separation (idem, this study Part 6 of the SI). Differences in energy of agitation during the contact, an ill-defined partial extraction process: rotary tumbler, shake and over, 5 to 10 rpm. Yasutaka et al. (2017) have demonstrated that differences in agitation creates differences in concentration due to differences in concentration of particles estimated by turbidity in that study, and by difference of concentration between the 450 nm-filtered and the 100 nm-filtered leachate.

The solid/liquid separation process is critical. A centrifugation before the filtration eliminates the largest particles and avoid the build-up of a filter cake during the filtration by these large particles, which makes a supplementary filtration: in the present experiment, there are 2.5 to 4.8 times less particles when the leachate is not centrifuged (SI 6). For 27 samples analysed for 20 parameters, the leaching concentration is globally 13% higher when the leachates are centrifugated before filtration (n = 287 paired data without LOQ, p = 0.008) than when the leachates are not centrifugated. The 95% confidence interval of that result is [+3.5% ; +23.3%]. There is no clear individual pattern of effect. For the elements present in the leachate with a significant concentration (the concentration is > 1 mg/kg for total dissolved salt - TDS, total organic carbon - TOC, SO4, F, Zn, Ni, Phenol Index, Cu, Ba, Zn, Mo, As, and the concentration is > LOQ for Pb, Cr and Cd), the centrifugation prior to filtration increases or decrease the value or concentration of the parameters or elements (results with 12 samples). Four types of effect can be distinguished (Table 2). The effect of centrifugation cannot be predicted for an individual sample and an individual element.

As a conclusion, the high variabilities in leaching concentrations are due to the presence of particles < 450 nm, and their concentration is variable because there are op-

TABLE 2: Effect of centrifugation + filtration (C+F) of the leachate versus filtration (F) of the leachate on the concentration of parameters of the leaching test EN 12457-2 (12 samples) - details in SI 6.

Parameters	C+F > F	C+F < F	C+F < > F	C+F = F
Physico-chemical	-	EC (2 samples)	-	pH
		TDS (1 sample)		
Organics	TOC (2 samples)	Phenol Index (1 sample)	-	
Anions	SO4 (2 samples)	F (2 samples)	-	Cl
Heavy metals	As (1 sample) Cd (1 sample) Mo (1 sample) Pb (4 samples) Zn (2 samples)	Cu (1 sample)	Ba (2 samples) Cr (2 samples) Ni (4 samples)	Hg Sb Se

tions in agitation energy and options in solid/liquid separation in the EN 12457 series. For agitation, the experts should agree to narrow down the options offered in the standard (rolling, tumbling, speed between 5 and 10 rpm). For solid/liquid separation, the optional Annex E of the standard details the preliminary centrifugation and should be made compulsory.

3.2.3 Partial extraction: accelerated column test prEN 16637-3

The validation data available in the validation report (Garcia-Ruiz et al. 2020) of the project of standard have been compiled. Individual concentration data are not available in the report. It is noticeable that the results of copper are not presented, despite that one sample was copper slag.

The column accelerated percolation test is an extremely variable proposal for construction materials from a waste stream: for elements, mean CVr = 0.24, n=328 > LOQ, mean CVR = 0.57, n=333 > LOQ , and for organic substances, mean CVr = 0.31, n=64 > LOQ, mean CVR = 0.79, n=63 > LOQ. The number of particles in the column (if there

is no fine fraction) and the residence time of 6-8 hours are probably too low compared to the original waste method and creates that variability.

The intra-laboratory CVr and inter-laboratory CVR are presented as a function of concentration, of L/S ratio, and by sample (Figure 4). The statistical analysis of variance indicates no influence of these factors neither of parameters on CVr and CVR (result not shown). The validation trials are not conclusive: the very high variability for all the elements (mean CVR = 0.57) and organic substances (mean CVR = 0.73), all waste and all percolation fractions indicate the simultaneous presence of low values and high values during repetitions, so that the results are not normally distributed. The only element with CVR < 0.4 in the three materials and for all the percolation fractions is silicon, a non-dangerous element in water. These variabilities are not accepted for compliance tests of industrial products. In a CEN/TC 351 document (CEN 2022) about quality assurance of release of dangerous substances of construction products, it is requested for CVR: main components: < 0.12; heavy metals < 0.19; amphoteric elements < 0.23.
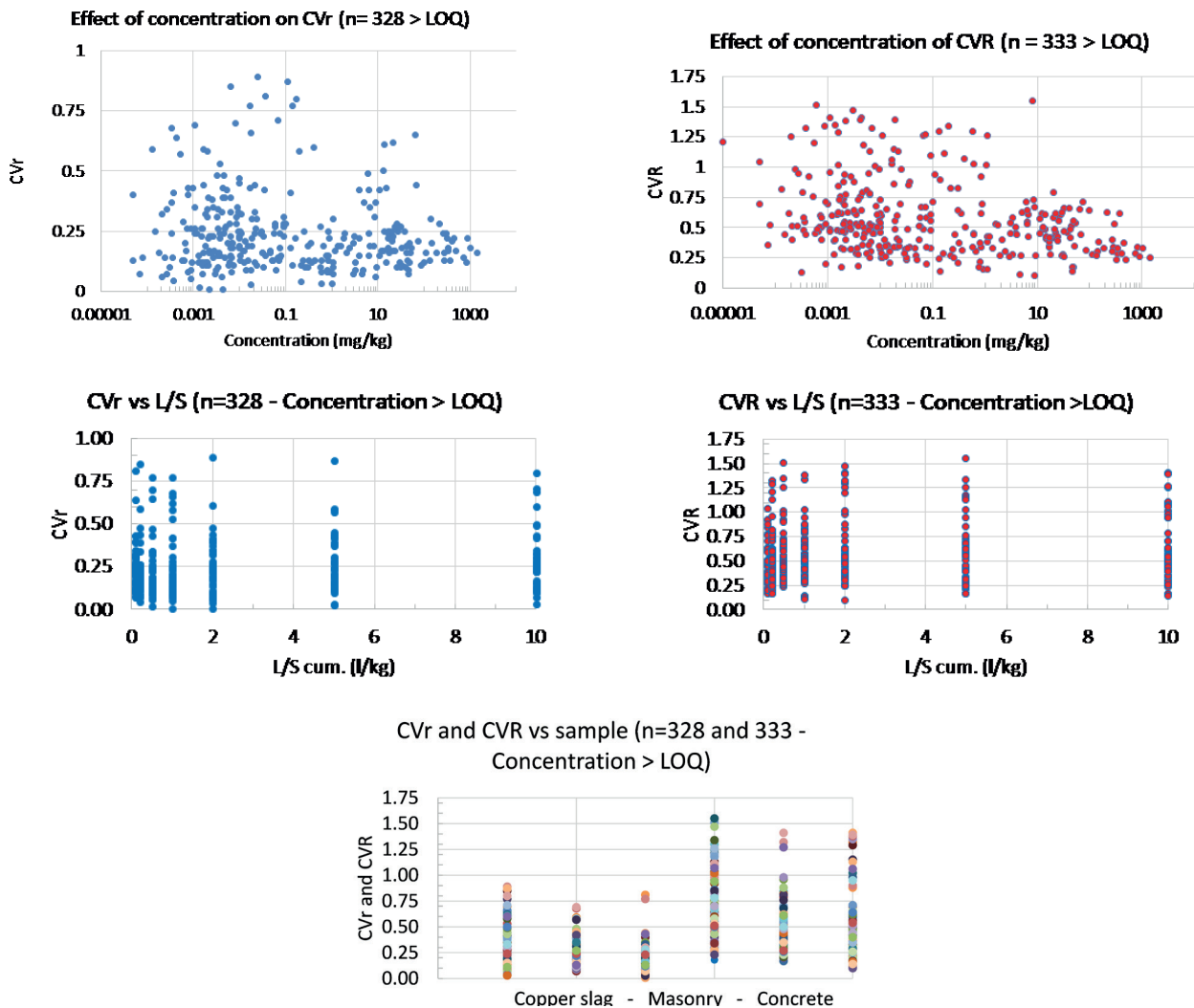

FIGURE 4: CVr and CVR of the accelerated percolation test of construction materials are high and not function of the concentration of the elements (upper figures), neither of the liquid-to-solid fraction (mid figures), nor of the sample (lower figure – three samples, for each sample left column CVr, right column CVR) - validation data of prEN 16637-3.

3.2.4 Partial extraction: ecotoxicological tests

These tests can be considered as "partial extraction" since the organisms react with the "bio-active" or "bioavailable" fraction and not the total concentration. Bioavailability depends on the organism, its development phase, its nutritional status, the time of exposure, the presence of other toxic(s), and the presence in the culture medium of substances that will enforce or weaken its reaction to toxic(s). Bioavailability cannot be defined as a firm general concept for waste.

An ecotox test is a dose-response test with typically a sigmoid function, from 0 to 100% inhibition or lethality with the increasing doses of ecotoxic chemicals or waste or soil in the culture medium. The maximum concentration that can be tested for liquid waste, waste leachate and solid waste, is not 100% but about 95%, the 5% being the culture medium and the organisms, with nutrients and acid/base buffer capacity. The result of the test is expressed as the concentration in the culture medium (mg/l or mg/kg) or the fraction of the culture medium in case of waste (liter leachate/liter liquid test medium, or kg waste/kg solid test medium) producing no effect (no observed effect concentration – NOEC) or 50% of effect (concentration producing 50% of effect, eventually lethality – CE50 or CL50). These tests are important for the classification of waste as hazardous by the hazard property HP 14 'Ecotoxic' (Hennebert 2018).

The results of two interlaboratory routines quality control in France in 2019 and 2020 with one synthetic solution and two liquid samples to analyse two times are presented in Figure 5. The intra-laboratory repeatability is good (mean CVr = 0.078), but the inter-laboratory reproducibility is too large (mean CVR including reference solutions and without sample 1 and 2 of Microtox test 2 = 0.77), being ten times higher than the mean CVr. One homogeneous sample sent to two laboratories will present very different results. The ecotoxicologists should improve that situation. A first step could be to remove any options in the methods, as suggested for instance for bioavailability tests by Henderson et al. (2014).

3.2.5 Synthesis of the variability of analyses

The findings of this paper are summarized in Figure 6. In the upper part, the maximum CVr or CVR of normal distribution (to avoid calculated negative values) is 0.50, and the maximum recommendation in an ISO document is 0.40. Sampling specialists propose for the sampling and the analysis CVR in all the case lower than 0.35 and better lower than 0.20 (Esbensen and Ramsey 2015). A maximum CVr and CVR of 0.10 is used for calculation of sampling granular waste and contaminated soils (Hennebert and Beggio, 2021) and should not be exceeded for analyses. That value is critical to calculate the number of particles and the size of representative samples and subsamples, up to the test portion. It has been showed in this paper that in routine quality control of service laboratory with home-made reference material, the CVr is in the range 0.02 – 0.08 (0.02 in Figure 1). In case of analysis of elements without extraction like XRF on homogeneous plastic material, the CVr is 0.01 – 0.03 (Hennebert and Beggio 2021). According
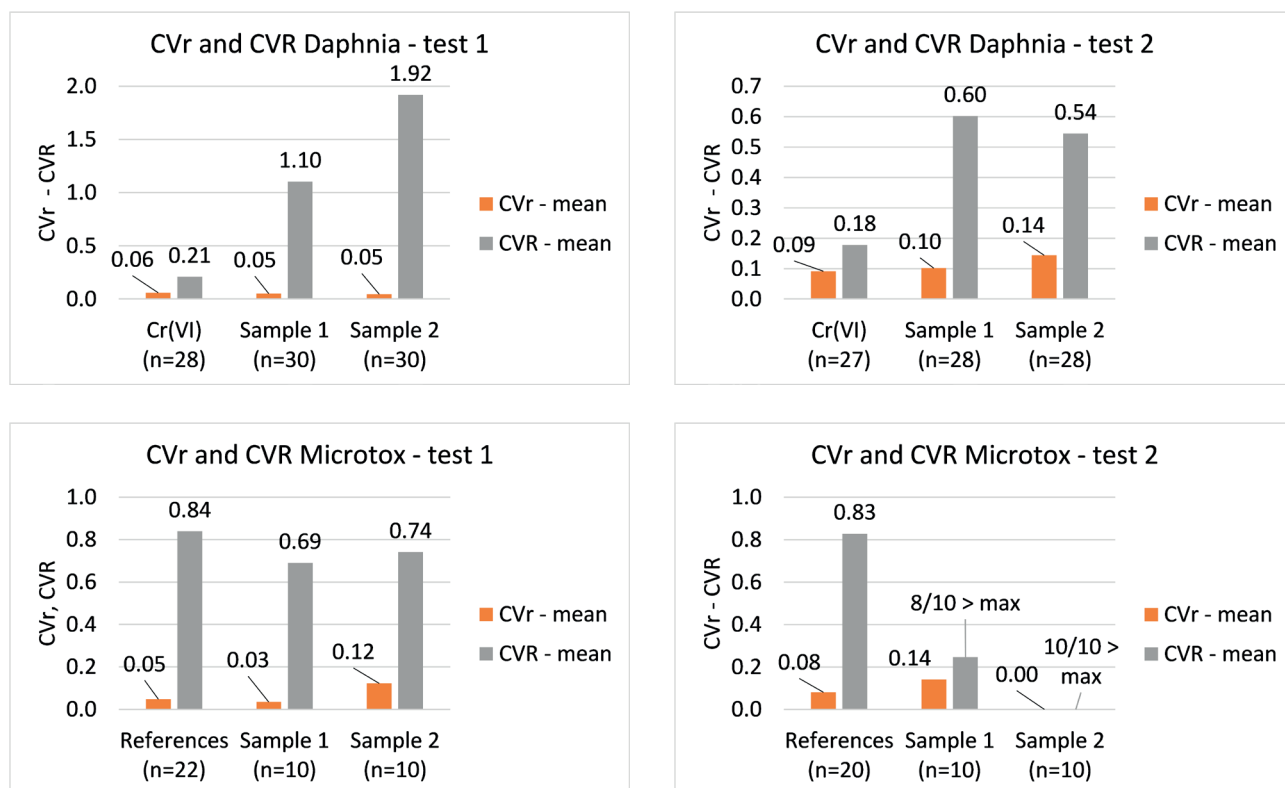

FIGURE 5: CVr and CVR of aquatic basic ecotox tests of round robin tests (France) for reference solutions and two water samples (n = number of data – "8/10 > max" means that 8 laboratories have EC$_{50}$ higher than the maximum concentration of the sample in the test).
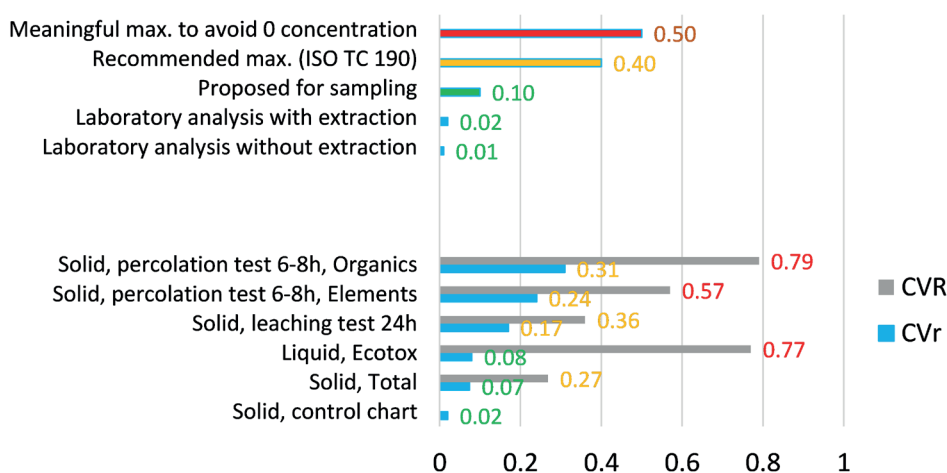
Mean CVr and CVRs of waste analyses

FIGURE 6: Synthesis of recommended and observed analytical variability of waste and environmental soil analyses.

to Gy (1996), the analytical control for production is < 0.01. In the lower part of Figure 6 are presented the CVr (blue) and CVR (grey) reported in this paper. The CVrs of total extraction tests are lower than 0.10, and of partial extraction are higher, as well as all the CVRs. Those methods should be improved.

The most frequent origin is non-homogeneous test portions, or ill-defined extraction and solid/liquid separation conditions. It should be noted that it is only in case of repetitions (eventually before studied sample) that a value can be identified as "high" or "low". In routine practice, the samples are not repeatedly measured, and that problem is not identified. A maximum acceptable CV could be 0.4, as in ISO (ISO 2016) , or USEPA methods (USEPA 2010). CV = 0.4 means that 95.4% of the results will be between [0.2 x – 1.8 x], which is in fact a very large range with a relative amplitude of a factor of 9... Larger variability indicates that the result of the method depends on the sample and the operator, or that the method is not adapted to the compound.

A table presenting some analytical methods by their intensity of extraction is presented in Part 7 of SI.

4. CONCLUSIONS

As the variability of the quantification step (after extraction) is limited in waste and soil analyses to about 0.01, the analytical variability stems from three main sources:

- non-homogeneous test portions due to the random presence of some concentrated particles in some test portions and not in others creating randomly high results. That question of variability of subsampling is solved in CEN TR 15301, EN 15002, EN 15413 by the simple approach of the number of particles;
- for partial extraction methods, variable extraction rate, due to ill-defined conditions or presence of options in the method (leaching or percolation test, biotests). The extraction step is a kinetic process that reaches solid/liquid equilibrium or not during the extraction time, depending on the chemical and mineralogical composi-

tion of the sample, on the grain size of the extracted test portion and on the operating conditions (agitation energy, self-grinding by tumbling, temperature).
- solid/liquid separation (leaching or percolation tests), critical since there are colloids and nanoparticles in the leachates, representing from 0 to 100% of the element fraction in the leachate. The leachate concentration is not a dissolved concentration. Counter-intuitively, the centrifugation before a 450 nm filtration (annex E of EN 12457 series) delivers leachates more concentrated in particles and statistically more concentrated in elements (+13%).

These sources of variability must be identified during the robustness tests of the method and be limited in any standardized method. A troubleshooting scheme for the different origins of intra- and inter-variability from analytical results is available in Hennebert and Beggio (2021). An intra-laboratory variability of CVr = 0.10 and inter-laboratory variability of CVR = 0.20 are suggested here as target value for standardisation. For the present total extraction methods, the mean CVr value is 0.07 and the mean CVR value is 0.27 (Table 1). The values proposed here are in line with the 0.15 proposed for waste analysis by Gerlach and Nocerino (2014) and the 10% for repeatability and 20% for reproducibility for bioaccessibility testing of metals (Henderson et al. 2014). That reduction of variability is ambitious for partial extraction methods. The methods with higher CVr and CVR should be revisited to reduce options and not jeopardise the sampling and characterisation efforts of waste and soil, particularly for valorisation in the circular economy.

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