4.01 Representative Sampling, Data Quality, Validation – A Necessary Trinity in Chemometrics

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Symbols

A	general symbol for 'analyte' (component of interest)
a_i	concentration of fragment/increment (grade)
a_L	average lot concentration (grade)
a_m	mass of unit
a_n	grade of sampling volume
C	sampling constant (material dependent)
d	top particle diameter, also known as d_{95}
G_n	group with index n
$\bar{G_n}$	average group mass
h_i	individual heterogeneity contributions
h_m	heterogeneity of unit
h_n	heterogeneity of group
j	lag parameter
m^2	mean squared
M_i	mass of fragment
$\bar{M_i}$	average fragment mass
M_L	lot mass
$\bar{M_m}$	average unit mass
N_F	number of fragments in lot
N_G	number of group in lot
N_U	number of units
r^2	representativeness
s^2	variance
$V(j)$	variogram function
θ	distance between unit pairs
θ_{min}	minimum distance between unit pairs

> *All naturally occurring materials are heterogeneous. Sampling should not be gambling*
> Pierre Gy (founder of the Theory of Sampling)

4.01.1 Introduction: Sampling of Heterogeneous Lots

All naturally occurring materials are heterogeneous at all operative scales related to sampling,[1–15] at scales larger than the prospective volume of a primary sample (termed distributional heterogeneity (DH)) as well as regarding the heterogeneity inside this volume (compositional heterogeneity); the latter also gains importance at scale commensurate with all mass reduction subsampling stages in the analytical laboratory. Sampling thus cannot be carried out without a working understanding of the phenomenon of heterogeneity and how it can be described and quantified, but most importantly, how it can be counteracted in the sampling process. There exists a more than 50-year-old, comprehensive, complete theory of sampling (TOS) encompassing this objective, which unfortunately is still not included in most university curricula in statistics, data analysis, analytical chemistry, geology, and within engineering and process technologies – chemometrics is no exception.[15]

Any sampling process (following the tenets of TOS, or not) interacts with the heterogeneous material making up the lot. Because of this, sampling is far from trivial as all sampling procedures unavoidably will be affected by the heterogeneity of the lot material at all scales larger than the operative sampling unit volume/mass. In addition, the sampling process creates sampling errors of its own nature, due to noncompliance with the practical, mechanical, maintenance, and operative procedural tenets of TOS. There are always two main contributors to the total sampling error (TSE): the heterogeneity of the lot material and the sampling process itself. For stationary lots, this generates five principal types of sampling errors, to which must be added two errors specific for the dynamic case, that is, process sampling.

Caveat: There exist two classes of materials that are exempt from the stringent principles and rules regarding naturally occurring materials delineated in this chapter, namely 'fine' or 'pure' chemicals, reagents, powders, and liquid solutions. Fine powders can be of uniform composition and sampling variability less than any predetermined threshold, say, 1% (rel.) or less, either because they have been manufactured for this specific purpose (production of reagent grade fine/pure chemicals inevitably includes the most thorough mixing conceivable) or because of exceedingly thorough comminution and mixing. Liquid solutions are of course very much easier to mix as they practically only show compositional heterogeneity at the molecular level. Thus, analytical chemistry often differentiates sampling of 'homogeneous' liquid solutions prepared by mixing chemicals in the laboratory. Although both of the above classes of materials may give rise to some comfort within the analytical laboratory, they are rare exceptions to the complete suite of material types in need of analytical characterization (qualitative, quantitative) where a substantial amount of sample preparation (especially representative mass reduction) is needed – so the analytical chemist is not exempt from the imperative of mastering the principles of TOS.

Uniform materials are the only case in which the devastating sampling bias problems dealt with here are practically absent. Sampling of such materials does not give rise to specific problems and can be accomplished on a basis of conventional statistics, in which the precision follows an inverse square root of the number of samples, etc. There exist scores of statistical textbooks and numerous textbooks on analytical chemistry, which deal comprehensively with this ideal situation; references can be found in Chapters 1.01–1.08. However, it is imperative to recognize that this constitutes but a very minor part of the gamut of materials arriving in the analytical laboratory, which are all characterized by heterogeneity...

4.01.2 Heterogeneity

Heterogeneity can be divided into two fundamental parts: constitutional heterogeneity (CH) and distributional heterogeneity (DH).

CH describes the heterogeneity dependent on the physical or chemical differences between the individual basic lot units, with TOS termed 'fragments' ('grains' would be a useful imaginary metaphor for 'fragments' in the following: mineral grains and seeds). Any given system (lot, geometry, material, state, grain-size distribution) will exhibit a CH, which can only be reduced by altering the physical state of the material, specifically only by comminution. CH plays its role at the scale of the individual fragments, grains, kernels, seeds, etc.

The DH complements this issue by describing all aspects of heterogeneity dependent upon the spatial distribution in the lot as gauged by operative sampling units corresponding to the sampling volume/mass used (in a full analysis this is also ultimately related to CH[1–4,15]); this sampling unit can conveniently be imagined as a scoop (the proverbial sampling scoop). The physical manifestations of DH are stratification, segregation, and/or local groups of fragments with a significant higher/lower concentration of the analyte than the average lot concentration, a_L. DH can actively be reduced by using a suite of 'correct' sampling methods to be delineated later. DH can never be larger than CH and CH can never be strictly zero.

Dependent on the purpose and scale of sampling ('scoop size'), CH may be close to negligible, but it is never nil. Homogeneity is defined as the (theoretical) limiting case of zero heterogeneity. Indeed if such a thing as a homogeneous material did exist, sampling would not be needed – as all sampling errors would be zero, all 'samples' would be identical.

4.01.2.1 Constitutional Heterogeneity

Tche heterogeneity between individual fragments is of interest. TOS's most fundamental theoretical achievement comes in the form of the heterogeneity contribution to the total heterogeneity of the lot, defined by focusing on an individual fragment: TOS characterizes all fragments according to the component of interest (the analyte, A), described by the proportion (or grade), a_i, and the fragment mass, M_i. If a lot consists of N_F individual fragments with individual masses, M_i, with an average fragment mass, $M_{\bar{i}}$, with lot grade a_L, and a lot mass, M_L, then the heterogeneity contribution from each individual fragment, h_i, can be calculated as follows:[3]

$$h_i = \frac{(a_i - a_L)}{a_L} \frac{M_i}{M_{\bar{i}}} = N_F \frac{(a_i - a_L)}{a_L} \frac{M_i}{M_L}$$

This definition of heterogeneity contribution is dimensionless and hence can be used for any intensive unit used in characterizing the material, for example, concentration, %, size. Delineating the compositional deviations of each fragment, it also compensates for variation in the fragment masses; larger fragments result in a larger influence on the total heterogeneity than smaller ones. This viewpoint constitutes a major distinction from 'classical statistics' where all units contribute equally (with equal statistical mass). h_i constitutes an appropriate compound measure of mass-weighed heterogeneity as contributed by each fragment in the lot.

The total CH of the lot, CH_L, can now be defined as the variance of the distribution of the heterogeneity contributions of all individual fragments:

$$CH_L = s^2(h_i) = \frac{1}{N_F} \sum_i h_i^2 = N_F \sum_i \frac{(a_i - a_L)^2}{a_L^2} \frac{M_i^2}{M_L^2}$$

For the above derivations as well as the one given below, whenever increment/sample masses are not identical, estimation of the total lot mass, a_L, must be done as a weighted mean from the analytical results, lest an additional increment weighing error (IWE) be introduced.[16]

$$a_L = \frac{\sum M_m a_m}{M_L}$$

4.01.2.2 Distributional Heterogeneity

Ascending one hierarchical scale level – from the scale of fragments, grains, etc. to the operative level of one sampling unit (sampling scoop) – one moves into the realm of DH of the lot, DH_L. Parallel to the conceptual division into N_F fragments, at the present scale the lot can alternatively be considered as divided into a number of potential sampling volumes, N_G, commensurate with the operative volume of the sampling tool. Other than this operative scale difference, the focus is identical, namely quantitative description of the differences in the composition (concentration) of the analyte, A, between these sampling volumes (index n), a_n. DH_L can be calculated via a strict analog to the above definition of heterogeneity carried by a single fragment. A group of fragments, 'group' for short (index n), G_n, similarly carries an amount of heterogeneity, h_n, which can be

calculated from the grade of the group in question, a_n, the group mass, M_n, the average group mass, $M_{\bar{n}}$, and the average grade over all groups, $a_{\bar{n}}$:

$$b_n = \frac{(a_n - a_L)}{a_L} \frac{M_n}{M_{\bar{n}}} = N_G \frac{(a_n - a_L)}{a_L} \frac{M_n}{M_L}$$

The DH for the entire lot can again be calculated as the variance of all group heterogeneity contributions:

$$DH_L = s^2(b_n) = \frac{1}{N_G} \sum_n b_n^2 = N_G \sum_n \frac{(a_n - a_L)^2}{a_L^2} \frac{M_n^2}{M_L^2}$$

By observing that the sum of all (virtual) groups actually constitutes the physical lot in its entirety, it can be appreciated that DH_L in fact is a measure of the spatial heterogeneity residing in(side) the lot. This alternative scale-dependent understanding at the two levels – fragments versus group of fragments (sampling unit) – constitutes a most elegant and effective theoretical concept in TOS.[1–4,15]

DH_L quantifies the material heterogeneity in a specifically relevant form, namely that dependent upon the specific sampling size (mass/volume) chosen, M_S. It is now possible to ascertain the quantitative effect of the lot heterogeneity interacting with alternative sampling processes, for example, using alternative sampling volumes. TOS terms this fundamental sampling volume the *increment*. All increments may be used either for making up a composite sample (see the following text) or occasionally as a single increment sample, termed a grab sample. The most important element in the sampling process delineation is the particular M_S employed. From TOS, it is clear that a single-scoop sample is almost never acceptable, *ibid*, so M_S has to be always understood as the compound mass of a composite sample, unless specifically stated otherwise.

Unlike CH_L, which is only a function of the material properties, DH_L can actively be altered (reduced), especially by choosing a smaller sampling tool volume, thereby increasing the number of increments in composite sampling (in process sampling, this means increasing the sampling frequency), and/or the lot can be thoroughly mixed, blended, and so on. In large lots, forced mixing is often impractical or impossible; in such cases, increasing the number of increments is often the only option and always a good choice of action. If there is a significant segregation or grouping (clustering) in the lot, increasing the sample size, M_S, reduces only the effect of CH on the mean (a comparatively minor effect). For process sampling, increasing the sampling frequency (number of samples) reduces both CH and DH.

TOS has much to say (all negative) regarding the universal futility of grab samples, which are never representative in practice against all realistic heterogeneous lots and materials. Grab samples are thus never reliable and accordingly must never be used. Full details can be found in any TOS literature.

4.01.3   Types of Sampling Errors Versus Practical Sampling

Full analysis of the phenomenon of heterogeneity[1–4,15] signifies that basically only three factors are responsible for the magnitude of the DH:

- CH_L (constant for a given material/given grain-size distribution state)
- Grouping (depends on the size (volume/mass) of the extracted increments)
- Segregation (depends on the spatial distribution of fragments in the lot).

Both segregation and grouping can be quantified, and methods and equations are described in detail in the pertinent main literature, *ibid*, and further references herein.

In order to extract samples from heterogeneous materials with sufficiently low variation, it is necessary to minimize DH_L. For any given material state, the case of reducing the two phenomenological factors grouping and segregation can principally be achieved in only two ways:

- Decreasing the size of the extracted increments, thereby increasing the number of increments (or increasing the sampling frequency) combined to form a given sample mass, M_S (counteracts grouping and segregation on the scale of the sampling tool volume).
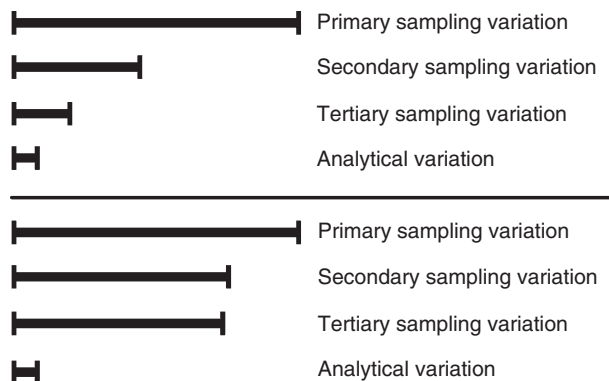- Mixing/'homogenizing' the lot (reduces macroscale lot segregation).

Figure 1   Variation at all sampling stages identified by a 0-D replication experiment; correct sampling is an obligation.[1–4,15] It is easy to identify any stage that contributes most to the total variation and to intervene here first. In the upper frame, the primary sampling step is responsible for most of the variation, as would be expected; this can be considered the normal scenario. In the lower frame, the third step is responsible for most of the sampling variation (e.g., an inferior mass reduction).

If these measures are insufficient for a given sampling process and total error specification, it is necessary to reduce the CH itself, which necessitates physical reduction of the fragment sizes, comminution (grinding or crushing), and/or increasing the total sample mass, M_S. Comminution is by far the most effective of these two options, following

$$\text{var}(\text{FSE}) = \frac{Cd^3}{M_S}$$

in which C is the material's constant (constant for a given grain-size distribution state) and d is the top diameter of the material (termed d_{95}).[1–4,15]

It is important to note that the quantitative sampling effect of DH_L can easily be estimated in practice by extracting and analyzing a replicate number of samples 'covering the entire geometry of the lot' and calculating the resulting empirical variance. Often a relatively small number of primary samples will suffice, though never less than 10. This procedure is termed a replication experiment (see **Figure 1**). It is critical that replication covers the entire sampling-and-analysis chain, especially that the primary sampling is replicated in a completely independent manner, including all subsampling and mass reduction stages, including sample preparation.[6] It is a requirement that all incorrect sampling errors (ISEs) have been eliminated, that is, only correct sampling is employed.[2]

4.01.3.1   Total Sampling Error – Fundamental Sampling Principle

All analytical results are associated with some nonzero uncertainty, often taken to be the analytical uncertainty *sensu stricto*, that is, the variance of the total analytical error (TAE). Following the analysis of the entire sampling process, TOS in addition collects all other sources of error from sampling and sums up these in the TSE; TAE and TSE together form the global estimation error (GEE) (see **Figure 2**).

Often TAE is under strict control in the laboratory, and is usually of no significant concern in comparison to sampling, as TAE is always significantly smaller than the sum of errors stemming from sampling (TSE). In fact, TSE is very often 50–100 times larger than TAE;[1–8] exceptions are exceedingly uniform materials with a truly exceptional small heterogeneity – such materials are rare indeed.

TSE has many sources. Indeed the primary objective of representative sampling is to identify, eliminate, or reduce all contributing sampling errors. The compound sampling variance, as delineated above, is specifically influenced by the heterogeneity of the material as well as the sampling procedure. Although much of this effort is to some extent under the control of the sampler, the part from CH is dependent on the material properties
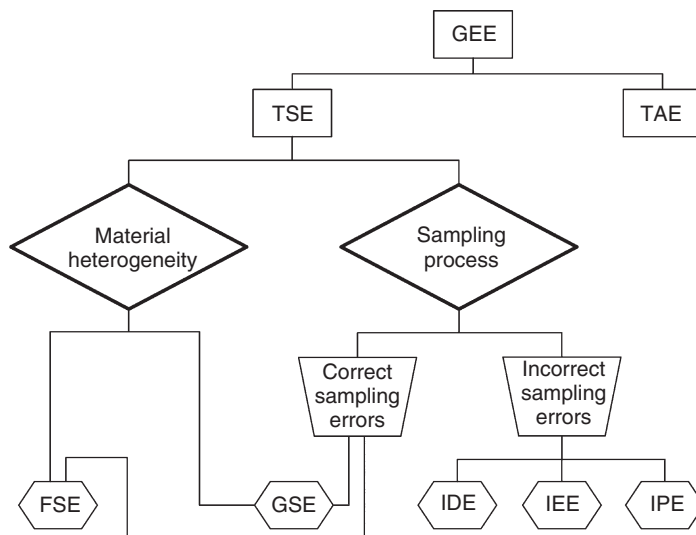
Figure 2 Overview of the five 0-D sampling errors and their interrelations. Reproduced with permission from Petersen, L.; Minkkinen, P.; Esbensen, K. H. Representative Sampling for Reliable Data Analysis: Theory of Sampling. *Chemom. Intell. Lab. Syst.* **2005**, *77* (1–2), 261–277.

only. This error is termed the fundamental sampling error (FSE), as it cannot be altered for any given system (lot, geometry, material, state, size distribution); altering FSE necessitates physical intervention, crushing, comminution. On the contrary, the contribution from the spatial distribution of the material is not fixed and can be altered. This is dependent not only on the material characteristic itself but also on the sampling procedure and whether counteraction measures are invoked (e.g., mixing). The variation stemming from distribution heterogeneity is collected in the grouping and segregation error (GSE).

The single rule to respect in regard to selecting smaller increments is that all possible extractions from the lot (all possible virtual increments) must have the same probability of being selected. This is called the fundamental sampling principle (FSP) – FSP must never be compromised, otherwise all possibilities of documenting accuracy of the sampling process are abandoned. FSP implies physical access to all geometrical units of the lot. TOS contains many practical guidelines of how to achieve compliance with FSP.[1–18]

TOS employs a strict terminology, in which all aspects of noncompliant sampling can be specifically named. Thus, TOS specifies as 'correct' only those features that will contribute toward the ultimate goal of being able to demonstrate representativeness of the particular sampling process employed, *ibid.*

The sum of FSE and GSE is termed the 'correct sampling errors' (CSEs), as they are not due to erroneous sampling or wrong procedures; in fact, CSEs occur even when the sampling procedure is 'correct' (meaning representative), hence perhaps at first sight somewhat peculiar naming. Errors that are connected to erroneous sampling procedures are contrarily summed in the ISEs.

ISEs comprise three parts: one stemming from not delineating correct increments from the lot, the second from not extracting exactly what was intended, and the third form of error is induced after the extraction of the increment (or sample). The increment delineation error (IDE) can be avoided by always selecting (delineating) an increment that completely covers the relevant dimensions of the lot, for instance a complete cross-sectional slice if the lot is a (very) long pile of material, or a 'drill core' to the very bottom of the layer(s) of interest if the lot is a 3-dimensional (3-D) volume or of a similar shape. The increment extraction error (IEE) arises when particles inside the delineated increment do not end up in the sample, for instance by bouncing or dusting, or if particles outside the delineated increment find their way into the sampling tool, contamination. It is normally stated that (only) particles or fragments with their center of gravity inside the delineated increment should become part of it.[1–4,12–14]

The last incorrect error arises when the sample is altered after extraction, for instance by absorbing moisture, by spillage, cross-contamination, or some similar phenomenon. Sample tampering and downright fraud is also a type of 'error', which is likewise collected under the term incorrect preparation error (IPE).

All these errors can be minimized, and some can indeed be completely eliminated, by full understanding of the guidelines in TOS for 'correct', that is, representative, sampling: There are many practical and mechanical aspects of this issue, all relatively simple and almost trivial to implement, but only if they are properly recognized. The TOS literature deals with all these issues at great length, with a focus on explaining the connection between individual errors and how they can be minimized completely. The selected literature list below is sufficiently comprehensive for this introduction, but not complete;[1–15] further references can be found in abundance here.

4.01.3.2   Lot Classification

The above analysis of heterogeneity, types of sampling error, and criteria for practical representative sampling holds for all lots/types of materials that are stationary, that is, nonmoving. Although the physical and geometrical configuration of lots may vary, 3-D, 2-D, and 1-D, sampling from all nonmoving lots is governed by the above features.

TOS recognizes this invariant issue by defining a generic, nonmoving type of lot, termed a 0-D lot (**Figure 3**). The 0-D lot is characterized by displaying no internal correlations between all increments, thus opening up for relatively easy practical sampling. 0-D lots can in principle be manipulated at will; however, the work necessary may vary significantly, primarily as a function of the total mass, M_L, but also of other features, for example, 'stickiness' and irregular fragmental forms. All basic stationary lots/materials and sampling process considerations described above are defined with respect to 0-D sampling.

As mentioned earlier, two additional errors are found when dealing with the dynamic case, that is, in process sampling.
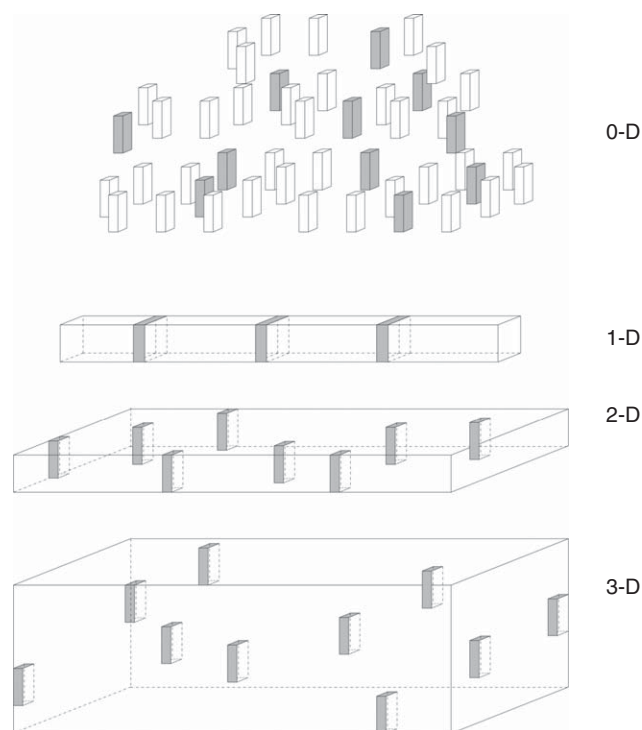

Figure 3   Classification of lot dimensionalities according to TOS. Reproduced with permission from Petersen, L.; Minkkinen, P.; Esbensen, K. H. Representative Sampling for Reliable Data Analysis: Theory of Sampling. *Chemom. Intell. Lab. Syst.* **2005**, *77* (1–2), 261–277.

4.01.4   Representative Mass Reduction

Very often the focus is on selecting the final sample mass way too early in the sampling process. Contrary to this erroneous objective, it is necessary, and far more beneficial, to focus only on how to make the primary sample be representative – even if this means procuring an 'oversized' sample, in order to overcome problems with heterogeneity that cannot be dealt with satisfactorily *in situ*. This of course necessitates sample masses to be significantly reduced prior to analysis; this section delineates all necessary principles and equipment types for representative mass reduction.

Any and all mass reduction steps (whether singular or in series) will generate sampling variation, no matter how well it is performed. Hence, it is only a matter of minimizing this inevitable contribution to the variation of the final result.

Any mass reduction method must be in appliance with FSP, that is, all parts of the lot (or subsamples) must have an equal probability of ending up in the final sample (subsample). This means that a correct device or method must ensure complete randomness at the lowest possible scale, ideally at the fragment level, which is however very rarely obtained in practice (only with very small lots comprising relatively large fragments).

An extensive benchmark study has been carried out in order to identify the optimal mass reduction principle(s).[6] This was practically achieved by investigating the world's most often used mass reduction approach, grab sampling, as opposed to a comprehensive series of more advanced techniques and methods, 17 in total. In the following, only a summary of this study is outlined, along with a series of conclusions and recommendations on practical mass reduction. All techniques and methods were tested with regard to a long list of parameters, some scientifically important, others related to cost and minimizing operating expenses. The most important merit of any mass reduction method, however, is the ability to deliver an unbiased split of material with the smallest possible variation in repeated runs, that is, best possible accuracy and precision. These two features are summed in TOS' quantitative measure of representativeness:

$$r^2(\text{SE}) = m^2(\text{SE}) + s^2(\text{SE})$$

where the sampling 'selection error' (SE) describes relative deviation of the sample concentration, a_S, from the true concentration, a_L (known here):

$$\text{SE} = \frac{a_\text{S} - a_\text{L}}{a_\text{L}}$$

r^2 summarizes the contribution from both the (squared) bias and the sampling variance; this quantitative measure of representativeness universally needs to be minimized.

The mass reduction techniques and methods investigated cover

- Grab sampling (a single increment used as the sample).
- Fractional and alternate shoveling (dividing sequentially into two (alternate) or more piles, scoop by scoop).
- Riffle splitters, with varying number of chutes, chute width, feeding mechanism, dust minimizing systems.
- A widely used circular riffle splitter for seeds and grains (Boerner divider).
- Rotational dividers in which samples are distributed over radial chutes by a rotating feeding nozzle.
- An elaborate manual technique recommended in international seed and grain communities (the 'spoon method'), which involves a rudimentary form of bed blending, followed by selecting a few spoonfuls in a composite sampling context.

In Petersen *et al.*,[6] an exhaustive evaluation resulted in an overall ranking of all 17 assessed methods, expressed with regard to representativeness (see **Figure 4**).

The conclusions and recommendations regarding mass reduction are clear:

It is evident that any method involving manual shoveling, grabbing, or similar simplistic selection of some material is by far the worse: grab sampling, fractional shoveling, alternate shoveling, or the 'spoon method'. The simplest riffle splitting method forms a transition from these totally unacceptable methods to a suite of 12 acceptable methods.

Optimal under all conditions are only riffle splitters or methods based on the same underlying principle (Boerner and rotating devices), namely that all material is distributed uniformly over an equal number of
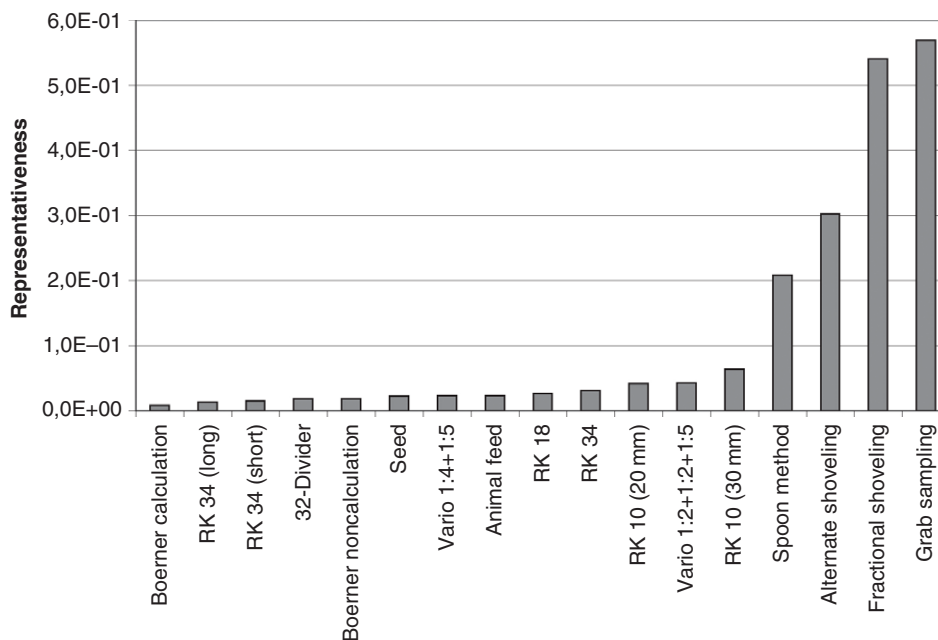
Figure 4 Mass reduction devices ranked as a function of lowest possible representativeness. Better a sampling process (here a mass reduction process), the smaller the r^2 index. In practice, all but the five rightmost methods are acceptable according to the compound evaluation in Petersen et al.,[6] in which one can find a full description of all methods and equipment summarized in the figure. Reproduced with permission from Petersen, L.; Minkkinen, P.; Esbensen, K. H. Representative Sampling for Reliable Data Analysis: Theory of Sampling. *Chemom. Intell. Lab. Syst*. **2005**, *77* (1–2), 261–277.

equally sized chutes facilitating a representative split into well-specified portions of the original material (lot). Standard riffle splitters end up with two identical 50% portions, necessitating a stepwise repeated procedure to achieve larger reduction ratios. This is easily evaded using the slightly more technical rotating 'Vario' dividers, where the total sample mass can be reduced to a lower proportion sample and a larger proportion ('waste' or bypass), as all chutes are used many times, yielding a large total number of effective chutes. The Vario device principle is comparable to using a static, but significantly cheaper, riffle splitter in sequence, but many more times over.

Furthermore, it is crucial that the equipment is operated correctly. There are a number of practical rules to be respected when using any of the acceptable devices – neglecting one or more of these can end up in the entire mass reduction being biased, or result in unnecessary large variation.

The complete benchmark report[6] contains all essential aspects of mass reduction in full detail.

4.01.5   Process Sampling (1-D Lots)

A 1-D object is a lot in which two dimensions are negligible in size, compared to the third, and where a distinct spatial or temporal correlation exists along the singular elongated dimension. A 1-D lot for example can appear as an ordered series of units from a production line (time or space) or as a flowing stream of material. The operative implication of this is that all increments must be in the form of complete, planar-parallel cross-stream cuts[1–5] in order to uphold FSP. 1-D increments are often compositionally correlated but need not be; everything depends on the 1-D heterogeneity characteristic of the lot.

In order to sample a 1-D lot correctly, one of only three possible sampling schemes (systematic, stratified random, or random) must be selected, and further a set of rules regarding the design of equipment must be respected in order to have an unbiased sample with minimum sample variation.[8–15]

A variogram is used to characterize autocorrelation (1-D heterogeneity) of 1-D lots as a function of the distance between extracted units (increments). A variogram is superior in identifying trends (increasing/decreasing) and periodic cycles (often hidden to the naked eye) in process data.

4.01.5.1   Heterogeneity of 1-D Lots

One-dimensional sampling requires some understanding of the nonrandom heterogeneity fluctuations along the extended dimension of the lot, that is, the hereogeneity between the extracted increments. Correct increments must be a discrete, complete planar-parallel cut across the entire stream of material, or similar extractions of material, chronologically ordered ($m = 1, 2, 3, \ldots, N_U$).

The heterogeneity contribution, h_m, of each such increments U_m is defined as

$$h_m = \frac{(a_m - a_L)}{a_L} \frac{M_m}{M_{\bar{m}}} = N_U \frac{(a_m - a_L)}{a_L} \frac{M_m}{M_L}$$

where M_m is the unit mass, $M_{\bar{m}}$ is the average unit mass, N_U is the number of units in the lot, a_m is the grade of the unit, and a_L is the true lot concentration.

The heterogeneity contribution, h_m, from a 1-D increment is comprised of three parts:

- A short-range fluctuation component, describing the heterogeneity within that particular increment (actually all the 0-D sampling errors + TAE).
- A long-range fluctuation contribution that describes the longer term trends in the process.
- A cyclic term that describe any periodic variation of the lot.

To characterize the heterogeneity of a 1-D lot, the chronological order of the units must be included in the analysis; a variogram is the perfect tool.

4.01.5.2   Variography

A variographic analysis requires a complete set of analytical results based on representative increments, all extracted equidistantly over a sufficiently long interval so as to cover the expected process variation well. Clearly, some first-hand knowledge of the process to be characterized/analyzed/sampled is advantageous, but *ab initio* variogram analysis is always possible. The variographic analysis will provide valuable information in the form of the 'nugget effect', the 'sill', and the 'range', three important parameters describing different aspects of the process variation.

4.01.5.3   Variogram Calculation

Normally, 50–60 increments are considered minimum for a thorough variographic analysis.[2,3,14,15] The variation is always problem-specific, that is, may be manifested in minutes, hours, days, or weeks – or in series of manufactured units, etc. It may at times be necessary to perform two experiments, if both short- and long-range variation is expected to be of importance, a short-range variogram being additional in such cases.

A dimensionless, relative lag parameter, j, describes the distances between any two increments:

$$j = \frac{\theta}{\theta_{min}}$$

where θ is the distance between extracted increments (minutes, meters, ordering index, etc.) and θ_{min} is the smallest sampling interval chosen. **Figure 5** illustrates examples of intervals between increments/unit pairs.

If a number of increments, N_U, are extracted and analyzed, $N_U - 1$ increment pairs with space θ and $N_U - 2$ unit pairs with space 2θ can be calculated. Normally, pairs are not calculated for lags higher than half the length of the measurement series, $N_U/2$.
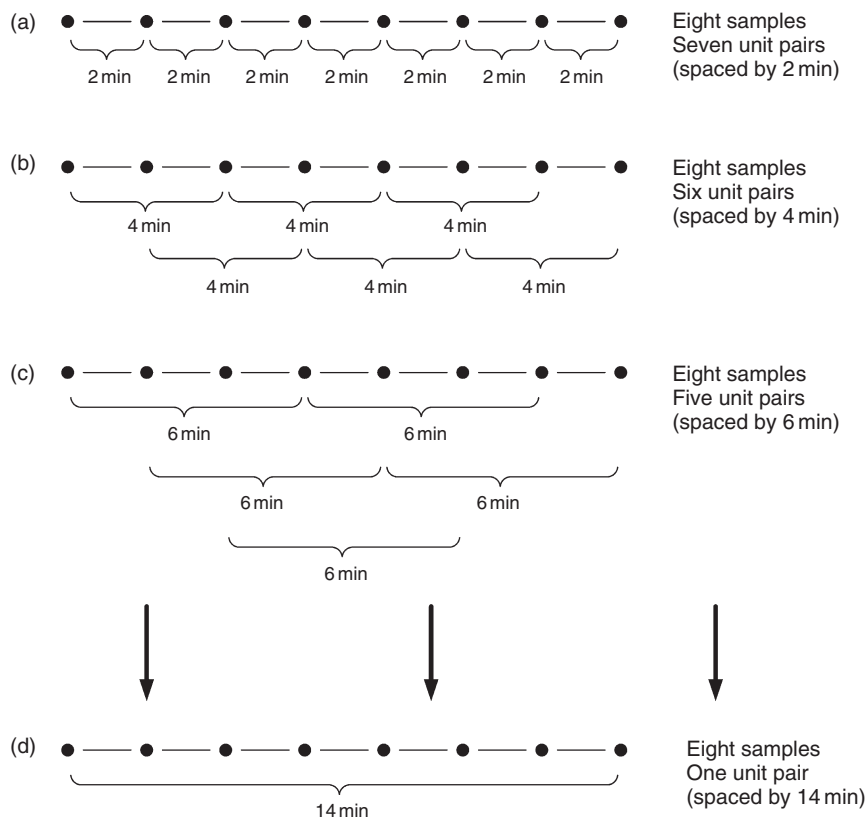
Figure 5   Example of increment extraction in a variographic experiment. Eight increments (units) are extracted 2 min apart. (a) Seven increment pairs spaced by 2 min, (b) six increment pairs spaced by 4 min, (c) five increment pairs spaced by 6 min, (d) one increment pair spaced by 14 min. The lag, j, can take any value from 1 to 7 (in general $N_U - 1$). Reproduced with permission from Petersen, L.; Esbensen, K. H. Representative Process Sampling for Reliable Data Analysis – A Tutorial. *J. Chemom*. **2005**, *19* (11–12), 625–647.

The variogram function, $V(j)$, is defined as $1/2$ times the average of the squared difference in heterogeneity between the pairs of increments as a function of j:

$$V(j) = \frac{1}{2(N_U - j)} \sum_m \left(h_{m+j} - h_m \right)^2$$

4.01.5.4   Interpretation of Variograms

The practical interpretation of the resulting variograms is the most important step in a variograpghic analysis. The variogram level and form provide extensive information on the process variation captured. Normally, only three primary types of variograms are encountered:

1. An increasing variogram (normal variogram shape).
2. A flat variogram (no autocorrelation along the defining dimension).
3. A periodic variogram.

The above variograms are outlined in **Figure 6**.

When the variogram type has been identified, information on optimized 1-D sampling can be derived. The increasing variogram (**Figure 7**) can be used as an example.

All variograms are not defined for lag $j = 0$, as this would correspond to extracting the exact same material twice. Even though this is not physically possible, it is still highly valuable to have the information of the expected variation if it would have been possible to repeat the sampling of the exact same increment. TOS identifies this
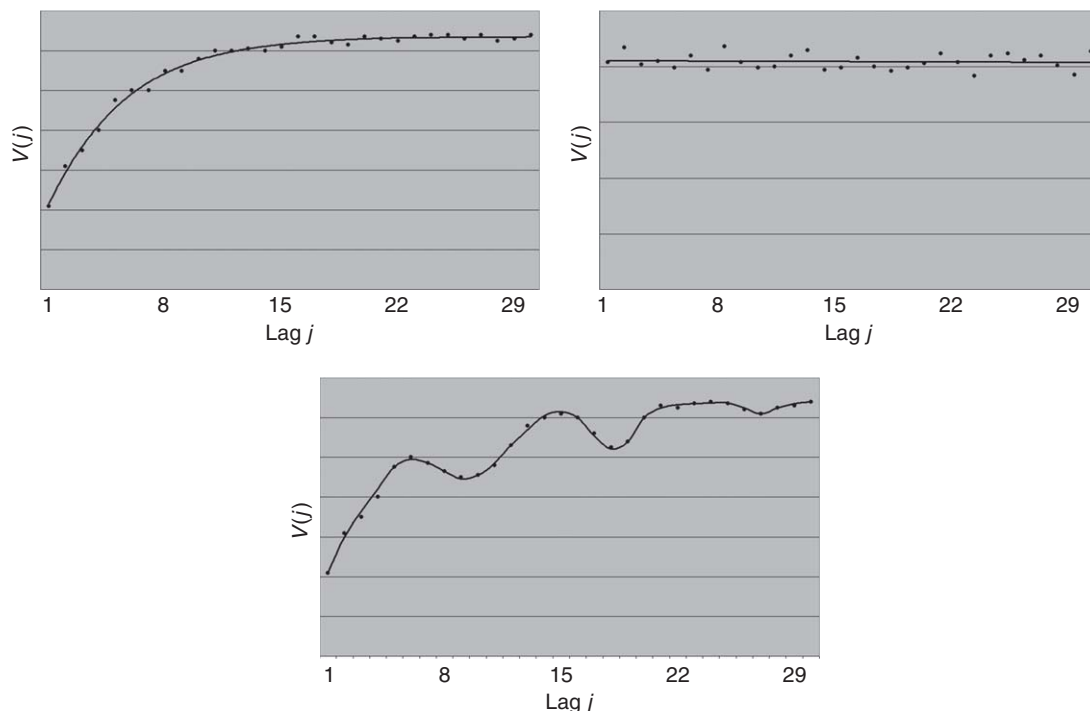
Figure 6   The three basic variogram types. In the lower frame, a period of ~9 is observed. Reproduced with permission from Petersen, L.; Esbensen, K. H. Representative Process Sampling for Reliable Data Analysis – A Tutorial. *J. Chemom*. **2005**, *19* (11–12), 625–647.

Figure 7   A generic increasing variogram, schematically defining the nugget effect, the sill, and the range. These standard parameters contain the essential information pertaining to all sampling errors involved and of the essential process variation; full details in Gy,[9] Petersen and Esbensen,[12] Halstensen,[13] and Esbensen *et al.*[14] Reproduced with permission from Petersen, L.; Esbensen, K. H. Representative Process Sampling for Reliable Data Analysis – A Tutorial. *J. Chemom*. **2005**, *19* (11–12), 625–647.
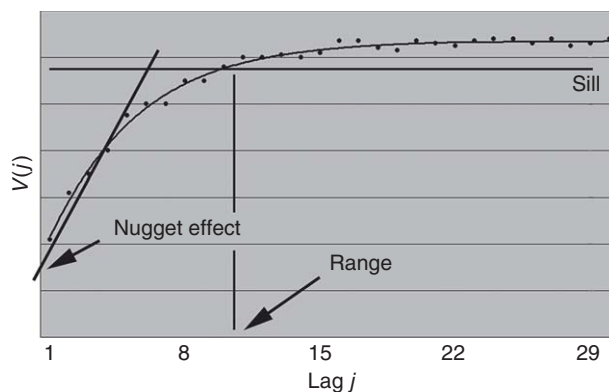
variation as minimum practical error (MPE). Normally, the first five points of the variogram are extrapolated backwards to intercept the ordinate axis to provide the 'nugget effect', which is a practical estimate of MPE.

MPE includes several error components, FSE, GSE, TAE, and all ISEs, and hence is an appropriate measure of the absolute minimum error that can be expected in practice using the existing or the contemplated sampling scheme at hand.

When the increasing variogram becomes more or less flat, the 'sill' of the variogram has been reached. The sill provides information on the expected maximum sampling variation if the existing autocorrelation is not taken into account. The 'range' of the variogram is found as the lag beyond which there is no autocorrelation. These primary characterizing variogram parameters are illustrated in **Figure 7**.

If a significant periodicity is observed, the sampling frequency must never be similar! Also the specific sampling mode (random sampling (ra), systematic sampling (sy), and stratified random sampling (st)) becomes critically important; full details can be found in Gy,[9] Petersen and Esbensen,[12] Halstensen,[13] and Esbensen *et al.*[14]

From the variographic experiment, a sampling plan can be derived (see Gy,[2] Pitard,[3] Heikka and Minkkinen,[8] Gy,[9,11] Gy and Marin,[10] Petersen and Esbensen,[12] Halstensen,[13] and Esbensen *et al.*[14] for detailed descriptions):

- Avoid extracting increments with a frequency coinciding with a period. Doing so will significantly underestimate the variation of the process.
- In general, the stratified random sampling mode (st) will always lead to optimal results (absolute lowest TSE), but systematic sampling (sy) will in many cases be marginally just as effective, and very often much easier to implement. Random sampling (ra) is never used in the process realm, *ibid.*
- Sampling with a frequency below the range will ensure that the process autocorrelation in effect reduces the sampling variation. The variogram is an effective tool to simulate alternative sampling strategies without making real-world experiments. The N_U variogram increments/samples contain all necessary information.
- Use $V(0)$ to estimate the minimal practical sampling error MPE. From this, further breakdown of the constituent error sources is often possible.[1]

4.01.5.5 An Example of Variographic Analysis

The data in this example are simulated, but patterned from many real-world examples and therefore realistic.

A factory produces a powder mixture with three components in a continuous process. The normal sampling scheme implies extracting one increment of 1 kg at random within every hour window by a (according to TOS) correctly designed cross-stream sampler.[2,3,14,15] The sampling is performed automatically and extracts the increments immediately before packaging of the final product. A variographic experiment will reveal whether the process yields a product with satisfactory constant composition. Sixty increments are extracted in a 1-h window (exactly every minute) and are subsequently analyzed to yield the percentage of component 'A', which is considered the most important for characterizing the mixture quality (of course the other parameters are also measured, but not shown here). According to the product specifications, component 'A' is present in the final optimal product at 5.14%.

Figure 8 shows the analytical results for each increment in the experiment (average content: 5.14%), along with the weight of the increments, which in this example practice varies only little around the set-point of 1 kg.
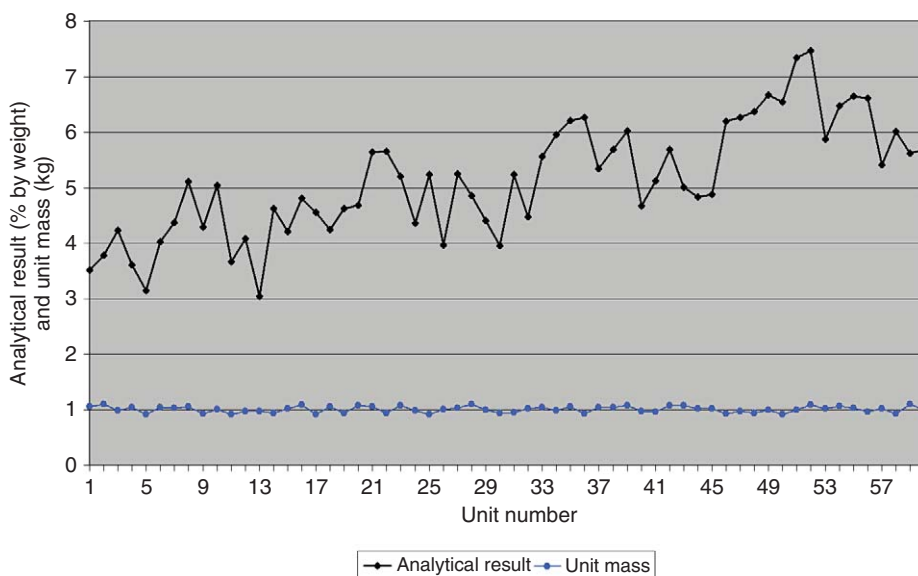
Figure 8 Results after 'analysis' of 60 increments (upper part) extracted at 1 min intervals during a full 1-h variographic experiment. The lower part describes the individual weights of the increments, which should ideally be 1 kg, but which vary slightly in practice. Reproduced with permission from Petersen, L.; Esbensen, K. H. Representative Process Sampling for Reliable Data Analysis – A Tutorial. *J. Chemom.* **2005**, *19* (11–12), 625–647.

The corresponding heterogeneity contributions of the individual increments can easily be calculated, as displayed in **Figure 9**. From these data, the variogram can be calculated (see **Figure 10**). The so-called auxiliary functions in **Figure 10** are derived technical help-functions, explained in depth in Petersen *et al.*,[1] Gy,[2,9] Petersen and Esbensen,[12] Halstensen,[13] and Esbensen *et al.*[14]

From the variogram in **Figure 10**, the nugget effect, $V(0)$, can be estimated to be 0.007 – by extrapolating a line through the first five points backwards to the ordinate axis. It may be appreciated that among other merits, this back-extrapolation is actually more precise using the so-called auxiliary functions (which is only one of
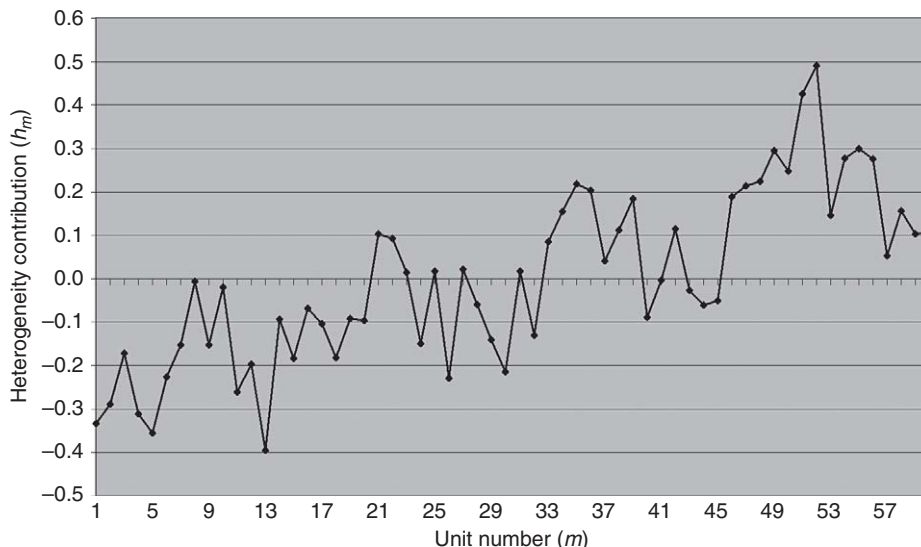
Figure 9 Heterogeneity contributions (h_m), calculated for the 60 increments in **Figure 8**. Reproduced with permission from Petersen, L.; Esbensen, K. H. Representative Process Sampling for Reliable Data Analysis – A Tutorial. *J. Chemom*. **2005**, *19* (11–12), 625–647.

Figure 10 Variogram, $V(j)$, and auxiliary functions for the experiment. The auxiliary functions are not crucial to the primary variogram analysis. Reproduced with permission from Petersen, L.; Esbensen, K. H. Representative Process Sampling for Reliable Data Analysis – A Tutorial. *J. Chemom*. **2005**, *19* (11–12), 625–647.

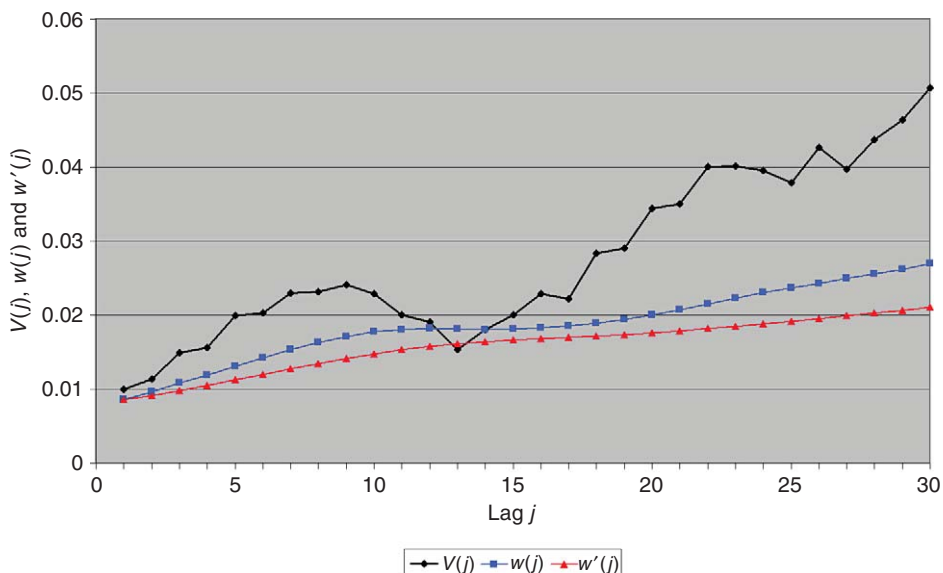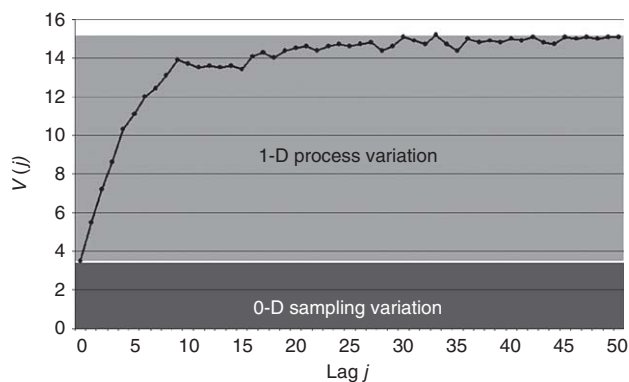**Figure 11**   Breakdown of 0-D/1-D sampling errors in a variogram. Reproduced with permission from Petersen, L.; Minkkinen, P.; Esbensen, K. H. Representative Sampling for Reliable Data Analysis: Theory of Sampling. *Chemom. Intell. Lab. Syst.* **2005**, *77* (1–2), 261–277.

their functions). They are however instrumental with regard to estimating the TSEs associated with alternative sampling strategies, namely ra, sy, and st.[1–3,12–14]

From the variogram, a minimum at $j = 13$ can be clearly observed (repeated, albeit less clearly, at $j = 26$ – because of the drastically smaller number of degrees of freedom available at these very large lags). This indicates that the process varies periodically with a cycle of 13 min. In the raw data, the periodicity is not easily identified, underlining the strength of the variogram as a powerful indicator of any periodicity.

This example only illustrates how to identify process behavior (trends/periods) from the variogram. A full analysis on how to identify optimal number of increments to form a composite sample, how to zoom in on an optimal sampling interval, and sampling strategy can be found in Petersen and Esbensen[12] and Halstensen[13] where these data are analyzed further. In the companion study on practical 1-D sampling,[14] it is further shown how the variogram can be used for a powerful breakdown, decoupling all 0-D errors from the process variation proper (1-D variance), as illustrated in **Figure 11**.

Variographic analysis, in the form of kriging and related spatial interpolation methods, is also used extensively in the science of Geostatistics as well as in geographical information systems (GIS). These aspects are essential also when considering sampling and prediction in mining, mineral processing, geochemical mapping, and environmental monitoring programs for example. The pertinent literature is vast; suffice here to direct the attention to Pitard,[3] Gy,[9] Esbensen *et al.*,[14] and Esbensen and Minkkinen[15] in which one can find extensive references in addition to those mentioned below. Freeware variographic software exist[23] as do commercial counterparts.

4.01.6   Sampling Errors – Summary

It is now possible to summarize all errors defined by TOS, governing both the 0-D and 1-D sampling scenarios.

The concept of 0-D errors identifies and summarizes every sampling variation source attributed to 0-D sampling:

- FSE: FSE is related to CH, which is a reflection of the material state of the lot.
- GSE: This error arises because of meso- and macroscale groupings and segregation and grouping in the lot material.
- IDE: When the geometrically outlined increment cannot be made to comply completely with the ideal increment requirements, this error crops out. It can be completely eliminated.
- IEE: When the material extracted is not 100% coinciding with what occupies the delineated increment, this error results. It can be completely eliminated.
- IPE: The error that sums up all sources of nonstochastic variation after extraction of the material, for example, evaporation, moisture uptake. This error should always be nil.

- IWE: Where appropriate, Minkkinen[16] points out one more error, IWE. This may be relevant, significant or not, depending on the specific context.

For 1-D sampling scenarios, a three-part error due to process variation is added:[2,3,9,12,13]

- The so-called continuous selection error (CE) is made up of three parts (only two are new in addition to the 0-D case):

  o CE1: Random fluctuation (identical to the sum of all 0-D errors).
  o CE2: Time fluctuation error (TFE). Error contributions due to trends in the process, which are not captured by the increment.
  o CE3: Cyclic fluctuation error (CFE). Error contributions from periodic variation of the process, which are not captured by the increment.

All the above errors form the TSE:

$$\text{TSE} = [\text{FSE} + \text{GSE} + \text{IDE} + \text{IEE} + \text{IPE}] + [\text{TFE} + \text{CFE}]$$

4.01.7   Seven Sampling Unit Operations

A basic set of sampling unit operations (SUOs) has been formulated, which constitute a complete set of procedures and general principles regarding practical sampling.[1] These unit operations can be grouped according to their use:

Three general principles – normally utilized only once in planning or optimization of sampling procedures:

- Transformation of lot dimensionality (transforming 'difficult to sample' 2-D and 3-D lots to 'easy to sample' 1-D lots). It is always possible to acquire some form of specimen from 3-D and 2-D lots, but whether this is based on probabilistic, correct, unbiased methods is a much more difficult issue – estimates of the primary sampling errors are difficult, sometimes impossible to come by, as are useful estimates of lot heterogeneity and composition a_L.
- Characterization of 0-D sampling variation by a replication experiment.
- Characterization of 1-D (process) variation by variography.

Four practical procedures – often used several times during practical sampling:

- Lot or sample homogenization by mixing or blending.
- Composite sampling, using the smallest possible increments.
- Particle size reduction (comminution).
- Representative mass reduction.[6]

The theory pertaining to the individual SUOs is explained in various sections of the present chapter and in full detail in Petersen *et al.*,[1,6] Petersen and Esbensen,[12] Halstensen,[13] Esbensen *et al.*,[14] and Esbensen and Minkkinen.[15]

4.01.8   Data Quality

Data quality is a very broad, often only loosely defined, term; a suite of problem- and discipline-related definitions can be found in the literature. Here we shall not try to define data quality in any comprehensive far less complete sense, but shall be content to specify that any definition that does not include the specific aspect of sample representativity is suboptimal and very likely to be inferior for its use in any broader sense.

The term 'data' is often equaled with 'information'; however, it should be obvious that this can only be in a hidden, latent, potential form. Only data analysis + interpretation may reveal 'information' and in a particular problem-specific context only.

Such issues have not been problematic in chemometrics, where, in general, issues pertaining to the prehistory of a data table ('data') usually receive but very little attention. One relevant major exception is the work of Martens and Martens,[19] which by its very nature focuses sharply on 'multivariate analysis of quality'. But even here, there is focus on only 'quality of information', defined as '. . . dependent on reliability and relevance'.

Inasmuch as the present TOS exposé has specified very clearly that 'reliable analytical information' derives from 'reliable analytical results (data)' only, meaning analytical results exclusively stem from representative samples and adequate sampling plans only, it stands to reason that any definition of data quality per force must include reflections/reference to representative sampling. Thus, it is crucial to contemplate the specific origin(s) of any data set. From the present perspective, dealing with 'modeling of data' without any considerations as to their representativity (strictly speaking, the representativity of the samples analyzed) cannot be considered safe and thus not reliable.

Without following the basic rules delineated in TOS, focus on 'data' alone, including derived issues, such as data quality, constitutes a sin by omission. In the context of process analytical technologies (PATs) for example, all aspects related to process analytical sampling (0-D and 1-D TOS) are nonexisting: TOS constitutes a veritable missing link in PAT.[20]

The type of errors known as 'measurement errors' in chemometrics typically only relate to the X-data ('instrumental signal errors'), and the magnitude of this type of error is inherently only of the same order of magnitude as the analytical errors – making this type of error almost as irrelevant as TAE compared to the physical sampling errors (TSE and its breakdowns) treated here.

4.01.9 Validation in Chemometrics

Section 4.01.8 has a direct bearing on the evergreen issue of proper validation in data analysis/data modeling in general and chemometrics in particular. Validation is concerned with validating the performance of any specific data analytical model, be it for prediction, classification, time-series forecasting, or similar procedures.

In statistics, data analysis, and chemometrics, a much favored method of validation is cross-validation, in which a subset of the training set apparently performs as an 'independent test set' in a sequential manner. Depending on the fraction of training set samples (totaling N) held out of the contemporary modeling (to be used for validation), an optional range of no less than $(N-1)$ potential cross-validation segments will always exist, the specific number of segments falling in the interval $[2,3,4,. . .,(N-1),N]$. Various 'schools of thought' of cross-validation have developed within chemometrics, some favoring the so-called 'full cross-validation' (one object per segment; N segments in total), some defining 10 as the canonical number of segments – and other schemes, whereas a minority do see more complexity than this in selecting from the space of $(N-1)$ optional variants of cross-validation segments. But usually there is more focus on strict adherence to some form of cross-validation procedure, or other, than openness to investigate what exactly are the precise assumptions and prerequisites behind cross-validation. This comprehension has hitherto been mostly lacking in chemometrics.

Against this background, Esbensen[21] makes a first analysis of all aspects of cross-validation versus test set validation, which is further much corroborated and powerfully illustrated by Esbensen and Lied.[22] The general conclusion arrived at is that cross-validation is but a simulation of test set validation, in form strikingly similar but not with regard to the essential characteristic: All arguments for cross-validation notwithstanding, the fact remains that there is ever only one data set involved in cross-validation, namely the training set. This precludes any possibility for more than one realization of the set of N data, namely the training set. Given the fact, exposed in this chapter, and in Petersen *et al.*,[1] Gy,[2] Pitard,[3] Smith,[4] Minkkinen,[7] Heikka and Minkkinen,[8] Gy,[9,11] Gy and Marin,[10] Petersen and Esbensen,[12] Halstensen,[13] and Esbensen *et al.*,[14] and Esbensen and Minkkinen[15] in full, that sampling errors overwhelmingly dominate, typically 10-50-100 X analytical errors alone, it is evident that any N-object data set constitutes but only one specific realization of an N-tuple of individual TSE materializations.

The main lesson from TOS' more than 50 years of practical experience is that there is no such thing as a constant sampling bias – sampling bias changes with every new sampling from a heterogeneous material. From this it follows that there can never be any guarantee that the specific training set realization will also be representative of all future similar data sets, each of which also repeats N individual TSE materializations.

Therefore, it is always necessary to test all implicit assumptions regarding sampling bias constancy, in practice every time, say, when a prediction model is to be used for its designated purpose: when predicting this is also based on a bona fide new data set, that is, a new N-object data set. Sampling will here per force have been involved in exactly the same fashion as for the training data set – only the associated TSE for the new data set has never been assessed. For this to be possible, a test set becomes an absolute necessity. Incorporating this second data set is the only way in which to incorporate information from both TSE materializations, for example, in prediction performance validation:

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^{n} \left(\hat{y}_{i,\text{val}} - y_{i,\text{val}} \right)^2}{n}}$$

where RMSEP is the root mean square error of prediction. From this discussion, one can conclude with complete generality that all types of variants or schematics of the cross-validation ilk by necessity must be inferior, indeed unscientific,[20,22] precisely because the dominating TSE contributions from all possible future data sets are not validated, not even from one such data set – which would be the test set. Cross-validation must logically and scientifically be discontinued unless absolutely no option for test set validation exists. Only test set validation can stand up to the logical demands of the validation imperative itself.

It is interesting to note that this highly compressed argumentation is made infinitely easier to express – and comprehend – by invoking the heterogeneity characteristics embedded in TOS.

Caveat: Within process sampling, there are many opinions on the market as to the optimal definition of the training set versus the test set. In a 5-year data series for example, would the first 3 years constitute a viable/optimal training set, with the last 2 years serving as an appropriate test set? Or, would pruning over the entire 5-year set, for example taking out every fifth sample to make up the test set (of size 20% relative to the 80% training set), be a better solution? Specifically regarding process sampling, there are always many options: Local, problem-specific schemes are legion, but only seldom comprehensive and authoritative enough to hold up to systematic scrutiny. The specific process sampling scenarios in TOS are in fact (much) more complicated than what simple carrying over of 0-D notions allow for. Suffice here to mention only seasonality, trends, or even more complex issues (process upsets a.o.). Indeed TOS has made specific allowance for the first two general factors in the form of TFE and CFE, respectively. Current experience would indicate that these features have stood process sampling in very good stead so far...

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Biographical Sketches

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