SPECIAL GUEST EDITOR SECTION

Materials Properties: Heterogeneity and Appropriate Sampling Modes

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The target audience for this Special Section comprises parties related to the food and feed sectors, e.g., field samplers, academic and industrial scientists, laboratory personnel, companies, organizations, regulatory bodies, and agencies who are responsible for sampling, as well as project leaders, project managers, quality managers, supervisors, and directors. All these entities face heterogeneous materials, and the characteristics of heterogeneous materials needs to be competently understood by all of them. Before delivering analytical results for decision-making, one form or other of primary sampling is always necessary, which must counteract the effects of the sampling target heterogeneity. Up to five types of sampling error may arise as a specific sampling process interacts with a heterogeneous material; two sampling errors arise because of the heterogeneity of the sampling target, and three additional sampling errors are produced by the sampling process itself—if not properly understood, reduced, and/or eliminated, which is the role of Theory of Sampling. This paper discusses the phenomenon and concepts involved in understanding, describing, and managing the adverse effects of heterogeneity in sampling.

In this paper the phenomenon heterogeneity and its manifestations in naturally occurring, manufactured, or processed materials, are described. Heterogeneity is responsible for the effects of the two fundamental correct sampling errors, and a specific sampling process may itself result in effects from up to three additional incorrect sampling errors (1, 2). All samplers must have a basic grasp of the nature and manifestations of heterogeneity in order to be able to assess the appropriateness of existing sampling procedures and equipment. Representative sampling is heterogeneity-counteracting mass reduction.

Materials

In the world of science, technology, and industry, the wide diversity of sampling target materials reveals a bewildering array of different types and degrees of heterogeneity with many diverse physical manifestations (Figure 1). The food and feed sectors are no exception. Materials appear as discontinuous or continuous solid(s), as discrete materials composed of varying types of mixtures of component units (foods, particles, fragments), aggregates, two-phase systems, e.g., slurries (solids, liquids), or three-phase systems (solids, liquids, gases). Examples of heterogeneous materials are legion. Below are shown just a few examples, intended to cover a broad range of potential application fields of interest for readers with differing backgrounds. The examples focus on the generic aspect of heterogeneity and its interaction with the sampling process; the examples can easily be translated into the typical or more specific type of material(s) of interest to the reader.

One of the most powerful features of Theory of Sampling (TOS) is that it offers universal principles for representative sampling that covers all manifestations of heterogeneity. While dramatically different in their apparent physical manifestations (Figure 1), all materials present identical heterogeneity challenges, which only differ in degree, and are treated in identical fashion by TOS.

The examples in Figures 1–7 illustrate that many heterogeneities are deterministic, resulting from specific processes, e.g., manufacturing/processing, stock laying-up processes, transport and pouring processes, and flow processes. This nearly always involves some form of dynamic activity, i.e., heterogeneous 3-D sampling targets are temporarily present in a moving 1-D configuration (flowing, ducted, conveyed, transported). Such sampling targets are by far the easiest to sample with the highest fidelity, i.e., by being intercepted by a cross-cutting sampling tool (2–6).

Homogeneity–Heterogeneity

To understand the heterogeneity concept, it is necessary to define its opposite, homogeneity, or rather what constitutes a homogenous material. Several definitions can be found in the literature, but we prefer the most stringent: A homogeneous material is composed of strictly identical fragments (3), identical in a complete, fully comprehensive sense, i.e., all fragments must be of exact same size, composition, density, surface morphology, and features (e.g., wettability), and electrical charge. Having strictly identical fragments is a very strong requirement that leaves almost no candidate in the real world of naturally occurring, manufactured, or processed materials. There is no such thing as a homogeneous material in the food and feed realm, nor in almost any other sector. In this context, it is therefore safe to state that all materials that are to be sampled are heterogeneous (4, 5, 7). This is a prudent and a

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Figure 1. Primary manifestations of heterogeneous materials. Top left: Grab sampling (discrete sampling) of highly heterogeneous slurry (grapes/must) at a winery intake. Top right: Array of optional increment sizes for sampling of soil with intermediate heterogeneity. Lower left: Sampling targets as big bags offers the dubious complacency of not observing the material and its heterogeneity when sampling (but the heterogeneity very much exists nevertheless). Lower right: Manual process sampling (grab sampling) of apparently uniform material. The heterogeneity manifestations shown cover the range from high to low, from visible to hidden, from the considered to the neglected.

sound scientific attitude that will ensure that heterogeneity is always part of the sampling agenda.

Heterogeneity Versus Sampling—Conceptual Introduction

A didactic framework for understanding TOS heterogeneity concepts, using a scale hierarchy progressing from fragment to decision unit (DU) scale, is presented below. Even though the number of real-world different heterogeneous materials is enormous, understanding their common feature heterogeneity is paradoxically easy, as long as one is not overwhelmed by their multitude of physical manifestations and visual appearances (Figures 1–5). It is only necessary to focus on their inherent heterogeneity, which is understandable from three concepts only: constituent units (of various kinds, at various scales); three scale levels; and simple summary statistics (average, SD, and variance). The scale levels alluded to are also known as "observation scale" in the TOS literature, which may also refer to "observation volumes."

All materials are made up of constituent units, for example, at the smallest scale of interest, molecules. At a scale level commensurate with a sampling tool volume, the constituent units would be grains, particles, and coherent aggregations (coherent enough so as not to be fragmented in the sampling process). At the highest scales of interest, the unit would be the sampling target itself. This three-tiered scale hierarchy constitutes the essential scaffolding for TOS theoretical and practical concepts regarding heterogeneity.

Regardless of which analyte of interest, any constituent

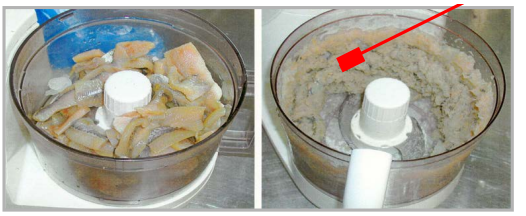

Figure 2. Primary manifestations of heterogeneous material in the laboratory. Here herring filets are subjected to sample processing and preparation before aliquoting. The food control laboratory in question believes that the resulting homogenate (right) is sufficiently well comminuted and mixed to allow direct aliquoting with a spatula (grab sampling), extracting only the precise, very small amount needed for analysis. The homogeneity is routinely assessed by visual inspection only; however, a Relative Sampling Variability characterization allows a fully quantitative heterogeneity characterization.

unit will be characterized by a certain quantity. In general this quantitative measure, the concentration, will vary from 100 to 0%. We shall follow the TOS tradition in which grains, as well as their possible fragments (fragmented during the sampling process), are termed "fragments." It is generally convenient to term both the original unaffected grains as well all possible fragment cascades induced in/by the sampling process itself as generic fragments. This makes it possible to deal with all types of original materials and their undisturbed constituent units at all scales up to the full scale of the target, as well as those sub-parts, which are made up of fragmented grains. This constitutes an extremely complex spatial arrangement of meso-scale and local-scale heterogeneity (Figures 3 and 7), but still only a particular set of untouched units and fragments. In other words, one can speak with complete generality and deal conceptually with any type of sampling target, which are then simply made up of fragments.

All materials to be sampled are heterogeneous because all fragments in general do not carry an identical concentration, or amount of heterogeneity. It is of no consequence if only a few,

Figure 3. Left: Significant compositional and distributional heterogeneity of a composite material clearly related to its preceding laying-up (filling of the beaker). Sampling of this type of very irregular heterogeneity must cover all three sampling target dimensions, but may alternatively have taken place prior to, or simultaneously with an earlier transportation stage. Right: Significant compositional heterogeneity; here the end state resulting from thorough mixing of a batch of herring filets in a food processer. By using high-powered illumination and a camera UV-filter, hitherto invisible compositional differences among individual particles are emphasized, revealing an appreciable residual heterogeneity in what is normally called the homogenate.

or an overwhelming proportion of the fragments, turn out to be identical in practice; the material is still heterogeneous. Think of a material consisting primarily as a uniform set of grains but contaminated with trace amounts of an extraneous (or intrinsic) analyte (8). Such sampling targets present some of the more difficult cases to deal with because the heterogeneity reflects a necessarily irregular spatial distribution of the sparse units carrying the contaminant, and in general, all fragments will not necessarily carry the same concentration. Many materials also display a distribution of grain sizes (very few materials are truly mono-disperse), in which case the units differ with respect to their mass and their analyte concentrations. This type of heterogeneity can be said to be a structural property of the material.

TOS defines two conceptual types of heterogeneity, which are complementary and inclusive. It is necessary to start with a strict definition of constitutional heterogeneity at the scale level of fragments.

Constitutional Heterogeneity (Compositional Heterogeneity)—CH_L

CH_L—CH_L is brought about because of intrinsic compositional differences between a set of individual fragments. A material is heterogeneous (it has a non-zero constitutional heterogeneity) if it consists of different constituents. Because fragment differences are structural characteristics of the material in question, mixing will have no effect on this type of heterogeneity. It will be the exact same ensemble of fragments regardless of the degree to which they are mixed up. They will remain equally different.

One can perform a one-to-one transformation of the concentration level of the analyte in the sample (or in the full DU), a_S, or a_{DU}, into a heterogeneity contribution concept, which is often used in theoretical and practical considerations in TOS. Here we remain with the above analytical concentrations, which are fully able to delineate the intricacies of heterogeneity (1, 2). However, the heterogeneity contribution format makes it easier to understand the concept of heterogeneity, because the individual fragment masses are factored in. Large fragments (masses larger than the average fragment mass) may carry a large concentration deviation from a_{DU}, with the consequence that the heterogeneity contribution from this fragment will be large. However, if a fragment, identically large in size, happens to have a concentration very close to, or equal to a_{DU}, its contribution to the full DU heterogeneity will be insignificant, maybe even zero, regardless of its size (mass); it is simply a large fragment with almost precisely the average material composition. From the perspective of a significant compositional deviation, large fragments will contribute the most to CH_L, while small particles (grains of dust, for example) will not contribute much to the total material heterogeneity.

The physical appearance of a lot (as made up of discernible fragments) may well lead to a false impression of heterogeneity, e.g., large fragments dominate the visual grain size distribution impression, while the inherent concentrations involved may well differ without any visual clue. Similarly, a material made of apparently almost identical grains (e.g., coffee, soy beans, or wheat grains) can nevertheless be display significant heterogeneity, for example, toxins, mycotoxins, or even gene modified organisms (GMOs). Some grains may actually be GMOs throughout, while many others may not as described in a case regarding GMO presence in kernel lots (9). There is one lesson to be learned: The visual impression of heterogeneity can be grossly misleading. The visual impression must never be used as a basis for heterogeneity assessments.

Figure 4. Illustration of the proverbial white powder with a normal grain-size distribution in which the larger-than-average particle sizes have been dyed blue, allowing detailed insight into grain-size differentiation and segregation behavior. The original powder visually makes a totally homogeneous impression. Shown here are two different DH_L manifestations (left, center). The powder state pictured center was produced by a single 90 degree rotation around the vertical axis of the container, attesting to significant DH_L handling sensitivity, illustrating that specific DH_L manifestations are always transient, a sensitive function of a number of factors (production, handling, transportation, manipulation while being sampled). This phenomenon applies to very many similar aggregate materials at all scales. The right hand illustration shows the effects of pouring segregation and the resulting problems acquiring a representative single-sample aliquot using a laboratory spatula. Discrete sampling (grab sampling) operations can never be representative. Illustrations courtesy of Peter Paasch-Mortensen (shown with permission).

To produce a complete heterogeneity characterization of a sampling material it would be necessary to analyze and weigh all constituent fragments. Because this is obviously not possible, nor desirable in sampling practice, sampling is foremost. Only a part of the lot will be physically sampled and eventually analyzed.

What would constitute an ideal sample? Following the fragment heterogeneity formalism, an ideal sample would have to be composed of a subset of individual fragments selected individually from the sampling target, completely at random, i.e., based on total free access to the full geometrical target volume. The salient issue is here that there must be free access to absolutely every grain. This demand is codified as the Fundamental Sampling Principle (here developed at the fragment scale). It is clear, however, that logically, nobody would wish to collect an ideal sample in practice. A set, i.e., a collection of neighboring fragments, will have to suffice.

In TOS, a coherent set of neighboring fragments is termed a group-of-fragments, or a group for short. While any disposition and size of a group can be envisaged, TOS is really only interested in the special group-of-fragments that will end up in the sampling tool after a unitary sampling operation. For sampling reasons, TOS is only interested in those practical groups that make up extracted *increments*. Sampling, therefore, in practice takes place by extraction of increments of a size that needs to be optimized (1, 2).

The exact same material, which was described above with respect to a fragment scale level, can alternatively be considered as made up of groups-of-fragments. This change in observation scale also applies to the heterogeneity analysis. This jump from fragment scale to the group scale level is all we need to be able to derive the second feature of heterogeneity, the spatial, or the distributional heterogeneity. Enter the distributional heterogeneity of the lot, DH_L, which is defined in a completely

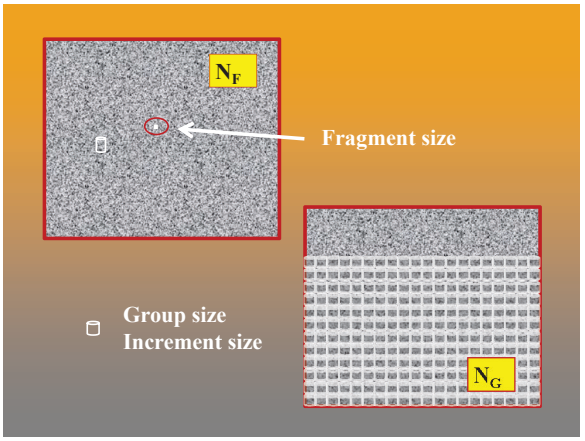

Figure 5. Pierre Gy's inspired conceptual scale-jump from fragment-scale to group-scale which facilitates definition of the distributional heterogeneity, DH. These two observation scales correspond to the different heterogeneity-carrying units indicated, fragment versus group. The lot can either be viewed as consisting of N_F fragments or as N_G groups (virtual increments), the latter indicated lower right (shown for 80% of the lot only for clarity). A third scale level in TOS corresponds to the sampling target (DU, lot) itself. All sampling targets can be viewed from these three vantage points, which is all that is needed for a complete description of heterogeneity.

similar fashion as CH_L. Note that distributional here means distribution in space, distribution within the geometrical volume occupied by the sampling target.

TOS definitions of CH and DH are usually made invoking a few statistical equations, which interested readers can find in their standard mathematical format in (1, 2).

Distribution Heterogeneity—DH_L

DH_L.—The distributional heterogeneity is a reflection of compositional differences between groups. Before sampling, only virtual groups exist in the sampling target, i.e., delineated increment groups that have not yet been extracted (Figure 5).

Because the entire ensemble of different fragments is available for manipulation, mixing now has an effect on the compositional differences between groups, e.g., shaking a pitcher with different types of solid particles; mixing of a segregated slurry tank; whisking whey and yolk; shaking a cocktail. Mixing has a deterministic influence on between-group differences; the virtual groups become more and more similar as mixing progresses. However, there is a limit to mixing; infinite mixing will not lead to a homogenous material state, but only to a minimum residual heterogeneity state, after which more mixing only results in a steady-state mixing/de-mixing around this state, or it may even increase DH locally (de-mixing, segregation). All relevant materials within the food and feed sectors will never achieve true homogeneity, but will instead reach their salient minimum state of heterogeneity; neither will they ever constitute the much-wished-for-but-unrealistic goal of a random mixture.

The between-group variability should logically be termed the group Constitutional Heterogeneity, since it is based on compositional differences in a completely identical fashion as for the definition of CH_L. At the group scale, however, the heterogeneity carried by all groups in the lot is specifically defined as Distribution Heterogeneity following the rationale laid out below.

Why isn't CH_L simply defined as the compositional heterogeneity at the group scale level? How is it possible to designate this as DH_L? Isn't this simply just a sleight-of-hand trick? What is the relationship between compositional and distributional heterogeneity thus defined? This is where the insight of the founder of TOS, Pierre Gy, comes into play. What is expressed as identical compositional differences in the basic definitions can be given a different physical meaning at the group scale level.

Consider a material made up of N_G groups (Figure 5). It follows that the full target volume, the next logical scale level jump, is completely defined as the sum-total collection of these N_G groups. That which statistically is defined as the variance of all group heterogeneity contributions (without spatial considerations) is in 3-D reality also the set of groups which physically occupies and fills up the target volume. Thus, when statistically summing over all group heterogeneity contributions, one is at the same time summing over the entire spatial lot volume. This variance physically expresses the spatial differences between all groups, which is therefore identical to viewing this variance as an expression of the total spatial heterogeneity of the material (lot). While theoretically and formally calculated based on identical compositional difference definitions for CH_L, DH_L quantifies the heterogeneity imparted to the whole lot originating from the spatial locations of the different groups within the lot.

It is no coincidence that TOS chooses to define DH_L in this fashion: the physical sampling takes place exclusively via groups, i.e., via increments. In practice, an increment is the result of a unitary sampling operation. An increment may form the whole sample (discrete sampling operation), if/when SQC considerations so define. But in all other instances, increments are sampled with the express purpose of being aggregated to form a composite sample.

While CH_L resides in the scale interregnum between fragment and group, DH_L quantifies the heterogeneity that resides in the realm between group scale and material sampling target scale (lot size). Both these heterogeneity aspects are needed to fully characterize the total heterogeneity of any material, but they cannot be physically separated from one another. CH_L and DH_L are conceptual, theoretical components that in practice always exist intricately interwoven for any material.

Two interrelated heterogeneity concepts of TOS form the basic element for all of practical sampling, helping practitioners to understand that one of the primary objectives must be to minimize the negative effects of both compositional and spatial heterogeneity (1, 2).

Sampling Modes for Heterogeneous Materials

Sampling must always be carried out in such a fashion so as to counteract the effects of heterogeneity as much as possible. As a case in point, taking just one discrete sample, a grab sample (Figure 5, upper left), cannot under any circumstances claim to be combating heterogeneity, with the logical result that discrete sampling (grab sampling) is to be avoided at all costs, at all times, at all scales.

The title of this chapter refers to appropriate sampling modes, but only grab sampling and composite sampling have

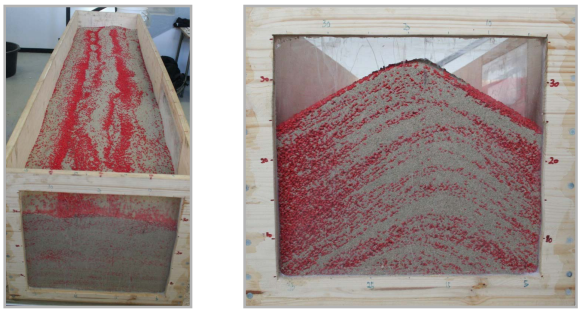

Figure 6. Two examples of strongly structured heterogeneity, brought about by different stacking processes, illustrating the type of spatial heterogeneity, DH_L often present in transportation or storage depots, vessels, and trucks as well as in train loads, containers, and ship cargo holds. Note that both examples have identical CH_L. Structured heterogeneity can be a major characteristic in the food and feed industry sectors, due to extensive stacking, reclaiming, and transportation processes involved in producing, processing, and manufacturing.

been discussed so far. Other sampling modes must also be classified within the present context, i.e., random, stratified, and systematic sampling. If a sampling target were ever truly a random mixture, these modes would result in equal uncertainties regarding the lot mean estimated from several samples, provided that increment sizes are equal and that an equal number is taken. However, there does not exist true random mixtures in science, technology, and industry (1–12), but many sources still overconfidently recommend random sampling as the optimal choice also in the case of segregated lots.

From the above, and based on the vast accumulated experiences with TOS over 60 years, it is clear that it is not one specific sampling mode that by itself will carry the day. It is the specific way this sampling mode is applied to counteract the specific heterogeneity met with that matters most. Thus, in the case of structured (segregated) heterogeneous lots, stratified random sampling will be the optimal heterogeneity counteracting procedure, because it forces the increment setup to cover the entire geometrical volume of the lot; several good illustrations of this deployment scheme are described by Wagner (8). When sampling moving lots or stationary elongated lots, collectively referred to as 1-D lot (1, 2), systematic sampling may on rare occasions encounter difficulties if the segregation or concentration fluctuation shows periodicity or the sampling frequency is a multiple of the frequency of the periodicity in the target. In this case the estimated lot mean will be biased. This situation mainly applies to 1-D lots. All matters regarding process sampling (i.e., sampling of 1-D lots) and sampling in the laboratory (mass-reduction) are described in a follow-up Special Section.

Structured Heterogeneity

Many materials in the food and feed sectors display particularly marked structured heterogeneity, e.g., layered, stratified, or hierarchically organized, irregular heterogeneity dispositions (clumpiness; Figures 6 and 7).

Figure 7 shows a generic example of a specific manifestation of a salami (minced meat, spices, and fat) occurring in a very irregular compound texture, the sampling of which is not straightforward. In many sectors, sampling of material with

Figure 7. Salami: an example of a highly irregular meso-scale heterogeneity. Any kind of tube-coring sampling is doomed to fail in procuring a representative sample. However, the principle of riffle-splitting can be applied even to this kind of material. Splitting can easily be obtained by selecting every other slice, or another fraction if a fractional sampling is desired. Even though not as easy as pouring free-flowing aggregate material through a standard riffle-splitter, the same general TOS principle guarantees a representative subsample (10).

similar high degrees of heterogeneity takes place with a tubular corer (thief, spear), but it is clear that a random core section of this material runs a severe risk of being nonrepresentative.

An alternative approach, inspired by the principle of riffle-splitting (9, 10), is shown in Figure 7. By slicing a sufficiently high number of slices, each covering the full width-thickness of the salami, a division of the material in all aspects identical to riffle-splitting is obtainable in spite of its specific sticky, decidedly not free-flowing nature.

By selecting every second slice, a mass-reduction (50/50%) can easily be achieved even for material with very high CH_L and DH_L. Despite the apparent heterogeneity difficulties, a 100% TOS-correct mass reduction can be realized, both in principle and in practice, but obviously dependent upon a certain necessary practical effort. The effectiveness, the representativeness of subsampling, however, is actually only a matter of practical implementation; i.e., how many initial thin slices one is willing to use. There is a substantial carrying-over potential for this type of creative sampling solution. Even more irregular heterogeneity can be handled with full confidence in an identical fashion. The riffle-splitting principle still holds, but it may be necessary to use a higher number of increments (slices). The guarantee that this will always constitute a representative sampling procedure comes from the demand that each increment must represent a complete slice across the two dimensions of the lot. This is a standard requirement originating from process sampling (1–5, 9, 13–15).

Problem-dependent usage of the principles of TOS allows many sampling processes to be designed carrying the key distinction, heterogeneity-counteraction. Because the principles of representative sampling (including subsampling) are not related to scale (scale-invariant), once these have been mastered, all materials are open to similar endeavors, because they differ only with respect to the degree of their inherent heterogeneities.

Complementing the theoretical analysis of heterogeneity, a practical guide to appropriate sampling modes can be formulated as follows:

(*1*) Before any sampling (subsampling) mix thoroughly wherever/whenever possible, to a state as close as possible to the residual minimum heterogeneity level for the particular material involved. Mixing is especially important after crushing.

(*2*) Wherever/whenever mixing is not possible, e.g., at the primary sampling stage (when the lot is larger than what allows forceful mixing), or because of other logistical constraints—but never because of work, effort, or cost considerations (13–15), use composite sampling, never grab sampling (1, 2).

(*3*) There is only one free parameter for composite sampling, the number of increments needed to control the total sampling error (Q) (1–4, 9, 13–15).

(*4*) A systematic classification of heterogeneity beyond irregular versus structured does not exist; there is unfortunately no heterogeneity typology which perhaps could have guided specific sampling procedures. There is only an ever-increasing degree of irregular heterogeneity with a bewildering array of apparently different manifestations. But as we have shown, all types of lots can be sampled with one universal procedure: composite sampling. It is always necessary to use an appropriate number of increments, Q, commensurate with the specific heterogeneity encountered. Riffle-splitting is but one special manifestation of composite sampling.

(*5*) Elsewhere in this Special Section the use of a Replication Experiment (16) to quantify the effective total sampling plus analytical error is presented. If this criterion is not satisfied, one must simply use a still higher Q than the contemporary choice. As with all composite sampling the imperative demand is that the Q increments cover the geometric lot volume as best as possible either using a regular grid basis, a stratified random approach, or a completely random deployment scheme.

(*6*) When facing heterogeneity, the appropriate sampling mode is composite sampling (Q). When possible, mix the lot thoroughly before sampling.

Laboratory Subsampling—Laboratory Mass Reduction

Laboratory mass reduction (subsampling) of free-flowing aggregate materials does not constitute a notable problem (9). A comprehensive benchmark study has been used as guidance extensively for a decade (10), which rates all existing approaches, methods, and equipment from a strict TOS representativeness point of view, except the significantly inferior coning-and-quartering method, which has been analyzed and rejected in (11).

Laboratory mass reduction (subsampling) of many types of material (fibrous, elongated, sticky, leafy green stuff, shelled, very hard, and very soft) from the food and feed sectors is not necessarily a simple matter, however. Examples of non-grainy, non-flowing units are numerous. The subject matter of proper mass reduction (subsampling in the laboratory) in the food and feed sectors will be addressed at a later occasion.

Measurement Uncertainty

A grey zone regarding responsibilities exists in the overlapping area between laboratory subsampling and analysis. The latter, known as Measurement Uncertainty (MU), is based on an extensive theoretical underpinning (metrology). Certain difficulties have been encountered regarding a logical but complicated responsibility demarcation between the frameworks of TOS and MU. This issue has recently been treated in a call for reconciliation rather than confrontation, however (12).

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