

Heterogeneity—the root of all evil (part 1)

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What is in common to all agents along the entire field-to-analysis pathway, e.g. process technicians and engineers, primary samplers, academic and industrial scientists, laboratory personnel, companies, organisations, regulatory bodies and agencies as well as project leaders, project managers, quality managers, supervisors and directors? All are dependent on reliable analytical data to make decisions, which in one way or another do not originate via aliquots alone. There is sampling, a lot of sampling (and sub-sampling), before a relevant, valid aliquot can be delivered to the analytical laboratory. And all sampling has to deal with materials which are heterogeneous at one scale or another (or at all scales). It is vital to understand the characteristics of heterogeneous materials. One form or other of primary sampling is always necessary which must counteract the effects of the sampling target heterogeneity. A total of five sampling errors arise because all sampling processes interact with heterogeneous lots: two arise because of the heterogeneity of the sampling target, and three additional sampling errors are produced by the sampling process itself—the latter if not properly understood and eliminated, which is the role of TOS. This column, and its sequel, introduces the phenomenon and concepts involved in describing, estimating and managing the adverse effects of heterogeneity in sampling.

The basics

Heterogeneity is responsible for the effects of the two fundamental “correct sampling errors” (CSE), and its interaction with the sampling process leads to

effects from three additional “incorrect sampling errors” (ISE). It is necessary for all competent samplers to 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. There are infinitely many manifestations of heterogeneity, yet for the competent sampler there is only one issue at hand. Representative sampling is nothing but *heterogeneity-counteracting* mass reduction, Figure 1.

Materials, sampling targets, lots

Materials (sampling targets, lots) present themselves in a bewildering array of

different types and degrees of heterogeneity with many diverse physical manifestations, Figures 1 and 2. Materials may appear as discontinuous or continuous solid(s), as discrete materials composed of varying types of mixtures of “component units” (components, particles, fragments...), aggregates, two-phase systems (e.g. slurries...), or three-phase systems (solids, liquids, gases). Examples of heterogeneous materials are legion, the few examples shown here are illustrations of the broad range of potential application fields of interest. The present description and examples focus on the *generic* aspect of heterogeneity and its interaction with the sampling process; the examples should be easily trans-

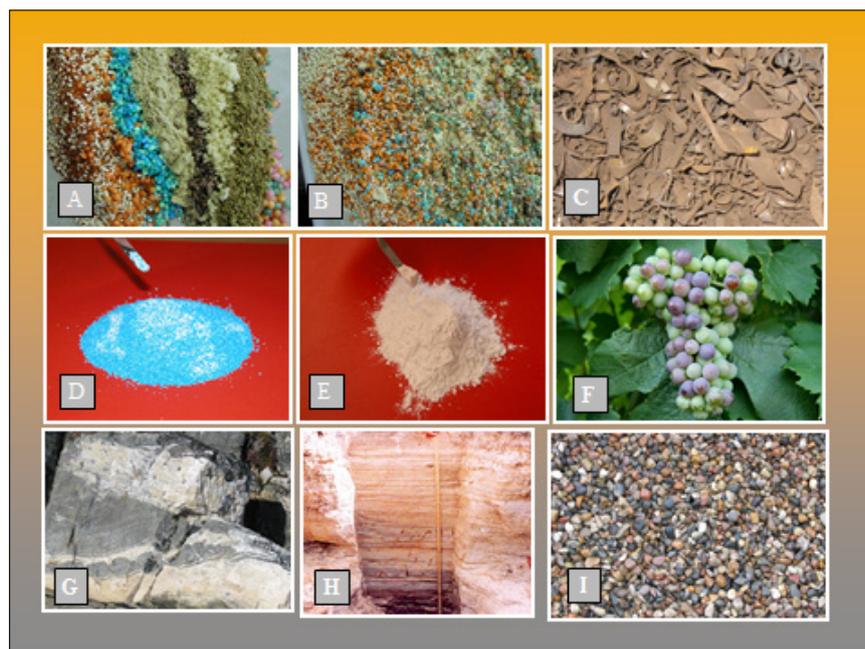


Figure 1. The many varied manifestations of heterogeneity—no homogeneous materials exist in the world of science, technology and industry. Consequently, the path from lot to aliquot is the most critical part—also for analysis.

SAMPLING COLUMN



Figure 2. Heterogeneity will always interact with sampling, and will determine the degree of TOS-compliant work needed to counteract its negative effort, which gives rise to sampling errors. Primary manifestations of selected heterogeneous materials and their sampling. 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, e.g. as “big bags”, offer the added difficulty of the sampler not being able to observe the material and its heterogeneity (but it certainly 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.



Figure 3. Example of primary manifestations of heterogeneous material in the laboratory, here herring fillets subjected to *sample processing and preparation* in a mixer. The laboratory technician may believe 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. This is a major fallacy, however, as shown in Figure 4.

lated into the typical type of material(s) of interest of the reader.

It is one of the most powerful features of TOS that it offers *universal principles* for representative sampling that cover all manifestations of heterogeneity. A first lesson is that, while dramatically different in their apparent physical manifestations, all materials present *identical* heterogeneity challenges, which *only* differ in *degree*, and they are therefore treated in identical fashion by TOS.

This is a tremendously liberating insight. Once we know how to deal with heterogeneity on one particular scale, we can deal with all manner of lots—at all scales.

Many meso- and large-scale heterogeneity manifestations are *deterministic*, in that they result from specific processes, e.g. manufacturing/processing, stock laying-up processes, transport and pouring processes, flow processes. This very nearly always involves some form of dynamic activity, i.e. heterogeneous three-dimensional sampling targets are temporarily present in a moving one-dimensional configuration (flowing, ducted, conveyed, transported). Such latter sampling targets can very easily be *intercepted* by a cross-cutting sampling tool. This type of Distributional Heterogeneity (DH) characterises the scale interregnum between increments and the whole



Figure 4. Significant compositional heterogeneity at the end state of “thorough mixing” of a batch of herring fillets in the mixer shown in Figure 3. *Invisible* compositional differences among individual unit fragments are emphasised by high-powered illumination and a UV camera-filter, revealing an appreciable “hidden” residual heterogeneity in what is normally called the “homogenate”. Compositional Heterogeneity (CH) is introduced in the text.

SAMPLING COLUMN

lot. (Process sampling will be covered in later columns.)

Homogeneity–heterogeneity

For the purpose of a precise understanding of the concept of heterogeneity, it is necessary to present a strict definition of its opposite: *homogeneity*, or rather of what constitutes a *homogenous material*. Several definitions abound in the general literature, but we here focus on the most stringent one (from the TOS): a homogeneous material is composed of *strictly identical fragments*—identical in the complete comprehensive sense, i.e. *all* fragments must be of the *exact* same size, composition, density, surface morphology and features (e.g. wettability), electrical charge (such differences will also lead to differential segregation or flow effects between fragments). It is clear that *strictly* identical fragments is a very strong requirement that leaves almost no candidate in the real world of naturally occurring, manufactured or processed materials. In this context, it is best and indeed safest always to assume that *all* materials that are to be sampled are heterogeneous. This is a sound scientific attitude that will ensure that heterogeneity always is the most important item on the sampling agenda.

Scale

It is necessary to focus on the *inherent* heterogeneity of lots, which turns out to be understandable from three concepts only: i) constituent “units” (of various kinds, at various scales), ii) three scale levels, iii) simple summary statistics (average, standard deviation, variance). The scale levels alluded to are also known as “observation scales” in the TOS literature, sometimes also referred to as “observation volumes”. All materials are made up of “constituent units”, e.g. at the smallest scale of interest: molecules; at a scale level commensurate with a general sampling tool volume the constituent units would be: grains, particles, fragments 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 (the

lot scale). This three-tiered scale hierarchy constitutes the essential scaffolding for TOS’ theoretical and practical concepts regarding heterogeneity; nothing more is needed.

Heterogeneity vs sampling

Regardless of which analyte is of interest, any “constituent unit” will be characterised by a certain quantity thereof, and this quantitative measure, the concentration, will vary from 100% to 0%. We shall here follow the TOS tradition in which grains, as well as their possible fragments (fragmented during the sampling process), shall all be termed “fragments”. From a generalisation point of view it is convenient to term both the original unaffected grains as well as 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 now made up of fragmented grains. This undoubtedly constitutes an extremely complex spatial arrangement (meso-scale and local-scale heterogeneity), but still only a *particular* set of fragments. In other words one can speak with complete generalisability of, and deal conceptually with, *any* type of sampling target, which are then, to the first conceptual consideration, 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, 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. Such sampling targets are presenting one of the more difficult cases to deal with because the heterogeneity is reflecting a necessarily irregular spatial distribution of the sparse units carrying the contaminant (and quite possibly not all fragments carry the same concentration). In general, when

just one non-zero number of fragments are different from one another, the material is heterogeneous. Many materials also display a distribution of grain sizes (very few materials are truly monodisperse), in which case the units differ both with respect to their mass as well as 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, but when the different scales of interest in sampling are factored in, it turns out there are three manifestations to deal with, although two are closely related. It is necessary to start with a strict definition of constitutional heterogeneity at the scale level of fragments, which will be the theme of the next column.

Acknowledgement

This and the next column on heterogeneity are summarised and edited versions based on Reference 1. Some illustrations are presented here with kind permission of the *Journal of AOAC International*.

References

1. K.H. Esbensen, C. Paoletti and N. Thiex, “Representative sampling for food and feed materials: a critical need for food/feed safety”, *J. AOAC Int.* in press (2015). doi: <http://dx.doi.org/10.5740/jaoacint.14-234>

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