Estimating the heterogeneity invariant using size-density classes – the case of contaminated soil and complex materials

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For the important material class of aggregate mixtures comprised by both analyte-enriched and *analyte-coated* particles, Gy's classical s^2(FSE) formula has often been reported to yield estimates of the fundamental sampling variance *greater* than the empirically estimated sampling variance. Which, however, is physically impossible according to the tenets of the Theory of Sampling (TOS), both physically and logically, since the fundamental sampling variance is, by definition, the minimum sampling variance remaining after all other sources of sampling errors have been eliminated. This situation has for many decades hindered rational use of the Theory of Sampling for this kind of complex systems. We here focus on contaminated soil as a typical illustrative example of great interest, as well as more generally in the field of environmental site assessment. This uncomfortable situation is exacerbated by the fact that sampling in these fields is still, after 70+ years of TOS, largely conducted by grab sampling, which assuredly lead to significant uncertainty and bias.

However, there is a solution to this at first sight 'intractable' problem to be found, specifically within TOS. In some of his earlier publications, Gy developed a variant the s^2(FSE) formula based on consideration of both size- and density classes, but quickly dismissed this approach as being inapplicable to « the metal, mining, and processing industries […] due to the unusual density contrast between the components » typical of matrices sampled in these fields. This size-density class variant was consequently then left out of sampling awareness and literature for a long time.

We revisit herein development of the heterogeneity invariant on this basis and show this to represent a general option which can be adapted to distinct and specific matrices and analytes *beyond* the original restricted realm. As an example, a size-density class variant is applied to data from studies on sampling complex contaminated soils for which the use of Gy's classical formula yielded such 'impossible' estimates of s^2(FSE) *larger* than empirical sampling variances by *several orders of magnitude*. This size-density class s2(FSE) variant now provides estimates for all cases and examples, which are systematically smaller than the empirical sampling variances, and thus in full accordance with the Theory of Sampling. This generalised approach is also applied with similar success to *controlled materials*, which were made to represent analyte-enriched and/or analyte-coated matrices, as used in recent studies on sampling bias and representativeness.

The results in our studies all show that it is not Gy's classical formula which was at fault when applied outside the traditional domains, e.g., to contaminated soils, it is that the critical assumptions behind the formula were broken, unwittingly, or worse, with blunt carelessness. In analyte-coated materials, or for mixed matrices, the original full size-density class-based formula now provides the proper starting point for developing TOS-compliant matrix-specific approaches on a much broader scale. With this new scope, analysts no longer must forego the revolutionary advantage of Gy's classical formula, i.e., the capacity to estimate the fundamental sampling variance *a priori*. Now, only at the cost of a pilot sampling stage, the augmented size-density class formula provides the analyst with the capacity to adapt sampling protocols also to the challenging task of taking on practically all natural systems *sesu lato*, however complex.

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