

# Theory of sampling (TOS)— fundamental definitions and concepts

Kim H. Esbensen<sup>a</sup> and Claas Wagner<sup>b</sup>

<sup>a</sup>Geological Survey of Denmark and Greenland (GEUS) and Aalborg University, Denmark. E-mail: [ke@geus.dk](mailto:ke@geus.dk)

<sup>b</sup>Sampling Consultant. E-mail: [cw@wagnerconsultants.com](mailto:cw@wagnerconsultants.com)

The Chinese sage Confucius is claimed to have stated: “Speak precisely—and wars can be avoided”



Photo Wikipedia

For the record, despite extensive searching with today's many internet facilities, we have been unable to confirm this attribution with certainty. Be that as it may, this is very powerful insight: this dictum addresses what is needed for effective communication, and for the relationship building thereupon and the meaning is clear: communication must at all costs avoid uncertainty, imprecision, vagueness in oral, written, technical, scientific communication. Exactly the same holds for those who want to communicate in science, technology and industry, especially concerning a topic that traditionally has been considered “difficult”—and of this claim there is probably only a very few better examples than the Theory of Sampling (TOS). It is crucially important to be able to speak with the outmost precision.

This second Sampling Column introduces the most important fundamental definitions and principles of the Theory of Sampling without which no rational understanding and appreciation can be established. We begin with a typology of *lot dimensionality*, a term defining both the geometrical dimensions as well as the effective number of dimensions involved in sampling.

Samples are extracted for various reasons, using many different sampling procedures in a wide range of application fields addressing a bewildering array of different material types. One would think that many potentially different sampling procedures would be needed. However, the main purpose of sampling is the same—to be able to extract a small mass of the target lot that is to be characterised (analysed), i.e. to obtain a sample, which accurately and precisely *represents* the lot (see definition below). Sample representativity is therefore the sole criterion that must be honoured in order to be able to draw valid conclusions about the characteristics of the original lot, while non-representative samples (termed “specimens” in TOS) will result in a risk of erroneous decisions and conclusions without any possibility of knowing to what degree this is the case.

The Theory of Sampling, the only fully comprehensive approach to representative sampling, allows a complete analysis of representativity regarding all sampling methods, procedures and equipment. Based on a set of scale-invariant sampling unit operations (SUO), TOS defines sampling as a multi-stage

process, allowing a complex sampling task to be broken down into its individual stages and to apply individual, or any required combination of, SUOs to be able to cover all sampling situations. TOS's sampling unit operations will be described in full detail in future sampling columns. TOS focuses on the sampling process and not the sample itself. Once extracted, there is no possibility to evaluate whether a *specific* sample is representative of the target lot, or not. The sampling process is the only guarantee for a representative sample. Disobeying or compromising TOS's principles will unavoidably lead to non-representative sampling procedures, which only will lead to “specimens” instead of “samples” (distinction to be fully defined).

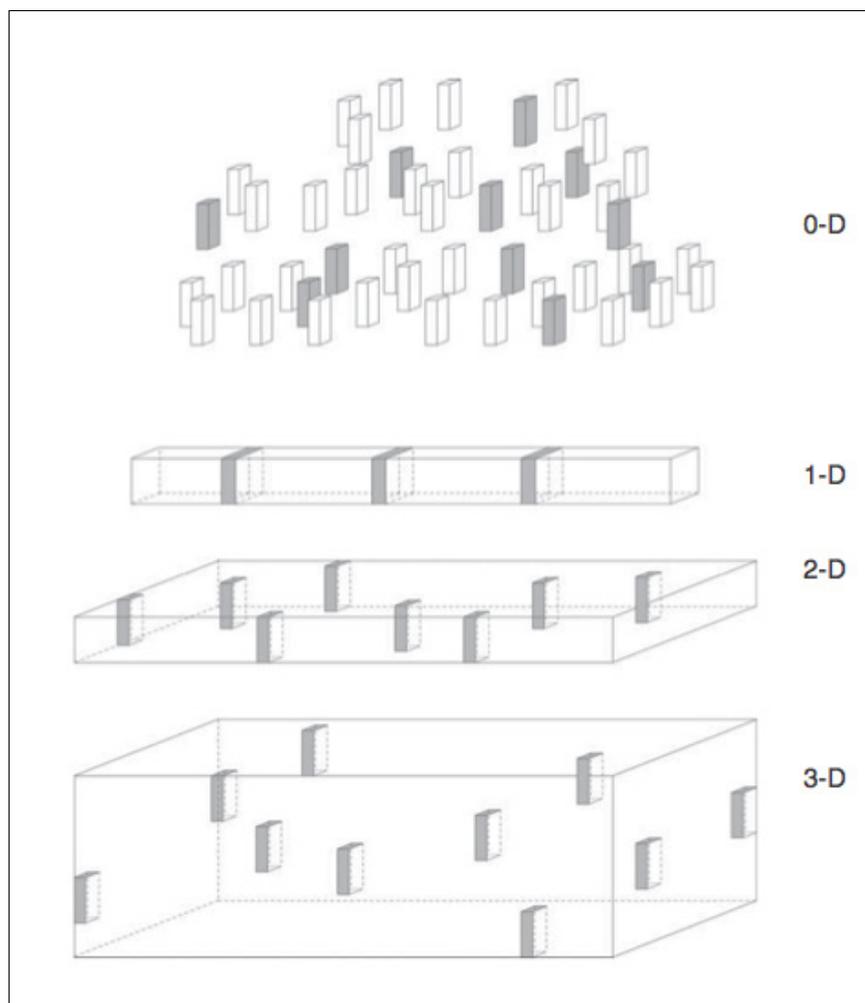
This column presents a fundamental set of TOS's terms and definitions without which it is not possible to fully understand, nor discuss TOS in a meaningful way.<sup>1</sup> It has been found convenient to start out by defining “lot dimensionality”.

## Lot dimensionality

Lot dimensionality is characterised by specifying the number of *effective* dimensions that need to be covered by the sampling process. This approach allows definition of one-, two- and three-dimensional (1-D, 2-D and 3-D) lots as well as the “zero-dimensional” (0-D) lot.<sup>2</sup> Figure 1 compares TOS's four cases of lot dimensionality.

The concept of lot dimensionality becomes clear, for example, when considering an elongated material stream, such as the case of dynam-

# SAMPLING COLUMN



**Figure 1.** Lot dimensionalities: 0-D, 1-D, 2-D and 3-D lots. Potential increments are marked in grey. Note how extracted increment can be made to cover the transverse dimensions only for 1-D and 2-D lots but not for 3-D lots. The special 0-D lot is defined in full in the text.

cally moving material on a conveyer belts (Figure 2). This lot can loosely be described as one-dimensional, since one dimension of the physical geometrical aspect dominates (the conveyer belt transportation direction). According to TOS, however, it is essential to consider how the specific sampling method applied is interacting with the *effective* number of dimensions during the sampling process. Employing grab sampling (extracting a single increment as the “sample”) on such an elongated material stream, which is a widely-applied but fundamentally-flawed extraction method, would in reality make this a 3-D lot *not* a 1-D lot, since grab samples are most likely only taken from the top surface part of the moving material flux,

and so are far from *covering* both the transverse lot dimensions fully (i.e. width and thickness). This “covering” aspect is a fundamental issue for TOS.

By contrast, a cross-stream cutter (a sampling device especially designed for elongated material fluxes, which shall be extensively illustrated in one of the future sampling columns) will cover the entire depth and width of the stream, thereby fully reducing the sampling lot to one dimension, i.e. the longitudinal dimension of the material stream. See Figure 2 for clarification of the practical aspect of lot dimensionality definition.

According to the TOS, 1-D lots represent the *optimal* sampling situation, preferred over 2-D and 3-D lots (e.g., industrial, geological or environmental

strata, stacks, stockpiles, silos) which should, wherever possible, be transformed to comply with a 1-D sampling situation. In practice, this is often possible by locating a situation where the lot already is in transport. Sometimes even original 0-D lots are also transformed into the desired 1-D configuration, because this offers unbeatable optimal sampling conditions (later column). Lot dimensionality transformation constitutes one of the governing principles (GPs) of the TOS.

The reason for being this specific about lot dimensionality is the inherent (complex) heterogeneity of all naturally-occurring materials, which makes sampling far from a trivial materials handling issue. Proper understanding of the heterogeneity phenomenon, its influence on the sampling correctness and, most importantly, how heterogeneity can be counteracted in the sampling process require a certain level of knowledge. The purpose of the Sampling Columns is to gradually build up this knowledge. The first instalment of definitions follows.

## Sampling terminology— the tower of Babel

### Lot

The complete entity of the original material being subject to sampling, e.g. truck load, railroad car, process stream, ship’s cargo, batch etc. The lot (also termed the sampling target or decision unit) refers both to the physical, geometrical form and size, as well as the material characteristics of the material being subject to sampling.

### Heterogeneity

Heterogeneity is the prime characterisation of all naturally occurring materials, including industrial lots. Heterogeneity manifests itself at all scales related to sampling for nearly all lot and material types. The only exception is uniform materials,<sup>3</sup> which are such a rare example that no generalisation about them with respect to sampling can be made here. TOS differentiates between two types of heterogeneity, one concerning the spatial distribution (distributional heterogeneity, DH) of the target material and one

# SAMPLING COLUMN



**Figure 2.** Lot dimensionality. Upper left: 1-D lot; right: 2-D lot; lower left: 3-D lot. TOS outlines that the principles behind representative sampling are scale-invariant (see text).

referring to the compositional differences between the individual “units” of the target material (compositional heterogeneity, CH). The next sampling column will deal extensively with these two types of heterogeneity.

### Sample

Correctly extracted material from the lot, which can only originate from an unbiased, representative sampling process. The term sample should always only be used in this qualified sense of “representative sample”. If there is doubt as to this characteristic, the term “specimen” (see below) should be used instead.

### Specimen

A “sample” that cannot be documented to be the end result of a bona fide representative sampling process. It is not possible to ascertain the representativity status of any isolated small part of

a sampling target by itself. It is only the *sampling process*, which can be termed representative or not.

### Correct sampling

TOS uses this term to denote that efforts have been executed, that has resulted in successful elimination of the so-called “bias-generating errors”, a.k.a. the Incorrect Sampling Errors (ISE). Incorrect sampling errors will be discussed more in one a future sampling column.

### Representativeness

Representativeness implies both correctness as well as a sufficiently small sampling reproducibility (sampling variance).

### Sampling bias

Systematic deviation between the average analytical sampling result and the true lot concentration, a.k.a. *accuracy*.

Elimination of the sampling bias is the first obligation for any sampling process in order to be correct.

### Reproducibility

Sampling variance, after removal of sampling bias, a.k.a. imprecision.

### Increment

Correctly delineated, materialised unit of the lot which, when combined with other increments, provides a multi-increment sample. This procedure is termed “composite sampling” in TOS, with the result being a “composite sample”.

### Composite sample

Aggregation of several increments, the number of which is designated as  $Q$ . A composite sample represents “physical averaging”, as opposed to arithmetic averaging of analytical results from individual increments.

# SAMPLING COLUMN

## Sub-sample

Correctly mass-reduced part of sample (primary, secondary...). A sub-sample is a result from a dissociative (disaggregation) process; a composite sample is a result from an integrative process.

## Fragment

Fragment refers to the smallest separable unit of the material that is not affected by the sampling process itself (e.g. particles, grains etc.). By naming the smallest unit-of-interest a *fragment*, TOS is also able to treat the situation in which the sampling process results in fragmentation of some of the original units.

## Group

A number of spatially correlated fragments, which act as a coherent unit (increment) during sampling operations. In practical sampling, the only group of interest is the actual increment being extracted, i.e. the material in the

sampling tool. The group size depends on the sampling tool (mass/volume) and the sampling process as well as how the tool is implemented and operated.

## Scale

The principles described by TOS are *scale-invariant*, i.e. the same principles apply to all relevant scales and stages in the sampling pathway (lot, sample, sub-sample).

## Zero-dimensional lot (0-D lot)

The 0-D lot is characterised by displaying no internal correlations between all potential increments, thus opening up for relatively easy practical sampling. A 0-D lot can be manipulated—at least in principle—for example, by mixing or direct *in toto* splitting, the work necessary may vary significantly as a function of the lot mass,  $M_L$ , but also by of other relevant features, e.g. stickiness, irregular fragment forms.

For a full set of necessary and sufficient definitions, referral is made to the horizontal sampling standard *DS 3077* (2013).<sup>4</sup>

## Notes and references

1. Currently there is a debate on "Alternatives to Gy's Sampling Theory?" on LinkedIn. This is a good example of the critical need for precise speaking. We shall return to this discussion in these columns but, significantly, after all the necessary basic concepts, definitions and principles have been properly introduced.
2. The special case of a zero-dimensional lot refers to a lot that can be effectively, mixed, moved and sampled throughout with complete correctness. Usually these are small lots, which can easily be manipulated. A full definition of the 0-D lot is given in the definition section of this sampling column.
3. Uniform materials: Materials with a repeated (correct) sampling reproducibility lower than 2%. Such materials do not occur naturally (exception gasses and infinitely diluted solutions etc.).
4. *Representative Sampling—Horizontal Standard*. Danish Standards DS 3077 (2013). [www.ds.dk](http://www.ds.dk)

continued from page 17

2. S. Cotton, *Lanthanide and Actinide Chemistry* (2<sup>nd</sup> Edition). Wiley, Chichester (2006).
3. A.Y. Vasiliev and M. Sidorov (Eds), *Uranium: Characteristics, Occurrence, and Human Exposure*. Nova Science Publishers, Hauppauge, NY (2012).
4. E. Faulques, R.E. Russo and D.L. Perry, "Raman spectral studies of uranyl sulfate and its urea complex structural isomers", *Spectrochim. Acta A* **49**, 975–983 (1993). doi: [http://dx.doi.org/10.1016/0584-8539\(93\)80216-W](http://dx.doi.org/10.1016/0584-8539(93)80216-W)
5. E. Faulques, R.E. Russo and D.L. Perry, "Raman studies of uranyl nitrate and its hydroxy bridged dimer", *Spectrochim. Acta A* **50**, 757–763 (1994). doi: [http://dx.doi.org/10.1016/0584-8539\(94\)80013-8](http://dx.doi.org/10.1016/0584-8539(94)80013-8)
6. T.R. Ravindran and A.K. Arora, "Study of Raman spectra of uranium using a surface-enhanced Raman scattering technique", *J. Raman Spectrosc.* **42**, 885–887 (2011). doi: <http://dx.doi.org/10.1002/jrs.2926>
7. R.L. Frost, J. Cejka and M.L. Weier, "Raman spectroscopic study of the uranyl oxyhydroxide hydrates: becquerelite, billietite, curite, schoepite, and vandendriess-cheite", *J. Raman Spectrosc.* **38**, 460–466 (2007). doi: <http://dx.doi.org/10.1002/jrs.1669>
8. G. Guimbretiere, A. Canizares, P. Simon, Y.A. Tobon-Correa, M.R. Ammar, C. Corbel and M.F. Barthe, "In-situ Raman observation of uranium dioxide weathering exposed to water radiolysis", *Spectrosc. Lett.* **44**, 570–573 (2011). doi: <http://dx.doi.org/10.1080/00387010.2011.610857>
9. P.C. Burns, "U<sup>6+</sup> minerals and inorganic compounds: insights into an expanded structural hierarchy of crystal structures", *Can. Mineral.* **43**, 1839–1894 (2005). doi: <http://dx.doi.org/10.2113/gscan-min.43.6.1839>
10. R.L. Frost, "An infrared and Raman spectroscopic study of the uranyl micas", *Spectrochim. Acta A* **60**, 1469–1480 (2004). doi: <http://dx.doi.org/10.1016/j.saa.2003.08.013>
11. N. Sanchez-Pastor, A.J. Pinto, J.M. Astilleros, L. Fernandez-Diaz and M.A. Goncalves, "Raman spectroscopic characterization of a synthetic, non-stoichiometric Cu-Ba uranyl phosphate", *Spectrochim. Acta A* **113**, 196–202 (2013). doi: <http://dx.doi.org/10.1016/j.saa.2013.03.094>
12. R.L. Frost, J. Cejka and G. Ayoko, "Raman spectroscopy study of the uranyl phosphate minerals phosphuranylite and yingjiangite", *J. Raman Spectrosc.* **39**, 495–502 (2008). doi: <http://dx.doi.org/10.1002/jrs.1868>
13. R.J.P. Driscoll, D. Wolverson, J.M. Mitchels, J.M. Skelton, S.C. Parker, M. Molinari, I. Khan, D. Geeson and G.C. Allen, "A Raman spectroscopic study of uranyl minerals from Cornwall, UK", *RSC Adv.* **4**, 59137–59149 (2014). doi: <http://dx.doi.org/10.1039/C4RA09361E>
14. <http://rruff.info/Metauranocircite/R070721> and <http://rruff.info/Metauranocircite/lbidem/Saleeite;lbidem/Ulrichite>
15. G. Meinrath, S. Lisc, Z. Strylad and C. Noubactep, "Lifetime and fluorescence quantum yield of uranium(VI) species in hydrolyzed solutions", *J. Alloy. Compd.* **300–301**, 107–112 (2000). doi: [http://dx.doi.org/10.1016/S0925-8388\(99\)00739-2](http://dx.doi.org/10.1016/S0925-8388(99)00739-2)
16. J.B.M. Novo, F.R. Batista, C.J. da Cunha, L.C. Dias, Jr, and F.B.T. Pessine, "Time-resolved studies in hydrogen uranyl phosphate intercalated with amines", *J. Lumin.* **124**, 133–139 (2007). doi: <http://dx.doi.org/10.1016/j.jlumin.2006.02.009>
17. S.J. Formosinho, H.D. Burrows, M.Da Graca Miguel, M.E.D.G. Azenha, I.M. Saraiva, A.C.D.N. Ribeiro, I.V. Khudyakov, R.G. Gasanov, M. Bolte and M. Sarakha, "Deactivation processes of the lowest excited state of [UO<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> in aqueous solution", *Photochem. Photobiol. Sci.* **2**, 569–575 (2003). doi: <http://dx.doi.org/10.1039/B300346A>
18. E. Hashem, J.A. Platts, F. Hartl, G. Lorusso I.M. Evangelisti, C. Schulzke and R.J. Baker, "Thiocyanate complexes of uranium in multiple oxidation states: a combined structural, magnetic, spectroscopic, spectroelectrochemical, and theoretical study", *Inorg. Chem.* **53**, 8624–8637 (2014). doi: <http://dx.doi.org/10.1021/ic501236j>
19. M. Mohapatra, B. Rajeswari, R.M. Kadam, M. Kumar, T.K. Seshagiri, N.K. Porwal, S.V. Godbole and V. Natarajan, "Investigation of uranium luminescence in SrB<sub>4</sub>O<sub>7</sub> matrix by time resolved photoluminescence, thermally stimulated luminescence and electron spin resonance spectroscopy", *J. Alloy. Compd.* **611**, 74–81 (2014). doi: <http://dx.doi.org/10.1016/j.jallcom.2014.05.096>
20. S. Tsumihama, C. Gotz and K.F. Dr, "Photoluminescence of uranium(VI): quenching mechanisms and role of uranium(V)," *Chem. Eur. J.* **16**, 8029–8033 (2010). doi: <http://dx.doi.org/10.1002/chem.201000408>