## Theory and Practice of Sampling of Heterogeneous Materials and Processes (TOS)

## (3-day comprehensive course)

A set of six Governing Principles (GP) and four Sampling Unit Operations (SUO) cover all practical aspects of sampling and provides a comprehensive framework for scientists (academic staff, Ph.D. students), process engineers, process operators, laboratory and industry personnel, including the critical issue of securing that all of primary sampling, splitting, sub-sampling and sample preparation is fully <u>representative</u> (procedures, equipment, maintenance). This 3day course provides a comprehensive introduction to the Theory of Sampling (TOS) for <u>stationary lots</u> as well as dynamic <u>process lots</u>. The course outlines the critical connections to process engineering, Process Analytical Technologies (PAT) and to multivariate data analysis (chemometrics).

The common characteristic of all naturally occurring, technological and industrial materials and processes is heterogeneity (raw materials, food, feed, rocks, alloys, mineralisations, ores, concentrates, environmental samples, mixtures and aggregates, interim and final process and manufacturing products), which have a much more complex spatial distribution that what can be encompassed by classical statistics. A lot cannot be view as but a collection of analytical results. TOS provides a rational description of lot heterogeneity and all sampling error types involved in sampling of heterogeneous materials and processes - as well as all necessary tools for their evaluation, elimination and/or minimisation. This course presents a comprehensive introduction to the basic principles of the Theory of Sampling (TOS), sufficient to understand how sampling errors influence the full lot-to-analysis pathway by adding significantly to the total measurement uncertainty. TOS provide professional competence on how to identify faulty, inefficient or suboptimal sampling procedures and equipment – and offers the necessary tools for rational sampling. The principles of TOS are generic and applies to all materials and lot types, at all locations and at all scales: A set of six Governing Principles (GP) and four Sampling Unit Operations (SUO) cover all practical aspects of representative sampling and provides a comprehensive toolbox for field personal, process engineers, laboratory personnel, quality units as well as management who has to make critical decisions about process status, product specification, laboratory sample adequacy and many other attributes based on valid analytical results. Sampling understanding is also of critical importance for those in management who are responsible for the bottom line.

The *sampling bias* has a fundamentally different nature than the analytical bias, unfortunately negating all attempts of 'bias-correction' in sampling. Instead TOS provides a set of practical ways to achieve "sampling correctness" (unbiasedness) by informed understanding, design and application to the generic *sampling process*. The course overview gives full insight into how to guarantee that all primary sampling, and subsequent sub-sampling (splitting) and sample preparation before analysis is documentable as representative (procedures, equipment, maintenance). After the critical primary sampling step, correct (unbiased) mass reduction (splitting) in the subsequent sub-sampling in the laboratory also needs to be 100% compliant with TOS in order to ensure <u>valid</u> analysis analytical results. It is often unknown, or is wilfully neglected, that the Total Sampling Error (TSE) is by far the dominating contribution to the total Measurement Uncertainty (MU), 10-25 X *larger* than the Total Analytical Error (TAE).

This course provides a comprehensive overview of the Theory of Sampling (TOS) for *stationary lots* as well as *process lots* and has a special focus on setting up experiments to characterise lot heterogeneity (replication experiments and variographic experiments), and how to use variographic analysis for process understanding and total process system measurement system validation.



## Literature documentation

The course includes a comprehensive literature documentation, including the world's first standard dedicated exclusively to representative sampling, DS 3077 (2013) <u>https://webshop.ds.dk/da-dk/standard/ds-30772013</u>

Esbensen, K.H. & Julius, L. (2013) "DS 3077 Horizontal—a new standard for representative sampling. Design, history and acknowledgements", NIR news 24, 8, p. 16–19.

Esbensen, K.H. (2015) *Materials Properties: Heterogeneity and Appropriate Sampling Modes*. J. AOAC Int. vol. 98, pp. 269-274. http://dx.doi.org/10.5740/jaoacint.14-234

Esbensen, K.H., Wagner, C. (2014). Theory of Sampling (TOS) vs. Measurement Uncertainty (MU) – a call for integration. Trends in Analytical Chemistry (TrAC) vol 57, 93-106.

Esbensen, K.H. & Julius, L.P. (2009). Representative sampling, data quality, validation – a necessary trinity in chemometrics. *in* Brown, S, Tauler, R, Walczak, R (Eds.) COMPREHENSIVE CHEMOMETRICS, Wiley Major Reference Works, vol. 4, pp.1-20. Oxford: Elsevier

Petersen, L, C. Dahl, K.H. Esbensen (2004). Representative mass reduction in sampling – a critical survey of techniques and hardware. *Chemometrics and Intelligent Laboratory Systems*, vol. 74, Issue 1, p. 95-114

Esbensen, K.H. & Mortensen, P. (2010). Process Sampling (Theory of Sampling, TOS) – the Missing Link in Process Analytical Technology (PAT). <u>in</u> Bakeev, K. A. (Ed.) Process Analytical Technology. 2.nd Edition. pp. 37-80. Wiley. ISBN 978-0-470-72207-7

Minnitt, R.C.A. & Esbensen, K.H. (2017) Pierre Gy's development of the Theory of Sampling: a retrospective summary with a didactic tutorial on quantitative sampling of one-dimensional lots. TOS Forum **7**, p. 7-19. doi: 10.1255/tosf.96

Esbensen, K.H. Paoletti, C, Theix, N. (2015) (Eds) Journal AOAC International, Special Guest Editor Section (SGE): Sampling for Food and Feed Materials. pp. 249-320 <u>http://ingentaconnect.com/content/aoac/jaoac/2015/00000098/00000002</u>

The REPLICATION EXPERIMENT (RE). https://www.spectroscopyeurope.com/system/files/pdf/Sampling%2028-1.pdf

Esbensen, K.H, Geladi, P. & Larsen, A. (2013). *Mythbusters in Chemometrics, 5: The replication Myth - 1*. NIR news, 24, 1. p. 18-20

Esbensen, K.H, Geladi, P. & Larsen, A. (2013). *Mythbusters in Chemometrics, 6: The replication Myth – 2: Quantifying empirical sampling plus analysis variability.* NIR news, 24, 3. p. 15-17

Esbensen, K.H., Paoletti, C. & Minkkinen, P. (2012). Representative sampling of large kernel lots – I. Theory of Sampling and variographic analysis. Trends in Analytical Chemistry (TrAC), <u>32</u> pp.154-165

Minkkinen, P., Esbensen, K.H. & Paoletti, C. (2012). Representative sampling of large kernel lots – II. Application to soybean sampling for GMO control. Trends in Analytical Chemistry (TrAC), 32 pp. 166-178

Esbensen, K.H., Paoletti, C. & Minkkinen, P. (2012). Representative sampling of large kernel lots – III. General considerations on sampling heterogeneous materials. Trends in Analytical Chemistry (TrAC), <u>32</u> pp. 179-184