Practical Applications of Sampling Theory

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Analytical determination is usually a multistep process, which may contain several sample and sample preparation steps. It is also an error generating process where each step generates its own error component. The errors may be *random* or *systematic*. When the overall reliability of an analytical determination is estimated the variances (squared errors) of the individual error generating steps of the *whole* analytical process are additive and, consequently, the weakest link in practice determines the overall quality of the result. Sampling and the probable error components generated by doing it cannot be neglected, therefore, when optimal analytical strategy for a given determination is considered. The optimum analytical strategy, and the error components to be considered, depend on the purpose of the determination, *i.e.*, whether point estimates of the concentration at sampling locations or a general description (average) of the lot is what is needed. The aim of chemometric methods is to interpret chemical and analytical data. Therefore, the reliability of chemometrics also depends on the quality on analytical results – and ultimately on the quality of sampling

An advanced sampling theory for analytical purposes has been developed by Pierre Gy [1, 2, 3], but is not very well known yet by analytical chemist and chemical metrologists. A short introduction to Gy's theory is given by Smith [4]. Too often sampling plans are made without the help of the sampling theory. This concerns both industrial and process analytical problems and large national campaigns, when, e.g., the overall state of the quality river and lake waters is evaluated or the intake of chemical constituents in daily diets is estimated. By using sampling theory it often possible to cut down the assay cost and to improve the reliability of the results.

The sampling theory exists. The lecture will show how this theory can be used in practice:

- To audit existing sampling flow-sheets
- To design and evaluate new analytical laboratory methods for solid samples
- To evaluate the reliability of time series measurements
- To design cost-optimal sampling and analytical procedures

1. Gy, P., *Sampling of particulate materials, Theory and practice*, Developments in Geomathematics 4, Elsevier, New York, 1982.
2. Gy, P., Sampling of heterogeneous and dynamic material systems, Theories on heterogeneity, sampling and homogenizing, Elsevier, Amsterdam, 1992.
3. Gy, P. Sampling for Analytical Purposes, Wiley, New York, 1998.
4. Patricia L. Smith, *A Primer for Sampling Solids, Liquids, and Gases: Based on the Seven Sampling Errors of Pierre* Gy, ASA-SIAM Series on Statistics and Applied Probability 8, Philadelphia, 2001.