T14. Comparison of independent process analytical measurements — a variographic study

Pentti Minkkinen
Lappeenranta University of Technology, Finland

Process analytical measurements can be based on samples cut from the process streams and analyzed in the laboratory. On-line and in line process analyzers and sensors are nowadays widely used to control and monitor chemical processes. Process analyzers need regular checking and updating of their calibration and all analytical systems should also go through proficiency testing which sometimes are mandatory. Both the calibration check and proficiency tests provide independent measurement sets from the same target. There are two main reasons which make comparisons of the mean values of independent measurements difficult. One is weighting error [1], which can cause systematic errors, if the flow-rate varies and correlates with the analyte concentration. To eliminate this error source the mean of the measurement set should be calculated as weighted mean by using flow-rates of sampling time as weights. Weighting error is the reason why often the mean estimated by process analyzers and by laboratory measurements do not agree.

Another reason is that the process data are often autocorrelated. In this case the standard deviation of the mean of the measurement set depends on sampling mode: whether *random*, *stratified* or *systematic* sample selection is used. Consequently, the statistics based on the assumption on normality cannot be used to estimate the uncertainty of the mean. Instead some form of chronostatistics has to be used. Pierre Gy has developed a variographic technique [2, 3] especially process analytical measurements in mind. Variography is a practical tool for characterizing the process heterogeneity. It also provides variance estimates for the different sampling modes for different sample intervals (lags) which take into account the effect of autocorrelation. The method is elucidated by using real and simulated data sets. The simulations are also based on real data sets.

References:

1. Minkkinen, P., Weighting Error — Is it Significant in Process Analysis?, WCBS3 Conference Proc., Publ. Ser. Fundacão Luis Englert 1/2007, 59-68
2. Gy, P.M., *Sampling of Heterogeneous and Dynamic Material Systems*, Elsevier, Amsterdam, 1992
3. Pitard, F.F., Pierre *Gy's sampling theory and sampling practice* (2nd edn.), CRC Press LLC: Boca Raton, USA, 1993