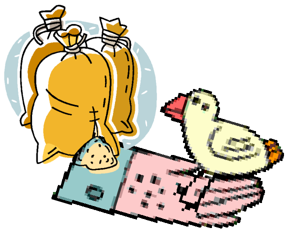
Sampling Uncertainty and Uncertainty for Compliance Assessment, Berlin15-16 April, 2008

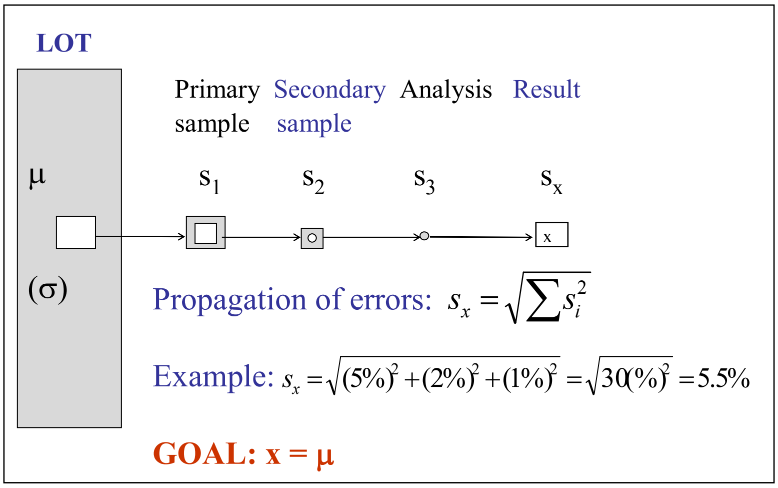
Uncertainty from Sampling Animal Feed: Applications of Fundamental Sampling Error Model



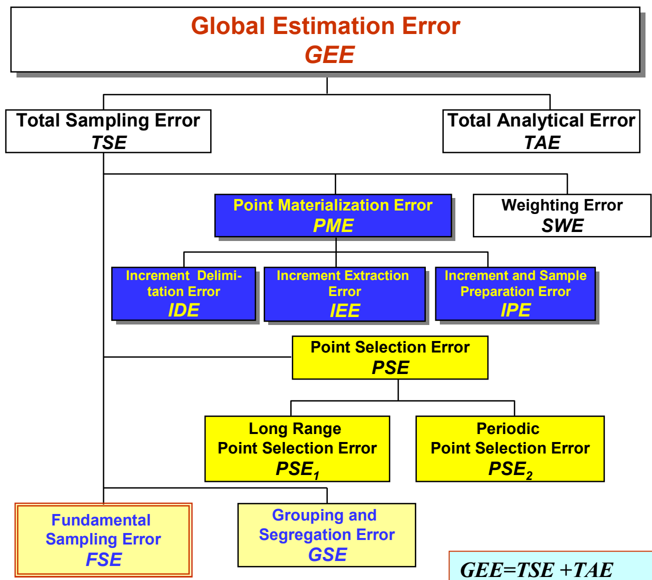
Pentti Minkkinen
Lappeenranta University of Technology
e-mail: Pentti.Minkkinen@lut.fi

Outline

- Sources of sampling error
- Definition of Fundamental Sampling Error (*FSE*)
- Estimation of sampling uncertainty based on *FSE* calculations
- Design and optimization of sampling procedures



Analytical process usually contains several sampling and sample preparation steps

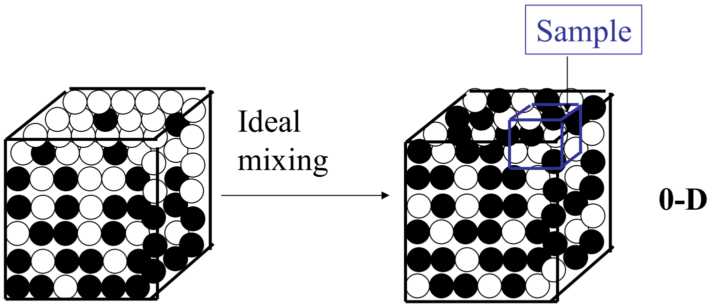


GEE=TSE +TAE

TSE= (PSE+FSE+GSE)+(IDE+IEE+IPE)+SWE

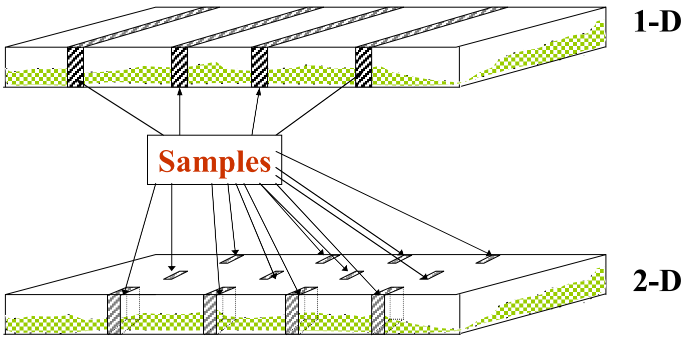
Error components of analytical determination according to P. Gy

Dimensionality of sampling targets (lots)



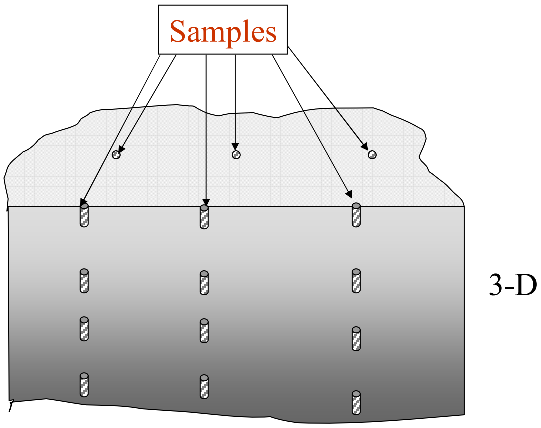
Sampling target 0-dimensional, if
1) The whole target can be taken as the sample
2) If the lot to be sampled can be mixed before sampling it can be *treated* as a 0-dimensional lot.

Fundamental Sampling Error determines the *correct sampling error* of 0-D targets **and it can be estimated by using binomial or Poisson distributions as models, or by using Gy's fundamental sampling error equations.**



If the lot cannot be mixed before sampling the dimensionality of the lot depends on how the samples are delimited and cut from the lot. Auto-correlation has to be taken into account in sampling error estimation.

***PSE* is likely the dominating sampling error component.**



Lot is 3-dimensional, if none of the dimensions is completely included in the sample.
***PSE* is likely the dominating sampling error component.**

Fundamental sampling error, *FSE*

- The component of sampling error caused by random variation in an ideally mixed material consisting of different kind of particles, i.e., *the error of ideal sampling process.*
- *FSE* is the only sampling error component that cannot be completely eliminated.
- *FSE* is function of the number of the analyte particles in the sample.
- *FSE* can be used as the *TSE* estimate *only* for 0-dimensional sampling targets

P. Gy's Fundamental Sampling Error Model

Sampling constant

Nominal particle size (95 % top size)

$$\sigma_r^2 = Cd^3\left(\frac{1}{M_S} - \frac{1}{M_L}\right)$$

.. Relative variance of *FSE*

Lot size

Sample size

Simplifies to $\sigma_r^2 \approx \dfrac{Cd^3}{M_s}$ if $M_s << M_L$

where $\sigma_r = \dfrac{\sigma_a}{a_L}$ = relative standard deviation

a_L = average concentration of the analyte in the lot

SAMPLING CONSTANT *C*

$$C = f \cdot g \cdot \beta \cdot c$$

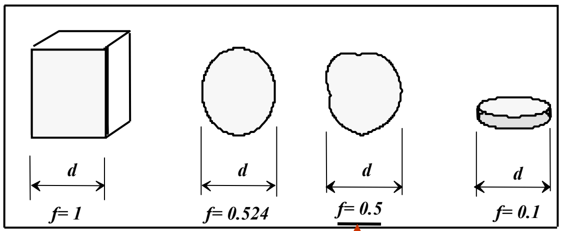
composition factor

liberation factor

size distribution factor

shape factor

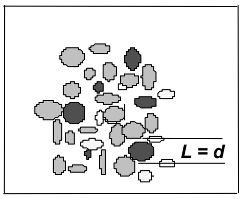
Estimation of the *shape factor, f*

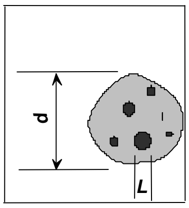


default in most cases

If the particle has a nominal particle size *d* which is equal to side length of a cube, its shape factor is the ratio of their volumes

Estimation of the *liberation factor, β,* for liberated and non-liberated particles





$\beta = 1$

$$\beta = \left(\tfrac{L}{d}\right)^x$$

Current proposals: $x = 0.5...1.5$ ($probably \approx 3$)

After grinding below liberation size, *L*: $\beta_{\max} = 1$

Estimation of size distribution factor, g

Approximate estimation:

Wide size distribution	($d/d_{0.05} > 4$) **default**	$\mathbf{g = 0.25}$
Medium distribution	($d/d_{0.05} = 4...2$)	$g = 0.50$
Narrow distribution	($1 < d/d_{0.05} < 2$)	$g = 0.75$
Identical particles	($d/d_{0.05} = 1$)	$g = 1.00$

Calculation of g if complete size distribution is measured:

$$g = \sum_i \left(\frac{d_i}{d}\right)^3 a_i$$

d_i = particle size in class i, d = 95% cut-off value of the size distribution, a_i = mass fraction for size class i

Estimation of constitution factor, c

density of critical particles

average concentration of the lot

$$\boxed{c = \frac{\left(1 - \frac{a_L}{\alpha}\right)^2}{\frac{a_L}{\alpha}} \rho_c + \left(1 - \frac{a_L}{\alpha}\right) \rho_m}$$

density of matrix

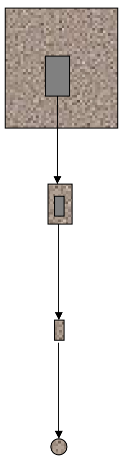
concentration of determinand in critical particles

Example:

A chicken feed (density = 0.67 g/cm^3) contains as an average 0.05 % of an enzyme powder that has a density of 1.08 g/cm^3. The size distribution of the enzyme particle size d =1.00 mm and the size range factor g = 0.5 could be estimated.

Estimate the fundamental sampling error for the following analytical procedure:
First a 500 g sample is taken from a 25 kg bag. This sample is ground to a particle size -0.5 mm. Then the enzyme is extracted from a 2 g sample by using a proper solvent and the concentration is determined by using liquid chromatography.

The relative standard deviation of the chromatographic measurement is 5 %.



M_L =25000 g; $d = L$=1 mm
ρ_c = 1.08 g/cm^3 ; α = 100 % ; $\beta = 1$
ρ_m = 0.67 g/cm^3 ; a_L = 0.05 % ; f = 0.5
c =2160 g/cm^3

d_1 = 1 mm; M_{S1} = 500 g ; M_{L1} =25000 g; g_1 = 0.5;
C_1 = 540 g/cm^3
➔ s_{r1} = 0.033 =3.3 % (primary sample)

d_2 = 0.5 mm; M_{S2} =2 g ; M_{L2} =500 g; g_2 = 0.25;
C_1 = 270 g/cm^3
➔ s_{r2} = 0.13 =13 % (secondary sample)

s_{r3} = 0.05 = 5 % (analysis)

Total relative standard deviation:

$$s_t = \sqrt{\sum s_{ri}^2} = 0.143 = 14.3\ \%$$

Optimising the sampling plan

The weakest link of the measurement chain is the secondary sampling. It can be improved by grinding the material finer. If the target relative standard deviation for this step is set to 3 %, solving the maximum particle size from Gy equation gives, d_2 = 0,189 mm.

This plan gives the following result

1) PRIMARY SAMPLE: M_{s1} = 500 g, d_1 = 1 mm, s_{r1} = 3.3 %
2) SECONDARY SAMPLE: M_{s2} = 500 g, d_2 = 1 mm, s_{r2} = 3.0 %
3) ANALYSIS: s_a = 5.0 %

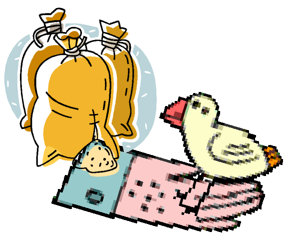
TOTAL RELATIVE STANDARD DEVIATION s_{tot} = 6.7 %

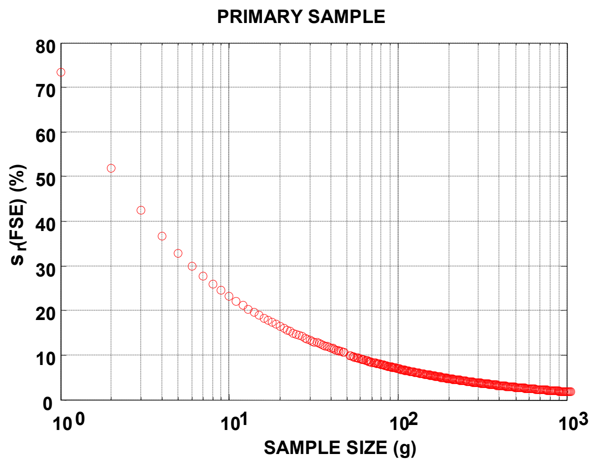
The expanded uncertainty from *FSE* is $U_r = 2\, s_{tot}$ = 13.4 %

NOTE: *FSE* gives realistic results only if ALL sampling steps are carried out by using correct devices and procedures (e.g. rotating sample splitters or correctly designed riffles).

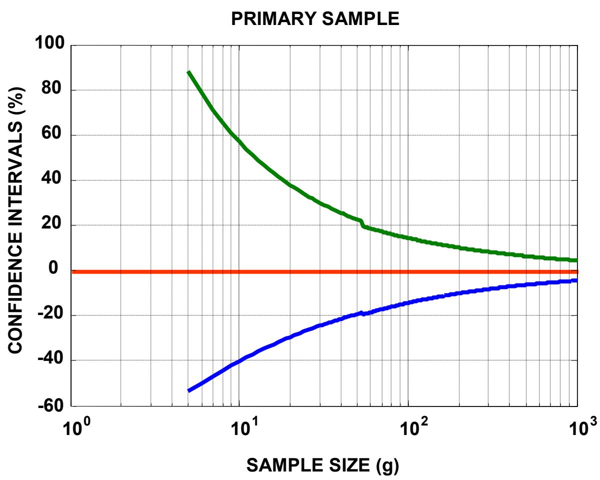
Implications

- Does direct blending and mixing provide a good product?
- Consider the end-user's sampling error as function of the sample size.





Relative standard deviation of *FSE* in primary sampling of the animal feed for enzyme content as function of the sample size



Approximate relative 95 % confidence intervals of the nominal enzyme content as function of the sample size based on *FSE* calculations for the primary sample

Nominal amount of enzyme and its 95 % confidence intervals for some selected sample sizes

Sample mass (g)	Enzyme mass (mg)	Lower bound (mg)	Upper bound (mg)
5	2.5	1.16	4.70
10	5.0	2.99	7.85
15	7.5	4.98	10.9
20	10.0	7.04	13.8

Uses of Gy's fundamental sampling error model

1. s_r of a given sample size:

$$s_r = \sqrt{C\,d^3\left(\frac{1}{M_s} - \frac{1}{M_L}\right)} \approx \sqrt{\frac{C\,d^3}{M_s}} \quad if\ M_s << M_L$$

2. Minimum M_s for a required s_r:

$$M_s = \frac{C\,d^3}{s_r^2 + \frac{C\,d^3}{M_L}} \approx \frac{C\,d^3}{s_r^2} \quad if\ M_s << M_L$$

Uses of Gy's fundamental sampling error model (continued)

3. Maximum d for given M_s and s_r

a) liberated material or material ground below the liberation size

$$d = \sqrt[3]{\frac{s_r^2}{f\,g\,c\left(\frac{1}{M_S}-\frac{1}{M_L}\right)}} \approx \sqrt[3]{\frac{M_s s_r^2}{f\,g\,c}} \quad \text{if } M_s << M_s$$

b) non-liberated material ground above the liberation size, L

$$d = \left(\frac{s_r^2}{f\,g\,c\sqrt{L}\left(\frac{1}{M_S}-\frac{1}{M_L}\right)}\right)^{\frac{1}{3-x}} \approx \left(\frac{M_s s_r^2}{f\,g\,c\sqrt{L}}\right)^{\frac{1}{3-x}}$$

assuming that $\beta = \left(\frac{L}{d}\right)^x$

4. Audit and design of multi-step sampling procedures

References

[1] P.M.Gy, *Sampling of Particulate Materials, Theory and Practice*, Elsevier, Amsterdam, 1982.
[2] P.M.Gy, *Sampling of Heterogeneous and Dynamic Material Systems*, Elsevier, Amsterdam, 1992.
[3] P.M. Gy, *Sampling for Analytical Purposes*, John Wiley & Sons Ltd, Chichester, 1998.
[4] F.F. Pitard, Pierre Gy's *Sampling Theory and Sampling Practice,* CRC Press, Boca Raton, Second Edition, 1993.
[6] P. Minkkinen, Practical Applications of Sampling Theory, *Chemom. Intell. Lab. Syst.*, **74** (2004) 85-94.
[7] L.Petersen & K.H. Esbensen, Representative process sampling for reliable data analysis - a tutorial, *J. Chemometrics*, **19** (2006) 625-647.
[8] L. Petersen, P. Minkkinen and K. H. Esbensen, Representative Sampling for reliable data analysis: Theory of Sampling, *Chemom. Intell. Lab. Syst.*, **77** (2005) 261-277.

DANKE SCHÖN,
THANK YOU,
kiitos, tack, tak, dekuji, merci, gracias, obrigado, grazie, teşekkür ederim, sukran