

# Estimation of the sampling variance of fragments cut from solid materials containing analyte as embedded nuggets

P. Minkkinen

Lappeenranta-Lahti University of Technology, Finland

If particles of interest (nuggets) are randomly distributed in a solid matrix the number of nuggets in fragments originating from that material are also randomly distributed. If the size distribution of nuggets is known, the mass variance and number variance of the nuggets as a function of sample mass can be theoretically estimated, provided that the nuggets are randomly distributed within the matrix. In industrial processes where the products are made by granulating mixtures of powders, comparison of the observed to theoretical variances can be utilised in quality control. In natural materials the distribution of the particles or nuggets in the matrix is not normally known and the distribution of the target analyte may be negatively skewed (mainly for bulk commodities), normal for alumina and coal, or lognormal for precious and base metals. Irrespective of the distribution, experimental results give nominal values for the size and number of nuggets embedded in analysed samples. The nominal results are specific to the fragment sizes and material studied. This paper shows how these experimental results can be utilised.

## INTRODUCTION

Many materials, natural and industrial, consist of target analyte as nuggets (particles) embedded in continuous matrix. In mineral industries materials are crushed to separate the valuable component embedded in matrix materials. In many industries, e.g., production of pharmaceuticals, food, fertilisers, animal feed; also in mineral and metallurgical processes, powders and particles are mixed and granulated either to produce intermediate or final products. The processes are controlled based on analytical results which include sampling errors – usually the largest error component of the whole analytical procedure. To optimise the sampling protocols, it is important that sampling errors can be estimated and minimised. That is especially important when modern in-line process analysers are used. Most of the analysers get information off a small volume from the surface of the target. While the frequency of measurements can be high, the actual sample size is thus very small.

Pierre Gy gave his first international presentation of his sampling theory at a conference in Germany (Gy, 1955). At that time calculations were time-consuming as they were manual, at best with mechanical calculators. Gy wanted to provide a quick method to enable a reasonable estimate for the sampling variance of particulate materials embedded in continuous matrix. Making several simplifying assumptions he presented an equation that later became known as the 'Gy Equation' [1]:

$$s_r^2 = C d^3 \left( \frac{1}{m_s} - \frac{1}{m_L} \right) \approx \frac{C d^3}{m_s}, \text{ if } m_L \gg m_s \quad [1]$$

Here  $m_s$  is the sample mass, or fragment mass if individual fragments are analysed and  $m_L$  is the size of the lot from which the samples are extracted.  $C$  is the sampling constant and  $d$  the nominal particle size (if estimated by sieving  $d$  is the sieve opening that retains about 5% of the material). Sampling constant is the product of four factors:  $C = f g l c$ , where  $f$  is the shape factor,  $g$  the size distribution factor,  $l$  the nugget liberation factor and  $c$  the constitution factor, which can be calculated from the properties of the matrix and embedded nuggets:

$$c = \frac{(1-a_L)^2}{a_L} \rho_n + (1 - a_L) \rho_m \quad [2]$$

Here  $a_L$  is the average mass fraction of the nuggets in the lot,  $\rho_n$  and  $\rho_m$  the densities of the nugget and matrix materials, consecutively. If the size distributions of the of the fragments and nuggets are available, exact values of  $g$  and the nominal particle size  $d$  can be calculated. Gy gave approximate values for usual cases taking the examples mainly from mineral processing. E.g., for wide size distributions, using the nominal particle size  $d$  as described above, an approximate value of  $g = 0.25$  was recommended. The difficulty with this model is the liberation factor. Gy gave a list for  $l$  that was roughly based on the volume ratio of the fragments and the embedded nuggets. The shape factor is the ratio of the volume of a nugget with nominal particle  $d_n$  to the volume of a cube with the same side length,  $f = (d_n/d_{cube})^3$ . The basic assumptions here are that the nuggets and fragments have similar shapes, and that the nuggets are randomly distributed within the matrix. These approximations have caused a lot of problems, when the practitioners, oblivious of the rough approximations, have tried to solve the value of liberation factor by fitting simple models like  $f = (d_n/d_{cube})^{3-x}$  to experimental data.

Gy's original purpose before computers was to provide practitioners with a simple tool that gives correct answers - at least with an order of magnitude, i.e., one should not try to solve sampling and analytical problems by taking 10 g samples when at least 10 kg is needed. In books by Gy published in 1982, 1992 and 1999 sampling error estimates are based on the concept of *heterogeneity*, estimated from experimental data. A good review of these is given by Pitard and François-Bongarçon, (2011). The relative heterogeneity contribution of the target analyte in individual particles ( $h_i$ ) in a mixture of fragments from broken solid materials is defined as follows:

$$h_i = \frac{(a_i - a_L) m_i}{a_L m_L} \quad \dots \text{(relative)} \quad [3]$$

Here  $m_L = \sum m_i$ , the total mass of analysed fragments or particles of the lot,  $a_i$  the mass fraction of analyte in individual particles,  $m_i$  the sample mass, and  $a_L = \sum(m_i \cdot a_i)/m_L$ , the weighted mean mass fraction of all analysed particles. From the relative heterogeneities Gy defined two new quantities, the constitution heterogeneity  $CH_L$  and the heterogeneity invariant  $HI_L$  of the lot studied.

$$CH_L = s^2(h_i^2) = \text{mean}(h_i^2) \quad [4]$$

and

$$HI_L = CH_L \bar{m} \quad [5]$$

$CH_L$  is thus the relative variance of the individual particles or fragments obtained by crushing a solid target. If the individual fragments cannot be analysed the experiments can be done using samples consisting of groups of fragments. Then  $m_i$  in Equations [3]–[5] is replaced with sample mass,  $m_s$ . These values define the distribution heterogeneity  $DH_L$ :

$$DH_L = s^2(h_s^2) = \text{mean}(h_s^2) \quad [6]$$

If the nuggets within the lot that is crushed are *randomly* distributed (or the lot of liberated particles randomised)  $DH_L$  can be predicted from  $HI_L$ :

$$DH_L = HI_L / \bar{m}_s \quad [7]$$

The experimental value of natural materials  $DH_L$  is usually significantly larger than the predicted value (Equation 7). The reason being that the nuggets in natural materials are seldom truly randomly distributed in the matrix. Some form of segregation is usual, e.g., nugget size variation or clustering within different sections of the lot. The calculations above are estimates of the analytical results given as mass fractions of the analyte material of the target analytes embedded as nuggets in the matrix materials. In the following section a new way is proposed for analysing the experimental results.

### ESTIMATION OF SAMPLING VARIANCE FROM AVERAGE MASS OF NUGGETS

Variance estimates calculated from the sample heterogeneities are relative variances of the analytical results  $a_i$ . Derivation of the heterogeneity variance from the material properties is complicated even in simplified cases if the densities of the nugget and matrix are different, because the random variable  $n_i$  (number of nuggets/fragment) is a factor both in the numerator and denominator (Equation 10). That is elucidated in Figure 1. Derivation is much simpler if it is based on the average mass of nuggets in fragments.

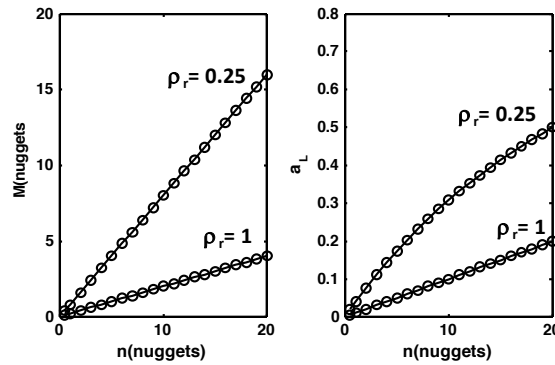


Figure 1. The total nugget mass increases linearly with an increasing number of nuggets if the fragments of equal sizes contain nuggets; whereas the mass fraction of the nuggets in the fragments increases linearly only in the case when the densities of the nugget and matrix materials are equal (density ratio  $\rho_r = 1$ ).

If a fragment of a material contains  $n_i$  embedded nuggets the following properties of the materials are needed for calculating the total mass ( $m_n$ ) and mass fraction ( $a_i$ ) of the nuggets in the fragment: densities of nuggets and matrix,  $\rho_n$  and  $\rho_m$ , density ratio  $\rho_r = \rho_m / \rho_n$ , the mass of nugget ( $m_{n0}$ ) the mass of the fragment not containing nuggets ( $m_{fr0}$ ). With these data Equations [8]–[10] can be derived.

If the nuggets have equal masses the total mass of nuggets within the fragment and the mass of the fragment are:

$$m_n = n_i \cdot m_{n0} \quad [8]$$

$$m_{fr} = m_{fr0} + n_i \cdot m_{n0}(1 - \rho_r) \quad [9]$$

Mass fractions  $a_i$  of nuggets in fragments are thus:

$$a_i = \frac{m_n}{m_{fr}} = \frac{n_i \cdot m_{n0}}{m_{fr0} + n_i \cdot m_{n0}(1 - \rho_r)} \quad [10]$$

The total mass of nuggets within a fragment is proportional to the number of nuggets but the mass fraction  $a_i$  of the nuggets is proportional to the number of nuggets only in the special case when the nuggets and matrix have the same density and  $\rho_r = 1$  (Figure 1).

If the nuggets, in general particles of the component of interest, in the lot from which the fragments originate are randomly distributed, then  $n_i$  follows a Poisson distribution. Poisson distribution has a property that the variance of  $n_i$  is equal to the mean value of  $n_i$ :  $s_{n_i}^2 = \bar{n}$ . Based on this simple relationship the variance of the nugget mass in individual fragments, and in samples consisting of groups of fragments can be estimated theoretically for random distributions. The nugget mass variance can be estimated from experimental data for unknown mixtures from the analytical data. This relationship was used in deriving variance estimates for three model cases verified by simulations.

### Variance of the nugget mass in fragments obtained from a lot of known composition

In many industries products are made by mixing and granulating powders or particles into granules of desired concentration of the active component. The pharmaceutical industry is a good example. In these cases, the average number of the valuable particles is known or can be reliably evaluated. In cases where the distribution is random, the properties of Poisson distribution can be used to estimate the theoretical variance achievable. If grains or nuggets of equal mass are mixed in the matrix, then from Equation (8) it follows that the variance of the nugget mass in an average fragment is:

$$var(m_n) = s_{m_n}^2 = var(n_i) \cdot m_{n0}^2 = \bar{n} \cdot m_{n0}^2 \quad [11]$$

The assumption is that the lot with mass  $m_L$  contains randomly distributed nuggets with mass  $m_{n0}$ . The lot may consist of the granulation process with equal size granules or fragments with mass  $m_{fr}$  originating from a solid target. The average analyte content of the lot is  $a_L$  (mass fraction of analyte nuggets of mass  $m_{n0}$ ). If these basic properties are known, the theoretical sampling variance can be estimated for three different cases.

**Case 1:** Individual granules are analysed, sample size is the size of a granule,  $m_s = m_{fr}$ .

Nugget concentration (average number of nuggets/mass) =  $c_n = a_L/n_0$  (Equation 16). In this case the estimate of the variance of the nugget mass in granules is:

$$s_{m_n}^2 (m_s = m_{fr}) = \bar{n} \cdot m_{n0}^2 = c_n \cdot m_{fr} \cdot m_{n0}^2 \quad [12]$$

**Case 2:** Samples to be analysed are groups of  $n_{fr}$  granules or fragments,  $m_s = n_{fr} \cdot m_{fr}$ . The estimate of the variance of the nugget mass in samples is:

$$s_{m_n}^2 (m_s = n_{fr} \cdot m_{fr}) = n_{fr} \cdot \bar{n} \cdot m_{n0}^2 = n_{fr} \cdot c_n \cdot m_{fr} \cdot m_{n0}^2 \quad [13]$$

**Case 3:** The granules contain nuggets as an average  $\bar{n}(j)$  nuggets of different size  $m_{n0}(j)$ . In this case the variance of the nugget mass in samples is:

$$s_{m_n}^2 (m_s = n_{fr} \cdot m_{fr}) = n_{fr} \cdot \sum ([\bar{n}(j) \cdot (m_{n0}(j))^2] \quad [14]$$

This offers an easy way to check if the randomising in the mixing process has succeeded by comparing these theoretical results to experimental results with the sample sizes used in these calculations. If the variance estimates differ significantly by using an appropriate statistical test, it is a strong indication that the mixing process could (should) be improved. The difference between the experimental and theoretical variance can be used as the theoretical measure of segregation or nuggets in the test materials.

### Estimation of the liberation mass of nuggets from experimental data

With natural materials the nugget size and distributions are difficult to estimate. Based on the equations given above the liberation mass of the nuggets can be estimated from the experimental variances. If the nuggets have approximately equal sizes and are randomly distributed in the matrix, the estimated nugget mass  $m_{ne}$  is close to the correct value. If that is not the case, the solution gives a nominal (or virtual) nugget size that gives an equal sampling variance estimate with the variance calculated from the experimental data.

By analysing samples of approximately equal masses consisting of one or more fragments from a lot of crushed material the analytical results give the mass of the nuggets in each sample. Analytical results provide the following data:

$$\text{Mass of nuggets in samples } (i) = m_n(i) = a(i) \cdot m_s(i) = n_{fr}(i) \cdot m_{n0}$$

$$\text{Mean of nugget masses in samples } (i) = \bar{m}_n(i) = \bar{a}(i) \cdot \bar{m}_s(i) = \bar{n}_{fr}(i) \cdot m_{n0}$$

$$\text{Variance of nugget mass} = s_{mn}^2 = \text{var}(m_n(i)) = \bar{n}_{fr}(i) \cdot m_{n0}^2$$

From these data the estimate of the nugget mass  $m_{n0e}$  of the nuggets is obtained (Equation 15).

$$m_{n0e} = \frac{s_{mn}^2}{\bar{m}_n(i)} = \frac{\bar{n}_{fr}(i) \cdot m_{n0}^2}{\bar{n}_{fr}(i) \cdot m_{n0}} \quad [15]$$

From the estimated nugget size the average number of nuggets per sample, i.e., nugget number concentration  $c_n$  can also be estimated for each nugget size in the sample:

$$c_n = \frac{\bar{n}}{m_{n0} \cdot m_s} = \frac{\bar{a} \cdot \bar{m}_s}{m_{n0} \cdot \bar{m}_s} = \frac{\bar{a}}{m_{n0}} \quad [16]$$

Table I presents simulation results of Case 1 (samples of single fragments) and Case 2 (samples of groups of fragments). The tables show that if the basic assumption about random distribution of nuggets within the fragments holds, the nugget mass can be predicted from the variance (Equation 15). Nugget concentration  $c_n$  (Equation 16) is constant (independent of sample size), if the nuggets are randomly distributed within the lot, from which the fragments, or product granules originate.

Table 2 gives simulation results for Case 3, where sample includes randomly distributed nuggets of different sizes. If the size distribution of the nuggets is known, the variance of the total nugget mass in fragments can be estimated (Equation 14). If samples contain nuggets of different sizes analytical results give the total nugget mass in the samples,  $m_n(i) = a(i) \cdot m_s(i)$ . In this case the estimates ( $m_{n0e}$ ) and  $c_n$  are nominal values, i.e., the nominal values (nugget size and  $c_n$ ) accurately predict the sampling variance as a function of sample mass (Equation 17). This means that in the case of the nuggets in the original lot being randomly distributed, the sampling variance as a function of sample size is proportional to sample mass,  $m_s$ :

$$s_{m_n}^2(m_s) = c_n \cdot m_s \cdot m_{n0e}^2 \quad [17]$$

Table I. Simulation results where the nugget size was 0.2 g and the average number of nuggets per fragment was 1.5 (columns 2 – 6) and  $5 \times 1.5$  (last column)

Estimate	$c_n = \bar{n}_n/m_s = 1.5 \cdot g^{-1}$					$\frac{\bar{n}_n}{m_s} = 7.5 \cdot g^{-1}$
$var(n_i)$	1.506	1.503	1.497	1.502	1.498	7.526
$mean(n_i)$	1.499	1.500	1.495	1.500	1.498	7.491
$Relvar(n_i)$	0.670	0.668	0.670	0.668	0.668	0.134
$var(m_n)$ , (g <sup>2</sup> )	0.060	0.060	0.060	0.060	0.0599	0.301
$mean(m_n)$ , (g)	0.300	0.300	0.299	0.300	0.300	1.498
$Relvar(m_n)$	0.670	0.668	0.671	0.668	0.667	0.134
$m_{n0e}$ , (g)	<b>0.201</b>	<b>0.200</b>	<b>0.200</b>	<b>0.200</b>	<b>0.200</b>	<b>0.201</b>

Table II. Simulation results with nugget sizes  $m_{n0}(j) = [1, 0.5, 0.25, 0.125, 0.0625]$  and nuggets per sample  $(j) = [1, 2, 3, 4, 6]$ . Columns 2 – 6 give the results when samples are made from single size nuggets and the last column gives the result when the samples include all five nugget sizes.

Estimate	Samples: $\bar{m}_n(j) = n(j) \cdot m0(j)$					$\Sigma(\bar{m}_n)$
$var(m_n(j))$	1.001	0.497	0.188	0.0625	0.0235	1.778
Mean $m_n(j)$	0.999	1.001	0.751	0.500	0.375	3.626
$m_{ne}(j)$	<b>1.002</b>	<b>0.497</b>	<b>0.250</b>	<b>0.125</b>	<b>0.063</b>	<b>0.490</b>
$c_n = n_{ne}/m_s$	<b>0.997</b>	<b>2.016</b>	<b>3.003</b>	<b>4.002</b>	<b>6.001</b>	<b>7.395</b>

Equation 15 accurately predicts the average nugget size and number of nuggets per sample, but only if the nuggets are randomly distributed in the sample material. If individual granules or fragments are analysed the estimated nugget size is close to the actual nugget size. In cases where the nuggets have different sizes the estimated values, nugget size ( $m_{ne}$ ) and  $c_n$ , are nominal values for this material. Still, in both cases, if the nominal values,  $c_n$  and nugget sizes are estimated experimentally, the sampling variance can be estimated as a function of sample size independent of fragment size (Equation (17)). On the other hand, if the assumption of randomness is not correct, then repeated experiments with different fragment or sample sizes will give significantly different  $c_n$  and nugget size  $m_{n0}$  estimates compared to the first experiment. Equation 17 is valid only for the fragment size used in the experiment. If it is important to optimise the sampling plan in the latter case, it can be done by performing sampling experiments using different fragment sizes.

#### Examples: Analysis of a real data sets

*Example 1.* Data for this example was taken from WCSB1 proceedings (Pitard 2004). A so-called heterogeneity test on gold ore was carried out by analysing 100 samples. The average mass of samples was 50.1 g consisting of 52 fragments. Only the analytical results  $a(i)$  and total sample masses  $m_s(i)$  were needed in calculations, because the total mass of Au nuggets in samples is:

$$m_n(i) = a(i) \cdot m_s(i) \quad [18]$$

Equation (15) can now be applied to estimate the nominal nugget size:

$$m_{n0e} = \text{var}(m_n) / \text{mean}(m_n) \quad [19]$$

Now when the nominal nugget size is estimated the average number of nominal size nuggets in samples as a function of nugget size can be calculated:

$$n_{n0e}(m_s) = \bar{m}_n / m_{n0e} \quad [20]$$

Nominal nugget concentration  $c_n$  in samples is:

$$c_n = n_{n0e} / \bar{m}_s \quad [21]$$

To check if the nugget number distribution fits a Poisson distribution the samples were ordered according to the increasing Au content. First estimates were calculated from samples 1 – 81 and then the number of samples was increased to 100. The results were then checked to see how they fit a Poisson distribution. These results are presented in Table III and in Figure 2. The results were compared to a Poisson distribution by comparing the lowest and highest nominal numbers of nuggets in fragments to cumulative Poisson probabilities calculated from the average values of the estimated number of nuggets in samples 1 – Nmax. Samples up to sample 91 fit a Poisson distribution giving an almost exactly symmetric 95% confidence interval. Figure 2 shows the total nugget mass in samples and the number of nominal size nuggets in the average size fragments. Figure 2 also shows that samples beyond 91 begin to deviate from a typical Poisson distribution.

The following conclusions can be drawn from this example: 1) The majority of the fragments (background) contain randomly distributed nuggets with a similar size distribution to Case 3 in the simulation part above. The nominal nugget size in this group is 4.79  $\mu\text{g}$  (Table III, column 6). However, the results (two last lines, column 6) indicate that including samples 91 – 100 in calculations increases the estimated nominal nugget size to 9.73  $\mu\text{g}$ . These results could be explained if these samples contain some fragments which have a much higher nugget concentration ( $c_n$ ) than the 91 first samples. E.g., some fragments contain clusters of nuggets, or exceptionally large nuggets. These results alone are not conclusive. If the fragments originate from a target where the nuggets are segregated into clusters or contain large random nuggets, repeating the experiment using samples crushed to a different fragment size in comparison to this experiment also gives different nominal values for different fragment sizes.

Table III. Results of repeated calculations for of samples 1 – Nmax. Columns: 2) estimated nugget size; 3) minimum, 4) average and 5) maximum number of nuggets in samples. 6) and 7): Cumulative Poisson probability values of the estimated minimum and maximum numbers of nuggets per fragment in in samples from 1 to Nmax

<b>Samples 1 – Nmax</b>	$m_{n0e}$ <b><math>\mu\text{g}</math></b>	$n_{nug}(1)$	$n_{nug}(\text{average})$	$n_{nug}(\text{max})$	<b>Pc(n=<math>n_{nug}(1)</math>)</b>	<b>Pc(n=<math>n_{nug}(i)</math>)</b>
1 – 81	3.58	2.63	6.77	12.75	0.035	0.978
1 – 82	3.70	2.55	6.62	11.88	0.039	0.962
1 – 83	3.77	2.50	6.56	11.21	0.041	0.964
1 – 84	3.94	2.39	6.34	12.03	0.048	0.987
1 – 85	3.96	2.38	6.35	10.15	0.048	0.941
1 – 86	4.10	2.30	6.20	11.37	0.054	0.975

1 - 87	4.11	2.29	6.23	9.96	0.052	0.899
1 - 88	4.41	2.14	5.88	12.50	0.067	0.992
1 - 89	4.44	2.12	5.89	9.81	0.067	0.924
1 - 90	4.70	2.01	5.63	11.68	0.080	0.987
<b>1 - 91</b>	<b>4.79</b>	<b>1.96</b>	<b>5.57</b>	<b>10.09</b>	<b>0.025</b>	<b>0.973</b>
1 - 92	4.95	1.90	5.45	10.54	0.028	0.976
1 - 93	5.16	1.83	5.29	10.73	0.032	0.980
1 - 94	5.31	1.77	5.19	10.15	0.034	0.982
1 - 95	5.59	1.69	5.00	10.93	0.040	0.986
1 - 96	6.19	1.52	4.59	11.79	0.057	0.997
1 - 97	6.55	1.44	4.40	10.49	0.066	0.994
1 - 98	7.90	1.19	3.74	12.13	0.113	1.000
1 - 99	8.65	1.09	3.48	9.78	0.138	0.997
<b>1 - 100</b>	<b>9.73</b>	<b>0.97</b>	<b>3.16</b>	<b>10.02</b>	<b>0.042</b>	<b>1.000</b>
<b>Samples</b>	<b>Average sample (g)</b>	<b>Av. number of fragments</b>	<b>Av. size of fragments (g)</b>	<b>Av. number of nuggets/ fragment</b>	<b>Nominal nugget (<math>\mu\text{g}</math>)</b>	<b><math>c_n</math> (<math>\text{g}^{-1}</math>)</b>
1 - 91	50.12	51.7	0.969	<b>5.57</b>	<b>4.79</b>	<b>5.75</b>
1 - 100	50.11	51.6	0.971	<b>3.16</b>	<b>9.73</b>	<b>3.26</b>

Powders and materials ground to liberation size can be randomised, at least in principle. The case is different with fragments: while the fragments can be randomised by mixing it does not change the nugget concentration and distribution within the individual fragments. Repeating the sampling experiment with smaller fragment sizes would be informative. Nugget clusters break in crushing or grinding the material and these smaller clusters can be mixed more evenly. Therefore, if the fragment size is reduced so that the average number of nuggets approaches the value one per fragment the randomisation of nuggets is possible. The case is different if a few fragments in the lot contain exceptionally large nuggets or tight nugget clusters. In repeated experiments by decreasing the fragment size the clusters begin to break when the fragment volume approaches the volume of the clusters in fragments. Exceptionally large nuggets or tight nugget clusters in fragments show up as exceptionally high values (peaks) of the results. Thus, random high peaks in smaller fragment sizes usually refer to large nuggets, gradually decreasing values to clusters with fragment size.



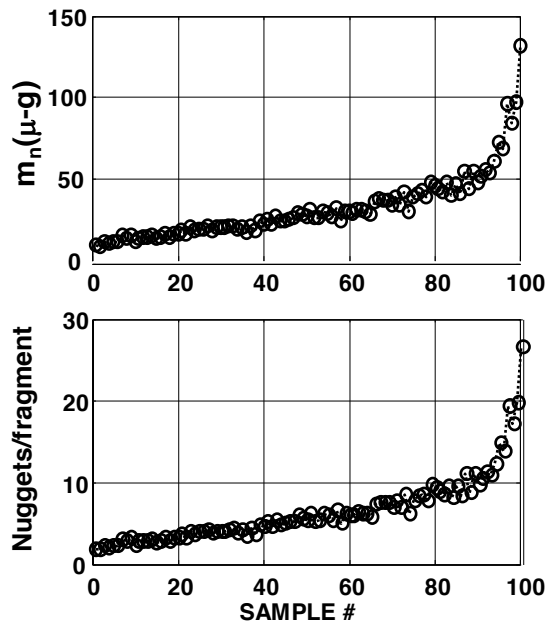


Figure 2. The upper panel shows the total Au mass in ordered samples. Lower panel shows the estimated number of Au nuggets of nominal size  $4.79 \mu\text{g}$  in the average size fragments of the samples.

*Example 2.* In this example the data published in WCSB5 (Minnitt, François-Bongarçon, and Pitard, 2011) were analysed by using the proposed method. In the original study 164.4 kg of crushed gold ore were sieved into 14 different fragment size classes. Each size class was further divided into 32 samples which were analysed for gold. The nominal nugget size in each of the 14 size classes was estimated the same way as in the previous example. Figure 3 shows the summary of the analytical results of each size class: total nugget mass in the samples of each size class together with the estimated nominal nugget size. Three coarsest size classes include about 60% of the total mass of subplot and eight coarsest 89%. The total gold approximately follows the total mass of the size classes. Average gold content increases with decreasing fragment size. Figure 4 shows the total gold mass of the samples in each of the 14 size classes. One sample in size class  $0.566 \text{ cm}^3$  has an anomalous gold content, about ten times higher than the average in that class. This could be explained by some large nuggets or tight nugget clusters in the material from which the samples were crushed.

All results are presented in Table IV. This is obviously a very complex mixture of fragments originating from some parts of the deposit where the clustering and possibly also nugget sizes differ from the majority of the samples. In most cases the estimated nominal nugget size decreases and number increases with the decreasing size class while the estimated number of nuggets per fragment remains almost constant down to the nominal fragment size class  $0.102 \text{ cm}^3$ . In smaller size fractions the nominal nugget sizes decrease and the nominal number of nuggets per fragment increases. The result is compatible with the assumption that the lot consists of fragments where nuggets are at least partly clustered. The only clearly anomalous value is in the size class  $0.566 \text{ cm}^3$  (line 3 in Table IV). In this size class one sample has gold content which is about ten times higher than the other samples of this size class (Figure 4). Two coarsest size classes also have samples with high gold content. That is compatible with the assumption that the lot contains a low number of fragments with tight clusters of nuggets, possibly also some exceptionally large nuggets. The higher Au content in smallest size classes can also be explained since the largest nuggets are first liberated during crushing, especially if the clusters are mainly located in grain boundaries within the rock.

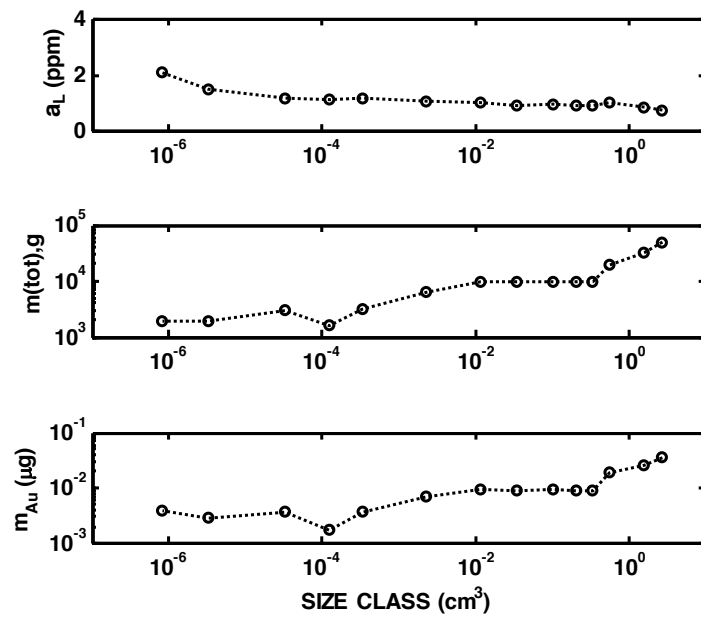


Figure 3. Panels from top down show the average properties of all 14 size classes: 1) average gold content as mass fraction 2) total mass of samples in size classes and 3) total mass of gold.

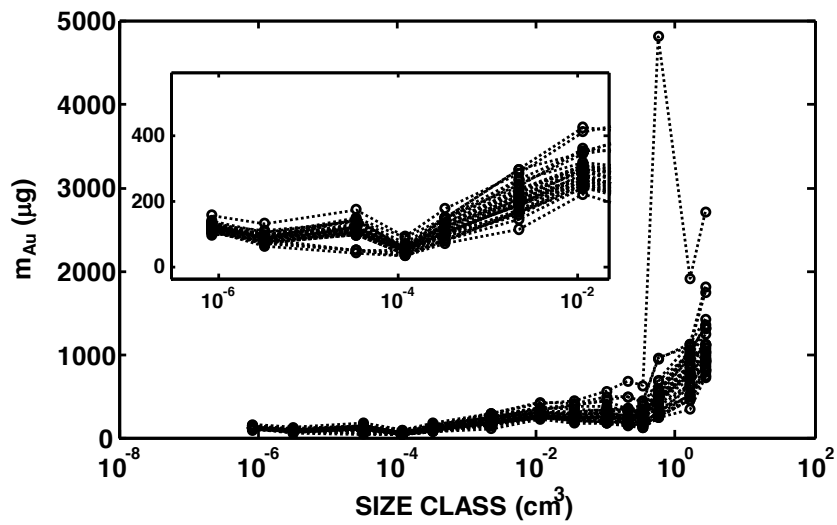


Figure 4. Total Au mass in the samples of all size classes.

Table IV. Results of the second example for different size classes. Estimated nugget sizes and numbers per fragment are nominal values specific for this lot

<b>v(frag)</b> <b>cm<sup>3</sup></b>	<i>Average</i> <b><math>a_i</math></b> <b>ppm</b>	<i>Average</i> <b>fragment (g)</b>	<b>Fragments</b> <b>in</b> <b>samples</b>	<b><i>mAu</i> in</b> <b>samples</b> <b>g</b>	<b><i>m0</i>(est)</b> <b>μg</b>	<b>Nuggets/</b> <b>fragment</b>	<b><math>c_n</math></b> <b>g<sup>-1</sup></b>
2.74	0.749	7.26	206	0.0359	137	8.2	0.0055
1.60	0.844	4.23	227	0.0261	109	7.5	0.0078
<b>0.566</b>	<b>1.001</b>	<b>1.50</b>	<b>403</b>	<b>0.0194</b>	<b>1020</b>	<b>0.6</b>	<b>0.0010</b>
0.342	0.884	0.907	334	0.0086	40.6	6.6	0.0217
0.203	0.895	0.538	560	0.0086	47.0	5.8	0.0191
0.102	0.963	0.270	1118	0.0093	29.4	9.9	0.0328
0.0354	0.912	0.0937	3189	0.0087	15.9	17	0.0574
0.0114	0.975	0.0302	10015	0.0094	7.58	39	0.129
0.002225	1.034	0.00596	33870	0.0067	9.19	23	0.113
0.000340	1.160	0.00090	110670	0.0037	5.35	22	0.217
0.0001121	1.092	0.00032	153430	0.0017	3.03	18	0.360
0.0000337	1.185	0.000089	1052000	0.0036	7.99	14	0.148
0.00000322	1.476	0.000085	6949000	0.0028	2.30	38	0.642
0.00000084	2.056	0.000022	264800000	0.0039	1.29	94	1.596

As these values are nominal values based on experimental data, they can be used to make an optimised sampling plan for this deposit. The results cannot be generalised to other types of deposit having different nugget size and nugget clustering.

The sampling plan of this study is a good example of stratified sampling of 14 strata each divided into 32 samples. The advantage of stratified sampling is that when the total variance of the stratified lot is calculated, and samples are taken from every stratum, the between-strata variance is cancelled and only the within-strata variances propagate to variance of the lot average. In this case the total mass of gold in the 164 kg lot is 0.148 g and its relative standard deviation 4.3%. An optimised stratified sampling plan may significantly reduce the analytical costs (Minkkinen 2004).

## SUMMARY

Many attempts have been made to estimate the variance of the analytical results of analytes which are embedded as nuggets or particles in fragments of solid matrices. Common amongst these methods is that the variance of analytical results has been estimated either empirically or theoretically, making simplifying assumptions. A short account of the developments is reviewed.

Here a different approach is proposed. Analytical results give the analyte mass in the samples and the variance of the mass in the target material in the samples is estimated. The method is based on the following property of Poisson distribution: the variance of the number of random events is equal to their mean. In many industrial processes particles of the critical, valuable, or active ingredients are mixed in the matrix and then pressed into granules; e.g., pharmaceuticals, fertilisers, and animal feeds are just a few examples. In these cases, the properties of the constituents are known, and the variance of randomised mixtures can be predicted as proposed in this study. The theoretical result can be used as reference in quality control, e.g., as the measure of the effectiveness of the mixing and blending processes. If the experimentally estimated variance of the number of the active particles differs significantly from the theoretical variance it indicates that the mixing process does not work effectively and should be improved.

In cases where natural materials are investigated the properties of the constituents are usually not known. From the variance estimates of designed pilot studies, as this study shows, it is possible to estimate the nominal nugget size and nominal number of nuggets per sample mass ( $c_n$ ). If the results are compatible with Poisson distribution,  $c_n$  is independent of the fragment size and sampling variance is proportional to the sample mass. If the number distribution in the fragments deviates from the Poisson values, the estimates, e.g., nominal nugget size  $m_{n0e}$  and number concentration of nuggets  $c_n$  can be used to predict the sampling variance as a function of sample mass with the limitation that the average fragment mass is not changed. The results in this case are specific only to the material and fragment size that was used in the sampling experiment. A detailed study, which can be used for optimising the sampling steps of the whole analytical procedure, requires that the sampling study is repeated with different fragment sizes. Two different empirical data sets were analysed by using the proposed method.

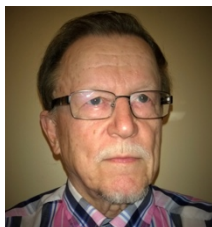
## ACKNOWLEDGEMENTS

The author is grateful to Richard Minnitt and Francis Pitard for publishing the original data used in this study. Without the results of well-designed and -conducted experiments this kind of study would have no relevance.

## REFERENCES

- Gy, P. (1955). Erforderliche Probemenge-Kurvetafeln (Minimum sample mass – Graphs and Curves). Internationales Kongress für Erzaufbereitung. Third International Mineral Processing Congress, Goslar, Germany, May 1955. *Erzmetall*, 8, B, 199–220.
- Gy P. (1982) *Sampling of Particulate Materials – Theory and Practice*. Second revised edition. Elsevier, Amsterdam
- Gy, P. (1992). *Sampling of Heterogeneous and Dynamic Material Systems. Theories of Heterogeneity, Sampling and Homogenizing*. Elsevier, Amsterdam.
- Gy, P. (1999). *Sampling for Analytical Purposes*. 2<sup>nd</sup> ed. John Wiley, Chichester, 1999.
- Minnitt, R.C.A., François-Bongarçon, D. and Pitard, F.F. (2011), Segregation free analysis for calibrating the constants K and  $\alpha$  for use in Gy's formula, *Proceedings of WCSB5*, Santiago, Chile, Gecamin, pp. 133–150.
- Minkinen, P. (2004) Practical applications of sampling theory, *Chemometrics and Intelligent Laboratory Systems* 74, 85–94.
- Pitard, F.F. (2004) Effects of residual variances on the estimation of the variance of the Fundamental Error, *Chemometrics and Intelligent Laboratory Systems* 74, 149–164

Pitard, F.F. and François-Bongarçon, D. (2011), Demystifying the fundamental sampling error and the grouping and segregation error for practitioners, *Proceedings of WCSB5*, Santiago, Chile, Gecamin, pp. 39-55.



### **Pentti Minkkinen**

Professor emeritus  
Lappeenranta-Lahti University of Technology

Pentti Minkkinen is a fully served professor of inorganic and analytical chemistry at Lappeenranta Lahti University of Technology (LUT) in Finland. He started teaching the theory and applications of sampling and chemometrics already in 1978 as integral parts of process analytical chemistry. He is the recipient the following three international awards, as the only person so far: The Kowalski Prize (2002) and Herman Wold Gold Medal in Chemometrics and Pierre Gy Sampling Gold Medal (both 2007). He was Co-Chairman at WCSB1 and has published over 30 articles on sampling in refereed journals and conference proceedings.

