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BULK SAMPLING: SOME STRATEGIES FOR IMPROVING QUALITY CONTROL IN CHEMICAL INDUSTRIES

Thesis submitted for the degree
of Doctor of Philosophy

by
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To *Angela*, *Bruno*,

Felipe and *Mirela*

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The investigation of a fundamental theory is often (and this is no exception) the result of an intense interest on the part of an individual and a considerable forbearance on the part of his superiors in trusting him to use time and other facilities which normally bring in a better return of the investment.

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Declaration

I grant powers of discretion to **The City University of London** Librarian to allow this thesis to be copied in whole or in part without further reference to me. This permission covers only single copies made for study purposes, subject to normal conditions of acknowledgment.

Far better an approximate answer to the *right* question which is often vague, than an exact answer to the *wrong* question, which can always be made precise.

J. W. Tukey, 1962
"The Future of Data Analysis"
Ann. Math. Stats. 33, 1-67.

Abstract

An increasing number of industries are concerned about variability in the quality of chemicals. This thesis is devoted to these concerns, particularly to three underlying, but overlapping, strands: (i) Unfolding a Bulk Sampling Scheme; (ii) Sampling of Heterogeneous and Dynamic Material Systems; (iii) Designing of Experiments with Divisible Materials.

In **Unfolding a Bulk Sampling Scheme** we detail a *sampling protocol* to determine the sample size, the minimum amount of material, and an acceptance criteria centered on the characteristic variability of the particulate material to be assayed. Segregation, heterogeneity, particle size, randomization of solid-solid mixtures and all properties regarding every sort of lot — zero, one, two or three-dimensional — have a thorough examination not in conceptual terms but, indeed, within a mathematical model that allows for materialization of errors with predictable risks.

In **Sampling of Heterogeneous and Dynamic Material Systems** we consider the problem of serial measurements within the scope of Matheron's *Regionalized Variables*. The dependency of two neighboring samples from the same one-dimensional lot whether moving or stationary is studied to refine precision statements, minimize quality fluctuations and reduce heterogeneity of consignments. Moments of continuous selection errors and their computation using nonparametric methods are presented through Gy's bulk sampling approach. Simplified methods to assess variability of continuous materials are also considered.

In **Design of Experiments with Divisible Materials** we deal with the problem of isolating variance components associated with sampling — primary, secondary and tertiary increments — and measurement systems. The method of conducting multifactor experiments, particularly *Nested Experimental Design*, to identify where in the process the quality improvement effort needs to be focused mostly is studied in a practical viewpoint according to the required needs. *Balanced, staggered* and *Nested-factorial Design* are analyzed accordingly. The insight allows optimization of sample size, amount of replication and reduction of variability and cost.

In the last chapter **Designing a Bulk Sampling Test Station** some suggestions based on the ideas of *Unit Operations* are presented. Fundamental rules for a sound design and choice of equipment for guarding against estimation bias are also considered together with a full layout for a *Sampling Test Station*.

Contents

List of Figures

List of Tables

Chapter 1

Introduction

This thesis represents the current state of development of the *Sampling of Bulk Materials* and is designed for use in industry, particularly in the chemical industry, by engineers who feel that standard methods (Tables and Graphics) are inadequate since they only applied to indivisible materials. It is also directed towards training because sampling of particulate materials is so neglected in most courses in Chemistry, Chemical Engineering and Mining Engineering where students are led to think that sampling is a plant wisdom rather than a science.

A complete sampling plan for particulate material requires the study of two complementary models: a *discrete model* taking into consideration the discrete nature of the population of fragments submitted to the sampling operation, described by the fundamental notion of heterogeneity, and a *continuous model* taking into consideration the continuous nature of the space and time variability of its quality characteristics.

A good sampling is expected to provide estimation of quality and control of all sources of errors met in chemical plants: sampling errors, analytical errors, reduction errors, delimitation errors, extraction errors etc.

Possibly the first and most important step towards the development of a satisfactory sampling plan is to obtain a complete control of all variance components. They are caused by real changes in quality of the bulk, the random errors of the increments, and the combined errors cited before.

Two broad types of physical problems arise in industries dealing with chemicals in bulk:

1. materials are stockpiled in a zero-dimensional form, in packages, bales or bags

that may be subdivided into unique sampling units for a routine sampling operations, and

2. materials are stored in a one-dimensional form like piles in a bulk form, in which no unique subdivisions may be specified as sampling units for a routine sampling operations.

In performing a suitable sampling plan the quality engineer encounters a hard obstacle: while sampling plans for indivisible products have been cataloged in a number of tables for both *attributes* and *variables*, it has not yet been possible for divisible products (see Juran [67]). Therefore a sampling model must be created for each type of bulk material. The model should define a proper universe or lot of sampling, describe how the samples should be selected, determine the number of samples to be taken, describe how the samples should be treated in the laboratory and the meaning of chemical results in terms of lot.

What makes this plans even more difficult is the peculiarity of divisible material in comparison to indivisible material. The latter is formed only of primary units for sampling and testing, while the former is composed of primary units divided into a set of secondary units which once again may be divided into tertiary or even higher order units according to the model intended. Sometimes, to perform economical plans increments are gathered into a composite samples in any of these stages as long as the precision remains steady. The Figure 1.1 shows some practicable arrangements of increments.

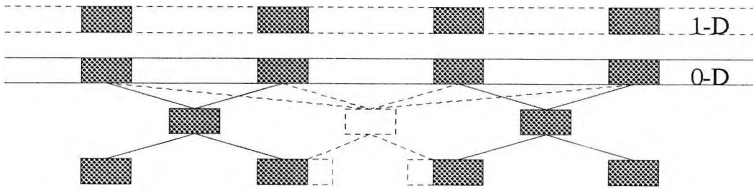


Figure 1.1: Arrangements of increments and replications within the boundaries of specified precision.

Economical reasons also drive manufacturers to define lots in distinct configurations according to type and charges of conveyance available. Chemicals from continuous processes are delivered in batches, batches are used as one-dimensional lots and vice-versa.

On rare occasions where the primary unit itself is the test portion, general sampling theory and standard sampling plans — Dodge & Romig Tables, MIL-STD-

105A, B, C, Phillips Standard Sampling System etc, may be of some help. That is a rule for mechanical sampling where the universe consists of pieces, parts etc., and, therefore, primary samples.

All the essential ideas about bulk material whatever the configuration — zero, one, two, and three-dimensional lots — are presented in Chapter 2. Relationships among both discrete and continuous functions, decomposition of overall sampling errors, notions of heterogeneity, segregation and group factors are considered to build up a sampling scheme and define the fundamental and segregation variances. Minimum weight of material and amount of sampling are considered together with the most common sampling models for systematic, stratified and isolated lots.

In Chapter 3 the sampling of dynamic material systems is considered through Content and Throughput Functions and Variographic Experiments. Auxiliary Functions are deduced to compute random, correlated and periodic parameters of variogram as well as the moments of quality fluctuation errors.

A better understanding of continuous models and fluctuations in the process is also aimed using the approach of both *Matheron* and *Gy*. The model applies to the different types of materials in industrial chemistry: materials moving or stopped in conveyor belts, pipes, ducts, streams and materials stationary in elongate piles. It presupposes the collection of a number of increments according to the type of consignment, intrinsic properties of material and equipment available. Increments collected during small fractions of time or space are analyzed and the data values are used to calculate an experimental variogram. From the data, analytical and graphical estimations are made and suggestions are presented to reduce fluctuations of the quality characteristics.

In Design of Experiments, *DOE*, the variance components are separated for analyses of the effects and interactions of the many sources of variations of the system. In this method the components of the variance of the continuous selection errors are added to analysis of quality fluctuations.

$$s_{CE}^2 = s_{CE1}^2 + s_{CE2}^2 + s_{CE3}^2 \tag{1.1}$$

Gy's model is based on time series analysis and can often be used to refine precision statements. In such cases the F-statistics between classical variance and the time series variance calculated from the squared differences between consecutive primary increments may be statistically significant. The following formula for calculation of geostatistical variance will based on the discrete variogram $[\gamma_x(h)]$ of the quality function $[x_j]$, flow of mass,

$$\gamma_x(h) = \frac{1}{n-r}\sum_{j=1}^{n-r}(x_{j+r} - x_j)^2 \tag{1.2}$$

where

r, is the number of unit-intervals in h,

h, is the lag of variogram, and

n, is the number of data values.

Multi-stage experiments with particulate materials are described in Chapter 4.

In classical statistics we use experimental data for a better understanding of population. We also can compare the sample means of two populations by the two samples t-test. *DOE* enlarges this view to situations in which we want to compare two or more population variances or materialize the net effect of the combined action of analyst, equipment, temperature, pression, reagent, standards etc. Any of these factors may produce excessive variability in the process. We have to isolate variances and measure their relative effect. The theoretical approach is to choose a simple linear mathematical model that expresses individual and interaction effects. An example is the multivariate response function that includes lot, batch, sampling, measurement effects and assumes interaction effects.

$$y_{ijkl} = \mu + a_i + b_j + c_{ij} + d_{ijk} + \epsilon_{ijkl} \tag{1.3}$$

where l represents the number of measurements performed in the experiment, k represents the number of samples, j may represent the number of batches, i may represent the number of consignments.

μ is the overall mean of the response variable ;
a_i is the effect of treatment i;
b_j is the effect of treatment j;
c_{ij} is the $i \times j$ interaction effect;
d_{ijk} is the effect of sampling errors within interactions;
ϵ_{ijkl} is the effect of analytical errors.

Due to the importance of nested design for the chemical engineering the model has been used with few changes. Instead of Equation 1.3 we use the equation:

$$y_{ijkl} = \mu + a_i + b_{j(i)} + c_{k(ij)} + \epsilon_{l(ijk)} \tag{1.4}$$

where one effect is nested within others. The conventional fully replicated nested design is easy to administer and analyze but it doubles the number of tests as we go down the bottom and distorts estimates of variance. This disadvantage is overcome by other designs that keep similarity among the degrees of freedom. Two types are also considered: *Staggered Nested Design* and *Nested-factorial Design.*

An economical plan is suggested for which the number of tertiary and secondary units per primary unit are optimized by analysis of variance through *DOE* without any damage to the precision of the experiment.

When sampling bulk materials the increments must often depend on human judgment because the material, even packaged, is not divisible into identifiable units. Experience has demonstrated that such dependence is hazardous and severe biases regularly take place. Statistics may be of little or no help if our sampling has been done poorly.

It is paradoxal how much progress chemical analysis has been made in the recent years and yet how little sampling work has been changing. Presently is quite common for chemical laboratories to perform chromatographical analyses and make use of sophisticated infrared equipment that produce accurate results in seconds and at the same time display in sampling laboratories the same equipment bias of the early 1900's. Some plants keep withdrawing increments by shovel, by scoop and reducing samples by coning and quartering. In many cases the lot is not available at one time or place, in others, all the lot is available for sampling but some parts are not accessible, in clear disregard of the principles of reliability and representativeness.

In Chapter 5 the production of reliable data, less dependent on human judgment, is considered and a *Sampling Test Station* is suggested. It follows the fundamental rules of correctness and representativeness of fragments in the light of *Unit Operations, Design of Equipment* and *Mineral Processing* for a sound design and/or the choice of equipment for guarding against estimation bias.

As we arrive at the consolidation of a broad sampling procedure for chemicals three fundamental areas of knowledgement are necessary: *Statistical Theory, Chemical Engineering* and *Chemistry.* The diagram in Figure 1.2 provides the relationships among these three not mutually exclusive areas within the scope of Quality Control of Chemicals.

The strategies proposed here in this work do not include the area of Chemistry and measurement errors involved in Analytical Chemistry for obvious reasons — 80% of worldwide standards are about analitycal tests and errors of analysis are

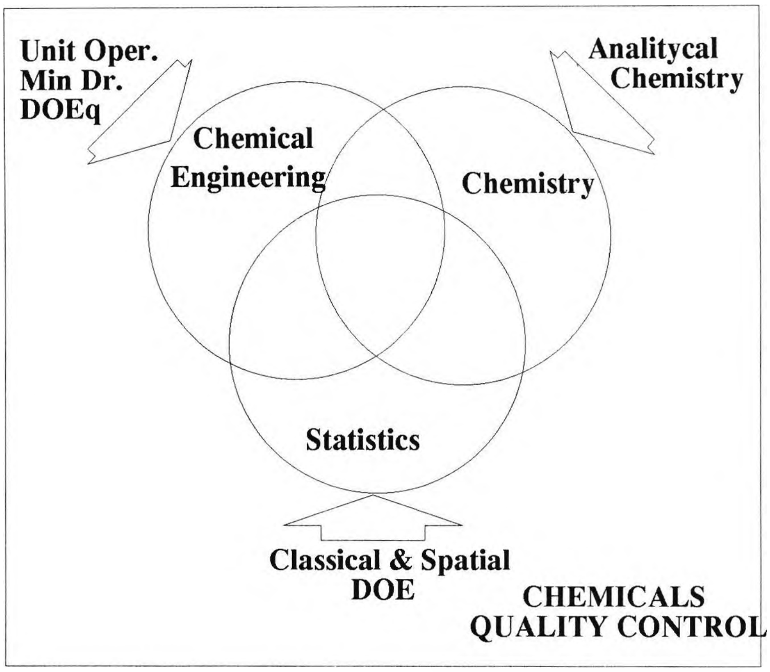


Figure 1.2: Relationship among areas studied in this work.

relatively low when compared to the sampling errors.

From the *Statistics* we use *Classical Statistics, Design of Experiments* and *Spatial Statistics.* From the Chemical Engineering we use *Unit Operations, Design of Equipment* and *Mineral Processing.*

The application of the methods and indeed the design of the Sampling Test Station will depend on the application and require adjustment to local conditions. This thesis attempts to develop best practice to the point of industrial usefulness.

Chapter 2

Unfolding a Bulk Sampling Scheme

Sampling plans for discrete indivisible product have been catalogued in a number of tables. They are used to accept or reject the immediate lot of the product at hand or to determine if the process which produces the product is within acceptable limits.

The most serious limitation of these plans is that they consider increments from bulk materials as a discrete pieces. In fact, it is not suitable for particulate materials to have such plans even when they come in clearly uniform remarked segments not to mention those unpackaged consignments in which the sample increments must be *created* from a pile, a truck, a railroad car or a conveyor belt.

A detailed sampling protocol must be written for each type of bulk material and it should include details of when, where and how the samples increments are to be taken.

To determine the sample size, the minimum amount of material, the acceptance criteria for specific applications and to control a manufacturing process centered on the variability of the product some knowledge of segregation, heterogeneity, particle size and randomization of solid-solid mixtures are essential. Not merely in conceptual terms but, through a mathematical model that allows for materializing of errors and decisions over materials and processes with predictable risks.

2.1 Establishment of a Sampling Model

In designing a sampling plan for bulk materials, one must firstly consider:

- How many samples should be taken from the lot?
- How large should each increment be?
- From where in the bulk material (population) should they be taken?
- Should individual samples be analyzed or a composite be prepared?

These questions cannot be answered accurately without some knowledge of the relative heterogeneity of the system. Gross samples should be unbiased with respect to the different sizes and types of particles present in the bulk material. The size and the amount of gross sample is often a compromise based on the heterogeneity of the particulate material one the one hand, and the cost of one the sampling operation on another.

The sample value will generally differ from the true, unknown value of the material consignment. This difference, called Total Error (TE), has a frequency distribution with a mean value and a variance. It is defined as follows:

$$TE = \frac{a_S - a_L}{a_L} \tag{2.1}$$

where

a_S Critical content of the sample S, perfectly defined but unknown;

a_L Critical content of the lot L, perfectly defined but unknown;

It is necessary to estimate each sort of error before the quality evaluation can be reported with any degree of assurance or precision. The sampling errors [SE], for example, are brought about depending on the nature of the material, size, shape, density, number of fragments, on the manner of sampling — random, systematic, stratified, multi-stage — and on the physical presentation of consignments — stationary, moving etc.

All these factors add bias and variability components. When the selection is probabilistic in the strictly sense, TE, is a random variable with three defined moments:

$m(SE)$ Expected value or bias of SE;

$s^2(SE)$ Variance of the distribution of SE;

$r^2(SE)$ Mean square of the distribution of SE;

The first moment $m(SE)$ measures the selection *accuracy*. The second moment, $s^2(SE)$, measures the selection *reproducibility* or *precision*. The last moment measures the sample *representativeness* and it is defined as follows:

$$r^2(SE) = m[(SE)^2] + \frac{1}{N}\sum_{i=1}^{N}(SE)_i^2 = m^2(SE) + \sigma_{SE}^2$$

The unusual characteristic of bulk materials rests on the huge flexibility of configurations. They are liable to be arranged according to the number of dimensions of their representative models: three dimensions when extending in the three dimensions of space, two dimensions when having a nearly constant thickness, one dimension when having a nearly constant sections and zero dimension or discrete model. This continuous perspective shown in Figure 2.1 can only be related to the discrete reality of Figure 2.2 through a mathematical model that takes into consideration the scale of observation, despite the fundamental discontinuity of the matter. To do so we define:

dX : The elementary volume centered at point X;

dM : The weight of active components present in dX;

dA : The weight of critical components present in dX.

P : An index for the model.

Defining the functions indexed:

$$\mu_P(x,y,z) = \lim_{dX\to 0}\left[\frac{dM}{dX}\right]$$

$$\alpha_P(x,y,z) = \lim_{dX\to 0}\left[\frac{dA}{dX}\right]$$

The first function, μ, refers to the weight of active components per unit of volume at point X, or *quality function* and the second one, α, to the weight of critical components per unit of volume at point X, or *weighting function.* These functions are related to one another through $a_p(x,y,z)$, the *critical content* at point X:

$$a_p(x,y,z) = \lim_{dX\to 0}\left[\frac{dA}{dM}\right] = \frac{\alpha_p(x,y,z)}{\mu_p(x,y,z)}$$

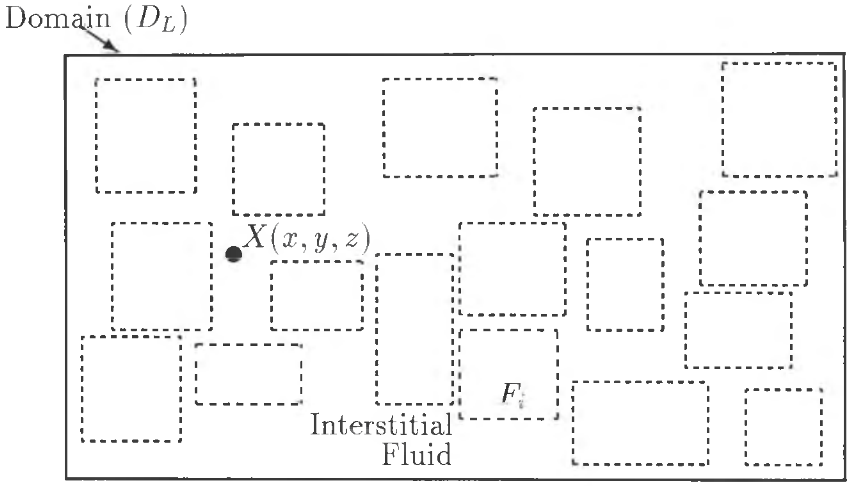


Figure 2.1: Schematization of the continuous model of lot L for particulate materials. The dotted lines represent the boundaries of the ideal rectangles fragments F_i.

Then by taking into account the continuous definition of the lot L, within the domain D_L represented by a three-dimensional model, P, we can express, $[M_L]$, the weight of active components of lot L, and A_L, the weight of critical components as follows:

$$M_L = \int\int\int_{D_L} \mu_P(x,y,z)dxdydz \tag{2.2}$$

$$A_L = \int\int\int_{D_L} \alpha_P(x,y,z)dxdydz \tag{2.3}$$

Similarly defined, a_L, the critical content of the lot L :

$$a_L = \frac{A_L}{M_L} = \frac{\int\int\int_{D_L} \alpha_P(x,y,z)dx.dy.dz}{\int\int\int_{D_L} \mu_P(x,y,z)dx.dy.dz} \tag{2.4}$$

From this we can essential represent any 3-dimensional model. Particularly important is the one-dimensional models of stationary elongate piles and dynamic lots like those obtained in blending systems and flowing stream on a belt conveyor.

Considering Figure 2.3

$x^{'}$: The projection of X on the x axis;

$(D_L^{'})$: The projection of D_L on the x axis;

Z_x: The section of D_L by the Λ plane parallel to $y0z$ at point $x^{'}$.

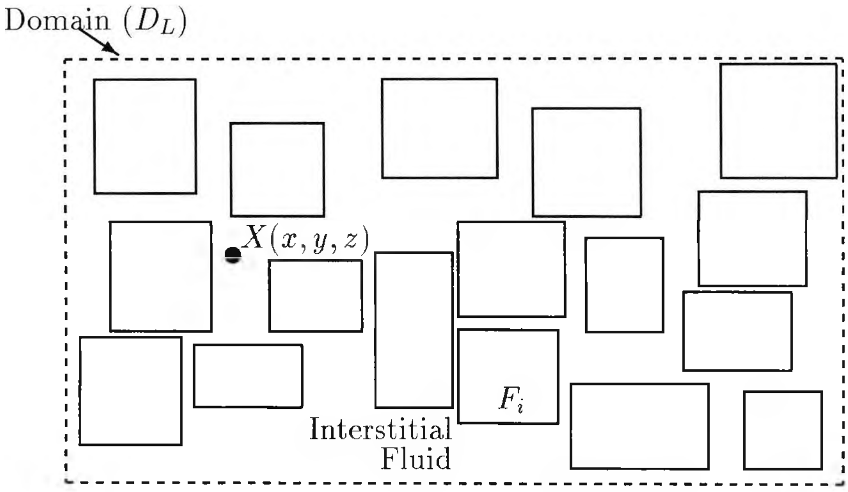


Figure 2.2: Schematization of the discrete model of lot L for particulate materials. The dotted lines represent the boundaries of the domain (D_L).

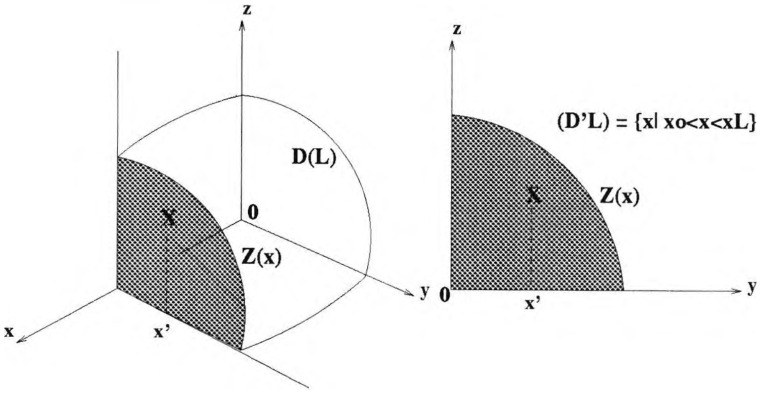


Figure 2.3: Slice of an elongate Pile considered three-dimensional but represented by a one-dimensional model over the x axis.

$\mu_P(x)$: The accumulation of active components at point x';

$\alpha_P(x)$: The accumulation of critical components at point x';

$a_P(x)$: The critical content at point x';

$$a_P(x) = \frac{\alpha_P(x)}{\mu_P(x)}$$

where

$$\mu_P(x) = \int\int_{Z(x)} \mu_P(x,y,z)dy.dz$$

$$\alpha_P(x) = \int\int_{Z(x)} a_P(x,y,z)\mu_P(x,y,z)dy.dz$$

Therefore, when spaced sampling is used,

$$a_L|_x = \frac{\int_{(D_L')} \alpha_P(x)\mu_P(x)dx}{\int_{(D_L')} \mu_P(x)dx} \tag{2.5}$$

By analogy, we can think of one-dimensional temporal models. These models together with certain basic concepts of elementary physics such as velocity of the belt, V_B, velocity of cutter, V_C, time t passing by a point x' in a range of time between t_0 and t_L in the beginning and end of the flow of L (belonging to the domain of the lot L) define the critical content $a_L|_t$ for dynamic lots:

$$a_L|_t = \frac{\int_{(T_L')} \alpha_P(t)\mu_P(t)dt}{\int_{(T_L')} \mu_P(t)dt}$$

This model is to be dealt with in Chapter 3 and will yield relevant practical results in understanding the fluctuation of content in continuous lots.

2.2 Relationships among Functions

The mathematical model presented so far uses point functions characterized by their subscript x, t, D_L. These functions describe the characteristics of the material included in the elementary fraction dx.

Two difficulties arise when converting this theoretical approach into a real model:

- extension from the fraction dx to a nonelementary volume representing the real volume taking into consideration in a simple operation of the sampling device;
- substitution of this fictitious model by an actual group of particles.

To fill the gap between the theory and the discrete reality two kinds of functions were created besides the point version: *Extended Functions* and *Fragmental Functions*. See Gy [37].

The extended functions illustrated in Figure 2.4 are characterized by the subscript $[e]$ since it represents a extension volume.

To understand these functions let us define some variables:

D_e : a given domain with either three, two or one dimensions represents the lot L. It is usually small when compared to the total extent D_L of the lot L;

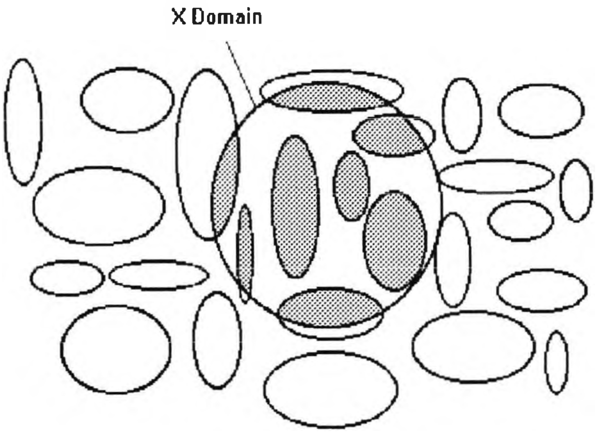


Figure 2.4: Extended Increment. Domain with isotropical properties in a bidimensional perspective.

$D_e(X)$: the domain D_e centered at point X;

$\mu_e(X)$: the average weight of active components per basic volume at the scale of D_e. By definition its value is:

$$\mu_e(X) = \frac{1}{D_e}\int_{D_e(X)} \mu_p(X')dX'$$

$\alpha_e(X)$: the average weight of critical components per basic volume at the scale of D_e :

$$\alpha_e(X) = \frac{1}{D_e}\int_{D_e(X)} \alpha_p(X')dX'$$

$e(X)$: the average critical content around the point X at the scale of D_e:

$$a_e(X) = \alpha_e(X)/\mu_e(X)$$

The fragmental functions are characterized by the subscript f. They describe the properties of the groups $G_e(X)$ of fragments whose center of gravity and center of mass fall within the boundaries of the extension domain $D_e(X)$. This definition is not arbitrary but also dependent on the "rebounding rules" to be explained afterwards. In Figure 2.5 is illustrated the fractional function. It is possible to declare

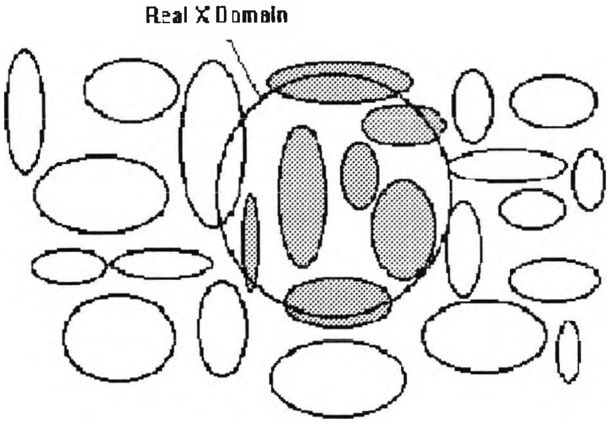


Figure 2.5: Fragmental Increment. Domain with isotropical properties in a bi-dimensional perspective.

that $\mu_f(X)$ is a discrete estimator of $\mu_e(X)$ which is itself an extended estimator of the point function $\mu_p(X)$. The same remains true for $\alpha_f(X)$ and $a_f(X)$.

Therefore,

$$a_L = \underbrace{\frac{\int_{(D_L)} a_P(X)\mu_P(X)dX}{\int_{(D_L)} \mu_P(X)dX}}_{Point} \approx \underbrace{\frac{\int_{(D_L)} a_e(X)\mu_e(X)dX}{\int_{(D_L)} \mu_e(X)dX}}_{Extended} \approx \underbrace{\frac{\int_{(D_L)} a_f(X)\mu_f(X)dX}{\int_{(D_L)} \mu_f(X)dX}}_{Fragmental}$$

The first equality is rigorous, but the others are only approximations. They are satisfactory under the following conditions:

- The size of the fragments is small when compared to the extension domain D_e;

$$\lim_{d \to 0} a_{L(f)} = a_{L(e)} = a_{L(p)}$$

- The size of the extension domain D_e is small when compared to the isotropic domain of D_L of the lot L.

The smaller the ratio D_e/D_L and the smaller the fragment size the better is the approximation. It could be useful to create a theory for optimizing the particle size in addition to logical steps that respect: (i) the selection of certain number of point increments I_p; (ii) the delimitation of the same number of extended increments I_e; (iii) the extraction of the same number of fragmented increments I_f and the reunion of the fragmented increments making up the discrete sample.

For the continuous model, where it is crucial to keep variability down to zero, the increment sampling process covers:

1. The selection of the *point increments* when applied to the model of point functions;
2. The sequence *point selection — increment delimitation* when applied to the extended functions;
3. The sequence *point selection — increment delimitation — increment extraction* when applied to the fragmental functions;

This increment property justifies the definition of the extended and fragmental functions that provide the necessary link between the continuous model and the discrete reality.

2.3 Decomposition of Overall Estimation Errors

The estimation of qualitative or quantitative properties of a batch of particulate material involves a certain numbers of error-generating operations. Some of these errors can be completely eliminated, others only partially eliminated; some can be minimized while others remain invariant. Therefore, their generation and properties must be controlled, and distinguished one from the other.

The Figure 2.6 shows a general decomposition of the Overall Estimation Error (OE).

The Total Error, TE, consists of two component errors: Preparation Error, PE, characterized by non-selective operations and Sampling Error, SE.

$$TE = \sum_{i}^{n} TE = PE + SE$$

The Sampling Error, SE, consists of two components: the Integration Error, IE and Materialization Error, ME. Both continuous and discrete models are interrelated through IE.

$$SE = ME + IE = DE + EE + IE$$

The continuous model describes the large-scale properties of IE while ignoring the small-scale particulate structure. The discrete model describes the small-scale

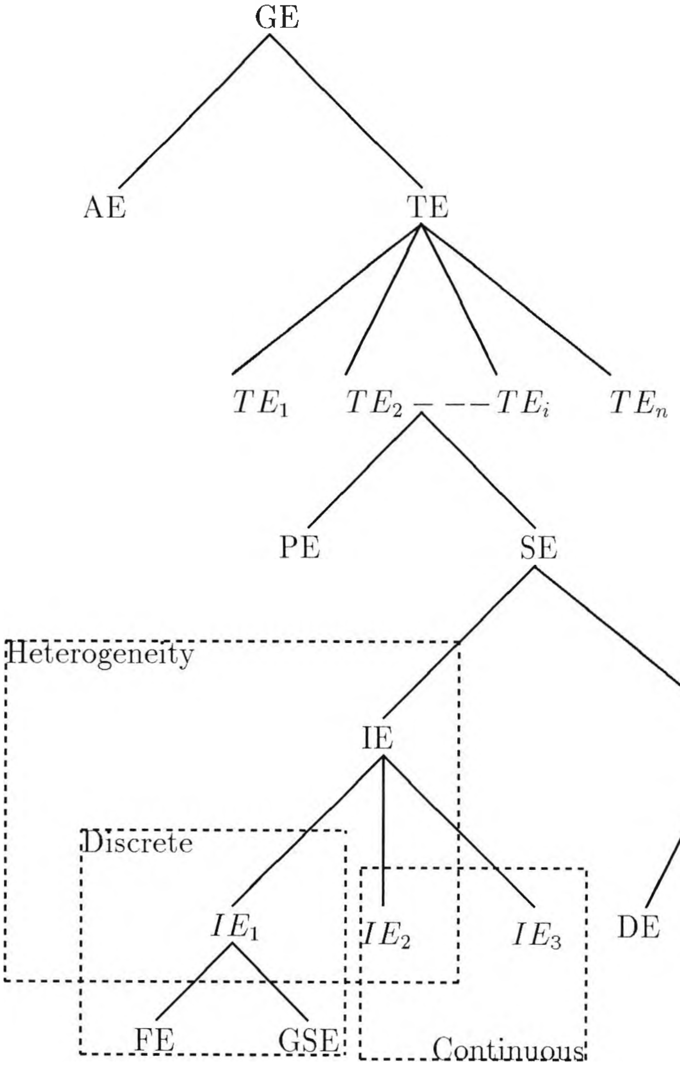


Figure 2.6: Decomposition of Global Estimation Error. The short-range fluctuation long-range and periodic errors are also represented by dashed boxes.

particulate properties of ME. Under certain conditions of sampling correctness, ME is nil and consequently, also Delimitation Error, DE and Extraction Error, EE.

In fact, IE represents quality and weight errors. The first corresponds to the intrinsic constitution of material and the latter is due to fluctuations in the flowrate of the material been sampled past the device used to take the increments. If the flowrate is constant, it is negligible and IE is due only to the fluctuations in the quality of material. Its decomposition includes a short-range quality error, IE_1, a long-range nonperiodic quality error, IE_2 and a periodic quality error, IE_3. Therefore,

$$IE = IE_1 + IE_2 + IE_3 = FE + GSE + IE_2 + IE_3$$

or in terms of continuous selection errors [CE]:

$$IE = CE = CE_1 + CE_2 + CE_3$$

When EE is nil, and only in that case, it is possible to carried out an experiment for both discrete and continuous lots and estimate all actually existing components of integration errors. These errors include the variance between individual test-units and interclass correlation coefficient between test-units in the same increment. Therefore, streams of material sampled in time or space are much more complete because it is possible to estimate not only the scalar variance of quality errors but also the variability of process as a whole.

The estimation of the variance of the IE is nothing other than the determination of the sampling precision and takes the one-dimensional time correlation into account when sampling one-dimensional moving streams. This approach may be used to analyze several sampling strategies. For example, random sampling is shown to be significantly inferior compared to systematic sampling and stratified random sampling.

The discrete model and the continuous model are connected through the deeper analysis of the short-range quality error. This requires a quantitative concept of particle heterogeneity and leads to the quantitative definitions of Constitution Heterogeneity of the lot, CH_L (an intrinsic characteristic of the material and greatly affected by comminution), and Distribution Heterogeneity of the lot, DH_L (truly affected by segregation). Both CH_L and DH_L can be determined nearly exactly if each particle is individually measured. Even though they are rather difficult to determine in practice, the necessary information can be approximated quite well by a size-density analysis.

IE_1 consists of two components: the Fundamental Error, FE and the Grouping Segregation Error, GSE. The mean of FE is nonzero which entails that even when increment sampling is theoretically correct, a bias exists. However, except for low grade materials, this bias is negligible (see Merks [76] for details). The variance of FE, [$\sigma^2(FE)$] is proportional to the constitution heterogeneity of the lot and inversely proportional to the number of sample fragments N_F.

$$\sigma^2(FE) \propto CH_L/N_F$$

Even without actually measuring $\sigma^2(FE)$, the theoretical analysis is useful since it shows when $\sigma^2(FE)$ theoretically completely cancels and how it can be in practice minimized. Moreover $\sigma^2(FE)$ is zero only when either the sample is equal to the lot or when CH_L is zero — never attainable in practice and $\sigma^2(FE)$ can be minimized by increasing the sample weight or by comminution. As it brings about cost, the economical optimum is reached by compromise. On the other hand, GSE is minimized by:

- minimizing FE;
- extracting increments as small as possible;
- minimizing segregation by homogenizing;

The Materialization Error, ME, consists of two components: a Delimitation Error, DE, and an Extraction Error, EE. These errors are caused by incorrectly constructed sampling devices and/or incorrectly operated devices.

All components of the GE are assumed independent in probability with the consequence that can be directly transposed to the means and variances of the errors:

$$GE \equiv \int_n TE_n + AE \equiv \int_n (SE_n + PE_n) + AE$$

which entails the following relationships:

$$m(GE) \equiv \int_n m(TE_n) + m(AE) \equiv \int_n [m(SE_n) + m(PE_n)] + m(AE)$$

$$s^2(GE) \equiv \int_n s^2(TE_n) + s^2(AE) \equiv \int_n [s^2(SE_n) + s^2(PE_n)] + s^2(AE)$$

Although the model applies equally well in one, two, three and zero dimensional, in practice, only one-dimensional streams can be sampled in such a way that the moments of SE can be determined. Sampling of two and three dimensional piles of stationary material is always subject to unavoidable and uncontrollable biases. These biases arise from the interaction of the sampling device with the particulate structure of the material. For sampling problems to be solvable, the material must either be in the form of moving stream or must be sampled by a splitting process. This process favors developing countries, since it is always possible to stop a stream on belts and collect increments by using a conventional sampler or dividers to split the lot.

2.4 Notion of Heterogeneity

Although optimization of the sampling protocols to minimize FE, GSE, IE_2, IE_3, and to eliminate DE, EE and PE is crucial for mastering the sampling techniques, the concept of heterogeneity is perhaps the most important part of the sampling strategy in determining the quality of both zero-dimensional lot and one-dimensional lots.

The problems of one-dimensional batch are a bit more complex since they involve variograms and long-range heterogeneity and periodic components they are postponed to a later stage. Here we deal with the general heterogeneity problem symbolized by h. The suffix m denotes the number of discrete units of a batch or lot L and is assumed to be assigned at random — $m = 1, 2, ...N_U$ where N_U is the total number of these discrete units. The following symbols are indexed by m.

U_m One of N_U typical units of the lot.

M_m Mass of all active components in unit U_m and $\sum_m M_m \equiv M_L$;

A_m Mass of critical component A in unit U_m and $\sum_m A_m \equiv A_L$;

a_m Critical content of unit U_m and $a_m \equiv A_m/M_m$.

The heterogeneity h_m, carried by U_m is proportional to the deviation $(a_m - a_L)$ or, in other words, the difference between this state and the complete homogeneity. Experiments by Gy [37] show that is much easier to deal with relative, dimensionless quantities. For this we define $M^*_m = M_L/N_U$. Then within the lot:

$$h_m \equiv \frac{(a_m - a_L)M_m}{a_l M^*_m} \equiv N_U \frac{(a_m - a_L)M_m}{a_l M_L} \tag{2.6}$$

When speaking of unspecified units U_m, it should be recalled that these units are formed of fragments of particulate material. Therefore, the unit U_m becomes the fragment F_i with $i = 1, 2, ..., N_F$ that can be similarly related to the descriptors M_L, A_L and a_L. Hence, any quality characteristic can be computed in terms of fragments.

$$a_L = \frac{\sum_i A_i}{\sum_i M_i} = A_L/M_L$$

For groups of fragments G_n of a lot and number of fragments within groups $j = 1, 2, ..., N_n$, the following relation is convenient:

$$a_L = \frac{\sum_n \sum_j A_{nj}}{\sum_n \sum_j M_{nj}} = A_L/M_L$$

In practical terms it will be better to consider the average number of fragments, $\bar{\imath}$, of the average fragment, $F_{\bar{\imath}}$, and the average number of groups, $\overline{n}$, of the average group, $G_{\overline{n}}$ and define the following relations:

$$A_L/M_L = a_L = A_{\overline{i}}/M_{\overline{i}} = a_{\overline{i}} = A_{\overline{n}}/M_{\overline{n}} = a_{\overline{n}}$$

We are interested in the heterogeneity between and not within fragments. The notion of heterogeneity h_i carried by a fragment is directly related to two descriptors: a *qualitative parameter* — critical component, A_i, a *quantitative parameter* — weight component, M_i, whose proportions characterize the critical content a_i.

As shown before, it is commonly accepted that the use of a relative and dimensionless rather than absolute characteristics is far more convenient. Considering this some remarks can be made:

- The sampling variance is a simple function of the variance of h_i;
- The calculation of h_i involves only parameters that are intrinsic properties of the material making up the lot and is independent of the size of lot considered;
- The descriptor h_i is dimensionless but requires the use of the same units;
- A set of fragments may be defined only by one descriptor when equal weight of bulk material is taken from the lot.

Thus, the average carried by the fragments of a lot is:

$$m(h_i) = \sum_i h_i/N_F = 0$$

and the sampling variance $s^2_{h_i}$ of the heterogeneity random variables is:

$$s^2_{h_i} = \frac{1}{N_F}\sum_i h_i^2 = N_f \sum_i \frac{(a_i - a_L)^2}{a_L^2} \times \frac{M_i^2}{M_L^2}$$

$s^2_{h_i}$ is equal to the relative variance of the content a_i of the fragments.

2.5 Constitution and Distribution Heterogeneity

There are two types of heterogeneities within dimensional lots:

- The heterogeneity consisting of a difference between the composition of the different units of a lot, such as between fragments of particulate material. This is defined as *Constitution Heterogeneity*, CH_L a micro property of a sampling unit;

- The heterogeneity consisting of a difference between the spatial distribution of the different units within the lot caused by differences in shapes, densities, sizes, weights of fragments. It is called *Distribution Heterogeneity*, DH_L, and it is a measure of both trends and the segregation phenomena — macro properties of the sampling units.

The *Constitution Heterogeneity* of a lot is defined as the relative and dimensionless variance of the heterogeneities h_i carried out by the N_F fragments F_i making up the lot.

$$CH_L = s^2_{h_i}$$

This variability is at its maximum in the case of one particle *primary increment* collected from a truly binomial sampling unit. However, the variability decreases rapidly as the number of particles in an increment increase. The composition variance is caused by differences in composition between particle and therefore a micro property of a sampling unit. When dealing with composite lots, it is easily demonstrated that CH_L is equal to the weighted averages of sublots:

$$CH_L = \frac{N_{F1}CH_{L1} + N_{F2}CH_{L2}}{N_{F1} + N_{F2}}$$

Therefore CH_L is a characteristic of the material making up the lot, irrespective of the size of the lot.

The difficulty in calculate CH_L resides in estimating N_F, which is generally very large. To overcome this difficulty we multiply CH_L by the term M_L/N_F which is the average weight of a fragment $M_{\bar{i}}$ and define the constant factor of constitution heterogeneity, IH_L:

$$IH_L = CH_L M_L/N_F = CH_L M_{\bar{i}} = \sum_i \frac{(a_i - a_L)^2}{a_L^2} \times \frac{M_i^2}{M_L} \qquad (2.7)$$

Thus, IH_L has the dimension of a weight and the property of a constant which characterizes the lot. Both CH_L and IH_L are two intrinsic parameters of the material under investigation. The former is always defined , but can only be calculated when the number of fragments is small enough to be counted like *movable* lots. The latter can always be calculated as a practical evaluation of the variance of fundamental error.

The hypothesis that the average weights $M_{\bar{i}}$ are almost equal implies that a comparison between various constant factors of constitution heterogeneity can only be made for materials having a similar particle size distribution.

At the cost of some approximation, IH_L can always be calculated, regardless of the large number of particles. Its great usefulness is in practical application, particularly to estimate the variance of fundamental error. For more information about FE see *short-range heterogeneity* later in this chapter.

The notion of distribution heterogeneity considering a lot made of N_F particles concerns not the microstructure of the particles but the isotropic module of observation. Two heterogeneity exist:

1. h_{nj}, carried by a fragment within a finite group of particles G_n with $j = 1, 2, ...N_n$ fragments F_{nj}. Following the same reasoning of Equation 2.6 in Section 2.4 the heterogeneity h_{nj} carried out by a fragment belonging to the lot is:

$$h_{nj} = \frac{(a_{nj} - a_{n\bar{j}})}{an\bar{j}} \frac{M_{nj}}{M_{n\bar{j}}}$$

   where M_{nj} and a_{nj} are the weight and critical content of the fragment F_{nj}; $a_{n\bar{j}}$ is the critical content of the average fragment $(a_{n\bar{i}} = a_n)$ and $M_{n\bar{j}} = M_n/N_n$.

2. h_n, carried by a group of fragments within a lot:

$$h_n \equiv \frac{(a_n - a_L)M_n}{a_L M_{\bar{n}}} \equiv N_G \frac{(a_n - a_L)M_n}{a_L M_L}$$

If there is no segregation and the size of particles are smaller than the liberation diameter, it is possible to accept that the heterogeneity carried by a group of fragments is equal to the heterogeneity carried by an average fragment in a group is $h_n = h_{n\bar{j}}$.

$$DH_L = s^2(h_n) = \frac{1}{N_G} \sum_n h_n^2 = N_G \sum_n \frac{(a_n - a_L)^2}{a_L^2} \times \frac{M_n^2}{M_L^2} \tag{2.8}$$

2.5.1 Relationship between CH_L and DH_L

Note first that G_n, group of particles, is a subset of the set of fragments L_F of the lot. Since $M_{n\bar{j}}$ and $M_{\bar{i}}$ are identical by definition,

$$\sum_i h_i^2 = \sum_n \sum_j h_{nj}^2$$

Assuming sampling correctness, the heterogeneity carried by fragments, h_i, is equal to the heterogeneity carried by a single fragment in a group,h_{nj}. Thus the following identity can be written:

$$h_i = h_{nj} = h_{nj} - h_n + h_n$$

Squaring both side,

$$h_i^2 = h_{nj}^2 = (h_{nj} - h_n)^2 + 2(h_{nj} - h_n)h_n + h_n^2$$

Summing up all over the lot with N_F fragments and N_n the number of fragments,

$$\sum_i h_i^2 = \sum_n \sum_j h_{nj}^2 = \sum_n \sum_j (h_{nj} - h_n)^2 + 2\sum_n \sum_j (h_{nj} - h_n)h_n + N_n \sum_n h_n^2 \quad (2.9)$$

Now by a simple algebra, using the Equation 2.9 and dividing each term by N_F

$$\underbrace{\frac{1}{N_F}\sum_i h_i^2}_{CH_L} = \underbrace{\frac{1}{N_G}\sum_n h_n^2}_{DH_L} + \underbrace{\frac{1}{N_F}\sum_n \sum_j (h_{nj} - h_n)^2}_{CH_{\overline{n}}} \quad (2.10)$$

where $CH_{\overline{n}}$ is the residual average constitution heterogeneity regarding different groups of fragments G_n in the lot.

From this underlying equation,

$$CH_L = DH_L + CH_{\overline{n}} \quad (2.11)$$

and several conclusions may be retained:

- All terms of Equation 2.10 are squares, therefore are positive and obey the inequalities:
$$CH_L \geq DH_L \geq 0$$
- The constitution heterogeneity of any lot of particulate material is always greater or equal to the distribution heterogeneity;

- When the material is completely homogenized, that is $a_i = a_L$, $CH_L = 0$. This implies that both DH_L and $CH_{\overline{n}}$ are also nil, therefore in this case there is no heterogeneity at all.
- Under natural conditions distribution heterogeneity is never nil and always positive despite the identity: $DH_L = CH_L - CH_{\overline{n}}$. Thus, DH_L being the variance of all h_n, can be nil only when the values of h_n are all equal to their average which is itself nil. Then, $DH_L \geq 0$ and due to the particulate nature of the material, can be only reduced to a minimum level $(DH_L)_{min}$ through CH_L and the mixing processes.

If we divide each term of Equation 2.9 by s^2, the variance of heterogeneity of prior lots, and assume standard normality, the analysis of variance terms are:

$$\sum_n \sum_j h_{nj}^2 / s^2 = N_F CH_L / s^2$$

which follows a $\chi^2_{N_F - 1}$ distribution;

$$\sum_n \sum_j (h_{nj} - h_n)^2 / s^2 = N_F CH_{\overline{n}} / s^2$$

which follows a $\chi^2_{N_F - N_G}$ distribution;

$$\sum_n N_n h_n^2 / s^2 = N_G DH_L / s^2$$

which follows a $\chi^2_{N_G - 1}$ distribution. We call N_n the number of fragments in a group and define $N_G = N_F / N_n$.

We can compute three independent unbiased estimators of variance:

1. The total variance:
$$s_t^2 = CH_L N_F / (N_F - 1)$$
2. The variance between groups:
$$s_b^2 = (DH_L)_{min} N_F / (N_G - 1)$$
3. The residual variance that corresponds to the variance within groups:
$$s_w^2 = CH_{\overline{n}} N_F / (N_F - N_G)$$

As N_F is generally very large, $s_t^2 \simeq CH_L$ and the minimum distribution heterogeneity may be written as follows:

$$(DH_L)_{min} = \frac{N_G - 1}{N_F - 1} CH_L \tag{2.12}$$

Therefore, $(DH_L)_{min} = f(N_G, N_F, CH_L)$ have a range:

$$DH_L = \begin{cases} min & \frac{N_G-1}{N_F-1} \times CH_L \\ max & CH_L \end{cases}$$

2.6 Segregation and Grouping Factors

Many of the difficulties of operating problems with particulate materials are caused by *segregation.* Segregation can be of two kinds: *size segregation*, in which particles of the same size, in a mass of bulk material containing a range of sizes, collect together and *density segregation*, in which particles of the same density or specific gravity in a mass of particles of varying density, gather together. However, all the available evidence shows that differences in particle size are by far the most troublesome. Because many industrial problems arise from it our attention should be focused on this characteristic.

The mechanism of segregation when handling mixtures is the shifting of fines through the voids of coarser particles. The Figure 2.7 shows a schematic of a typical cumulative percentages of fines and total corn as a function of radial distance from the charge point. In the study undertaken by Foster [100] an increase in fines content to 20% was found under the central charge point and practically no fines at the edges.

The best way to materialize these concepts of grouping and segregation factors related to distribution heterogeneity is by rewriting the Equation 2.12:

$$(DH_L)_{min} = \frac{N_G - 1}{N_F - 1} CH_L = \frac{1}{1+\zeta} CH_L \tag{2.13}$$

where grouping factor, ζ, is defined as the ratio of total number of fragments N_F to the total number of groups N_G,

$$\zeta = (N_F - N_G)/(N_G - 1)$$

or

$$\frac{1}{1+\zeta} = \frac{N_G - 1}{N_F - 1} \tag{2.14}$$

From the formula, we can see that ζ is a positive and decreasing function of G_n and an increasing function of the size of the groups. Also it reaches a minimum, equal

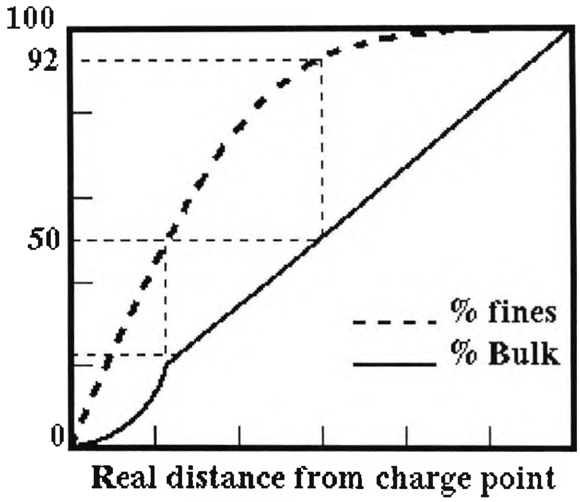


Figure 2.7: Effect on Segregation by Particle Size

to zero, when the number of groups is equal to the number of fragments ($N_G = N_F$) and very large when $N_G \to 1$. When $N_G = 1$ then $\zeta = +\infty \Rightarrow (DH_L)_{min} = 0$ and, therefore, as general rule $1 \ll N_G \ll N_F$.

In practice, however, is common to use $N_F/N_G = \zeta$ or $N_{\overline{n}}$ the average number of fragments in a group. Under the hypothesis of natural distribution heterogeneity $(DH_L)_{nat}$, remains always smaller than CH_L but superior to the minimum $(DH_L)_{min}$.

Using the Equation 2.13 it is possible to create the following useful inequality:

$$\frac{1+\zeta}{1+\zeta}CH_L \geq (DH_L)_{nat} \geq \frac{1}{1+\zeta}CH_L > 0 \tag{2.15}$$

In order to obtain $(DH_L)_{nat}$ through CH_L, Gy [37] defines a factor $\zeta\xi$ and calls ξ the segregation factor.

$$(DH_L)_{nat} = \frac{1+\zeta\xi}{1+\zeta}CH_L = (1+\zeta\xi)\frac{N_G-1}{N_F-1}CH_L \tag{2.16}$$

Then, using the Equation 2.15 and dividing both side by $CH_L/(1+\zeta)$

$$(1+\zeta) \geq (1+\zeta\xi) \geq 1 > 0$$

With additional algebra operations we obtain:

$$1 \geq \xi \geq 0$$

From this and Equation 2.15 we can conclude that:

$N_n = 1$		$N_F > N_n > 1$		$N_n = N_F$
N_F	$\geq$	N_G	$\geq$	1
0	$\leq$	ζ	$\leq$	$+\infty$
CH_L	$\geq$	DH_{res}	$\geq$	0

Table 2.1: Effective domain of the variables related to Grouping and Segregation Factor. Effect of observation scale on N_G, ζ and DH_L.

1. When the segregation factor approaches 0, the lot approaches the state of minimum distribution heterogeneity $(DH_L)_{min}$;

2. When the segregation factor approaches 1 the lot approaches the state of maximum distribution heterogeneity $(DH_L)_{max}$. Finally from Equation 2.14 and Equation 2.16:

$$(DH_L)_{nat} = (1 + \zeta\xi)(N_G - 1)\frac{N_F}{N_F - 1}\sum_i \frac{(a_i - a_L)^2}{a_L^2}\frac{M_i^2}{M_L^2} \tag{2.17}$$

The effective domain of these variables is collected in Table 2.1. To deduce the variance of grouping and segregation errors we have to analyze the influence of the size of increments on the variance of the first term $\sigma^2(CE_1)$. Then,

$$\sigma^2_{GSE} = \zeta\xi\sigma^2(FE)$$

2.7 The Minimum Weight of Material

The object of this section is to discuss the relationships between the size and amount of increments and accuracy of estimation, taking into consideration the characteristics presented so far and the nature of the material. The sampling protocol is carried out by extracting a suitable primary quantity from a representative lot, mixing, dividing into secondary increments or subsamples and analyzing. Sometimes subsamples are combined in order to increase precision.

The common assumption that a defined level of precision can only be attained by relating sample size to lot size is wrong, since truly random samples of the same size provide equally reliable estimates of bulk characteristics whatever the size of the lot. However, when large lots are being considered is always advisable to the increase sample size instead of the weight of material.

The amount of individual increments however, is taken so as not to exceed a predetermined level of sampling uncertainty. The material must be sufficiently homogeneous that variability between increment portions does not mask small variations due to the intrinsic properties of material.

There are three approach for the minimum weight of bulk material and each one is based on a sampling constant, k_s : Ingamells', Gy's and Visman's. The first approach is useful in describing the subsampling characteristics of the laboratory samples and submitted samples. The second is useful in controlling the reduction of field samples to a laboratory size. Visman's approach is for design of a field sampling procedure. From all these approach, the last two should claim for priority not only due to basic sampling principles involved but also due to the field of applicability.

Visman's sampling theory as described in his *General Sampling Theory* [105] applies to the analysis of unknown materials which are both heterogeneous and segregated. It requires the collection of two series of samples, one series of small samples and one series of large samples. The members of each series are reduced and then analyzed. Care must be taken that the variance in the results does not originate from sampling errors. His sampling constants are defined as follows:

$$A = \frac{w_1 \times w_2(s_1^2 - s_2^2)}{w_2 - w_1}$$

and

$$B = s_2^2 - \frac{A}{w_2}$$

where A is a constant of heterogeneity, B is a constant of segregation, s_1 is the small sample variance, s_2 is the large sample variance, w_1 is the small sample weight, and w_2 is the large sample weight.

The constants A and B being determined, the expected variance in the combined results of n samples of weight w is given by

$$s^2 = \frac{A}{W} + \frac{B}{n} \Rightarrow w = \frac{A}{ns^2 - B} \tag{2.18}$$

where $W = nw$ is the total weight of samples of weight w.

From his theory we can draw two underlying conclusions:

1. As the segregation increases the number of samples required become more critical to keep the variance down;

2. In case there is no segregation at all, B is zero and the number of samples has no effect.

With segregate materials there is an optimum field sampling weight w^* which will yield a most precise estimate of the attribute considered for any given total weight of field samples. By differentiating Equation 2.18 with respect to w and equating to zero, this optimum weight is found to be

$$w^* = A/B = W/n \tag{2.19}$$

Visman's sampling theory was developed semi-empirically and in the light of statistical theory its approximations when segregation, defined as $\xi = \sqrt{B/nA}$, is extreme, may not be tolerable in real circumstances.

For materials of unknown composition, the test requires collection of more than 25 small and large samples with an average weight of at least $100g$ and $5000g$ respectively. For the first series of small samples (w_1) are chosen to ensure that the first term (A/w) contributes more to the total variance than the second term. The total variance is computed using the following equations that provide maximum estimates, by first-order approximation. of the constants A and B.

To any preassigned accuracy the weight of the gross sample and the number of increments can be found.

More realistic however, is Gy's sampling constant. It takes into consideration the complex features of isolated particle, group of particles and size distribution. The theory assumes that the material is thoroughly mixed, there are no materialization errors inherent in the sampling tools or crushing machines and preparation errors are kept to a irreducible minimum. In this case of sampling correctness the short-range quality fluctuation errors IE_1 reduce to FE since GSE can be eliminated. From a practical view the fundamental error is the only error that never cancels.

The basic equation is defined as follows (for more details see in Section 2.4 and Section 2.5).

$$\sigma_{FE}^2 = (\frac{1}{M_s} - \frac{1}{M_L}) IH_L$$

Deverly in his Doctor thesis (1984) of size-density of minerals shows that

$$IH_L \equiv \underbrace{[\sum_x V_x \frac{M_{Lx}}{M_L}]}_{S_1} \underbrace{[\sum_y \delta_y \frac{(a_{xy} - a_L)^2}{a_L^2} \frac{M_{Ly}}{M_L}]}_{S_2}$$

where

M_{Lxy} Mass of the class M_{Lxy} of L_{xy};
V_x Volume of average fragment of the size-density class;
a_{xy} Critical content of F_{xy};
δ_y Specific gravity of F_{xy}.

He determines the precise relationship of both functions associated to practical factors:

$$S_1 = f\sum_x d_x^3 \frac{M_{Lx}}{M_L} = fgd^3$$

and S_2 being a function of several variables reaches the maximum and minimum when

$$[S_2] = \begin{cases} [S_2]_{min} & \rightarrow 0 \quad\quad a_{xy} = a_L \\ [S_2]_{max} & \rightarrow \varpi \quad\quad \text{otherwise} \end{cases}$$

$$\sigma_{FE}^2 = (\frac{1}{M_s} - \frac{1}{M_L})\varpi l f g d^3$$

in which:

ϖ = mineralogical composition factor;

f = a particle shape factor;

d = top size of bulk solid;

g = granulometric (size range) factor;

C = sampling constant;

l = liberation factor.

Liberation Factor — l It is defined as the maximum particle diameter that ensures the complete liberation of the critical component or the parameter to be estimated. The formula below defines its basic terms:

if $d \leq d_l$ then $l = 1$
if $d > d_l$ then $l = \sqrt{\frac{d_l}{d}}$

Liberation Factor—l	1	0.8	0.4	0.2	0.1	0.05	0.02
d/d_l	1	1—4	4—10	40—100	100—400	400	
Concentrate	h	h	$\rightarrow$	$(1-h)$	$(1-h)$		
Residues		h	h	$\rightarrow$	$(1-h)$		

Table 2.2: Liberation Factor l as a function of particle size d, and d_l is the particle size at which complete liberation occurs. h stands for heterogeneity and $(1-h)$ for homogeneity.

From its definition, l can vary between 0 and 1 but for all practical purposes we shall never use values smaller than 0.03. The liberation diameter, d_l, is the maximum particle diameter that ensures the complete liberation of material. When the maximum value of l is 1.0, occurring when the critical mineral is completely liberated. More crushing is too costly. Its value can be estimated visually. The Table 2.7 presents these ranges.

Particle Shape Factor—f The microscopical analysis of particles in general assumes as a standard of dimension, d, cubic particles in which is the sieve aperture retaining 5% oversize. This is taken as the size of the largest particles. In practice, particles are irregular in shape and may tend towards spheres rather than cubes. This factor can vary from between $f = 0.5$, when the shape is spheroidal, and f = 0.2, when particles are like plates or needles.

Mineralogical Composition Factor—ϖ It is defined whenever there is a constant proportional factor between chemical content and the corresponding physical content expressed in terms of mineralogical component

$$\varpi = \frac{(1-a_L)}{a_L}[(1-a_L)\delta_M + a_L\delta_G] = \frac{1-a_L}{a_L}\frac{\delta_M\delta_G}{\delta}$$

where a_L is the content of the chemical product;

δ_M is the specific gravity of the material;

δ_G is the specific gravity of the remaining constituent of the lot;

δ is the average density.

defined as

$$\delta = \frac{\delta_M\delta_G}{[(1-a_L)\delta_M + a_L\delta_G]}$$

Granulometric Factor—g It is the range of the sieve aperture (d) which retains 5 per cent oversize material, to the aperture which passes 5 per cent undersize material (d_o). Their values are standardized in Table 2.7.

Size Range	d/d_o	g
Large	> 4	0.25
Medium	4—2	0.50
Small	< 2	0.75
Uniform	=1	1.00

Table 2.3: Typical values of the granulometric size range factor, (g), the ratio of the sieve aperture d which remains 5% oversize material, to the aperture which passes 5% undersize material (d_o).

WORKED EXAMPLE:

The following is a reworking of an example of Royle [87] using the methods of previous section. Galena, PbS, is a mineral ore has a lead content $[a_I]$ around 5 percent in a calcite gangue. It is delivered at a size of 1 cm. The density of both gangue and galena is 2.7 and 7.5, respectively.

The sampling campaign was optimized by the analytical laboratory and was based on the equation below and on the nomograph of logarithm scale showing σ^2_{FE} as a function of sample weight and particle size. When the weight M_L is very large compared to M_S, the quickest way to determine the fundamental error is by

$$\sigma^2_{FE} = Cd^3/M_S$$

In order to give more robustness to our nomograph it is useful to transform the variables into a logarithmic coordinates. Therefore,

$$\log \sigma^2_{FE} = \log C3 \times \log d - \log M_S$$

For a given particle size, which, by definition, is a constant carrying a given sampling constant, the value of σ^2_{FE} is directly to $-\log M_S$ and the derivative function has a -1 slope on the nomograph presented. Every successive sampling and comminution stage is represented by a broken line. To reduce the σ^2_{FE} we have to optimize the nomograph depending on the costs allowed and the equipment available.

In the example presented, $10kg$ was collected from the galena ore delivered at a size of $1cm$. Comminution took it to $3mm$. Then it was split to $500g$, crushed to $1mm$, reduced to $50g$, grinding to $0.2mm$ and finally splitting to $2g$ for laboratory analysis.

Determination of IH_L in the equation

$$\sigma^2_{FE} = (\frac{1}{M_s} - \frac{1}{M_L})IH_L$$

- Percentage of pure Pb in the Galena:

$$Percent_{Pb} = 0.05Pb = 0.05[\frac{207+32}{207}] = 0.058PbS$$

- Mineralogical Factor ϖ :

$$\varpi = \frac{(1-a_L)}{a_L}[(1-a_L)\delta_M + a_L\delta_G]$$

$$\varpi = \frac{(1-0.058)}{0.058}[(1-0.058)\times 7.5 + 0.058 \times 2.7]$$

$$\boxed{\varpi = 117.30}$$

- Determination of IH_L:

$$IH_L = \varpi \times f \times g \times \sqrt{\frac{d_l}{d}} \times d^3$$

$$IH_L|_{(1cm)} = \underbrace{117.30 \times 0.5 \times 0.25}_{14.66} \times \sqrt{\frac{0.01}{1}} \times 1^3 = 1.47$$

$$IH_L|_{(3mm)} = 14.66 \times \sqrt{\frac{0.01}{0.30}} \times 0.30^3 = 0.072$$

$$IH_L|_{(1mm)} = 14.66 \times \sqrt{\frac{0.01}{0.10}} \times 0.10^3 = 146 \times 10^{-7}$$

$$IH_L|_{(.2mm)} = 14.66 \times \sqrt{\frac{0.01}{0.02}} \times 0.02^3 = 829 \times 10^{-7}$$

- Determination of Variance of Fundamental Error:

$$\sigma^2_{(FE)diam} = (\frac{1}{M_s} - \frac{1}{M_L})IH_{(L)diam}$$

but $M_L \gg 10M_S$. Then,

$$\sigma^2_{(FE)1cm} = (\frac{1}{M_s})IH_{(L)diam} = (\frac{1}{10000}) \times 1.47 = 1.47 \times 10^{-4}$$

$$\sigma^2_{(FE).3cm} = (\frac{1}{500} - \frac{1}{10000}) \times 0.072 = 1.44 \times 10^{-4}$$

$$\sigma^2_{(FE).1cm} = (\frac{1}{50} - \frac{1}{500}) \times 14610^{-7} = 0.3 \times 10^{-4}$$

$$\sigma^2_{(FE).02cm} = (\frac{1}{2} - \frac{1}{50}) \times 82910^{-7} = 0.4 \times 10^{-4}$$

The total variance is then:

$$\sigma^2_{FE} = \sigma^2_{(FE)1cm} + \sigma^2_{(FE).3cm} + \sigma^2_{(FE).1cm} + \sigma^2_{(FE).02cm}$$

$$\boxed{\sigma^2_{FE} = 3.61 \times 10^{-4}}$$

From this the 0.95 confidence limits for the mean of the lot will be given by

$$a_L = \overline{a}_S \pm t_{0.025}\sqrt{\sigma^2_{TE}} =$$

$$a_L = 0.05 \pm 1.96 \times \sqrt{3.61 \times 10^{-4}} = 0.05 \pm 1.96 \times 0.019$$

$$\boxed{0.05 \pm 0.037}$$

Many other questions can be solved by using these formulae. For example:

1) the weight that must be taken for a given particle size for a certain sampling error;

2) the size which the sample must be crushed if a particular weight is taken and a given sampling error for the mean of lot is deemed barely tolerable.

Basic computer programs for performing similar calculations are found in Wills [109].

2.8 Amount of Sampling: Models

Determining the minimum number of increments to be taken from the whole consignment depends on the knowledge of properties of the particulate material to be sampled (see Subsection 2.7) and categorizing of the identifiable portions of the lot.

The configuration of consignment divides the sampling into three classes: container sampling, stopped and moving belt sampling and wagon or ship's hold sampling. In the first case the material is packaged in unequivocally partitions or primary units which are not unequivocally identifiable as secondary units. There is a lot size N from which N_Q increments are selected. In the second case the lot is not divisible into unequivocally identifiable portions.

When the material is conducted past the selection point, the whole lot L of size, M_L, may be thought of as a series of uniformly distributed primary sampling units constituting the consignment in an pseudo-Euclidean space with Q increments I taken from it. These increments range from x_0 to x_Q with all x within the domain of the lot (L). It can be represented: $(x_Q) \equiv \{x|0 < x \leq x_Q\}$.

In a collection point, generally in a *Sampling Test Station* there will a random selection with a uniform probability of the increment being chosen. Let us call this probability density $\Pi(x)$, uniform throughout the domain (equals to Π_0) and zero outside it.

From a discrete viewpoint each increment composing the consignment has the same probability of being chosen,

$$P\{x_Q\} = \sum_0^{x_Q} \Pi(x_I) \Rightarrow \sum_0^{x_Q} \Pi(x_I) = 1$$

In a continuous perspective, the probability of selecting one and only one increment x_I is

$$\int_0^{x_Q} \Pi(x_0)dx_o = \Pi_o \int_0^{x_Q} dx = \Pi_o x_o = 1 \Rightarrow \Pi_o = 1/x_o$$

When sampling the increment at random from each stratum we can make inferences about the lot and/or the process through the key equality:

$$a_L = \overline{a}_s \pm t_{0.025}\sqrt{\sigma^2_{TE}} = \overline{a}_s \pm t_{0.025}\sqrt{\sigma^2_{SE} + \sigma^2_{PE} + \sigma^2_{ME}} \qquad (2.20)$$

where $t_{0.025}$ is the value for a $t-$distribution with $n-1$ degrees of freedom involved in the pilot estimate of the average variance of N_Q number of increments I. The other variables are: σ^2_{TE} the overall precision or total error of the process, σ^2_{SE}, the sampling error, σ^2_{PE} the preparation or subsampling error and σ^2_{ME} the measurement error. The combination of these variance components for two and more levels of sampling can be dealt with in a general way to illustrate the effect of varying the number of samples or subsamples at each level and the effect of composite samples prior to analysis.

With a substantial number of degree of freedom (DF) it is possible to establish the variability $[\sigma_{TE}]$ for different lots of chemicals for containers within lots, σ_b, for samples from containers, σ_w, and for a number of replications on the same samples, σ_{PE}, and σ_{ME}.

In order to reduce the risks, great improvements can be achieved by composing samples. For example, if we are controlling isolate lots and analysis made with half the portion, σ_{ME} is reduced by a half. If two samples are taken at random, one from any bag in one lot and the other from any bag in any other lot, the variance of the average quality is reduced by as many as half. Therefore, with little extra trouble other arrangements can be made so as to get more confidence in the decision. This is a good method of improving precision of the experiment.

Now let us see the influence of weight of increment. According to Merk [76], and Visman [105] the ideal sampling technique is to minimize the weight of gross sampling by using a large number of very small increments from a representative portion of the stream. A bit different view is presented by Bertholf [7]. He does not believe it is a totally acceptable procedure. Gy [37] however bases his theory on both authors.

He presents a general equation for a series of increments of weight M_i,

$$\sigma_{TE}^2 = \sigma_{trend}^2 + \frac{\sigma_I^2}{w} + \sigma_{PE}^2 + \sigma_{ME}^2$$

where

σ_{TE}^2 = the observed variance;
σ_{Trend}^2 = the trend variance;
σ_I^2 = variance of the increment of unit weight;
w = the increment weight;
σ_{PE}^2 = the preparation variance
σ_{ME}^2 = the measurement variance

If a series of samples is taken with each sample being composed of N_Q increments of weight w, then

$$\sigma_{TE}^2 = \frac{\sigma_{trend}^2 + \sigma_I^2/w}{N_Q} + \sigma_{PE}^2 + \sigma_{ME}^2$$

If R replications are prepared and measured out of the gross sample, the total variance observed is

$$\sigma_{TE}^2 = \frac{\sigma_{trend}^2 + \sigma_I^2/w}{N_Q} + \frac{\sigma_{PE}^2 + \sigma_{ME}^2}{R}$$

Solving for the required number of of increments

$$N_Q = \frac{\sigma_{trend}^2 + \sigma_I^2/w}{\sigma_{TE}^2 - \sigma_{PE}^2 - \sigma_{ME}^2} \tag{2.21}$$

and for the replications,

$$N_Q = \frac{\sigma^2_{trend} + \sigma^2_I/w}{\sigma^2_{TE} - \sigma^2_{PE} + \sigma^2_{ME}/R} \tag{2.22}$$

Substituting the denominator:

$$\sigma^2_{\overline{SE}} = \sigma^2_{TE} - \sigma^2_{PE} + \sigma^2_{ME} \tag{2.23}$$

or

$$= \sigma^2_{TE} - \frac{\sigma^2_{PE} + \sigma^2_{ME}}{R} \tag{2.24}$$

Substituting Equations 2.21 and 2.22 in Equation 2.23 and 2.24 and rearranging

$$N_Q = \underbrace{\frac{\sigma^2_{trend}}{\sigma^2_{\overline{SE}}}}_{Increments} + \underbrace{\frac{\sigma^2_I}{\sigma^2_{\overline{SE}} w}}_{Increments/w} \tag{2.25}$$

Multiplying the Equation 2.25 by w we will have

$$N_Q w = M_S = \frac{\sigma^2_{trend} w}{\sigma^2_{\overline{SE}}} + \frac{\sigma^2_I}{\sigma^2_{\overline{SE}}} \tag{2.26}$$

The plot for proportional variance components would present a function which is hyperbolic with the minimum number of increments per sample being a function of increment weight. It is possible to represent the minimum gross sample weight as a function of increment weight on a straight line. The approach of the Subsection 2.7 is based in this minimum weight of gross sample that allows for the properties of material.

2.8.1 Container Sampling

In sampling lots in identifiable portions we shall firstly make some assumptions about the consignment:

- The lot consists of N bags or cans or drums etc.
- It is randomly chosen n out of N containers;
- The material is completely mixed for guarding against segregation;

- The rules of delimitation and extraction for an unbiased sampling are all respected;
- Grinding follows the steps for minimum fundamental variance;
- The analytical errors are randomly distributed with zero mean and constant variance;

  The mean of these samples as an estimate of population is

$$\overline{a}_s = \frac{1}{n_1}\sum_{i=1}^{n_1} x_i + \frac{1}{n_2}\sum_{i=1}^{n_2} x_j + \frac{1}{n_3}\sum_{i=1}^{n_3} x_k \cdots \tag{2.27}$$

where x represents the error associated with stage i of measurement of certain characteristic such as mean of lot, deviation of the mean of the composite sample from the mean of the lot, deviation of the mean of the laboratory sampling from the mean of the composite sample, deviation of the ith test-unit from the mean of the laboratory sample, analytical error associated to the measurement etc..

The total sample variance of the lot, a_L, supposing two measurements and two preparation stages is

$$\sigma^2_{TE} = \underbrace{\frac{N-n}{N}\frac{s^2_b}{n} + \frac{\sigma^2_w}{n}}_{(1)} + \underbrace{\sigma^2_{SSE}}_{(2)} + \underbrace{\frac{\sigma^2_{PE} + \sigma^2_{ME}}{2}}_{(3)} \tag{2.28}$$

where s^2_b is the variance between bags and equal to

$$s^2_b = \sum_{j=1}^{N} \frac{[(a_S)_j - \overline{a}_S]}{N-1}$$

σ^2_w is the variance of increments obtainable from a container and assumed equal to all of them;

σ^2_{SSE} is the variance of subsampling, obtainable from the composite sample by the selected method of blending and reduction;

The terms of Equation 2.28 correspond to

(1) ⇒ sampling variance;
(2) ⇒ reduction variance;
(3) ⇒ measurement variance;

and tell us the number of samples $[n]$ required to achieve a given σ^2_{TE}.

$$n = \frac{S^2_b + \sigma^2_w}{\sigma^2_{TE} + S^2_b/N - (\sigma^2_{SSE} + (\sigma^2_{PE} + \sigma^2_{ME})/2)} \tag{2.29}$$

If there is no previous data from which to estimate the sampling variance directly from measurements on the lot itself, the pilot study is a good substitute for a reliable estimation of the mean quality of the current process.

A pilot study for obtaining tentative values by extensive research is also necessary. It will probably be very expensive as a initial cost but, in a long run, the average cost may be considerably less than the uncertainty of getting separately values for each lot.

2.8.2 Systematic Sampling

Increment are selected at regular intervals which have been determined beforehand and are part of a sampling plan subordinated to the sampling devices and machines available. It is called the random start when the first increment is taken at random. See Figure 2.8.

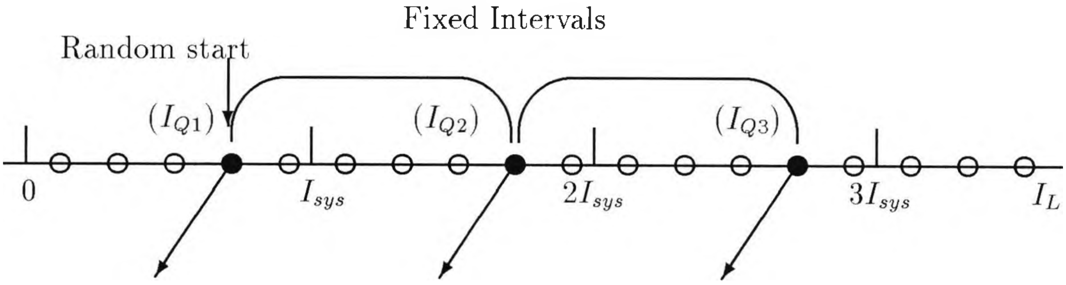


Figure 2.8: Systematic sampling intervals I_{sys} dividing the lot or consignment by a sub-domain (I_{Q1}) with N_Q increments

The increment I_1 is selected at random, within the domain of the first series of increments I_{Q1} from a number of increments chosen out of the lot. The number of increments is adopted according to the degree of representativeness. It is defined as:

$$(I_{Q1}) \equiv \{I | 0 < I \leq I_{sys}\}$$

In this sampling collection pattern, a series of increments I_Q follow I_1 in a consecutive order. If the number Q of increments I_Q belongs to an elongate pile or stopped conveyor belt then, within consignment, the following inequalities apply:

$$I_Q = I_1 + (Q-1)I_{sys} \leq I_L < I_1 + QI_{sys}$$

In this model the minimum number of increments to be taken is to be

$$N_Q = (\frac{\sigma_w}{\sigma_{SE}})^2 = \frac{\sigma_w^2}{(\frac{CV \times a_L}{100})^2 - \sigma_{PE}^2 - \sigma_{ME}^2} \tag{2.30}$$

In a carefully designed sampling plan, consideration should be given to periodic phenomena that could prejudice the information on the sample measured.

2.8.3 Stratified Sampling

Stratified Sampling is an important extension of Container Sampling. It involves division of the consignment into groups or strata. The sub-groups are usually sampled in proportion to their weight. It is very useful method when the consignment consists of different materials which are not easily mix or there are a number of widely differing grade.

As shown in Figure 2.9, consecutive increments are broken up into (I_Q) adjacent strata of, as far as possible, equal number of increments in the domain I_Q.

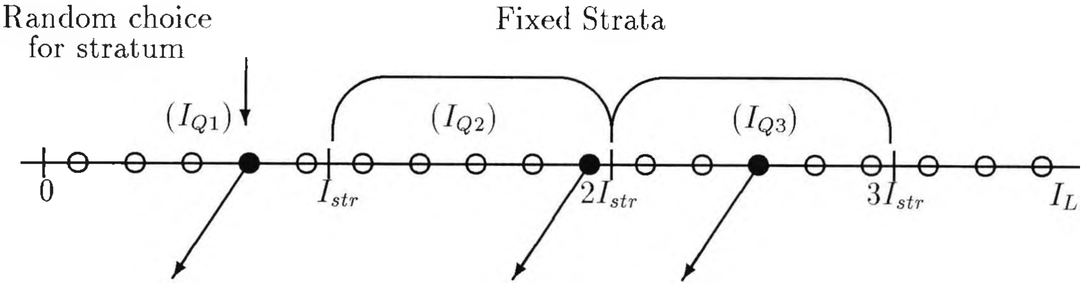


Figure 2.9: Stratified sampling intervals I_{str} dividing the lot or consignment by a sub-domain (I_{Q1}) with N_Q increments chosen randomly.

$$(I_Q) \equiv \{I|(N_Q - 1) < I \leq I_{stra}\}$$

It is advantageous to stratify the consignment so that the inside of the stratum becomes uniform as far as possible and the difference between the strata becomes large. In order to do so we call N the number of elements in the population, N_Q the number of extracted increments and k the number of strata.

The subscripts i and j correspond to the serial number of strata and number of elements in the $i-$th stratum, respectively.

The mean $\overline{a}_i$ is first calculated from n_i elements of the $i-$th stratum: $\overline{a}_i = 1/n_i \sum_{j=1}^{n_i} a_{ij}$. Since each stratum is considered a population on its own, the conditional expectation for each stratum is

$$E(a_{ij}|_i) = a_L|_i$$

Correspondingly there is also a conditional variance for the $i-$th.

$$\sigma^2(a_{ij}|_i) = \sigma_i^2$$

In practical terms an approximate value of the variance within strata is known from prior experiments or a pilot plant.

The conditional variance of the sample mean of the $i-$th stratum is

$$\sigma^2(\overline{a}_i|_i) = \frac{N_i - n_i}{N_i - 1}\frac{\sigma_{ij}^2|_i}{n_i}$$

The mean of $\overline{a}_i$ weighted by its respective stratum size N_i is

$$\overline{\overline{a}}_S = \overline{\overline{a}}_i = \frac{1}{N}\sum_{i=1}^{k} N_i a_i = \frac{1}{N}\sum_{i=1}^{k}\{N_i \frac{1}{n_i}\sum_{j=1}^{n_i} a_{ij}\} \qquad (2.31)$$

where $\overline{\overline{a}}_i$ the unbiased estimator of the parameter considered:

$$E(\overline{\overline{a}}) = \frac{1}{N}\sum_{i=1}^{k}\{\frac{N_i}{n_i}\sum_{j=1}^{n_i} E(a_{ij})\} = \frac{1}{N}\sum_{i=1}^{k}(a_L|_i) = E\{E(a_{ij}|_i)\} = E(a_{ij}) = a_L$$

The variance of the sample mean $\overline{\overline{a}}_S$ is given by

$$\sigma^2_{(\overline{\overline{a}}_S)} = \sigma^2\{\frac{1}{N}\sum_{i=1}^{k}(\frac{N_i}{n_i}\sum_{j=1}^{n_i} a_{ij})\}$$

$$= \sigma^2\{\frac{1}{N}\sum_{i=1}^{k}(N_i\overline{a}_i)\}$$

Considering the variance for strata and assuming the means $\overline{\overline{a}}_i$ independent of one another,

$$\sigma^2_{(\overline{\overline{a}}_S)} = \sum_{i=1}^{k}(\frac{N_i}{N})^2 \frac{N_i - n_i}{N_i - 1}\frac{\sigma^2(a_{ij}|_i)}{n_i} \qquad (2.32)$$

In industry, however, it is common to reduce cost by taking proportional allocation of stratified lots. The simplest way to do so it is to select, from each stratum, a constant fraction of sampling size such as $n_i/N_i = n/N$. If it is assumed that the individual strata are large ($N_i \gg 1$), the following equation for proportional subdivision may be used:

$$\sigma_p^2\overline{\overline{a}}_S = \sum_{i=1}^{k} \frac{N_i}{N^2}(1 - \frac{n_i}{N_i})\frac{N_i}{n_i}\sigma^2_{(a_{ij}|_i)}\frac{1}{N}$$

Simplifying, rearranging the equation and considering $\sigma^2(a_{ij}|_i) = \sigma_i^2$

$$\sigma_p^2\overline{\overline{a}}_S = (\frac{1}{n} - \frac{1}{N})E(\sigma_i^2)$$

But we know that

$$\sigma^2(a) = E_y[\sigma^2(x|y)] + \sigma_y^2[E(x|y)]$$

then we can compare the variance $\sigma_p^2\ \overline{\overline{a}}_S$ for proportional allocation with the variance without stratification.

$$\sigma^2(a_{ij}) = \sigma^2 = E(\sigma^2(a_{ij}|_i) + \sigma^2(E(a_{ij}|_i))$$

and therefore

$$\sigma^2 = \underbrace{E(\sigma_i^2)}_{\sigma_{w1}^2} + \underbrace{\sigma^2(a_S|_i)}_{\sigma_{w2}^2}$$

Finally, the variance of an stratified sample of size n is always large than the variance of an stratified sample of proportional subdivision having the same number of elements:

$$\sigma_p^2(\overline{\overline{a}}_S) = \sigma^2(\overline{a}_S) - (\frac{1}{n} - \frac{1}{N})\sigma^2(a_L|_i)$$

From the proportional subdivision of the lot we can conclude that the more the means (expectation $a_L|_i$) within the various strata differ from one another, the greater the effect of subdivision.

After choosing the approximate number of increments, further investigations are required to minimize the overall cost C through i-th stratum costs $n_i c_i$.

$$C = \sum_{1=1}^{k} n_i c_i \tag{2.33}$$

The necessary condition for a minimum of $\sigma^2(\overline{\overline{a}}_S)$ with the constrains of cost C is found by the total differential of Equation 2.32. Assuming that $n_i \ll N_i$

$$d\sigma^2(\overline{\overline{a}}_S) = \frac{\delta\sigma^2(\overline{\overline{a}}_S)}{\delta n_1}dn_1 + \frac{\delta\sigma^2(\overline{\overline{a}}_S)}{\delta n_2}dn_2 + \cdots \frac{\delta\sigma^k(\overline{\overline{a}}_S)}{\delta n_k}dn_k \tag{2.34}$$

Partial differentiation results in

$$(\frac{N_1}{N})^2\frac{1}{n_1^2}\sigma_1^2 dn_1 + (\frac{N_2}{N})^2\frac{1}{n_2^2}\sigma_1^2 dn_2 + \cdots (\frac{N_k}{N})^2\frac{1}{n_k^2}\sigma_1^2 dn_k$$

The total differential of Equation 2.33 results in

$$dc = c_1 dn_1 + c_2 dn_2 + \cdots + c_k dn_k$$

If this equation is multiplied with λ^2 and added to the Equation 2.34

$$\sum_{i=1}^{k}(\frac{N_i}{N})^2\frac{1}{n_i^2}\sigma_i^2 dn_i = \lambda^2\sum_{i=1}^{k} c_i dn_i$$

Comparing the coefficients leads to

$$n_i = \tfrac{1}{\lambda}\tfrac{N_i}{N}\tfrac{\sigma_i}{\sqrt{c_i}} \quad \text{where} \quad \lambda = \frac{\sum_{i=1}^{k}\frac{N_i}{N}\sigma_i\sqrt{c_i}}{C}$$

It can be seen that the cost-optimized subdivision is achieved if the number n_i of increments are proportional to the stratum proportions N_i/N and proportional to the standard deviations σ_i within the strata. The extent to which a stratum has to be taken into account increases with its size N_i and the heterogeneity within the stratum, expressed by σ_i.

In industrial processes, the cost of investigation of the sampling attribute are almost the same for any i–th stratum, say c^*, therefore, the real number of increments are

$$n_i = \frac{c}{c^*}\frac{N_i\sigma_i}{\sum_{i=1}^{k} N_i\sigma_i}$$

2.8.4 Nonstratified Segments and Series of Lots

For an isolate lot the sampling procedure is to select k increments out of n segments, comminute, split gradually each unit in steps and estimate the series of values. If n test results, a_{S1}, a_{S2}, ... a_{Sn}, an estimate of σ_{TE}^2 is given by

$$\sigma_{TE}^2 = \frac{1}{n}\frac{\sum_i (a_S|_i - \overline{a}_S)^2}{(n-1)}$$

Degree of Freedom	λ
2	2.76
3	2.16
4	1.61
6	1.26
9	1.00
14	0.79
19	0.68
29	0.54
49	0.42
74	0.33
99	0.29

Table 2.4: Table for Determining Sample Size.

For a given confidence interval, say $t_{0.025} \times \delta$ the amount of sampling may be determined if we take one increment from each segment. In this case $s_1^2 = \sum_i (a_S|_i - \overline{a}_S)^2/(n_1 - 1)$. Dividing, s_1^2 by $(\delta/1.96)^2$, we find the amount of sampling, where 2δ is the desired width of a 0.95 confidence interval. If its value is less than 30, then the trial-and-error method proposed by Duncan [30, 31] may be used:

$$\frac{s_1^2}{n} = [\frac{\delta}{t_{0.025(n-1)}}]^2$$

To obtain an acceptance sampling plan with the prescribed risks, a preliminary sample n_1 can be taken as shown before. The final sample size n, is obtained with $\lambda = \Delta/s_1$ from the Table 2.4. The meaning of Δ resides on the difference $L - \Delta$, the mean of a lot that is deemed barely tolerable, where L is the lower specification limit.

If this lot is one of a series, there will be always a need to check the quality in a long run and/or the continuity of the pilot study. On the assumption that n and k are relatively small compared with the number of segments and test units, the total variance of the isolate lot is

$$\sigma_{TE}^2 = \frac{\sigma_b^2 + \sigma_w^2/k}{n} + \sigma_{PE}^2 + \sigma_{ME}^2$$

We know that composite samples can be used requiring only a few measurements and consequently low costs. Then we may construct a sampling plan with n segments

Sample Size	d_2	D_2
2	1.128	3.686
3	1.693	4.358
4	2.059	4.698
5	2.326	4.918
6	2.534	5.078
7	2.704	5.203
8	2.847	5.307
9	2.970	5.394
10	3.078	5.469

Table 2.5: Factors for Computing Control Charts Lines, from Juran.

selected at random, from the lot and draw an increment of k test unit from each segment. Let h subgroups of n/h increments each be selected at random from the n increments and composite sample be reduced to a laboratory sample. The measurement of the h composite samples may be used to test the validity of the prior estimates of variance within a $R-$Chart whose central and upper limits are:

$$CL = d_2\sqrt{\frac{s_b^2 + s_w^2/k}{n/h} + s_{PE}^2 + s_{ME}^2}$$

and

$$UCL = D_2\sqrt{\frac{s_b^2 + s_w^2/k}{n/h} + s_{PE}^2 + s_{ME}^2}$$

where s_w^2, s_b^2, s_{PE}^2, s_{ME}^2 have been estimated from a pilot study and d_2 and D_2 from the Table 2.5.

If the range h falls below UCL the vality of prior estimates of variance is accepted. If not, further sampling must be undertaken in order to force them within the limits. In case of acceptance of validity, the mean of the h composite measurements $\overline{a}_{S(h)}$ is considered the lot mean and the sampling variance is

$$s^2_{\overline{a}_{S(h)}} = \frac{s_b^2 + s_w^2/k}{n} + \frac{s_{PE}^2 + s_{ME}^2}{h}$$

Finally the confidence limits are:

$$\overline{a}_{S(h)} \pm t_{0.025} s^2_{\overline{a}_{S(h)}}$$

and $t_{0.025}$ corresponds to a point of a $t-$distribution with

$$n = \frac{(s^2_{\bar{a}_{S(h)}})^2}{\frac{1}{f_b}(\frac{s_b^2}{n})^2 + \frac{1}{f_w}(\frac{s_w^2}{kn})^2 + \frac{1}{f_{PE}}(\frac{s_{PE}^2}{h})^2 + \frac{1}{f_{ME}}(\frac{s_{ME}^2}{h})^2} - 1$$

where f_b, f_w, f_{PE} and f_{ME} are the degree of freedom which of the respective prior estimates were determined with.

2.8.5 Other Sampling Procedures

There are other important procedures for sampling:

- *Random Mixture Sampling Scheme*

  It is often assumed in sampling that mixture is in the state of random distribution. The existence of mixture in this condition, usually called stochastic homogeneity, has to be proved. Tests of randomness provide procedures for checking non-stochastic homogeneous mixtures.

  The theoretical expected variance for random mixture is given by $\sigma^2(n_x) = np(1-p)$ where n is the sample size, N is the total number of elements and p the numerical concentration in the lot. If the concentration of a sample, $x = n_x/n$ is introduced into the theoretical equation the expected variance is:

  $$\sigma^2(x) = \frac{N-n}{N-1}\frac{p(1-p)}{n} \tag{2.35}$$

  and it must be compared with the sample variances of r replications of n elements each:

  $$s^2(x) = \frac{1}{r}\sum_{i=1}^{r}(x_i - p)^2$$

  and the confidence interval, assuming normality, will be given by chi-square distribution:

  $$\frac{\chi_p^2}{r-1} < \frac{s^2}{\sigma^2} \leq \frac{\chi_q^2}{r-1}$$

  In chemistry the proceeding is similar to this general method except for the number of elements. We use concentration by mass. Having individual grain masses g_x and g_y the sample concentration by mass $[\kappa]$ is:

  $$\kappa_x = \frac{n_x g_x}{n_x g_x + n_y g_y} = \frac{n_x g_x}{n_x(g_x - g_y) + n g_y}$$

The second equality is due to $n = n_x + n_y$. Then using property of variance and Taylor expansion, the variance of concentrations $[\sigma^2(\kappa)]$ is:

$$\sigma^2(\kappa) = (\frac{d\kappa(E(n_x))}{dn_x})^2\sigma^2(n_x) \quad (2.36)$$

$$= (\frac{ng_xg_y}{(E(n_x)g_x + E(n_y)g_y)^2})^2\sigma^2(n_x) \quad (2.37)$$

But the expectation of the sample mass is

$$E(n_x)g_x + E(n_y)g_y = E(g) = n\underbrace{(pg_x + (1-p)g_y)}_{\overline{g}_{xy}}$$

where $[\overline{g}_{xy}]$ is the average single-grain mass.

Finally from Equation 2.37 and Equation 2.35:

$$\sigma^2(\kappa) = \frac{g_x^2g_y^2}{n^2\overline{g}_{xy}^4}np(1-p)$$

- *Multi-stage Sampling Scheme*
  In this scheme each of the units of the first stage chosen for the sample is divided , in each case, into units of the second stage, of which, several other elements are selected into a third stage and so on. This is a typical case of nested designs to be studied in Chapter 4.

2.8.6 Constitution of Increment and Overall Precision

The specifications for the overall precision of a product determine the sampling plan for the constitution of increment — the formation of primary sampling units, sub-sampling, composite sampling, gross sampling, consequently, the amount of sampling. It depends on the consignment from which the samples are taken from, the cost it is allowed for, and the use intended for the product.

There will be always a compromise involving these decisions, however, one of the following models will be devised:

1. Increments, N_Q, are taken from whole consignment, weighing M_L, for isolated lot;

2. Increments, N_Q, are taken from consignment divided into several lots with N_P primary sampling constituting the consignment;

3. Increments, N_Q, are taken in two-stage sampling where some primary units, N_p , are taken from consignment and also some secondary sampling units n_w are taken from primary;

4. Increments, N_Q, are taken in stratified two-stage sampling, that is consignment is divided into some lots and some primary sampling units, N_p, are taken from each lot, and also some secondary increments, n_w, are taken from primary sampling unit.

From the Figure 2.10 using β_{TE} for overall precision, the following relationship may be computed:

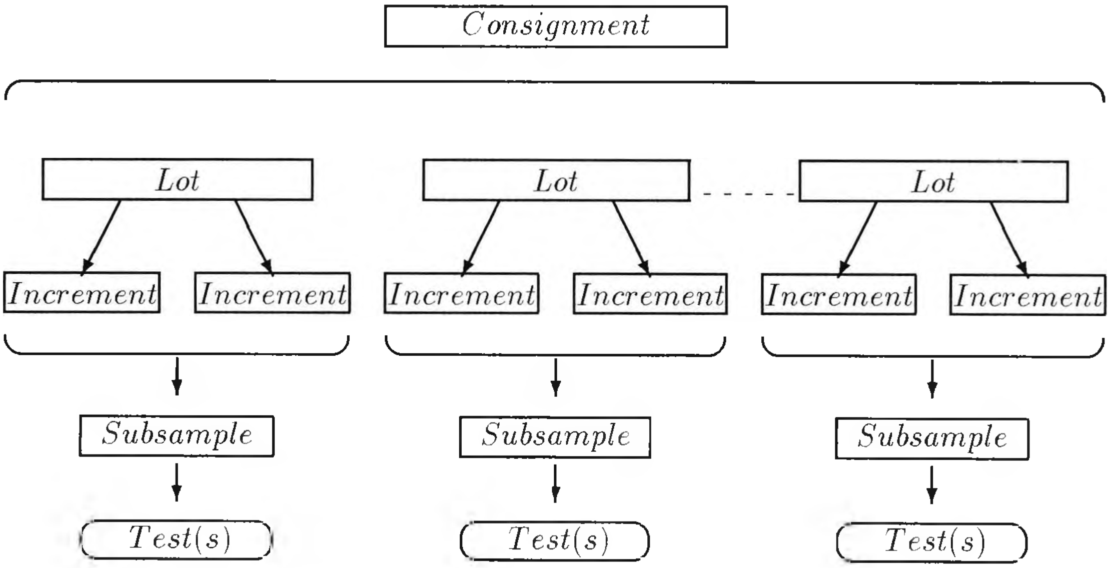


Figure 2.10: Case of consignment divided into several lots for computing of precision.

a) Where the test sample has been analized one time, the overall precision, being k the number of sub-samples is

$$(\frac{\beta}{2})^2 = \frac{\sigma_w^2}{n} + \frac{\sigma_{PE}^2 + \sigma_{ME}^2}{k}$$

b) where the test sample has been analised l times

$$(\frac{\beta}{2})^2 = \frac{\sigma_w^2}{n} + \frac{\sigma_{PE}^2}{k} + \frac{\sigma_{ME}^2}{kl}$$

If the increments collected from each lot to produce sub-samples were further collected, enough for one consignment, to produce the gross sample the overall precision for one test sample from the gross sample is

$$(\frac{\beta}{2})^2 = \frac{\sigma_w^2}{n} + \sigma_{PE}^2 + \sigma_{ME}^2$$

where the test sample has been analyzed l times, the overall precision is

$$(\frac{\beta}{2})^2 = \frac{\sigma_w^2}{n} + \sigma_{PE}^2 + \frac{\sigma_{ME}^2}{l}$$

When some primary sampling units are taking from the lot $[M]$ and then, some secondary sampling units are produced from primary sampling units, a two-stage sampling occurs with three distinct cases: See Figure 2.11.

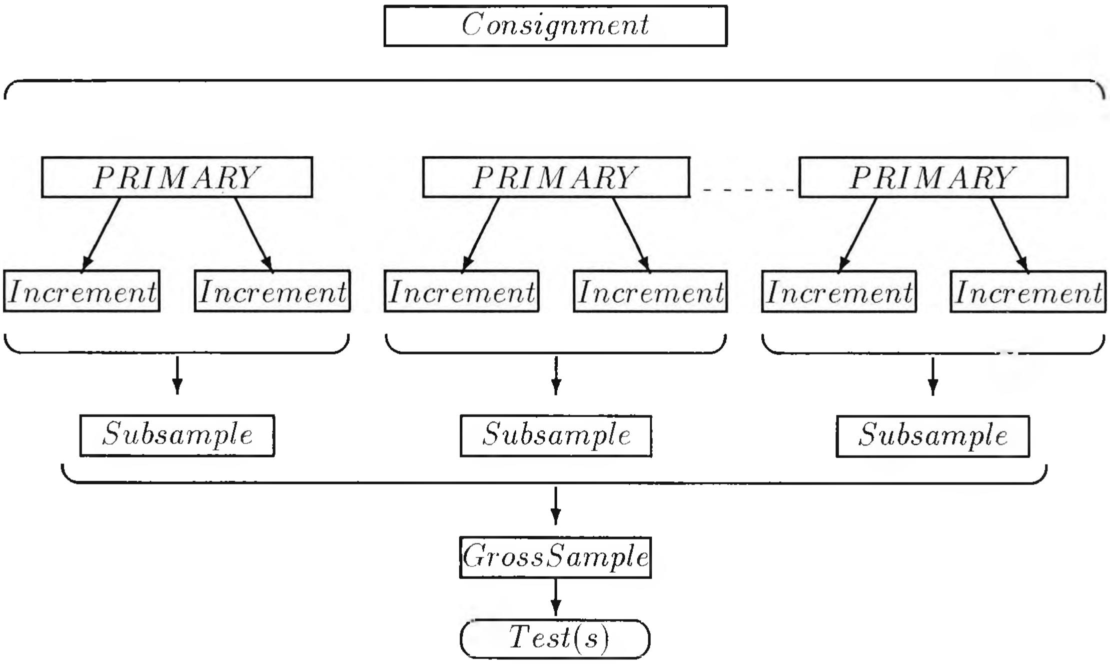


Figure 2.11: Two-stage sampling with primary and secondary sampling units.

1) when one test sample is produced from each increment and analyzed one time the overall precision is

$$(\frac{\beta}{2})^2 = \frac{M-m}{M-1} \times \frac{\sigma_b^2}{m} + \frac{\sigma_w^2 + \sigma_{PE}^2 + \sigma_{ME}^2}{mn_w}$$

2) when the increments for each primary sampling unit produce one sub-sample and one test sample, the overall precision is

$$(\frac{\beta}{2})^2 = \frac{M-m}{M-1} \times \frac{\sigma_b^2}{m} + \frac{\sigma_w^2}{mn_w} + \frac{\sigma_{PE}^2 + \sigma_{ME}^2}{k}$$

3) when the sub-samples are collected together to produce a gross sample, the overall precision is

$$(\frac{\beta}{2})^2 = \frac{M-m}{M-1} \times \frac{\sigma_b^2}{m} + \frac{\sigma_w^2}{mn_w} + \sigma_{PE}^2 + \sigma_{ME}^2$$

In each sample test there is measurement error $[\sigma_{ME}^2]$. If the test sample has been analyzed r times, then the number of replications must be considered accordingly.

2.9 A Test of Randomness for Particulate Mixtures

The physical relationship of particles in a mixture is said to be stochastic when there is at the same a random element and a non-random element involved in its structure.

Previously it was pointed out that reduction of the random variability of fundamental errors, s_{FE}^2, is only possible through comminution or other size reduction mechanism.

The other error also associated with both discrete and continuous model, S_{GSE}^2, can only be eliminated by mixing. When there is no thoroughly mixed system cluster points take place and concentration gradients increase the variability of a material. Such deviations in composition should not exceed a specified value in terms of batch homogeneity.

Naturally blending is not that easy. For example, natural segregating tendencies will be observed with extreme differences in specific gravity, size, or shape. The heavier, smaller, or smoother and rounded particles tend to sink through the lighter, larger, or jagged ones, respectively. In some cases, preparation of materials to avoid extreme differences in such ingredient properties can avoid the need for any type of segregation.

There are also other factors that can cause segregation. Eletrostatic charges may cause particles to repel each other, particularly in continued blending. Loss of material as dust must be considered as a possible means of segregation. If there are smear particles, frictional anchorage may be necessary in order to achieve a good mixing.

A well designed and preserved *Sampling Test Station* has remarkable effects in overcoming grouping and segregation problems. Thus, the manual or mechanical solids-mixing operation must be checked from the point of view of delivering a well-mixed batch to a certain point.

There are two sensitive criteria for testing randomness of particulate materials Pearson's χ^2-Test and Shortest Distance Test.

Both require some prerequisites for measuring the primary data and calculating the sample statistic:

1. The range in particle sizes is not excessively large;
2. The percentage of particle to be estimated must be kept low — less than 10 per cent or the complementary;
3. The particle must be distinguishable or made so by some optical method;
4. The distribution is assumed to be binomial, and is approximated by a Poisson sufficiently accurate for small percentages.

In the Table 2.6 both comparative test are presented with the significant differences in terms of χ^2_{n-1} and χ^2_{2n-1}.

	Real St.	*Ideal St.*	Criteria for random
Pearson Test	$\sum_{j=1}^{k}(f_j - f_{ave})^2/f_{ave}$	$\chi^2_{\alpha,n-1}$	$K_P > \chi$
Shortest Test	$K_S = 2\pi\mu\sum r_i^2$	$\chi^2_{\alpha,2n}$	$K_S > \chi$

Table 2.6: Typical Tests for detecting Randomness of particulate material

2.9.1 Creating Surfaces and Measuring Primary Data

Sample surfaces suitable for the proposed tests may be obtained in different ways. Of course the best configuration has a three dimensional character but observation is experimentally hard.

The easier method is to take some slice by using a transparent bottom sampler with a flat surface immediate ready for investigation.

Though the measurements may be made directly on the same surface enlarged by a microscope, Weidenbaum [107] suggests take micrographical photos.

The other kind of measurement is by using a freezing process — let a molded wax or any thin-flowing monomer seep into a large random sample and cool it. Then, using a bistoury or a microtome to slice flat surfaces for investigation.

2.9.2 Pearson's χ^2–Test

The Pearson's χ^2–Test is performed on the surface by using a grid and counting the number of particles in each cell of the grid. It is suggested to choose a grid that the average number of points in cell exceeds five. From the following relationship it is possible to calculate the Pearson's constant K_P:

$$K_P = \frac{\sum_{j=1}^{k}(f_j - f_{aver})^2}{f_{aver}}$$

in which k is the number of cells in the grid, f_{aver} is the average number of points in the cell and f_j is the actual number of points in the j-th cell.

If this quantity is larger than the central value $[\chi^2_{1-\alpha,k-1}]$ the null hypothesis of random mixing must be rejected and no other test is required. But, on the other hand, if the null hypothesis is accepted, it is usual to perform the shortest distance test.

2.9.3 Shortest Distance Test

This test is based on Weidenbaum [107] and Neyman and Pearson [79]. It computes the expected value and variance of r^2, a circle of radius r having, as a center, a selected random point. According to a Poisson law the probability of this circle just reaching the first random point is equal to $e^{-r^2\pi\mu}$ where μ is the average number of random points in unit area.

The cumulative distribution of r^2 exponential:

$$F(r^2) = 1 - e^{-r^2\pi\mu}$$

with probability density with respect to r^2

$$f(r^2) = \pi\mu e^{-r^2\pi\mu}$$

Its mean expected value, $E(r^2)$, is evaluated as

$$E(r^2) \equiv \int_0^\infty r^2 f(r^2) d(r^2)$$

$$E(r^2) = \frac{1}{\pi\mu} \int_0^\infty r^2\pi\mu e^{-r^2\pi\mu} d(r^2\pi\mu) = \frac{1}{\pi\mu} \tag{2.38}$$

The variance of this distribution, $V(r^2)$ is

$$V(r^2) \equiv \int_0^\infty [r^2 - E(r^2)]^2 f(r^2) d(r^2)$$

$$V(r^2) = \frac{1}{\pi^2\mu^2} \int_0^\infty (r^2\pi\mu)^2 e^{-r^2\pi\mu} d(r^2\pi\mu) - \frac{1}{\pi^2\mu^2} = \frac{1}{\pi^2\mu^2} \tag{2.39}$$

But the distribution of the squared distance may be transformed into a χ^2-distribution with two degrees of freedom in which $\chi^2 = 2r^2\pi\mu$. The density of the transformed variable $p(\chi^2)$ is

$$p(\chi^2) = f(r^2)\frac{d(r^2)}{d(\chi^2)} = \frac{1}{2}e^{-r^2\pi\mu} = \frac{1}{2}e^{-\chi^2/2} \tag{2.40}$$

But the distribution of the n independent squared shortest distances may be transformed into a χ^2distribution with $2n$ degrees of freedom by

$$\chi^2_{2n} = 2\pi\mu \sum_{i=1}^{n} r_i^2$$

This additive property is the basis of Shinnar and Naor [93] shortest distance test. It says: when a series of independent observations of squared shortest distances is taken, added up and multiplied by $2\pi\mu$, the result is distributed as χ^2 with $2n$ degrees, if the null hypothesis of random distribution is true. If not, clusters exist and $2\pi\mu\sum_{i=1}^{n} r_i^2$ will be much smaller than the ordinary χ^2.

Test criterion suggested: if $2\pi\mu\sum_{i=1}^{n} r_i^2$ falls short of the $\chi^2_{\alpha,2n}$ critical value, it is possible to conclude that the distribution of the points in the plane under investigation is not random. If $2\pi\mu\sum_{i=1}^{n} r_i^2$ exceeds $\chi^2_{\alpha,2n}$ the null hypothesis of random distribution cannot be rejected.

Chapter 3

Sampling of Heterogeneous and Dynamic Material Systems

The principles summarized in this chapter, are part of a new science called Geostatistics and it is concerned with the problem of determining the accuracy of estimates of quality characteristics. They are based on Matheron's Regionalized Variables [74, 75]. The essence of the Theory of Regionalized Variables is the use of information about autocorrelate data — spatial relationships. In this sense, the methods used in this chapter, are closely related to time-series analysis.

There is always a dependency of two neighboring samples of particulate materials from the same one-dimensional lot, whether moving or stationary. The theory of serial measurements, in this view, can be used to refine precision statements, minimize fluctuations of quality, reduce heterogeneity of lots, and study the moments of the continuous selection error.

We present the theoretical approach behind the variogram, the key tool for quality control in continuous processes, establish a sound comparison between classical and serial variance, derive the auxiliary functions to materialize the short, long and periodic parameters and model a variographic experiment including protocols. We suggest a simplified variographical method using only results for a linear variogram. We finish with an analysis of short and long-range fluctuations in an experiment on *Charcoal.*

3.1 Introduction

The theory for sampling bulk solids presented so far disregards space and time series data analysis. However lots of particulate material flowing past a sampling point are widespread in modern chemical industry plants particularly those dealing with fertilizers, mining, explosives pharmaceutic products etc.

For most manual sampling regimes and for many mechanical sampling systems, sampling frequency are too low to show a significant correlation between consecutive increments. Primary increments collected from moving belt at intervals of 15 minutes or less are generally correlated (Merks [76]). In such cases the $F-$ratio between the classical variance and the serial variance calculated from squared differences between consecutive primary increments is statistically significant. Traditional methods failed to express in any way this important character of chemicals, namely their continuous intrinsical variability.

Shewhart Control Charts and other methods of process capability in use for the sequential checking of variability are useful for zero-dimensional lots, or a lot made of random units but they are not suitable for materializing non-random characteristics of one-dimensional lots with autocorrelation.

We shall retain X as the average value of the quantity of interest, say a quantity of moisture, a metal content, a particular size fraction, and $X(t)$ the respective value at an instant t when passing a sampling point.

In this case where "time" expresses mass units or time units, the usual sample variance is

$$s^2 = \frac{1}{n-1}\sum_{i=1}^{n}(X(t_i) - \overline{X}_n)^2$$

where,

$$\overline{X}(n) = \frac{1}{n}\sum_{i=1}^{n} X(t_i) \tag{3.1}$$

being $X(t_1)$, $X(t_2)$, $\cdots$ and $X(t_n)$ the collected data at times ,t_1, t_2, $\cdots$ and t_3.

The true mean X for the whole lot is given by

$$\overline{X} = \frac{1}{T}\int_0^T X(u)du \tag{3.2}$$

Unfortunately, this formula neglects the effect of the smoothness of $X(t)$ and overvalues the sampling error. Therefore to assess the accuracy of X_n estimation we need a function that may be able to measure such smoothness. That is provided by *Variogram.*

The variogram at lag u measures the average stability of the process and it is defined as

$$\gamma(u) = \frac{1}{2}E[(X(t) - X(t-u))^2]$$

$\gamma(u)$ generally is small when u is small and increases in value as the lag get larger. It should be stressed that the function $\gamma(u) = \frac{1}{2}E[(X(t) - X(t-u))^2]$ is stationary as long as is is not time dependent but only lag dependent. When the factor 1/2 is used, it is called the semi-variogram.

To determine the accuracy of a certain set of data and define the confidence limits we need the estimation error variance $[s^2_{TE}]$ defined as

$$s^2_{TE} = E(\overline{X}(n) - \overline{X})^2 \tag{3.3}$$

From these equations and using Matheron's [75] identity,

$$2(X(u) - X(t_i))(X(v) - X(t_j)) =$$

$$-(X(u) - X(v))^2 + (X(v) - X(t_i))^2$$

$$+(X(t_i) - X(v))^2 - (X(t_i) - X(t_j))^2$$

then we may be able to evaluate s^2_{TE}

$$\begin{aligned}
s^2_{TE} &= E[(\frac{1}{T}\int_0^T X(u)du - \frac{1}{n}\sum_{i=1}^{n} X(t_i))^2] \\
&= E[\frac{1}{n^2T^2}\int_0^T\int_0^T \sum_{i=1}^{n}\sum_{j=1}^{n}(X(u) - X(t_i))(X(v) - X(t_j))dudv] \\
&= E[-\frac{1}{2n^2}\sum_{i=1}^{n}\sum_{j=1}^{n}(X(t_i) - X(t_j))^2 \\
&- \frac{1}{2T^2}\int_0^T\int_0^T (X(u) - X(v))^2 dudv \\
&+ \frac{1}{nT}\int_0^T \sum_{i=1}^{n}(X(u) - X(t_i))^2 du]
\end{aligned}$$

Finally, changing the terms position we have the exact value for the estimation error variance:

$$
\begin{aligned}
s^2_{TE} &= \frac{2}{nT}\int_0^T \sum_{i=1}^{n} V(u-t_i)du \\
&- \frac{1}{n^2}\sum_{i=1}^{n}\sum_{j=1}^{n}(V(t_i)-t_j) \\
&- \frac{1}{T^2}\int_0^T\int_0^T V(u-v)dudv
\end{aligned}
$$

3.2 Content and Throughput Functions

In the last chapter we presented three interdependent functions of any particulate material: amount of active components $[\mu(x)]$, amount of critical components $[\alpha(x)]$ and percent of critical content $[a(x)]$. Substituting the concept of mass by flow and x by t we are within the one-dimensional environment.

For studying these functions and expressing the moments of the sampling continuous selection errors, we must break up a general case $[f(t)]$ that characterizes the time variations of the flowing material, both in quantity and in quality, into a sum of four terms:

$$f(t) = f_0 + f_1(t) + f_2(t) + f_3(t)$$

where

f_0 : is the *nugget effect* describing the average property of the material in the same point, or time $t = 0$;

$f_1(t)$: is a *short-range term* representing non-periodic fluctuations of the general function;

$f_2(t)$: is a *long-range term* representing non-periodic fluctuations of the general function;

$f_3(t)$: is a *periodic term* representing cyclical variations of some lots.

From this general function Matheron [74, 75] deduces the variographical function $\gamma_f(\theta)$, where θ represents a regular interval of time (or space), assuming that both quality and quantity variations are:

- stationary of the *first order*: the first moment is time-stabilized and invariant towards the time axis. In this respect, their moving mean remains constant within a defined domain;
- stationary of the *second order*: the mean, standard deviation and mean square are time-stable. Under routine conditions, these fluctuations are likely to have time-stable properties, perhaps with a periodic term.

For computing quality and quantity variations of $0-D$ lots, Gy [38, 37] defines content and throughput functions whose details are analyzed to follow.

First, let us consider true random functions $A(t)$ and $W(t)$ defined at all points with a very large but finite number of discontinuities represented by a $X(t)$ function. By smoothing these discontinuities one defines graphically another function represented by $\xi(t)$.

Let x_j be the estimate of $X(tj)$, where x_j is a discrete function defined at a finite number of points, usually in a series of instants t_j at regular interval θ apart.

Because $A(t)$ and $W(t)$ are discontinuous and random functions, the analysis of autocorrelation of both functions may be carried out by examining the graph of the representative function x_j. If for the period considered the scatterplot is distributed about a parallel to the t-axis there is non-autocorrelation. On the contrary, if the graph presents points distributed about a trend curve there is an autocorrelation.

As declared before, the variogram of these functions, expresses the mean square of the differences between $X(t+h)$ and $X(t)$ as a function of the distance h, for any t value in the interval from 0 to T.

Let $\gamma_X(h)$ and $\gamma_\xi(h)$ be the variograms of $X(t)$ and $\xi(t)$, respectively. Then,

$$\gamma_X(h) = \frac{1}{T-h}\int_0^{T-h}[X(T+h) - X(t)]^2 dt \tag{3.4}$$

$$\gamma_\xi(h) = \frac{1}{T-h}\int_0^{T-h}[\xi(T+h) - \xi(t)]^2 dt \tag{3.5}$$

Considering Gy's definitions[46, 47]:

θ, the basic unit-interval between two consecutive measurements;

r, the number of unit-intervals in h and defined as h/θ;

n, the number of unit-intervals in t and defined as T/θ.

Define the discrete variogram $[\gamma_x(h)]$ of x_j as

$$\gamma_x(h) = \frac{1}{n-r}\sum_{j=1}^{n-r}(x_{j+r} - x_j)^2 \tag{3.6}$$

For a better understanding of the symbology used to determine the variographical functions, a flowing stream is presented in the Figure 3.1 illustrating the schematic computation of a variogam.

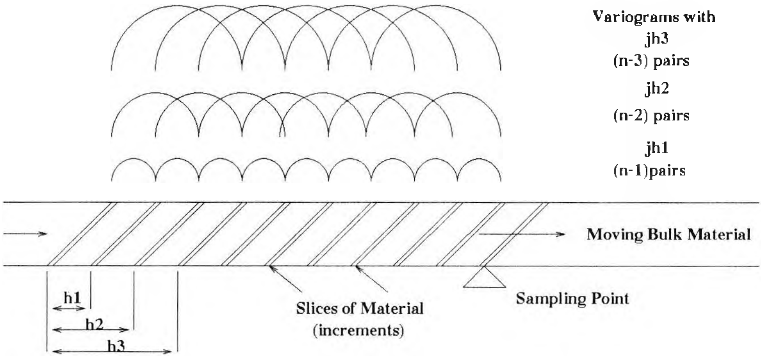


Figure 3.1: Schematization of Terms to Compute a Variogram, where $h1 = \theta$, $h2 = 2\theta$ and so on, $r = h/\theta$ and $n = T/\theta$.

From the definitions,

$$X_j = \frac{1}{\theta}\int_{tj-\theta/2}^{tj+\theta/2} X(t)dt$$

$$\xi_j = \frac{1}{\theta}\int_{tj-\theta/2}^{tj+\theta/2} \xi(t)dt$$

It is possible to estimate both variograms:

$$\gamma_X(h) = \frac{1}{n-r}\sum_{j=1}^{n-r}(X_{j+r} - X_j)^2$$

$$\gamma_\xi(h) = \frac{1}{n-r}\sum_{j=1}^{n-r}(\xi_{j+r} - \xi_j)^2$$

The variogram of one function is known through the other function. Also $\gamma_X(h)$ and $\gamma_x(h)$ are known through $X(t)$ and x_j respectively.

When $h = 0$, $X(t)$ presents a series of discontinuities, so some of differences of Equation 3.4 tends towards 0, then $\gamma_X(h)$ tends towards a positive value. Meanwhile, $\gamma_\xi(h)$ tends towards zero since $\xi(t)$ is a continuous function by definition. The random nature of the x_i means that it hardly ever takes this value towards zero. Consequently, $\gamma_x(h)$ has a positive limit as $h \to 0$. On the other hand as $h \to \infty$, all three variograms have a limited value.

The relationship of the three variograms may be expressed in terms of fluctuation of the estimate x_j about the trend curve $xi(t)$, equal to $[\alpha_j]$, fluctuation of X_j about the trend curve $xi(t)$, equal to $[\beta_j]$ and the measurements errors expressed by λ.

Assuming no determination bias the average of each function is nil and variance estimates are $\sigma_h^2(\alpha)$, $\sigma_h^2(\beta)$ and $\sigma_h^2(\lambda)$, where $\sigma^2(\alpha) = \sigma^2(\beta) + \sigma^2(\lambda)$.

Finally, combining Equations 3.4 and 3.5 together with the above assumptions we have:

$$\gamma_x(h) = \gamma_\xi(h) + 2\sigma_h^2(\alpha)$$

$$\gamma_X(h) = \gamma_\xi(h) + 2\sigma_h^2(\beta)$$

$$\gamma_x(h) = \gamma_X(h) + 2\sigma_h^2(\lambda)$$

Three conclusions are reached:

- Variogram of a random function: In this case, $X(t = h)$ and $X(t)$ are statistically independent, $\xi(t)$ is a constant X_0 and $\gamma_\xi(h) = 0$. Therefore, $\gamma_x(h) = 2\sigma_h^2(\alpha)$ and is represented graphically by a line parallel to the h axis.
- Variogram of a autocorrelated function: In this case, $X(t)$ is autocorrelated and $\xi(t)$ is not a parallel line but a continuous function. Its variogram is also a continuous function with $\gamma_\xi(h) = 0$ for $h \leq h_0$. This first part of variogram $\gamma_x(h) = 2\sigma_h^2(\alpha)$. Therefore, the real estimate of $\gamma_\xi(h)$ must be deducted of the average value of the variance of x_i about the trend curve $[2\sigma_h^2(\alpha)]$.
- Variogram of a periodic function: In this case, $\xi(t)$ is defined by a cyclic function and so is its variogram. There is a maximum and a minimum alternate values. Both amplitude and period can be determined by graphical and analytical methods.

3.3 Splitting the Variogram

A general function $f(t)$ and its stationary properties can be characterized by variographics functions that can be simplified considering its relative increase between $t - \theta/2$ and $t + \theta/2$:

$$\delta_f(t,\theta) = \frac{f(t+\theta/2) - f(t-\theta/2)}{f_L}$$

where f_L is the mean of $f(t)$ throughout the domain of the lot L.

These conventions merely create a dimensionless variogram, useful for any measurement unit and allow us to write:

$$\begin{aligned}
\gamma_f(\theta) &= \frac{1}{2(T_L-\theta)} \int_{\theta/2}^{T_l-\theta/2} \delta_f^2(t,\theta)dt \\
&= \frac{1}{2(T_L-\theta)f_L} \int_{\theta/2}^{T_l-\theta/2} [f(t+\theta/2) - f(t-\theta/2)]^2 dt
\end{aligned}$$

The variogram of $f(t)$ is a sum of three terms:

$$\gamma_f(\theta) = \gamma_{f1}(\theta) + \gamma_{f2}(\theta) + \gamma_{f3}(\theta)$$

being $\gamma_{f1}(\theta)$, $\gamma_{f2}(\theta)$ and $\gamma_{f3}(\theta)$ the variogram of the functions $f_1(t)$, $f_2(t)$ and $f_3(t)$, respectively.

Properties of $\gamma_{f1}(\theta)$: The variogram of $\gamma_{f1}(\theta)$ can be written:

$$\gamma_{f1}(\theta) = [1 - \rho_{f1}(\theta)]\gamma_{f1}$$

where γ_{f1}, the relative mean square of f_1 throughout the domain of (T_L) is a dimensionless quantity:

$$\gamma_{f1} = \frac{1}{T_L f_L^2} \int_{(T_L)} f_1^2(t)dt$$

The component $f_1(t)$ represents all discontinuities from the intrinsic particulate structure of material being analyzed. For values of θ larger than θ_{f1}, called *range* of variogram the autocorrelation function is surely nil. The Figure 3.2 shows a typical short-range variogram.

Hence, $\theta \geq \theta_{f1} \Rightarrow \rho_{f1}(\theta) = 0$ and $\gamma_{f1}(\theta) = \gamma_{f1} = constant$

The variogram $\gamma_{f1}(\theta)$ is said to *flat* in the useful domain of θ.

Properties of $\gamma_{f2}(\theta)$: Similarly the variogram of $\gamma_{f2}(\theta)$ can be written:

$$\gamma_{f2}(\theta) = [1 - \rho_{f2}(\theta)]\gamma_{f2}$$

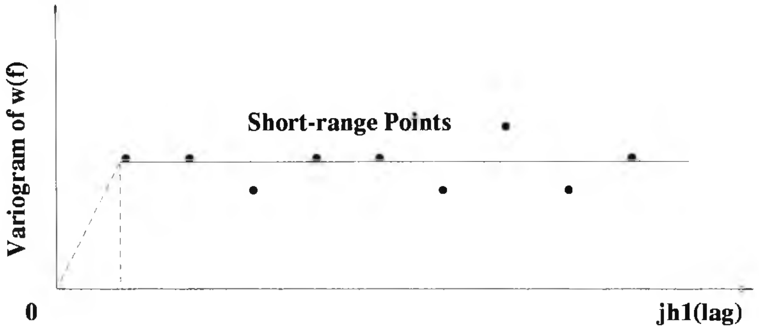


Figure 3.2: Flat Variogram $\gamma_{f1}(\theta)$ for $f_1(t)$ with random distribution.

where γ_{f2}, the relative mean square of f_2 throughout the domain of (T_L) is a dimensionless quantity:

$$\gamma_{f2} = \frac{1}{T_L f_L^2} \int_{(T_L)} f_2^2(t)dt$$

The function $f_2(t)$ shown in the Figure 3.3 represents the continuous trends of $f(t)$, all discontinuities being considered by $f_1(t)$. Therefore, when $\theta = 0 \rightarrow \rho_{f2}(\theta) = 1$ and $\gamma_{f2}(0) = 0$.

According to Gy [37], for values of θ larger than the range of variogram, the autocorrelation function is nil; $\theta \geq \theta_{f2} \rightarrow \rho_{f2}(\theta) = 0$ and $\gamma_{f2}(\theta) = \gamma_{f2}$. Between $\theta = 0$ and $\theta = \theta_{f2}$ the variogram $\gamma_{f2}(\theta)$ is an increasing function of θ.

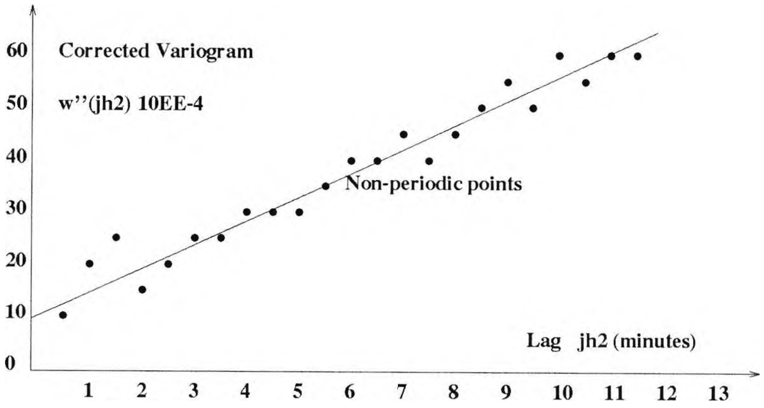


Figure 3.3: Long-range continuous Variogram $\gamma_{f2}(\theta)$ for $f_2(t)$ with autocorrelation.

Properties of $\gamma_{f3}(\theta)$: The periodic function is the summation of all terms of general form:

$$f_{31}(t) = f'_{31} sin 2\pi t/T_{P1} + f''_{31} sin 2\pi t/T_{P1}$$

$$f_{32}(t) = f'_{32} sin 2\pi t/T_{P2} + f''_{32} sin 2\pi t/T_{P2} \cdots$$

with f'_{31}, f'_{32}, f''_{31} and f''_{32} constant and T_{P1}, T_{P2} the component periods. These formulae are simplified by simple translation of time axis. For that reason we will use $f_{31}(t) = f_{31} sin 2\pi t/T_{P1}$ instead. The Figure 3.4 shows details of a periodic variogram $[\gamma_{f3}(\theta)]$ together with $[\gamma_{f12}]$ and $[\gamma_{f2}(\theta)]$.

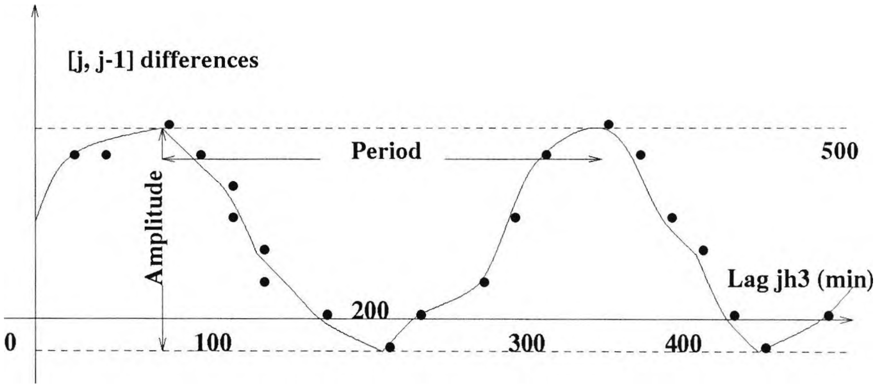


Figure 3.4: Periodic Variogram $\gamma_{f3}(\theta)$ for the simplest $f_3(t)$ considered.

Using the expression of $f_{31}(t)$ it is possible to compute $\gamma_{f31}(\theta)$:

$$\gamma_{f31}(\theta) = (1 - cos 2\pi\theta/T_{P1})\gamma_{f31}$$

where

$$\gamma_{f31} = \frac{f_{31}^2}{2f_L^2}$$

The variogram of a simple periodic function is also a periodic function with the same period.

The following properties remains:

$$K \text{ being an integer} \Rightarrow \begin{cases} \theta = 2KT_{P1}/2 & \rightarrow \quad \gamma_{f31}(\theta) = 0 \\ \theta = (2K+1)T_{P1}/2 & \rightarrow \quad \gamma_{f31}(\theta) = \gamma_{f31} \end{cases}$$

The variogram oscillates about γ_{f3} with amplitude equals to $2\gamma_{f3}$.

Periodic terms occurring in bulk materials have detrimental and unexpected consequences for industrial processes. Although expensive bed blending is always a suitable alternative to reduce the fluctuations of lots with periodic terms.

Properties of $\gamma_f(\theta)$: Considering a variogram with all terms $\gamma_{f1}(\theta)$, $\gamma_{f2}(\theta)$, $\gamma_{f3}(\theta)$ and calling γ_{fo} the largest value considered negligible in comparison with γ_{f1} (within confidence limits), the starting point of $\gamma_f(\theta)$, in the interval θ_{fo} is

$$\gamma_{f2}(\theta_{fo}) + \gamma_{f3}(\theta_{fo}) = \gamma_{fo} \ll \gamma_{f1}$$

Therefore, for values of θ as follows: $0 < \theta_{f1} < \theta \leq \theta_{f0}$

$$\gamma_f(\theta) = \gamma_{f1}$$

and for all values of θ such as $\theta \leq \theta_{f2}$:

$$\gamma_{f1}(\theta) = \gamma_{f1}$$

$$\gamma_{f2}(\theta) = \gamma_{f2}$$

$$\gamma_{f3}(\theta) = (1 - cos2\pi\theta/T_P)\gamma_{f3}$$

and

$$\gamma_f(\theta) = \gamma_{f1} + \gamma_{f2} + (1 - cos2\pi\theta/T_P)\gamma_{f3}$$

3.4 The Variographic Parameters

So far we have shown the continuous variogram $\gamma_f(\theta)$ broken into parts, separated by discontinuous functions. In order to implement a practical approach it is necessary to define a corrected variogram $[w^*_f(jh)]$ that represent an unbiased estimate of a discrete variogram $[w_f(jh)]$ estimator of $\gamma_f(\theta)$. As it is a discrete function, θ must be replaced by jh, where h is a variable time (or space) interval. That will be possible by defining an experimental variogram $[w'_f(jh)]$ that removes the error retained by $[w_f(jh)]$. We may be able to overcome most of difficulties, as long as there is a general idea of the model of variogram fitting the data, by defining and estimating the parameters.

Data obtained from a variographic experiment can, most of the time, fit a simple model as showing in the following, $[\theta_R]$ being the range of the variogram.

For $\theta < \theta_R$:

$$\gamma_f(\theta) = \gamma_{f1} + \underbrace{\gamma'_{f2}\theta + \gamma''_{f2}\theta^k}_{Range} + \gamma'_{f3}(1 - cos2\pi\theta/T_P)$$

For $\theta \geq \theta_R$:

$$\gamma_f(\theta) = \gamma_{f1} + \gamma'_R\theta + \gamma'_{f3}(1 - cos2\pi\theta/T_P)$$

In the presence of a complex periodic phenomena, these formulae may not be valid and the only possible interpretation of the variogram is given by the point-by-point calculation of the auxiliary functions to be shown in Section 3.5

When the variogram fits a *flat model*, $\gamma_f(\theta) = \gamma_{f1}$ but because of the random nature of this component, γ_{f1} represents the discontinuity of $\gamma_f(\theta)$ with mean equal to zero and variance s^2_{f1}. Every difference between units selected and extracted at very short intervals should have average converging to 0 and of variance $2s^2_{f1}$. For particles in suspension, the variability in this case approaches 0.

A *linear model*, shown in Figure 3.5 in the useful domain, is defined as follows:

$$\gamma_f(\theta) = \gamma_{f1} + \gamma'_{f2}\theta$$

which means that $\gamma_f(\theta) = \gamma_{f1}$ and $\gamma_{f2}(\theta) = \gamma'_{f2}\theta$.

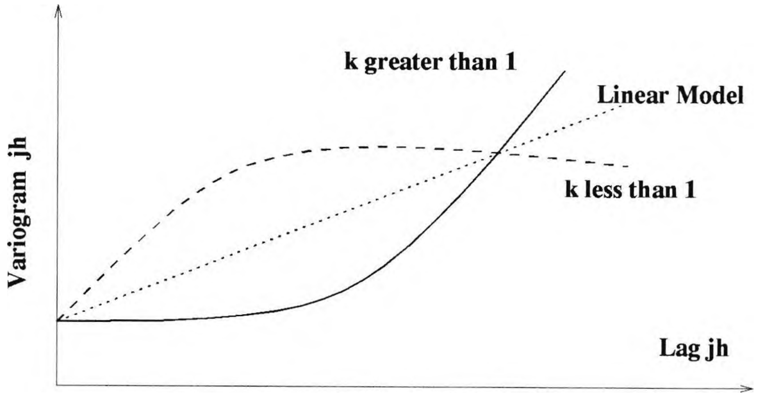


Figure 3.5: Linear and Generalized Linear Model for $\gamma_f(\theta) = \gamma_{f1} + \gamma'_{f2}\theta^k$.

It is usually accepted as an approximation for values of θ_{fu} larger than 30 mn, where θ_{fu} is the useful domain of θ. The upper limit of the uniform interval between increments or the uniform strata length is specified by selection scheme. As a general rule, Gy [47] it is always smaller than the range θ_{f2} and beyond which $\gamma_f(\theta)$ remains constant.

A *parabolic model* can be represented by

$$\gamma_f(\theta) = \gamma_{f1} + \gamma'_{f2}\theta + \gamma''_{f2}\theta^2$$

with $\gamma_{f1}(\theta) = \gamma_f$ and $\gamma_{f2}(\theta) = \gamma'_{f2}\theta + \gamma''_{f2}\theta^2$

It is generally concave downwards which entails γ''_{f2} negative acceptable within the useful domain. The expression for a non-periodic model

$$\gamma_f(\theta) = \gamma_{f1} + \gamma'_{f2}\theta + \gamma''_{f2}\theta^2$$

with γ_{f1}, γ'_{f2} and γ''_{f2} the *variographic parameters* to be determined.

Other models are of some interest such as *logarithmic* one, depicted in Figure 3.5 and represented for k integer as

$$\gamma_f(\theta) = \gamma_{f1} + \gamma'_{f2}\theta + \gamma''_{f2}\theta^k$$

and the *spherical model* which is a transitive model, consisting of two separate functions with discontinuity.

The typical equations are

$$\gamma_f(\theta) = \gamma_{f1} + \gamma'_{f2}\theta - \gamma''_{f2}\theta^3$$

This is perhaps the underlying geostatistics model for theoretical and practical purposes. It shows the variogram form with the relationship between classical variance $[\sigma^2]$, the spatial covariance $[C(\theta)]$ and $\gamma_f(\theta)$.

3.5 Auxiliary Functions

The Auxiliary Functions are used to determine the variogram $[\gamma_f(\theta)]$ consequently $f(t) - \mu(t)$, $\alpha(t)$ or $a(t)$ and their moments.

It is only possible to estimate a real discrete variogram and variographic parameters of the function $f(t)$ if it is assumed truly known in a series of Q increments sampled at instants t defined as follows:

$$t_q = (q - 1/2)h$$

with $q = 1, 2, \ldots Q$, and h uniform intervals between consecutive punctual increments I_q. The number Q is defined by the following inequalities:

$$(Q - 1/2)h \leq T_L < (Q + 1/2)h$$

where Q^{th} and the last increment must fall within the limits of the domain (T_L) in order to belong to the lot. Therefore, h is a submultiple of T_L and $T_L = Qh$. The estimates of f_L depend on the quality characteristic to be calculated:

- with $f(t) \equiv \mu(t)$ or $\alpha(t)$

$$f_L = \frac{1}{Q}\sum_q f(t_q)$$

- with $f(t) \equiv a(t)$

$$f_L = \frac{\alpha_L}{\mu_L}$$

- with any other function the proceedings are the same.

From these specifications we define the discrete semi-variogram $[w_f(jh)]$, estimator of the continuous variogram $\gamma(jh)$:

$$w_f(jh) = \frac{1}{2(Q-j)f_L^2}\sum_q [f(t_{q+j}) - f(t_q)]^2$$

for $q = 1, 2, \ldots, (Q-j)$ and $j = 1, 2, \ldots, j$.

There is a statistical minimum for $(Q-j)$. The number of squared differences must be larger than 25. As h tends towards 0, the product jh remains constant and equal to h_0. So $w_f(jh)$ tends towards $\gamma_f(h_0)$.

3.5.1 Towards the Corrected Variogram

The experimental estimates of the increments I_q are error-generating operations involving sampling, dividing, reduction, assaying etc. Therefore we should use $f'(t_q)$ instead of $f(t_q)$ and compute the experimental variogram $[w'_f(jh)]$,

$$w'_f(jh) = \frac{1}{2(Q-j)f_L^2}\sum_q [f'(t_{q+j}) - f'(t_q)]^2$$

If we call ϵ_{fq} the relative estimation error of $f(t_q)$ and define a dimensionless function:

$$\epsilon_{fq} = \frac{f'(t_q) - f(t_q)}{f_L}$$

By relative estimation error or standard deviation we call the relationship between the absolute standard deviation of sample reduction and/or assaying and the content a_L of the lot.

The use of ϵ_{fq} will depend on the characteristic considered:

- if $f(t)$ represents $\mu(t)$ then ϵ_{fq} is consequence of sampling and weighing errors;
- if $f(t)$ represents $\alpha(t)$ then ϵ_{fq} is consequence of sampling, reduction and assaying errors;
- if $f(t)$ represents $a(t)$ then ϵ_{fq} is consequence of the errors of both $a(t)$ and $\mu(t)$, therefore, sampling, reduction, weighing and assaying errors.

The variogram being a summation of mean squared differences of two values of $f(t)$ is biased as $w'_f(jh)$ includes s_f^2, an experimental estimate of the true value of the variance of e_{fq} distribution. Hence,

$$w'_f(jh) = w_f(jh) + s_f^2$$

and the corrected variogram

$$w^*_f(jh) = w'_f(jh) - s_f^2$$

The discrete variogram $w_f(jh)$ estimated by $w^*_f(jh)$ is in fact an unbiased estimate of the continuous variogram $\gamma_f(jh)$ following the removal of the biased term.

The determination of s_f^2 is based on assaying or weighing of the characteristics. It is nil for mass deviation $[s_\mu^2 = 0]$ as long as we respect materialization procedures.

3.5.2 Analysis of Periodic Variogram

Firstly we must check the existence of periodic terms. This is confirmed by analyzing the corrected variogram $w^*_f(jh)$ and its differential Δw^*:

$$\Delta w^* = w^*_f(jh) - w^*_f(j+1)h$$

and plotting the results $\Delta w^*/h$ against $\theta = (2j+1)h/2$. Naturally the choice of the interval plays an underlying role. It must be smaller than the period T_P the optimum value requiring, sometimes, a trial and error procedure.

1) Admitting positive and negative terms alternately, the variogram conveys a periodic component. The computation is carried on by considering the model variogram $\gamma'_f(\theta)$:

$$\gamma'_f(\theta) = \gamma'_{f1}(\theta) + \underbrace{\gamma'_{f2}(\theta) + \gamma'_{f3}(\theta)}_{\gamma'_{f+}(\theta)}$$

As we know the discrete value of $w^*_f(jh)$, estimation of $\gamma'_{f+}(\theta)$ is straightforward:

$$w^*_{f1}(jh) = w^*_f(h) = \gamma'_{f1}$$

and

$$w^*_{f+}(jh) = w^*_{f2}(jh) + w^*_{f3}(jh) = w^*_f(jh) - w^*_f(h)$$

which is always positive for values of jh larger than the domain of the flat variogram.

The mathematical function has two trigonometric terms to be determined: γ_{f3} and T_P. Assuming a cosine function

$$\gamma_{f3}(\theta) = (1 - cos 2\pi\theta/T_p)\gamma_{f3}$$

there will be a maximum for values $\theta = (2k+1)T_p/2$ when $\gamma_{f3}(\theta) = 2\gamma_{f3}$:

$$\gamma_f(\theta) = \gamma_{f1} + \gamma_{f2}(\theta) + 2\gamma_{f3}$$

and for $\theta = 2kT_p/2$,

$$\gamma_f(\theta) = \gamma_{f1} + \gamma_{f2}(\theta)$$

We must be cautious in order to save our experiment:

- use values of jh closer to extreme points of periodic variogram (precision);
- choose small values of h with high degrees of freedom ($\lim_{h\to 0} w_f^*(jh) \equiv \gamma_f(jh)$).

The differential test using the graphical method is probably the most accurate way to find the required parameters. The Figure 3.6 shows the use of test. It is based on drawing two curves that joins the extreme points of corrected variogram.

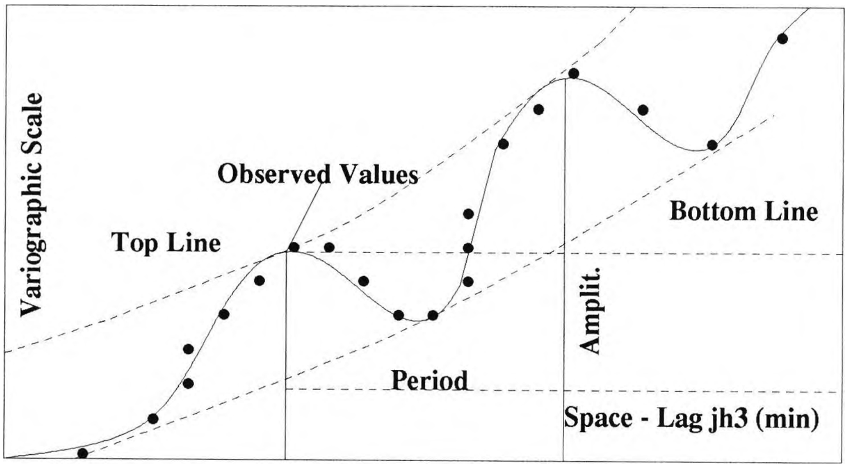


Figure 3.6: Graphical Representation of Periodic Variogram and Method for determination of both Period (T_P) and Amplitude (γ_{f3}).

The top curve represents values $\gamma'_{f1} + \gamma'_{f2}(\theta) + 2\gamma'_{f3}$ and the bottom curve values of $\gamma'_{f1} + \gamma'_{f2}(\theta)$. Therefore the abscissas of the first contacts with the bottom curve estimate the period T_P and the ordinate differences between both curves measure $2\gamma_{f3}$.

2) Admitting no periodic terms, $\gamma_{f3}(\theta) = 0$ and $\gamma_f(\theta) = \gamma_{f1}(\theta) + \gamma_{f2}(\theta)$. Then,

$$w^*_{f2}(jh) = w^*_f(jh) - w^*_f(h)$$

Plotting the positive values of $w^*_{f2}(jh)$ against jh, we may be able to fit the data through any interpolation techniques. According to Pitard [83] a straight line is suitable most of the time. If the curve is parabolic it is fitted by plotting $w^*_{f2}(jh)/jh$ against jh and estimating the the ordinate and gradient accordingly. In this case the long-range variogram is represented by the following equation:

$$\gamma'_{f2}(\theta) = \gamma'_{f2}\theta + \gamma''_{f2}\theta^2$$

and the complete variogram:

$$\gamma'_f(\theta) = \gamma'_{f1} + \gamma'_{f2}\theta + \gamma''_{f2}\theta^2 + (1 - cos2\pi\theta/T_p)\gamma_{f3} \tag{3.7}$$

3.6 Moments of Quality Fluctuation Errors

Assuming that all the variographic parameters have been estimated: γ'_{f1}, γ'_{f2}, γ''_{f2}, γ'_{f3} and T_P. The moments depends on the sampling model used — systematic (sys) or stratified (strat). There will be moments for each characteristic: a_S, A_S and M_S, the critical content a_s being defined as:

$$a_S = A_S/M_S \tag{3.8}$$

The continuous selection error CE is the sum of four independent errors:

$$CE = QE_1 + QE_2 + QE_3 + WE \tag{3.9}$$

The first moment is:

$$m(CE) = m(QE_1) + m(QE_2) + m(QE_3) + m(WE) \tag{3.10}$$

and the variance:

$$s^2(CE) = s^2(QE_1) + s^2(QE_2) + s^2(QE_3) + s^2(WE) \tag{3.11}$$

In order to relate the equations presented so far we need to define some other variables:

ε: relative deviation of mass of critical component $[A_S]$ from its mean;

η: relative deviation of mass of active component $[M_S]$ from its mean;

ϱ: difference between ε and η.

From these definitions we have:

$$A_S = (1+\varepsilon)m(A_S)$$

$$M_S = (1+\eta)m(M_S)$$

and the critical content:

$$a_S = \frac{A_S}{M_S} = \frac{(1+\varepsilon)m(A_S)}{(1+\eta)m(M_S)} = \frac{1+\varepsilon}{1+\eta}a_L \tag{3.12}$$

By definition, CE is the continuous selection error of the variables a_S and a_L within the lot. Then,

$$CE = \frac{a_S - a_L}{a_L} = \frac{\varepsilon - \eta}{1+\eta} = \frac{\varrho}{1+\eta}$$

All these quantities are random variables since $|\eta| < 1$, then $1/(1+\eta)$ is a convergent series equal to 1.

The moment of the quantities $m(\eta)$, $m(\varepsilon)$ and $m(\varrho)$ are nil by definition. As $\sigma^2(\varepsilon) = u^2(A_S)$, $\sigma^2(\eta) = u^2(M_S)$ and $\rho(\varepsilon, \eta) = \rho(A_S, M_S)$, then

$$\sigma^2(\varrho) = \sigma^2(\varepsilon) + \sigma^2(\eta) - 2\rho(\varepsilon,\eta)\sigma(\varepsilon)\sigma(\eta) \tag{3.13}$$

The relationships between the moments of a_S and CE are evident: $m(a_S) = \{1 + m(CE)\}a_L$ and $\sigma^2(a_S) = a_L^2\sigma^2(CE)$ or $u^2(a_S) = \sigma^2(CE)$

Assuming a general parabolic variogram:

$$\gamma_a^{'}(\theta) = \gamma_{a1}^{'} + \gamma_{a2}^{'}\theta + \gamma_a^{''}\theta^2$$

for the whole domain of the lot,

a) The mean of the continuous selection error CE is

$$m(CE) = u^2(M_S) - \rho(a_S, M_S)u(A_S)u(M_S)$$

coefficient of bias

$$b(CE) = |m(CE)|/s(CE)$$

b) variance of CE

$$s_{CE}^2 = u_{a_S}^2 = u^2(A_S) + u^2(M_S) - 2\rho(A_S, M_S)u(A_S)u(M_S)$$

where the relative variance of the sample weight $[M_S]$ for systematic sampling is

$$u^2_{sys}(M_S) = \frac{1}{T_L}(\gamma'_{M1} T_{sys} + \frac{\gamma'_{M2}}{6} T^2_{sys})$$

and for stratified sampling:

$$u^2_{strat}(M_S) = \frac{1}{T_L}(\gamma'_{M1} T_{strat} + \frac{\gamma'_{M2}}{3} T^2_{strat})$$

Relative variance of the weight of critical components $[A_S]$ for systematic sampling is

$$u^2_{sys}(A_S) = \frac{1}{T_L}(\gamma'_{A1} T_{sys} + \frac{\gamma'_{A2}}{6} T^2_{sys})$$

and for stratified sampling:

$$u^2_{strat}(A_S) = \frac{1}{T_L}(\gamma'_{A1} T_{strat} + \frac{\gamma'_{A2}}{3} T^2_{strat})$$

Breaking up the total variance $s^2_{(CE)} = s^2_{(QE)} + s^2_{(WE)}$:

- for systematic sampling:

$$s^2_{sys}(QE) = \frac{1}{T_L}(\gamma'_{a1} T_{sys} + \frac{\gamma'_{a2}}{6} T^2_{sys})$$

$$s^2_{sys}(QE_1) = \frac{T_{sys}}{T_L}\gamma'_{a1}$$

$$s^2_{sys}(QE_2) = \frac{1}{T_L}(\frac{\gamma'_{a2}}{6}) T^2_{sys}$$

- for stratified sampling:

$$s^2_{strat}(QE) = \frac{1}{T_L}(\gamma'_{a1} T_{strat} + \frac{\gamma'_{a2}}{3} T^2_{strat} + \frac{\gamma''_{a2}}{6} T^3_{strat})$$

$$s^2_{strat}(QE_1) = \frac{T_{strat}}{T_L}\gamma'_{a1}$$

$$s^2_{strat}(QE_2) = \frac{1}{T_L}(\frac{\gamma'_{a2}}{3} T^2_{strat} + \frac{\gamma''_{a2}}{6}) T^3_{strat}$$

Finally the variance of the sampling error is calculated by the difference:

$$s^2_{WE} = s^2_{CE} - s^2_{QE}$$

Each of these moments has an important meaning:

1) The mean of continuous quality errors $[m(CE)]$ and coefficient of bias must be negligible or at least small, say less than 1% for guarding against estimation bias.

2) The variance of weighting error $[s^2(WE)]$ relatively high means fluctuations of the increment weight due to fluctuations of the rate of flow. Care must be taken with lack of correctness of sampling devices: cutter speed, uniformity of moving belt etc.

3) The variance of short-range quality errors $[s^2(QE_1)]$ even with bed blending hardly can be reduced. Reducing size of particle may reduce fundamental error and mixing reduce but at an economical cost. The effective way to minimize $\sigma(QE_1)$ is by taking as much increment as possible.

4) The variance of long-range quality errors $[s^2(QE_2)]$ can be reduced by mixing and mainly bed blending techniques.

5) The variance of periodic quality errors $[s^2(QE_3)]$, depending on the complexity of function, it is better performed by modeling the variogram interpreting the total continuous selection errors. Even for the sinusoidal model neither the amplitude nor the period are strictly constant.

The relative importance of parameter γ'_{f3} resides in the relationship f_3/f_L, defined as

$$f_3 = f_L\sqrt{2\gamma'_{f3}}$$

3.7 Modeling a Simplified Variogram

As stated before, the spatial statistics is based on assumption of dependence of sample values, regarding the position in the lot. The essential step for the understanding the behavior of the material under analysis is through Variogram and Variograph Experiments.

Fitting data may lead us to one of the models presented before. A typical spherical semivariogram is presented in Figure 3.7. The correlation is hardly perfect and the random component is presented in the distribution values. The mathematical models will assume always the presence of the two sources of variability referred to as bias. In some cases a third term occurs: the periodic one.

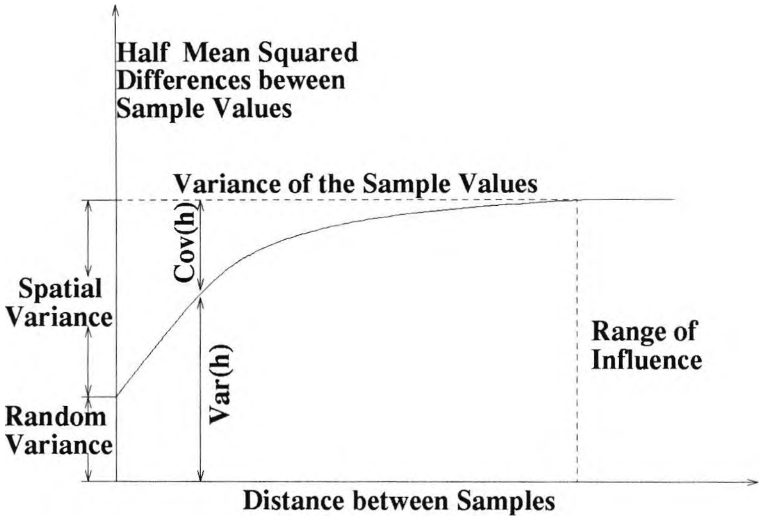


Figure 3.7: A typical Variogram showing relationship among Variance, Covariance and Variogram.

The bias is a function of the random component of the variogram and could be expressed in terms of random variance or nugget effect as termed by geostatisticians:

$$E = \frac{RandomVariance}{SpatialVariance}$$

where regular changes in the body of material are represented by the spatial variance while errors of analysis or measurements are represented by random variance. Instead of assume that the values are realizations of a random variable, like classical statistics, it assumes they are realizations of a random function of the distance or time between samples. This function displays spatial continuity between x_1 and x_2 for each distance and direction.

The scatterplot shows how continuous the data are, according to the symmetrical cloud of all possible pairs of data values whose location are separated by certain distance in a particular direction. As the location of any point can be described by a vector, it is convenient to label the x-axis $x(u)$ and y-axis $x(u+h)$.

The relationships between each one of an h-scatterplot and h is traditionally called the correlation function, the covariance function and the semivariogram. The three statistics are proposed for summarizing the fatness, but the most robust is the last one. It is presented below and rearranged to reflect the computational form in which the sample values are usually computed:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{(i,j)|h_{ij}=h} (v_i - v_j^2) \tag{3.14}$$

The values of $\gamma(h)$ are unaffected if all the i and j subscripts in the equation are switched. Instead of summing over all (i, j) pairs that are separated by h, it could be summed over all (j, i) pairs that are separated by h and so there will be this result:

$$\gamma(h) = \gamma(-h) \tag{3.15}$$

This result entails that γ for any particular direction will be identical to the one in opposition direction.

It is possible to extend the idea of h-scatterplot to that of a cross-h-scatterplot by using different variables at different locations. The equation used to define the variogram, $\gamma(h)$, can be extended to cross-variogram equation and it will become:

$$\gamma_{u,v}(h) = \frac{i}{2N(h)} \sum_{(i,j)|h_{ij}=h} (u_i - uj)(v_i - v_j) \tag{3.16}$$

In practice, however it is not possible to two samples at the same place. If a sample is evaluated twice, different values are obtained because of the valuation errors. On the other hand, if two samples are taken next to each other, different values are obtained again, not because of the sampling errors but because of intrinsic variations (micro-structures) of the body of material to be estimated. As a consequence, a discontinuity is usually observed near the origin which is called the Nugget effect.

The mathematical models of semivariogram can be classified according to whether or not they correspond to situations where the second order stationarity conditions are satisfied. If the second order stationarity exists, then a priori variance σ^2 of $x(u)$ also exists and is finite (sill). For large distances h such that $x(u)$ and $x(u + h)$ are not correlated (distance of influence), the semivariogram $\gamma(h)$ will reach a value equal to σ^2.

If only intrinsic hypothesis is satisfied, the sample variance is an increasing function of the size of the area or volume in which the samples are located, and the semivariogram $\gamma(h)$ will be a continuously increasing function of h.

Unfortunately, most of the particulate materials does not seem to satisfied all stationarity conditions. The moments of the variogram in these situations are only found out after the long computation of point-by-point fitting suggested by Gy [37].

When sampling materials from conveyor belt or bed blending systems and Matheron's conditions are all satisfy a simplified method has been suggested by Saunders

[91]. It is based on the following three points:

1. the estimation error variance [σ_E] is, to a close approximation, determined by the variogram at short lags;
2. the formulae for σ_E take very simple forms for linear variograms;
3. the variogram can be considered linear over short lags, in most practical situations.

The method consists of fitting a linear variogram model $V(h) = A + Bh$ to the observed data. The fitting should concentrate on the short lag variogram. As in systematic sampling, no two sampling times or spaces are less than one lag, it is necessary to extrapolate back to the interval zero to one lag. When systematic sampling is used, we should calculate the sample variogram:

$$\gamma(h) = \frac{1}{2(n-k)} \sum_{i=1}^{n-k} (X(t_i) - X(t_{i+k}))^2$$

for n samples and $k = 1, 2, \ldots$. Then we should fit a straight line $A + Bkh$ to the first few calculated values of the variogram.

When the sampling scheme is stratified the t_i values are not equally spaced. We should take into account the separation between each individual pair of sample times. The best way to compute the variogram is to take all pairs (t_i, t_j) such that $|t_i - t_j|$ is less than a specified cutoff, and for each pair calculate:

$$d_{ij} = |t_i - t_j|$$

$$v_{ij} = \frac{1}{2}(X(t_i) - X(t_j))^2$$

Then we may fit a straight line $A + B(|t_i - t_j|)$ using linear regression.

If the sample times are fairly evenly spaced we can use the same systematic technique used before.

Having calculated the parameters of the straight line we are able to compute [σ_E] for systematic sampling:

$$\sigma_E = \frac{1}{n}(A + \frac{1}{3}B(|t_i - t_j|))$$

for stratified sampling and

$$\sigma_E = \frac{1}{n}(A + \frac{1}{6}B(|t_i - t_j|))$$

for systematic sampling.

Worked examples of this simplified methods are given by Saunders [91] for worked examples and then relate to point-by-point techniques of Chapter 3.

3.8 Accuracy of Systematic Sampling

It has been stated that the only way of reducing the detrimental quality fluctuations is through bed-blending also known as one-dimensional homogenizing process. It is implemented on particulate materials worldwide. Statistical theories of bed-blending have been proposed. It includes stacking and reclaiming. It is costumary to sample such systems taking samples, cross-sectionnally, at fixed space or time intervals. Again, the increments are supposed to be evenly spaced along the stacking or the conveyor belt — stationary or moving. The increments taken at closer intervals than normal are analyzed individually or by interpenetrating samples, combined before analysis. Prediction of the standard error of the mean may be treated either by time series theory or analysis of variance. Jowett [66] refers to the the first treatment as worthwhile because it gives equally ready solution not only when the two interval sizes correspond but also when they do not. However when we want to asses nothing but accuracy, $ANOVA$ techniques are useful.

His time series techniques for coal is quite interesting because there is no restriction to the form of variogram and it is implemented in quite realistic situations. The data are collected from increments taken at about one-minute intervals from conveyor belt sections loaded into four trucks. It is supposed continuity between these sublots, a supposition rather artificial. He chose ash contents as a quality characteristic is but it could be any other. The data are collected in a serial way, one pair having a member in common with another pair.

After computing the semivariogram, a curve is plotted symmetrically about the origin, being each pair at a distance h apart like in Figure 3.8.

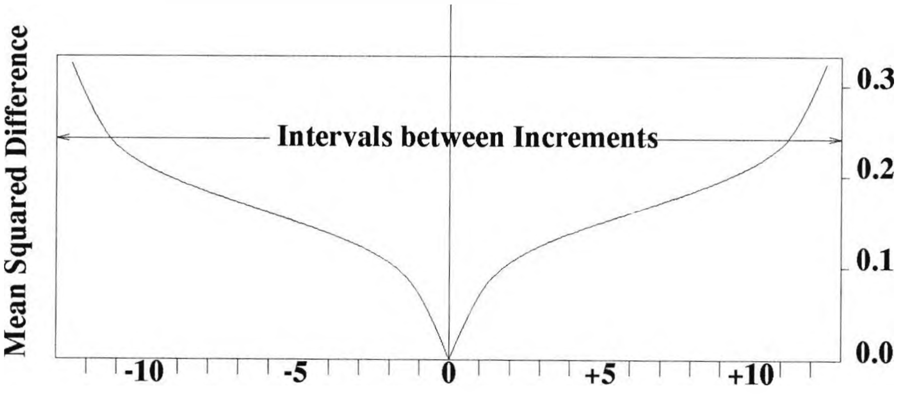


Figure 3.8: The Symmetrical Semivariogram with One-dimensional Variations.

The points are fitted by any numerical procedure or by eye. This curve is useful because it gives us basic information about the material itself and the variations of the material on one-dimensional basis. These variational properties is related to autocorrelation function and it indicates how closely any term of the series resembles its successors (positive values) or its predecessors (negative values).

The second curve in Figure 3.9 is then computed by multiplying the points of semivariogram for each h by a factor $1 - |h|/T$, where T is the length of the section in time units. For instance, he divided the truck in four zones and within each zone four increments were extracted at each minute, taking $T = 16min$ as a whole.

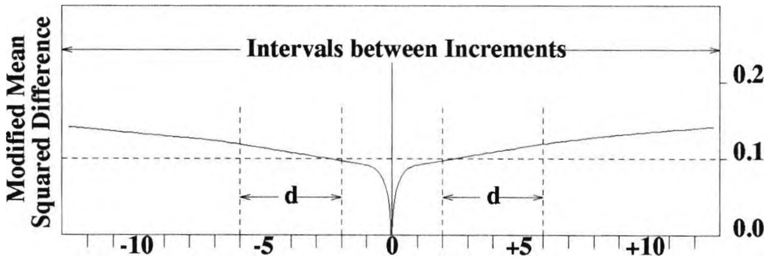


Figure 3.9: The Modified Semivariogram for Computation of Standard Error.

The sampling error of the mean is estimated as follows: the horizontal axis of Figure 3.9 is divided into intervals of width d, the length of each zone. Next the average ordinate is calculated in the central and in the adjacent intervals by subtracting the mid-ordinate from the average ordinate. The total is divided by $2n$, where 2 is due to semivariogram and n is the number of zones. The main contribution will come from the central interval, particularly when there is no sill.

$$\sigma^2_{\underline{x}} = \frac{1}{2n}\sum_{0}^{n}[Aver - Mid]$$

It is very interesting to notice the close agreement between the statistic procedure and the reasoning for those variations in both approaches by Gy [37] and Jowett [66]. The short-range variance is due to segregation, local disorder and intrinsic properties of material while the long-range variance is due to non-periodic trends of material. Both are based on systematic sampling variance due to Cochran [23]. The minimum sampling interval is a problem of some interest. One approach, using successive samples taken very closely together, is to compare the observed to expected distribution of ranges of pairs of measurements. The procedure is repeated several times eliminating some measurements until a significance test shows no differences between observed and expected distributions. The minimum spacing at which this kind of association is not present so that the minimum practical size of test or sampling interval may be determined.

It should be worthwhile express the same computation through classical statistics, firstly using all individual increments for computing the *ANOVA* table between and within zones. After that we should compute the individual results by combining them according to the model of interpenetrating samples. A different *ANOVA* table is also computed for between and within trucks.

Although these standard deviation may be smaller than those of time series it is not a correct approach because of supposition of continuity is somewhat artificial.

3.9 Worked Example

From a practical viewpoint, the main interest in conducting a variographic experiment is to predict in advance the order of magnitude of the continuous selection errors that is, the quality fluctuations. When performed with accuracy and precision it is possible to use this graphics as a model for comparisons with lots of the same product or supplier.

The following example will illustrate the use of this technique and the computation of variance estimate through Variographic Experiments. It was conducted in two stages. Firstly it was investigated the random term — $V(0)$ — and then, the continuous term — $V(j)$ — for *Charcoal*. It was chosen particle size as a quality characteristic (coarses greater than 900μ).

The short-range and long-range data were collected in the Research Center of *Geotechnical Engineering* at *The City University* and analyzed at *Pascall Engineering Ltd.*, London.

The first series of 30 increments were sampled in spaces of $20cm$ and analyzed using the sieve shaker method. From the data we obtained 15 points of the variogram. They are presented in the Table 3.1. The variogram is depicted in Figure 3.10 and appears flat with a sill. The second minimum point corresponds to the variance of short-range fluctuatutions.

Under these conditions we can consider the best estimate of V(0) is given by the first minimum of the circle. Therefore, $V(0) = 1.45EE - 03$.

A second series of long-range data were sampled with lag equal to $2m$ for testing of $CE2$. They were also analyzed at *Pascall Engineering Ltd.*, and the data values are presented in the Table 3.2.

Increment	*Values*	*Increment*	*Values*	$V(j) \times 10^{-3}$
01	0.71	16	0.74	1.65
02	0.73	17	0.73	2.60
03	0.69	18	0.67	2.75
04	0.67	19	0.69	2.98
05	0.73	20	0.70	3.20
06	0.73	21	0.63	2.62
07	0.74	22	0.64	1.45
08	0.70	23	0.68	2.15
09	0.71	24	0.71	3.00
10	0.69	25	0.69	2.40
11	0.65	26	0.74	2.43
12	0.74	27	0.65	3.65
13	0.74	28	0.63	4.19
14	0.69	29	0.59	3.82
15	0.70	30	0.62	4.50

Table 3.1: Experimental Data for Short-term *Charcoal* Fluctuations and computation of Variographic parameters V((j).

The variogram is depicted in Figure 3.11.

We can see from the figure, after the 10th. point the variogram remains flat following the second rule of stationatity, with a variance estimate equal to $4.7EE-03$. Finally assuming no periodical terms:

$$v_E^2 = 4.70EE-03 + 1.45EE-03 = 6.15EE-03$$

We have assumed that *Charcoal* has no periodic fluctuations, however it has to be confirmed with a complementary experiment of at least 80 data values.

The Fortran program used for calculations of variographic parameters is presented in Appendix 2.

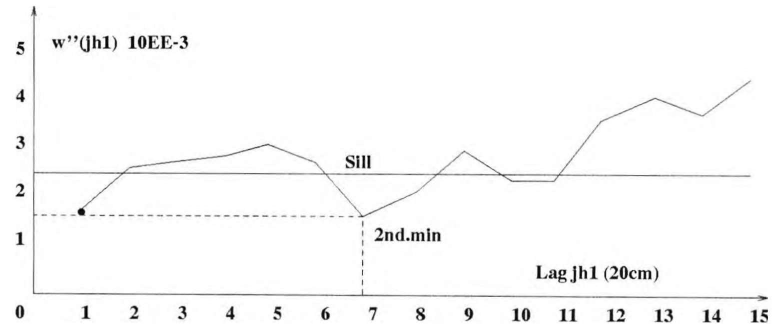


Figure 3.10: Graphical Representation of the Experimental Variogram V(j) of Short-term *Charcoal* Fluctuations. Quality Characteristic: Particle Size.

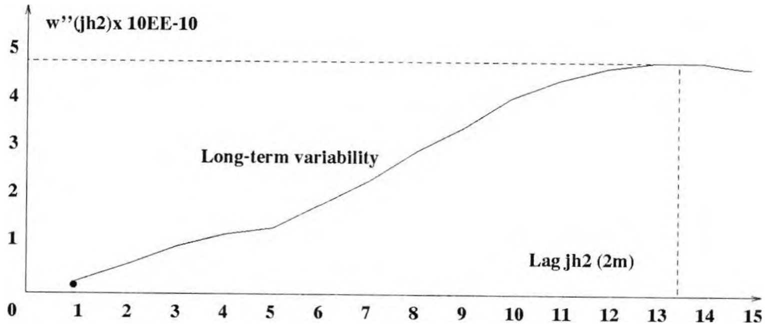


Figure 3.11: Graphical Representation of the Experimental Variogram V(j) of Long-term *Charcoal* Fluctuations. Quality Characteristic: Particle Size.

Increment	*Values*	*Increment*	*Values*	$V(j) \times 10^{-3}$
01	0.66	16	0.74	0.20
02	0.63	17	0.74	0.40
03	0.64	18	0.74	0.65
04	0.65	19	0.73	1.02
05	0.67	20	0.73	1.40
06	0.69	21	0.71	1.80
07	0.69	22	0.71	2.32
08	0.69	23	0.70	2.85
09	0.70	24	0.69	3.45
10	0.70	25	0.69	4.03
11	0.71	26	0.68	4.40
12	0.73	27	0.67	4.69
13	0.73	28	0.65	4.78
14	0.74	29	0.63	4.74
15	0.74	30	0.66	4.60

Table 3.2: Calculation of Experimental Variogram V(j) of Long-term *Charcoal* Fluctuations.

Chapter 4

Multi-stage Experiments with Bulk Materials

Bulk Materials such as coal, charcoal, sulphur, ore and the like are evaluated by their quality characteristics: purity, ash content, carbon proportion, moisture percentage etc. From the receiving of the raw material to the acceptance there is a long series of error-generating functions: selection, division, preparation, further division, analysis etc.

This chapter deals with the problem of isolating variance components associated with each stage sampling (primary, secondary and tertiary units) and measurement systems. The method of conducting multifactor experiment, particularly Nested Experimental Design is commonly used for variation studies because they identify where in the process of bulk materials the quality improvement effort needs to be focused. Three types of design are studied: balanced, staggered and nested-factorial according to the importance of each from a practical viewpoint and the required needs. They are presented with analytical solutions to detect, analyze and reduce such factors and therefore assign causes to process capability. The insight allows optimization of sample size, minimization of the amount of replication and reduction of both variability and cost. A case study is presented of the application of the methods to determination of error and their impact on cost.

4.1 Introduction

Companies dealing with bulk materials either in batch or continuous process, generally are faced with fluctuation of quality characteristics that can damage the quality of finished goods and produce failure to meet specifications. Even robust designs are at stake if the main sources of variations — Sampling Error(PE), Subsampling Error(SE) and Analytical Error(AE) — are not kept below some percentage of Total Error(TE) demanding by customers.

The overall variance of test results is generally the sum of these individual variances and their transition may be consolidated in the following equation:

$$\sigma^2_{(TE)} = \sigma^2_{(PE)} + \sigma^2_{(SE)} + \sigma^2_{(AE)} \tag{4.1}$$

The process of obtaining data (samples) from particulate materials is well known. Firstly we extract a *representative* primary samples from the lot or batch then reduce each primary sampling without altering the quality characteristics to a several subsamples and finally analyze them. The first step is selective and it is generally done in a *Sampling Test Station.* The second is mostly preservative and involve a sequence of non-selective operations such as transfer, crushing, grinding, pulverizing, drying, mixing,dividing and so on. The third is analytical and it is performed in laboratory by using a minute part of the subsampled portion. Since these systems add variability to the output from a process, they also affect directly the process capability.

The engineer must first discover which link is the weakest and since all data originate at the analytical system, it should be examine first. A primary analytical requirement is the capability to analyze homogeneous samples for the element X with the required accuracy, precision, speed and confidence. When successive subsamples shows an unacceptable variance, it is necessary to discover how much of this variance is due to analytical error, and how much to the sampling and subsampling errors.

The first objective of the quality improvement processes is to have processes that are in statistical control and are capable of meeting customer specifications. Process capabilities are calculated by comparing the distance between one specification limit and the lower specification limit (if they both exist.)

In chemical industries, the variability inherent in the analyzing systems, subsampling procedures and sampling techniques are the major limits on increasing process capability and bias and fluctuations. That is because the relationship between the process width and the specification limits is defined in terms of a process capability index, either C_p or C_{pk}. A C_p index measures potential process performance since only the process spread is related to the specification limits.

$$C_p = \frac{\begin{array}{lcl}\text{Upper} & & \text{Lower}\\ \text{Specification} & - & \text{Specification}\\ \text{Limit} & & \text{Limit}\end{array}}{\pm\sigma_{TE}(process\, definition)}$$

However, C_{pk} is related to the C_p index, but takes into account differences between the design nominal and the actual process average (or mean) and can be considered a measure of process performance. Thus

$$C_{pk} = C_p(1 - k) \tag{4.2}$$

and

$$k = \frac{(nominal - \mu)}{(USL - LSL)} \tag{4.3}$$

where μ is the process mean.

The difference between the final component value and the process mean is the Total Error, TE, which has three or more sources of error (variability) shown in Equation 4.1.

The inverse of the C_p index, considering a stable process with $6\sigma_{TE}$ is the fraction of the specification width that our process operates within. We can apply that same principle to our calculated variance components and since they are additive, we can combine related components of product, property and/or characteristics. The computation would include variability of components, percentage of total variability, by sources and degree of freedom, capabilities and specification width, and percentage out of specification according to the requirements of the process: in terms of $n \times \sigma_{TE}$.

There are two basic approaches to isolate such errors and establish the relationship among these sub-systems: *X—R Control Charts* and Analysis of Variance, particularly *Nested Experimental Design* (NED). This chapter is mostly about the second though both have the same target: isolating variances and measuring the relative effect of factors upon the response.

NED is preferred to *Charts* for several reasons: (i) it requires only one experiment not one for each isolated variance; (ii) it allows experimenters to compute significant effects within and between factors and get more hints about changes and/or adjustments; (iii) it is much more powerful because it permits a number of configurations such as balanced, staggered fractional and factorial designs; (iv) it allows analysis of the data as they are accumulated, preparing successive ANOVA tables as the experiment progresses (and, therefore, relating these measures of variation to specification).

4.2 Assumptions underlying Nested Design

Most industrial experiments to quantify sources of variability in chemical process are done through Nested Designs.

It is usually the case when the differences between the mean effect of the levels of one factor are due in part to differences between the unique effects associated with other factors they are confined to. For convenience reasons such proceeding is useful when some factors are very hard to vary and others are much easier.

The fundamental difference between a nested set of data and a fully randomized set lies in their error structures. In a fully randomized design there is only one homogeneous random error system with equal chance of perturbing each observation. In the nested structure, on the other hand, we have two independent sources of random disturbances: within factor levels that affects each nested group and the other set of random observation affects each observation separately as the nested factor levels are changed.

For better understanding of the error structure let us examine the simplest nested situation where two independent sources of random variation occurs:

$$y_{i(j)} = \mu + e_i + \epsilon_{i(j)}$$

If the sampling of factors and subfactors is random, then the errors are assumed to have zero expectation and are uncorrelated. The variance, however, has two independent terms: $Var(\epsilon_{i(j)}) = E(\epsilon^2_{i(j)})$ and $Var(e_i) = E(e^2_i)$. The first estimate we get from all observations by pooling the sum of squares within batches. The second one by using the grand mean against mean of batches.

The pooled mean sum of squares within batches is

$$\frac{1}{b(a-1)}\sum_{i}^{a}\sum_{j}^{b}(\overline{y}_{i(j)} - \overline{y}_{..})_2 = A,$$

The among batches mean sum of squares is

$$\frac{1}{(b-1)}\sum_{j}^{b}(\overline{y}_{i.}-\overline{y}_{..})_2 = B,$$

What characterizes these multifactor experiments is that the levels of one factor are similar but not identical to different levels of another factor. Analyzing is nested under the levels of subsampling and this factor under the levels of sampling. This idea may be extended to the case where some factors have a factorial relationship and others are nested within the factorial combinations or in levels of other factors. The Figure 4.1 illustrates a model embodying both nested and factorial design.

It is better understanding, let us synthesize the computational steps leading to an analysis of variances through the general nested model given in the Equation 4.4 below.

$$y_{ijkl} = \mu + A_i + B_{i(j)} + C_{k(ij)} + \epsilon_{(ijk)l} \tag{4.4}$$

where i = 1,2,...n; j = 1,2,...n_i; k = 1,2,...n_{ij}; l = 1,2,...n_{ijk} and $\sum_i \sum_j \sum_k n_{ijk} = N$, $\sum_j \sum_k n_{ijk} = N_{i..}$ and $\sum_k n_{ijk} = N_{ij.}$; μ is the overall mean; A , B and C are random and independent variables with zero means and variances σ_a^2, σ_b^2, σ_c^2 and σ_ϵ^2 and having a nested relationship within each other. The last term in the model can be considered the *residual* or error.

From the model it follows that the variance of grand mean ($\overline{y}_{....}$) is:

$$\begin{aligned} var(\overline{y}_{....}) &= var(\mu + N^{-1}\sum_i N_{i..}A_i + N^{-1}\sum_i\sum_j N_{ij}B_{j(i)}) \\ &+ N^{-1}\sum_i\sum_j\sum_k n_{ijk}C_{k(ij)} + N^{-1}\sum_i\sum_j\sum_k\sum_l \epsilon_{l(ijk)} \qquad (4.5) \\ &= N^{-2}(\sigma_a^2\sum_i N_{i..}^2 + \sigma_b^2\sum_i\sum_j N_{ij}^2 + \sigma_c^2\sum_i\sum_j\sum_k n_{ijk}^2 + N\sigma_\epsilon^2) \qquad (4.6) \end{aligned}$$

Similarly, the variance for the factor A is:

$$var(\overline{y}_{i...}) = \sigma_a^2 + N_{i..}^2(\sigma_b^2\sum_j N_{ij.}^2 + \sigma_c^2\sum_i\sum_j n_{ijk}^2 + N_{i..}\sigma_d^2)$$

For the factor B mean ($\overline{y}_{ij..}$):

$$var(\overline{y}_{ij..}) = \sigma_a^2 + \sigma_b^2 N_{ij.}^{-2}(\sigma_c^2\sum_k n_{ijk}^2 + N_{ij.}\sigma_d^2)$$

And for the factor C mean ($\overline{y}_{ijk.}$):

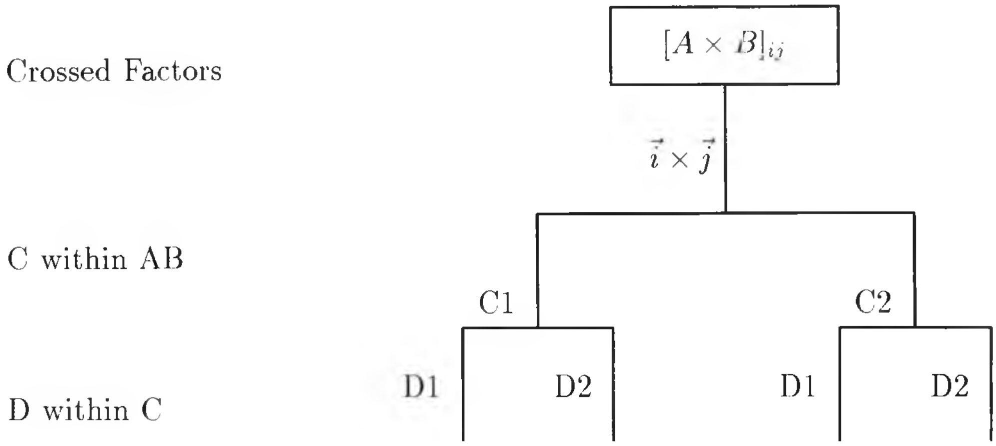


Figure 4.1: Balanced Nested Factorial Design.

$$var(\overline{y}_{ijk.}) = \sigma_a^2 + \sigma_b^2 + \sigma_c^2 + n_{ijk}^{-1}\sigma_d^2$$

Finally, the variance of y_{ijkl} is

$$var(y_{ijkl}) = \sigma_a^2 + \sigma_b^2 + \sigma_c^2 + \sigma_d^2$$

The sums of squares SS_T are:

$$\begin{aligned} &\underbrace{\sum_i^n N_{i..}(\overline{y}_{i...} - \overline{y}_{....})^2}_{SS_A} + \underbrace{\sum_i^n \sum_j^{n_i} N_{ij.}(\overline{y}_{ij..} - \overline{y}_{i...})^2}_{SS_B} \\ &\underbrace{\sum_i^n \sum_j^{n_i} \sum_k^{n_{ij}} n_{ijk}(\overline{y}_{ijk.} - \overline{y}_{ij..})^2}_{SS_C} + \underbrace{\sum_i^n \sum_j^{n_i} \sum_k^{n_{ij}} \sum_l^{n_{ijk}} (y_{ijkl} - \overline{y}_{ijk.})^2}_{SS_\epsilon} \end{aligned} \tag{4.7}$$

The statistical development presented, assumes all the variables are normally distributed and the functions SS_A, SS_B, SS_C and SS_ϵ are mutually independent.

4.3 Balanced Nested Design: The General Model

This a classical model in which the several levels of a factor are distributed among those of another in a balanced way when it is not possible to cross them or practical considerations make it advantageous.

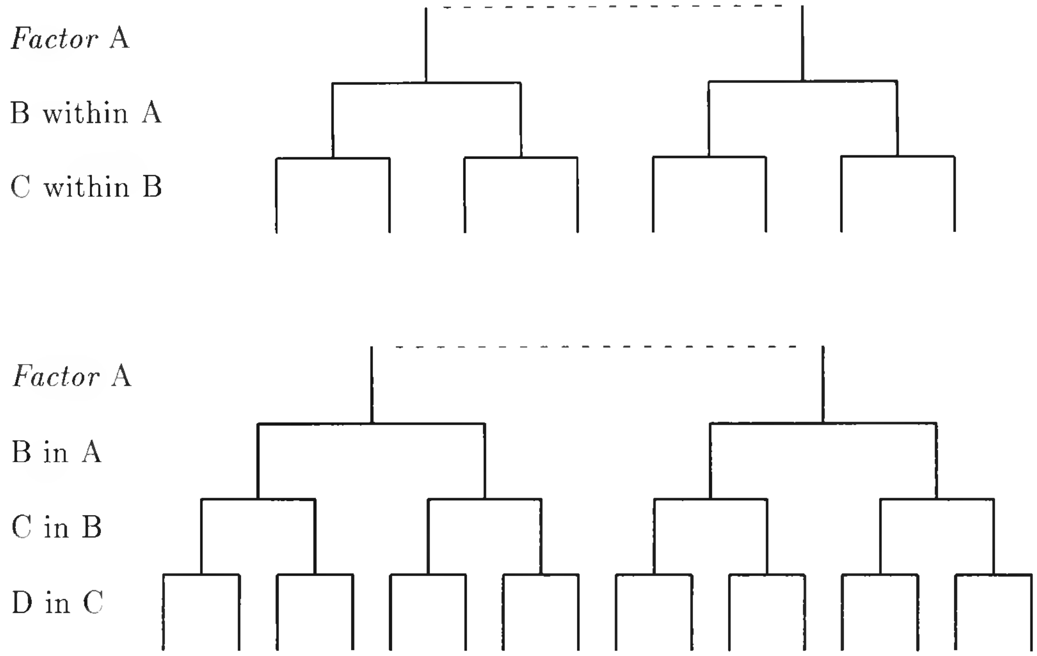


Figure 4.2: Three and Four-Stage Balanced Nested Designs.

Figure 4.2 shows two classical n-stage nested designs assuming duplicate tests on each of $k-1$ nested factors except for the top factor. A more general designation would be Factors A, B, C, D and so on. In addition, sample 1 may be called the first A-unit and sample a, the a-th A-unit, being A the determinant of the total degree of freedom. Note that these designs are completely replicated.

These nested configurations are similar to the one presented in Figure 4.1 except for the interaction term whose square sum has now been combined to the other factors.

A classical design is represented by Equation 4.4 with branches into 2^k following the first stage , is widely used in industrial experimentation. The factor A represents process and sampling errors. It could be a product in liquid or bulk form: barrels, casks, bags, portions continuous or discrete. The second nested factor, B, represents subsamples taken from the primary samples. The factor, C, is analyzed from secondary samples. It is the effect of analyzing within subsampling. The error term, ϵ, represents total errors of replications due to internal and external experimental conditions. The assumptions required for the model are: A_i , $B_{j(i)}$, $C_{k(ij)}$, $\epsilon_{(ijk)l}$ are random samples from a normal population, with mean zero and variances σ^2_{PE}, σ^2_{SE}, σ^2_{AE} and σ^2_{ϵ} respectively, and all of the random variables are mutually independent.

In addition, given the normality, confidence limits based on $\hat{\sigma}^2_\epsilon$, the direct estimate for σ^2_ϵ, can be calculated exactly using the well-known fact that $\nu\hat{\sigma}^2_\epsilon/\sigma^2_\epsilon$ is distributed as chi-square with ν degree of freedom. Further, a negative estimate of σ^2_ϵ is impossible.

The procedure for synthesizing the experimental results is to select randomly a first stage value, A_1, from a population $(0, \sigma^2_A)$. Then, two second-stage values (B_{11} and B_{12}), selected randomly from (A_1, σ^2_B). Following this, two third-stage values $(C_{111}, C_{112}, C_{121}, C_{122})$ are selected from each of $(B11, \sigma^2_C)$ and (B_{12}, σ^2_C).

Then, two four-stage values are selected from $(C_{111}, \sigma^2_\epsilon)$, $(C_{112}, \sigma^2_\epsilon)$, $(C_{121}, \sigma^2_\epsilon)$, $(C_{122}, \sigma^2_\epsilon)$.

At this point, eight four-stage values are obtained for inclusion in the design. Repeating this procedure for the remaining $[a]$ levels of the first stage yields the additional $[8a]$ fourth-stage values needed to complete the design.

Application of the usual analysis of variance provides estimates of the four variances as follows:

- $\sigma^2_A = (1/8)$ (mean square for Factor A - mean square for Factor B);
- $\sigma^2_B = (1/4)$ (mean square for Factor B - mean square for Factor C);
- $\sigma^2_C = (1/2)$ (mean square for Factor C - mean square for Factor D);
- $\sigma^2_D =$ (mean square for the last factor).

Hence, the mean squares for each factor are:

$$\left\{ \begin{array}{ll} 1: & (1/\mathrm{a})(1/\mathrm{a}\text{-}1)\chi^2_{\nu=a-1}(V_A) \\ 2: & (1/\mathrm{a})(1/\mathrm{a})\chi^2_{\nu=a}(V_B) \\ 3: & (1/2\mathrm{a})(1/2\mathrm{a})\chi^2_{\nu=2a}(V_C) \\ 4: & (1/4\mathrm{a})\chi^2_{\nu=4a}(V_D) \end{array} \right.$$

The sum of squares are similar to a factorial design with due combining.

$$\begin{aligned} SS_A &= \sum_i \frac{y^2_{i...}}{bcn} - \frac{y^2_{....}}{abcn} \\ SS_B &= \sum_i \sum_j \frac{y^2_{ij..}}{cn} - \frac{y^2_{i...}}{bcn} \end{aligned}$$

and so on.

As all the factors are random, the analysis of variance table and the expectations of the mean squares for this experiment is given in Table 4.1.

Sources	*SS*	*DF*	*MS*	*EMS*
Process&Sampling	SS_A	a-1	MS_A	$\sigma_\epsilon^2 + \mathrm{n}\sigma_{AE}^2 + \mathrm{cn}\sigma_{SE}^2 + \mathrm{bcn}\sigma_{PE}^2$
Subsampling	SS_B	a(b-1)	MS_B	$\sigma_\epsilon^2 + n\sigma_{AE}^2 + cn\sigma_{SE}^2$
analyzing	SS_C	ab(c-1)	MS_C	$\sigma_\epsilon^2 + n\sigma_{AE}^2$
Error (E)	SS_E	abc(n-1)	MS_E	σ_ϵ^2
Total (T)	SS_T	abcn-1		

Table 4.1: General Analysis of Variance for a Three-stage Design

Hence, the two basic moments are:

$$\overline{Y} = \frac{y_{....}}{N} = \frac{\sum_i \sum_j \sum_k \sum_l y_{ijkl}}{abcd} \qquad (4.8)$$

$$\sigma_{(TE)}^2 = \sigma_{\overline{Y}}^2 = \frac{\sigma_{(PE)}^2}{a} + \frac{\sigma_{(SE)}^2}{ab} + \frac{\sigma_{(AE)}^2}{abc} + \frac{\sigma_\epsilon^2}{abcd} \qquad (4.9)$$

Four hypotheses require our attention:

$1)H_oC: \quad \sigma_{AE(PE,SE)}^2 = 0$
$2)H_oB: \quad \sigma_{SE(PE)}^2 = 0$
$3)H_oA: \quad \sigma_{PE}^2 = 0$
$4)H_oE: \quad \sigma_\epsilon^2 = 0$

1) For the first hypothesis $H_oC : \sigma_{AE(PE,SE)}^2 = 0$ is tested by computing an F—statistic:

$$F^o = MS_C/MS_E$$

The null hypothesis is rejected if

$$F^o \geq F(1-\alpha), ab(c-1), abc(n-1)$$

2) For the second hypothesis $H_oB : \sigma_{SE(PE)}^2 = 0$ we are guided by the result of test of factor C. If H_oC is rejected we compute

$$F^o = MS_B/MS_C \tag{4.10}$$

and we reject H_oB if

$$F^o \geq F(1-\alpha), a(b-1), ab(c-1)$$

If H_oC is not rejected we compute a pooled mean square error, $\overline{MS}_A$:

$$\overline{MS}_E = \frac{SS_E + SS_C}{abc(n-1) + ab(c-1)}$$

and we calculate

$$F^o = MS_B/\overline{MS}_E$$

H_oB is rejected if $F^o \geq F(1-\alpha), a(b-1), ab(c-1)$

3) For the third hypothesis $H_oA : \sigma^2_{PE} = 0$ we are guided by the results of tests of factors B and C.

If H_oB is rejected we compute

$$F^o = MS_A/MS_B$$

and we reject H_oA if

$$F^o \geq F(1-\alpha), (a-1), a(b-1)$$

If H_oB is not rejected we compute a pooled mean square error, $\overline{\overline{MS}}_E$:

$$\overline{\overline{MS}}_E = \frac{SS_E + SS_C + SS_B}{abc(n-1) + ab(c-1) + a(b-1)} \tag{4.11}$$

and we calculate

$$F^o = MS_A/\overline{\overline{MS}}_E$$

H_oA is rejected if $F^o \geq F(1-\alpha), (a-1), abc(n-1) + ab(c-1) + a(b-1)$

4) The fourth hypothesis $\sigma^2_\epsilon = 0$ has several meanings. This term measures the random error. In this particular case, it measures the variation produced by disturbing factors, both known and unknown. Only a small part of it is directly attributable to the measurement system.

These values may mislead the experimenter to believe in effects that in fact do not exist. In some other cases it brings about an anomalous situation: it can lead to a negative difference for some factor. As a negative variance term has no meaning and there is no chance of interactions the only interpretation is that it is so large as to mask the variability between and within samples and/or subsampling. In this case it is made up of two terms: variability associated to sampling and/or subsampling errors or to unidentified causes. This source of variation must be investigated further through additional experiments.

If sound principles of *DOE* are used, a reasonable good gauge is to found the coefficient of variation (CV) for the total error. It does give the precision of the measurements when comparing to other similar past experiments.

$$CV = \sigma_\epsilon / \overline{y}_{....}$$

Regarding analytical error it appears in the final phases and is much easier to detect through NED by considering each analysis separately and focusing on the accuracy and precision of the system. It works like *Control Charts:* the *X Chart* monitors accuracy and *R Chart* precision. Both methods detect causes to be addressed: training, methods of analyses or laboratory equipments. The disadvantage of this method is that even with this minimum amount of replication, the amount of data in each A-unit quickly becomes very large as the number of factors increases.

The variance components become more difficult to estimate precisely as we move upward in such designs. As it was showed in Figure 4.2 those stages which have the fewest degrees of freedom, doubling for each factor beginning with C. The last factor contains essentially half of the degrees of freedom in the entire experiment. For example, see Table 4.2 a four-stage nested design with a levels of factor A and two levels for each other factors would have $8a - 1$ experiments:

Factors	*Type of Factors*	*DF*
A	Batches	a-1
B Within A	Sampling	a
C within B	Subsampling	2a
D within C	Analyzing	4a
Total		8a-1

Table 4.2: General Analysis of Variance for a Three-stage Experimental Design

As we increase the number of factors the size of the experiment is doubled and the cost increased. To keep the number of experiments the experimenter has three competing choices:

1. omit factors indispensable to the whole system;
2. reduce the number of levels and the precision of estimations;
3. distribute the degrees of freedom among the factors.

Some cares must be taken when using a few units at the top levels. The simplest algorithm is to use balanced Nested Design. In this case NED tends to provide little information on the upper levels. According to Bainbridge[5] more than 25 degrees of freedom at the top level of the design is imperative. He states that collecting more data than theoretically needed is possible as the cost of testing is usually minimal. In chemical industries cost of sampling and measurements are generally expensive and it is desirable to minimize the time, effort and cost of the experiments. Therefore the option for staggered and/or inverted design makes more sense. On the other hand there is a concern about the degrees of freedom at each level of the design. Balanced Design usually provides more than enough information at the bottom levels while as one moves upward variance components become much difficult to estimate precisely. Therefore unbalanced nested design should be used as an advantage to the classical nested design: the cost of experimentation is reduced and the variance estimation, particularly of sampling and analysis, is more reliable.

4.4 Staggered Nested Design

The staggered fully replicated nested design is not easy to administer and to analyze but it has a great disadvantage: there is no doubling the number of tests as we go down the bottom and so no distorting of estimates of variances in higher degree happens. In the Figure 4.3 these types of design for three and four factors are presented and may be compared to the ones of Figure 4.2 according to the format of A-units.

The purpose of using staggered designs is to balance the degree of freedom across it and reduce cost with number of tests. Getting more information on variances associated with the first stage without increasing the size of the experiment has a great impact on cost.

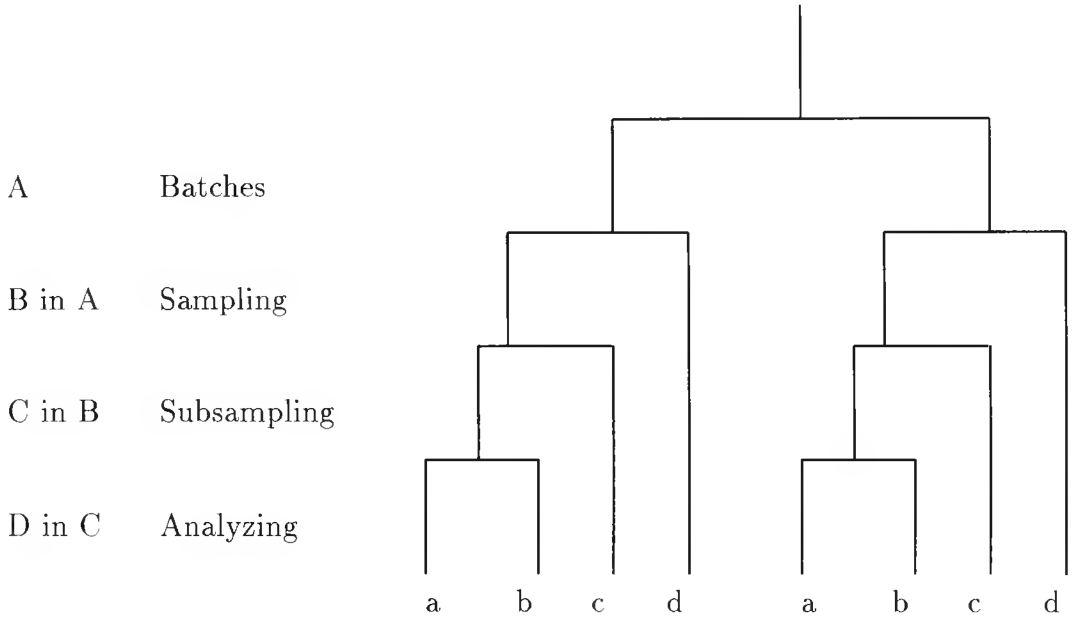


Figure 4.3: Staggered Nested Design.

In the Table 4.3 a comparative degrees of freedom breakdown for this design as compared to the classical is presented for forty observations.

Table 4.3: Comparative Degrees of Freedom for Design

Staggered		*Balanced*	
Source	DF	Source	DF
A	9	A	4
B	10	B	5
C	10	C	10
D	10	D	20
Total	39	Total	39

This problem and others are discussed in Davies [29] where comparative analysis of variance is presented with precise variance estimations for alternative designs.

As a first consequence there is no reason for pooling the variance components even when negative components ocurr. It can be thought of as a partially replicated nested design with about the same degree of freedom for each factor. If we consider an experiment with factors A, B, C and D, the layout is like this: each portion, batch, time or space (A) of bulk material is sampled (B) on two occasions with two subsampling (C) each time with two tests (D) one time and one (D) the other. Each day three samples will be run. Two analyses of sample 1 and one of the others.

The Table 4.4 and Table 4.5 that follows are based upon the work of Ganguli, see Anderson [1]. Their illustrate the expectations of mean squares, and methods of obtaining the sums of squares for three and four factor experiments.

As opposed to balanced designs the mean squares cannot be compared directly by F—tests since the coefficients for a given variance component are not the same in both equations. Because of incomplete replications, the expected mean squares have noninteger coefficients. As we are interested in estimating variance components, there is no objection in using them.

Table 4.4: Expectation of Mean Squares and Sum of Squares by Factor

Sources	*SS*	*DF*	*Expectations of MS*
Sampling	(5)-CF	a-1	$\sigma_c^2 + 12/3\sigma_b^2 + 3\sigma_a^2$
Subsampling	(3)+(4)-(5)	a	$\sigma_c^2 + 11/3\sigma_b^2$
Analysing	(1)+(2)-(3)	a	σ_c^2
Total (T)	(1)+(2)+(4)-CF	3a-1	
Portions	(7)-CF	a-1	$\sigma_d^2 + 11/2\sigma_c^2 + 21/2\sigma_b^2 + 4\sigma_a^2$
Sampling	(5)+(6)-(7)	a	$\sigma_d^2 + 11/6\sigma_c^2 + 1\ 1/2\sigma_b^2$
Subsampling	(3)+(4)-(5)	a	$\sigma_d^2 + 11/3\sigma_c^2$
Analyzing	(1)+(2)-(3)	a	σ_d^2
Total (T)	(1)+(2)+(4)+(6)-CF	4a-1	

Table 4.5: Totals needed to Sums of Squares

$(1) = \sum a^2$	$(5) = \frac{\sum(a+b+c)^2}{3}$	$(9) = \frac{\sum(a+b+c+d+e)^2}{5}$
$(2) = \sum b^2$	$(6) = \sum d^2$	$(10) = \sum f^2$
$(3) = \frac{\sum(a+b)^2}{2}$	$(7) = \frac{\sum(a+b+c+d)^2}{4}$	$(11) = \frac{\sum(a+b+c+d+e+f)^2}{6}$
$(4) = \sum c^2$	$(8) = \sum e^2$	$\text{CF} = \frac{(GrandTotal)^2}{No.Tests}$

The algorithm for getting coefficients of variance components it is quite similar to the EMS rules for fixed, random and mixed models by Hicks [52]. They depend on the number of factors. We will present the calculation for a five factors, a, b, c, d and e staggered nested experiment, similar to the one of Figure 4.3, with a levels for the factor A.

1) Set up a design and the table below:

Factors Chosen	Total Units	Analyses per Unit	Tree Tests				
Total	1	n	5a(1)				
A	a	n_i	5(a)				
B	2a	n_{ij}	4(a)				1(a)
C	3a	n_{ijk}	3(a)			1(a)	1(a)
D	4a	n_{ijkl}	2(a)		1(a)	1(a)	1(a)
E	5a	1	1(a)	1(a)	1(a)	1(a)	1(a)

2) Fit the design according to the Table, assuming a total of n split into $4a$ units. Therefore, for the factor A with $a-1$ degrees of freedom and all the others with a degrees, the coefficients of variance components for σ_ϵ^2 is 1.

Sources	*DF*	σ_e^2	σ_d^2	σ_c^2	σ_b^2	σ_a^2
A	a-1	1	$\sum_i\sum_j\sum_k\sum_l n_{ijkl}^2 f_i$	$\sum_i\sum_j\sum_k n_{ijk}^2 f_i$	$\sum_i\sum_j n_{ij}^2 f_i$	$\sum_i n_i^2 f_i$
B in A	a	1	$\sum_i\sum_j\sum_k\sum_l n_{ijkl}^2 f_{ij}$	$\sum_i\sum_j\sum_k n_{ijk}^2 f_{ij}$	$\sum_i\sum_j n_{ij}^2 f_{ij}$	
C in B	a	1	$\sum_i\sum_j\sum_k\sum_l n_{ijkl}^2 f_{ijk}$	$\sum_i\sum_j\sum_k n_{ijk}^2 f_{ijk}$		
D in C	a	1	$\sum_i\sum_j\sum_k\sum_l n_{ijkl}^2 f_{ijkl}$			
E in D	a	1				

3) Calculate each coefficient for the factor B :

$$\sigma_b^2 = \left\{ \sum_i\sum_j n_{ij}^2 \times f_i \sum_i\sum_j n_{ij}^2 \times f_{ij} \right.$$

Finally the coefficient for the last factor A, $\sum_i n_i^2 \times f_i$.

The constant values remaining unknown are $f's$.

$f_i = \frac{(1/n_i - 1/n)}{a-1}$ related to the factor A,
$f_{ij} = \frac{(1/n_{ij} - 1/n_i)}{a}$ related to the factor B in A,
$f_{ijk} = \frac{(1/n_{ijk} - 1/n_{ij})}{a}$ related to the factor C in B.
$f_{ijkl} = \frac{(1/n_{ijkl} - 1/n_{ijk})}{a}$ related to the factor D in C.

4.5 Staggered Nested-factorial Design

There are some constrains in industry that regular designs cannot meet. This turns out to be the case when some factors are crossed, some factors are nested but, different from the model of Hicks [52], the repeated nesting has not necessarily equal number in the subclasses.

An example, related to our theme is the case when A is sampling system using manual sampler and B represents sampling using automatical sampler. Both are crossed and having two factors related: subsampling nested in both A and B, and analyzing nested to subsampling.

A Balanced Nested Factorial Design is presented in Figure 4.4, and the equation is:

$$y_{ijkl} = \mu + A_i + B_j + \Lambda_{ij} + C_{k(ij)} + D_{l(ijk)} + \epsilon_{m(ijkl)}$$

The best way to work out this and any other model of the kind, is by using Bainbridge expressions [5] considering firstly the interaction [Λ] instead of A and B. This transforms the nested factorial into a nested design. To the expectations of the Table 4.4 we call the sample data r_{ij}, s_{ij}, t_{ij} and u_{ij}. See Figure 4.4.

From the model it is possible to construct the Table 4.6:

S	*DF*	*Sum of Square*
Λ	ab-1	$1/4\sum_i\sum_j(r_{ij}+s_{ij}+t_{ij}+u_{ij})^2\text{-}1/4ab[\sum_i\sum_j(r_{ij}+s_{ij}+t_{ij}+u_{ij}]^2]$
C	ab	$1/3\sum_i\sum_j(r_{ij}+s_{ij}+t_{ij})^2+\sum_i\sum_j u_{ij}^2\text{-}1/4\sum_i\sum_j(r_{ij}+s_{ij}+t_{ij}+u_{ij})^2$
D	ab	$1/2\sum_i\sum_j(r_{ij}+s_{ij})^2+\sum_i\sum_j t_{ij}^2\text{-}1/3\sum_i\sum_j(r_{ij}+s_{ij}$
E	ab	$\sum_i\sum_j r_{ij}^2+\sum_i\sum_j s_{ij}^2\text{-}1/2\sum_i\sum_j(r_{ij}+s_{ij})^2$

Table 4.6: General Analysis of Variance for Staggered Nested Experimental Design

where *EMS's* are computed below:

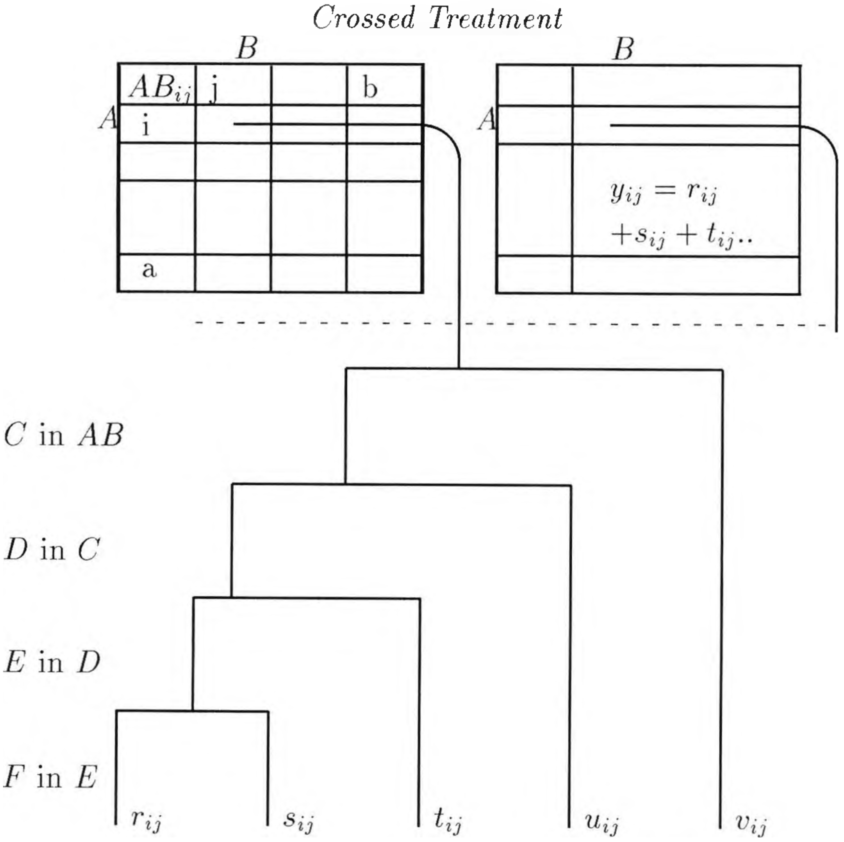


Figure 4.4: Balanced Nested Factorial Design.

Λ $\sigma_\epsilon^2+3/2\sigma_d^2+5/2\sigma_c^2+4\sigma_\Lambda^2$
C $\sigma_\epsilon^2+ 7/6\sigma_d^2 + 3/2\sigma_c^2$
D $\sigma_\epsilon^2+ 4/3\sigma_d^2$
E σ_ϵ^2

Finally we have to substitute the values of σ_Λ^2 by the Expected Mean Squares for Two-factor Factorial Designs.

$$EMS_\Lambda = \underbrace{\sigma_\epsilon^2 + 3/2\sigma_d^2 + 5/2\sigma_c^2}_{\sigma_{residual}^2} + 4\sigma_\Lambda^2$$

Considering A and B random and $n = 4$ replications the last terms will be:

$$EMS_A = \sigma_{residual}^2 + 4\sigma_{AB}^2 + 4b\sigma_A^2$$
$$EMS_B = \sigma_{residual}^2 + 4\sigma_{AB}^2 + 4a\sigma_B^2$$
$$EMS_{AB} = \sigma_{residual}^2 + 4\sigma_{AB}^2$$

4.6 Worked Example 1

The following example will illustrate the *NED* procedure for a balanced design of Section 4.3.

The experiment was conducted in Fabrica da Estrela, a branch of IMBEL, that produces Charcoal out of wood and consisted of sampling randomically four portions from the process (furnaces also chosen at random) and sending them, to the *Sampling Test Station.* Two subsamples were then taken randomly out of eight from each portion and sent to the laboratory ready to be analyzed. The analysts, equipment, days and time were always assigned at random.

The moisture content was measured by using Karl Fisher's method during a one-week experiment, and the results are recorded in the Table 4.7.

The process is defined at $x \pm 5\sigma$ as a control limit and the *representative* parameter chosen is *moisture content.*

The following relative capability indices for centered mean is required: $Cp = 1.66$ and defect rate .57PPM. Considering an expected change in process mean over a several manufacturing cycles equals to $\pm 1.5\sigma$, the process CP_k would be 1.66 and the defect rate would be 233PPM. This is to show the continuous concern with sampling and measurement systems in the company.

	Charcoal Moisture Content															
Sampling	*Portion1*				*Portion2*				*Portion3*				*Portion4*			
SSampling	*1*		*2*		*3*		*4*		*5*		*6*		*7*		*8*	
Analysis	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
	44	40	40	63	35	30	47	37	39	37	56	46	36	40	34	35
	48	38	53	50	38	31	49	36	41	44	53	46	42	39	34	32

Table 4.7: Charcoal: Data collected from Furnace 1.

There are a number of packages available for analyzing nested designs. Three are particularly important for balanced designs: *SAS*, *Statgraphics* and *SPSS*. The analysis of this experiment was carried out using $SPSS-PC$. The details of macro are given in *Appendix I*.

The output of the Analysis of Variance is summarized below:

Sources	*DF*	*SS*	*MS*	F^o	$F_{5\%\&1\%,dg1,dg2}$
Process & Sampling	3	659	219.7	5.10	2.95—4.57
Subsampling	4	575	143.8	2.99	3.84—7.01
— $SE_{j(i1)}$	1	162	162	10.8	4.49—8.53
— $SE_{j(i2)}$	1	153	153	10.2	4.49—8.53
— $SE_{j(i3)}$	1	199	199	13.3	4.49—8.53
— $SE_{j(i4)}$	1	61	61	4.1	4.49—8.53
Analyzing	8	390	48.8	3.2	2.59—3.89
Error (E)	16	240	15.0		
Total (T)	31	1865			

From this test we can see that although portions of material within lot were supposed to have no significant effect on the *moisture content* of Charcoal, in fact there is a big one both at 5% and 1% levels.

There is no interaction present as process—sampling and subsampling are nested, not crossed, but if we go down to subsampling rows, different effects take place. Subsampling errors are relatively low at the level of 5% and 1% and there are significant differences between subsamples within samples. It can be noted that what we took as subsampling effect (1*df*) and interaction effect (3*df*) is really subsampling—within—sampling effect (4*df*).

Considering our coding (×100) we have the following system of variance equations:

$$\begin{aligned}
2.20 &= \sigma_\epsilon^2 + 2\sigma_{AE}^2 + 4\sigma_{SE}^2 + 8\sigma_{PE}^2 \\
1.44 &= \sigma_\epsilon^2 + 2\sigma_{AE}^2 + 4\sigma_{SE}^2 \\
0.49 &= \sigma_\epsilon^2 + 2\sigma_{AE}^2 \\
0.15 &= \sigma_\epsilon^2
\end{aligned}$$

From our example the estimated variances were:

$$\begin{aligned}
s_\epsilon^2 &= 0.15 \\
s_{AE}^2 &= 0.17 \\
s_{SE}^2 &= 0.23 \\
s_{PE}^2 &= 0.10
\end{aligned}$$

The total variance is that associated with individual moisture content measurements of Charcoal

$$s_{(TE)}^2 = 0.65$$

We can observe from these values that the process—sampling error for Charcoal account for only 15% of the total variation, while sub-samples and analyses account for 36% and 26% respectively. That means 50% of deviation is due to sampling problems. On the other hand analytical error equals 26%.

These results might suggest some procedures:

- thorough adjustment and calibration of the measurement system;
- review of sampling techniques and equipment;
- correct subsampling preparation in the Sampling Test Station.

The next step consisted of performing a second nested design taking into consideration the correct sampling and sub-sampling procedures and using calibrated equipment.

We proved the effective decline in these systems by comparing past data and past performances in control charts regarding assignable causes.

We now discuss uncertainty and cost of three systems. They follow the equation:

$$V_{A,B,C} = \frac{\sigma^2_{AE}}{bcn} + \frac{\sigma^2_{SE}}{cn} + \frac{\sigma^2_{PE}}{n}$$

The renewed experiment yielded the following estimates: $\sigma^2_{AE} = 0.25$, $\sigma^2_{PE} = 0.12$ and $\sigma^2_{SE} = 0.11$. Therefore the variance of estimate of batch mean is

$$V_{A,B,C} = \frac{0.25}{8} + \frac{0.12}{4} + \frac{0.11}{2} = 0.12$$

Considering these limits as the minimum at current circumstances alternative sampling, sub-sampling and testing schemes may be reached in order to minimize both variance and cost. Assuming that it costs £2.00 for taking a sample, £4.00 to prepare the subsampling and £8.00 to make an analytical test. The Table 4.8 produces these results.

Samples n	*Subsampling* *c for cn*	*Replications* *b for bcn*	*Variance of* *batch mean*	*Cost(£) of* *procedure*
1	1	2	.36	28.
1	2	4	.20	52.
1	4	8	.15	84.
2	1	2	.18	56.
2	2	4	.10	128.
2	4	8	.07	104.
4	1	2	.09	96.
4	2	4	.06	122.
4	4	8	.04	144.

Table 4.8: Minimization of Variance and Cost.

In our case, due to the existing variability of the analytical error in relation to sampling and subsampling error, the variance of the estimate of batch mean for the process tend to reduce considerably as we increase the number of samples at a little extra expense and very little is gained by replicate testing.

4.7 Worked Example 2

The following example will illustrate the *NED* procedure for a Staggered Nested Design of Section 4.4. The data was taken from page 17 of Bainbridge [5]. We chose the first week of his six week experiment. The results agree with the variance component estimates given by Bainbridge. The output listing is presented in Table 4.9.

$\sum(Entries)^2$	*Values*
a	503.80
b	459.90
a+b	1916.70
c	375.30
a+b+c	3884.30
d	600.54
a+b+c+d	7492.70

Table 4.9: Comparative results of Summations.

The variance estimates are in Table 4.10.

Factors	*Degrees*	*MS*	*Variance*
Days	6	8.18	0.51
Machines	7	3.16	0.00
Long Term	7	5.54	3.58
Short Term	7	0.77	0.76

Table 4.10: Estimates of Variance Components.

A Fortran program for variance component estimates is included in Appendix 2.

Chapter 5

Designing a Bulk Sampling Test Station

The sampling theory presented so far accounts for continuous selection errors[CE] particularly in zero and one-dimensions. All the data are supposed to be free from Materialization [ME] and Preparation Errors [PE]. In fact, the most essential prerequisite for effective quality control in chemical engineering resides on a sampling system where correctness and representativeness exist. See Chapter 2, Section 2.1 and 2.3.

To a large extend the design of sampling systems for particulate materials has been undertaken in a somewhat empirical manner although some advances in the technology of equipment have been available for some time. Even with rules of design for constructing or buying sampling equipment, bias may occur and ruin any effort to minimize CE's. The fate of poorly designed systems is often its complete removal and a return to the imprecise manual sampling regimes of a zero-dimensional single increment.

In this chapter, basic considerations are presented in the light of so-called *Unit Operations* required for a sound design and choice of equipment for guarding against estimation bias. The system is designed for mechanical sampling because the manual sampling is always unaccurated and lacks reproducibility. A program for checking bias can be easily implemented in semi-automated sampling plants. To keep down the costs of running and maintaining the system it is designed to be located in a same place and called *Sampling Test Station.*

5.1 Introduction

Determination of quality characteristics in consignments of chemicals involves a sequence of typical operations such as sampling, subsampling, sample preparation and analysis. All these operation are error-generating as has been shown in previous chapters with errors caused by the intrinsic properties of materials and their influences on bias and variability. For simplicity we have assumed that data were collected in accordance to the theory of materialization presented in Chapter 2, Section 2.1 and respecting the extended and fragmental definitions of the increment presented in Chapter 2, Section 2.2.

Delimitation is a boundary that limits the extended increment. As we tend to match extended with fragmental functions the correctness of a given sampling system is a primary structural property. A chemical industry that makes the pretence of effective Quality Control must have some basic types of sampling equipments.

Materialization errors include preparation errors, which is a nonselective process, and delimitation errors, which is a selective process. There are interdependent operations of reducing, sampling, screening, comminuting, drying, mixing etc, that yield *sample data*.

The type of material to be processed, the amount of transportation and the level of quality required define the system. If the system is supposed to yield only random samples only a few items of equipment are required. Unfortunately, it is hardly ever true within modern chemical plants that require continuous quality control, particularly when preparing primary increments.

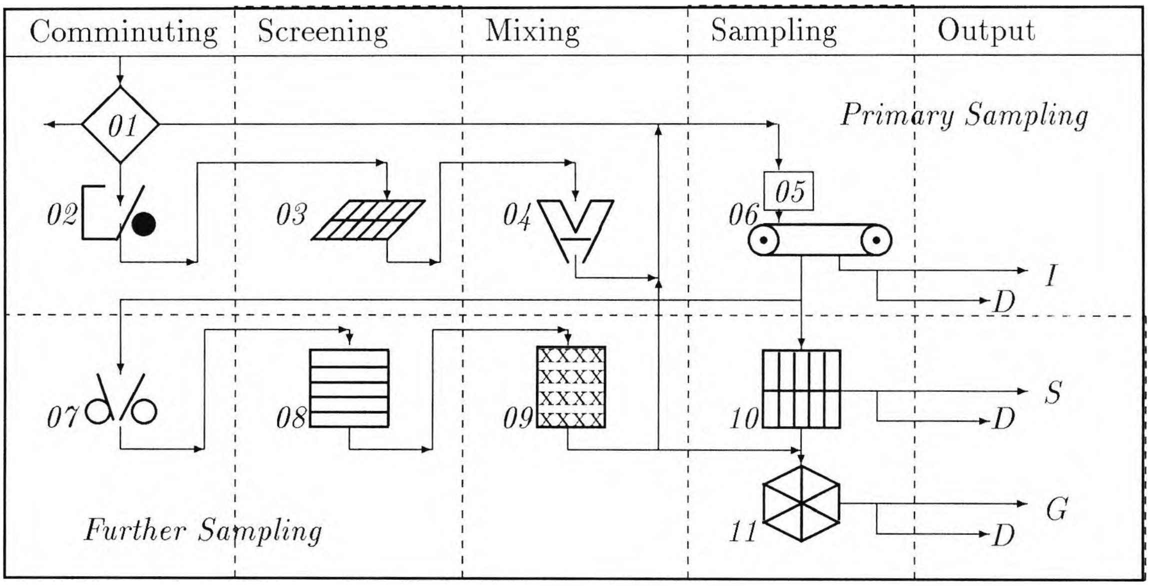
In a well-balanced sampling regime the variance of preparation should be of the same order of magnitude of the variance of sampling. In this case obtainning data free from estimation bias a minimum number of mechanical equipment is mandatory: a comminuter, a mixer, and a belt Conveyor with cutter, at least.

Manual sampling definitely fails to generate a sound set of data. By comparison to mechanical sampling it is costly, hazardous, tedious and statistically unreliable, particularly in plants that are continuously buying and selling large quantities of bulk materials.

An other great advantage of mechanical system is its flexibility in collecting samples in any regime: stratified systematic sampling on a constant time basis, systematic sampling on a constant mass basis or on a random regime.

5.2 Sampling System Design

A proposed sampling system that prepares primary, secondary and gross samples according to the procedures laid down in Chapters 2, 3 and 4 is shown in Figure 5.1.



LEGEND:
[*I*] = Increments
[*D*] = Discards
[*S*] = Subsamples
[*G*] = Gross Samples
[01] = Mechanical Feeder
[02] = Hammer Crusher
[03] = Bar-type Grizzlies
[04] = Vee Mixer
[05] = Screw Feeder
[06] = Moving Belt
[07] = Roll Mill
[08] = Vibrating Screen
[09] = Cube Mixer
[10] = Jones Riffle
[11] = Rotary Cascade

Figure 5.1: Flow sheet of the Model for Bulk Sampling Test Station.

Five underlying Unit Operations subsystems are proposed:

1. Sampling Subsystem;
2. Mixing Subsystem;
3. Comminuting Subsystem;
4. Screening Subsystem;
5. Sampling Accessories.

The choice of subsystem and/or equipment depends on the stage and the objectives. Inderdependent operations mean that every piece of equipment contributes to the reduction of variability of parameters not related to the intrinsic properties of material. The relationship among sources of error, equipment and results to be achieved are presented in Table 5.1. Back references to previous chapters are given in the text.

Sources of Errors	*Notation*	*Equipment/Legend*
Constitution Het.	CH_L	Comminuting System
Particle Size	d	[02] [07]
Shape Factor	f	[02] [07] [08]
Liberation	l	[02] [07]
Mineral Factor	ϖ	—
Granul. Factor	g	[02] [07] [08]
Sampling Constant	C	[02] [07] [08]
Distribution Het.	DH_L	Mixing Subsystem
Grouping Factor	ζ	[02] [07] [04] [09]
Segreg. Factor	ξ	[04] [09]
Delimit. Error	DE	[02] [05] [06] [07]
Extration Error	EE	[06] Acces.Tool
Preparation Error	PE	—
Sampling Size	N_Q	Sampling Subsystem
Increment Weight	w	[06] [10] [11]
Mass Concentr.	κ_x	[02] [07] [08]
Continuous Het.	CE	Sampling Subsystem
Critical Mass	η	[06] [10] [11]
Weight Function	ε	[01] [06]

Table 5.1: Relationship among Sources of Error, Equipment and Results.

5.2.1 Sampling Subsystem Design

The selection of sampling machines is described below. Within the scope of the application — pilot experiments — three underlying pieces of equipment are proposed:

1. Belt Conveyor;
2. Jones Rifler;
3. Rotary Cascade.

- **Belt Conveyor**:

  The selection of the conveyor belt is the most important design item of the station not only because it constitutes a large portion of the initial cost but also because it is responsible for delivering primary increments to the other sampling equipment. Its malfunctioning represents a summation of the long-range variability not due to the material itself but due to the errors. See Chapter 2, Section 2.2, 2.3, 2.7 and 2.8, Chapter 3, Section 3.1 and 3.6 and Chapter 4, Section 4.1.

  Selection and/or design requires careful definition of the belt itself — belt width, belt speed — and of other mechanical parameters such as, pulleys, shafts, type of sampler (on-the-belt or falling stream), sampler speed, sampler width etc.

  Our proposed Conveyor Belt is for a falling stream sampler similar to the one in Figure 5.2 where a represents the belt width and $b \times c$ the sampler aperture.

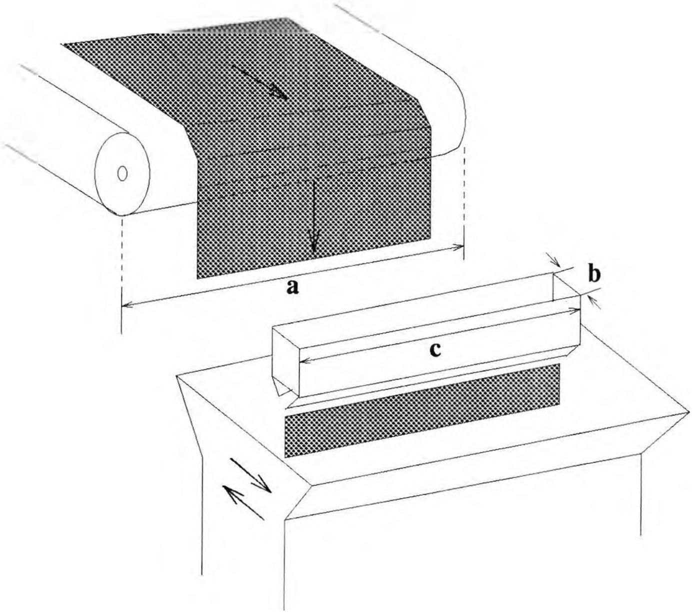


Figure 5.2: Conveyor Belt with Falling-stream Sampler: through-stream, cutter-bucket Type.

Some theoretical consideration should first be addressed. For a correct delimitation theory, the sampler should satisfy two conditions regarding the extended increment:

1. the slice of material should be extracted in constant thickness;
2. the slice should be representative of the entire stream;

This operation must be performed on the whole stream part of the time. Taking increments on part of the stream at any time generate incorrect delimitation, therefore it is incapable of performing probabilistic sampling. The Figure 5.3 shows some good and bad increments. B, C, $A4$ and $A5$ generate visible sampling mistakes while $A1$, $A2$ and $A3$ perform correct delimitation. All three design have parallel cuts across the stream.

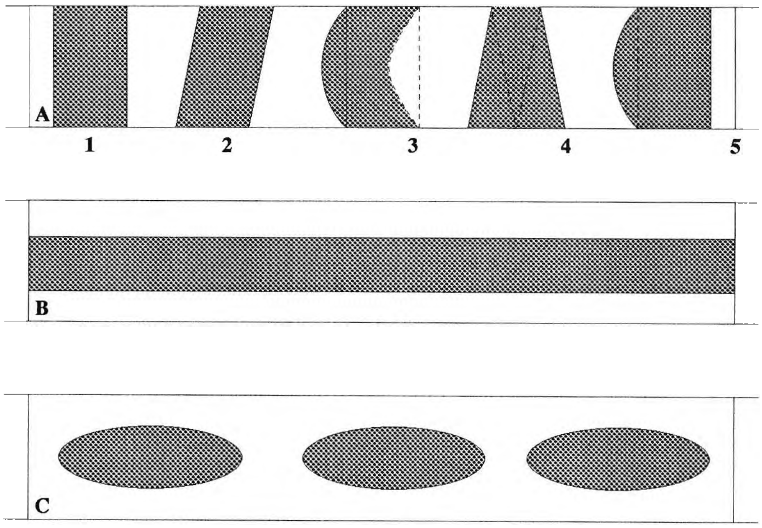


Figure 5.3: Taking increments: Correct Delimitation only with parallel cuts across the stream.

The extraction error introduces the largest biases encountered in this sort of equipment. In the Chapter 2, Section 2.2, we have seen that the fragments having their center of gravity inside the extended increment belonging to the model fragmental increment. The actual fragmental increment matches the correct fragmental increment only in two situations:

1) particles are punctual representatives; or

2) rebounding rule is respected.

The first hypothesis is cost-prohibited. The second requires further theoretical study.

For its better understanding let us define the following notations:

$v_{(c)}$ horizontal sampler speed;

$v_{(x)}$ horizontal velocity vector;

$v_{(y)}$ vertical velocity vector;

r radio of the edges of the sampler;

φ vertical angle of the fragment when colliding;

Figure 5.4 illustrates the position of a spherical fragment from the top size range moving towards the sampler opening at the moment of impact.

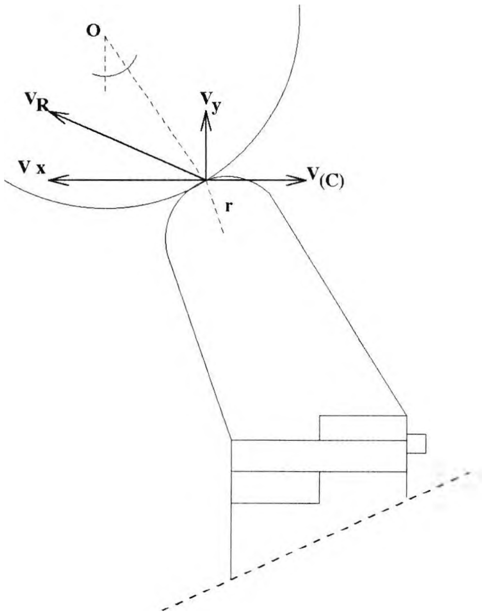


Figure 5.4: Collision of Particle with cutter edge.

If the fragment from the top size range collides with the cutter edges traveling against its direction, it bounces from one edge and may fall outside or into the sampler slot. Such probability depends on shape of the sampler cutter edges, the sampler speed $[v_c]$ and the time interval $[\Delta t]$ the fragment travel above the cutter edges.

The probability of falling inside the slot is also function of the distance between the leading edge and trailing edge. The chance of the fragment belonging to the sample is represented by a stochastic variable. It is function of several parameters: momentum of the fragment, collision angle, sharpness of the edge and number of fragments colliding at the same time. Some parameters suppress other ones in such way that when the fragment bounces backwards, the sampler width $[w]$ becomes reduced to $w - v_c\Delta t$. On the contrary, when the fragment bounces forwards: $w + v_c\Delta t$. Therefore the chances of a fragment to be part of a sample follows this relationship:

$$\frac{w + v_c\Delta t}{w - v_c\Delta t} = 1 + \frac{2v_c\Delta t}{w - v_c\Delta t} \qquad (5.1)$$

This situation is depicted in Figure 5.5.

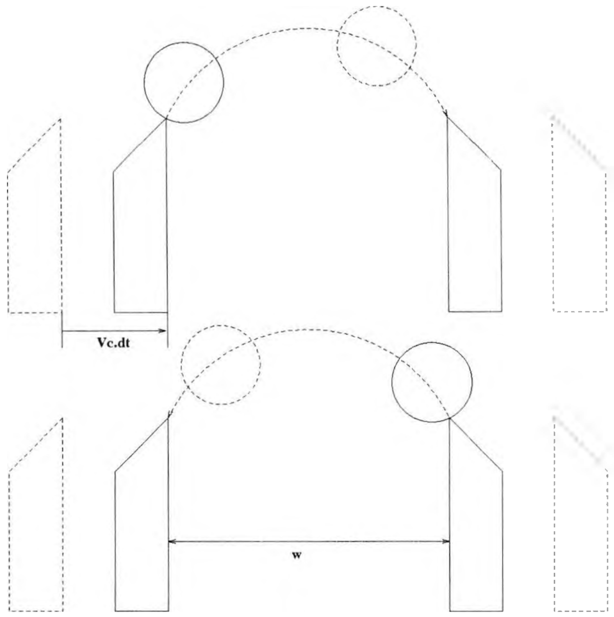


Figure 5.5: Collision of Fragments with Opposite Edges of the Cutter.

From the Equation 5.1, Merks [76] presents some interesting conclusions based on top size range definition of fragment:

1. It increases as $[v_c \Delta t \rightarrow w]$. If the probability of fragment bounce upwards is 5% and since no more than 5% of all fragments are part of top size range (definition) the real probability would be 0.25%. Therefore, there seems to be very low chance for bias to occur as the shape of the cutter edges are designed sharply. Some bad and good designs are shown in Figure 5.6. If edges are thick for mechanical reasons, they should be perfectly symmetrical. The last design in this figure, shows an angle between 45^o and 90^o. This design is likely to introduce unacceptable extraction errors.
2. The vertical angle $[\varphi]$ of the fragment when colliding with sampler and the speed that the material leaves the belt play an important role in defining characteristics of sampler. However bias may occur if the probability of the Equation 5.1 exceeds two-to-one. This is the case when the fragment bounces forwards from the trailing edge and falls into the inner walls of the cutter.
3. The vertical velocity vector of bouncing particles is greatly reduced due to collisions with other particles in free falling. Therefore, the chances of particles, bouncing from opposite edges, fall inside or outside the slot are greatly reduced.

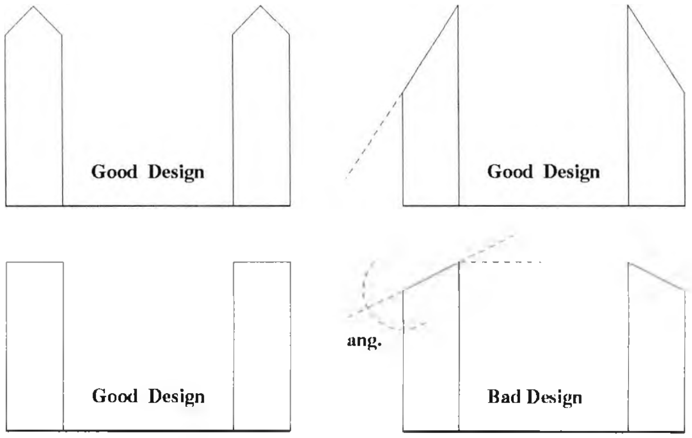


Figure 5.6: Correct and incorrect Designs for Cutter Edges.

The critical parameters for conveyor belt samplers are clearly defined in Gy's experiment [43]. The experiment establishes a sound scientific basis between the diameter of the coarsest particle [d] in the bulk material, the critical cutter width [w] and the critical cutter speed [v_C]. The schematic layout of the experiment is depicted in Figure 5.7.

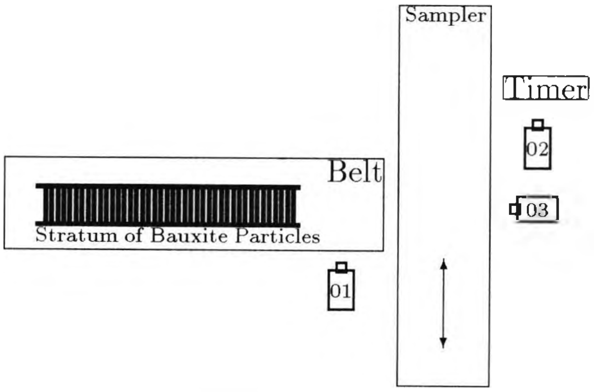


Figure 5.7: Schematic Layout of the Experiment for Critical Design Parameters.

The sampling unit consisted of narrow particle size fractions of hard bauxite. One series included fragments ranging from *40 mm* to *50 mm*, in the other *80 mm* to *100 mm*. Three cameras were required: 01 for recording the belt, 02 for recording the hand of a 1/100 chronometer and 03 for recording the cutter.

For each test the following variables were measured:

$N_{(F)}$ = number of calibrated fragments in the test;

B = length of the belt with $N_{(F)}$;

$v_{(C)}$ = cutter sampler velocity assumed to be uniform;

$v_{(B)}$ = belt speed assumed to be uniform;

D = belt loading rate assumed to be uniform — number of fragments per unit of length of belt — $[D = N_F/B]$;

w = width of the conveyor belt in m;

T = Time, in seconds, during which any element of the stream is cut , $T = w/v_C$.

R = rate of flow of the stream, in fragments per second.

$$R = \frac{v_B}{D} = \frac{v_B \times N_F}{B}$$

N_M = number of fragments theoretically expected if the probability for identical fragments that bounces from opposite edges of sampler were equal to

$$N_M = RT = \frac{v_B N_L w}{v_C B}$$

Under ideal conditions the actual number of fragments $[N_A]$ that is collected with the sampling device must be equal to the theoretical number of particles $[N_M]$. Their ratio should be close to the unity for the parameters considered.

The Table 5.2 produces the sampler efficiency when the size $[d]$ of the largest fragments is one-third or less the minimum cutter width $[w]$. The values of particle diameters were $100mm$ for this test.

The following rules must be borne in mind when designing any sampling device traveling against the stream:

1. The minimum width of the primary sampler must follow the specifications shown in Table 5.3. That is known as rule of extraction correctness.
2. The ratio between the sampler slot and a particle from the top size range must exceed, at least three times, the top by a considerable margin. In this case the speed of the sampler can be increased by a factor that is calculated with the following formula:

   $$v_S^* = [1 + (w/w^*)]0.3$$

   in which v_S^* is the critical speed of sampler in mps, w is the actual width of sampler in m and w^* is the critical width of sampler.

Width-w	*w/d*	*Speed-mps*	N_M	N_A	N_A/N_M
200	2.0	0.24	32.6	29.0	0.89
250	2.5	0.24	40.9	37.5	0.92
300	3.0	0.37	29.6	30.0	1.01
350	3.5	0.37	34.4	34.5	1.00
300	3.0	0.47	23.7	23.5	0.99
300	3.0	0.60	18.4	18.7	1.02
300	3.0	0.78	14.8	13.5	0.91
300	3.0	1.09	10.5	9.0	0.85

Table 5.2: Sampling Experiment showing the relationship among Particle Size, Sampler Width and Sampler Speed.

Coarse Diameter	*Cutter Width*
For d $\geq$ 3mm	w $\geq$ 3d
For d < 3mm	w $\geq$ 10mm

Table 5.3: Rules for Extraction Correctness.

3. The optimum solution for sampler speed is $v_C = 0.60mps$. The Table 5.2 confirm such optimization.
4. The minimum amount of material [δm] to be sampled in each primary increment will depend on the characteristics of both sampler and moving belt. An approximate mass may be computed when having the handling capacity [M/h] in *mtph*, width [w] in m and speed of sampler [v_S] in *mps*:

$$\delta m = \frac{M/h \times w}{3.6 \times v_S}$$

Characteristics of the Conveyor Belt *Belt Width*

The belts in use are generally made of synthetic fibers which gives them extraordinary resistant to corrosion and abrasion, particularly when handling active chemicals. Their dimension are standardized ranging from 18 to 96 inches with intervals of 6*in* in between. For pilot experiments with material in bulk, 24*in* width fits quite well if any combination of prevailing lumps and fines does not load the lumps too close to the edges of the conveyor belt.

The width of belt is governed by size of lumps to be handled. They determine all specifications. There is an empirical relationship between lump size and minimum narrow of belt.

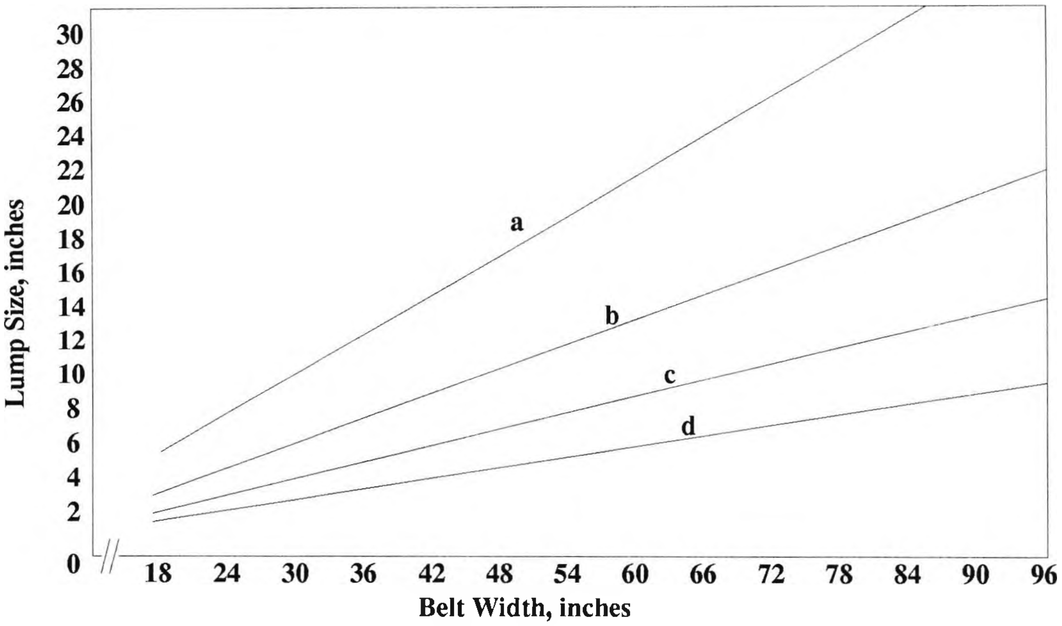


Figure 5.8: Belt width required for a given lump size.

The Figure 5.8 shows the required width for specific lumps in inches according to BRT Belting LTD [7]. Fines no greater than 1/10 maximum lump size. In case *a*, for a 20° surcharge with 10% lumps and 90% fines, the recommended maximum lump size is 1/3 the belt width [$b/3$]. The cases *b*, *c* and *d* represent respectively: all lumps for a 20° surcharge; 10% lumps, 90% fines with 30° surcharge; all lumps, 30° surcharge.

Belt Speeds

Determination of moving belt speeds are based on type of material to be conveyed. Powdery materials as largely used in chemical industries should be conveyed slowly through feeders to avoid segregation and dusting. Care must be taken both in loading and discharge points. Dusting particularly with dry and fines, causes losses of powder and endangers the environment. Fragile material and heavy, sharp-edged materials limit belt speeds. The first because of degradation, the latter because the sharp edges are likely to wear the belt itself. As far as wearing of belt is concerned the loading should be preferably done in the same direction of the belt travel. The Table 5.4 presents some recommendations for maximum speeds for conveyor belts based on *CEMA* [19].

As the choice for pilot plant should embrace many types of material, we propose the one for coal and soft ores with variable speeds.

Conveyor Belt Loading

Intermittent or regular feeding of material to the belt will result in alternate

Type of Material being Conveyed	*Belt Speed km/h*	*Belt Width cm*
Grain and other free- flowing non-abrasives	9.2 12.8	45 60—76
Coal, soft ores chrushed stones	7.3 10.4	45 60—91
Non-abrasive Materials discharging by plows	3.6 —	any width any width
Feeder, flat troughed non-abr. from hoppers	1.0 2.0	any width any width

Table 5.4: Maximum speeds of Conveyor Belts and Belt Width.

empty and overload portions. Such condition usually causes a loss of capacity and very likely spillage of material over the edges of the belt along the overload portions. The situation ruins any study on variability of continuous flow. Steady feeding must be provided and loading bias checked now and then, particularly when loading from hoppers, bags or bins. *Feeders* in this respect are very useful. For fine materials, smaller than 10mm, a Screw Feeder placed above the conveyor belt and below the loading bin to regulate the flow continuity is mandatory. See Figure 5.1. It is syncronized through sampler and belt speed . The latter should always be regulable from 0.3 to 0.6 m/s.

In the condition of the design, the conveyor belt should be horizontally installed with low tangential velocity. To obtain this optimum condition the fundamental force-velocity relationship should be recalled:

$$F_c = \frac{mv_B^2}{r} = \frac{Wv_B^2}{gr}$$

where F_c is the centrifugal force, v_B^2 the belt or tangential velocity, g the gravitational force, m, mass, W, gravity weight force, r, radial distance.

When the belt conveyor is horizontal to the discharge pulley, two conditions should be addressed (see Figure 5.9):

1. If the centrifugal force is equal to or greater than gravity weight force of the material, that means that the tangential speed is sufficiently high, the material leaves the belt in a vector tangent to the pulley. See Figure 5.9. In this case $v_B^2 \geq gr$.

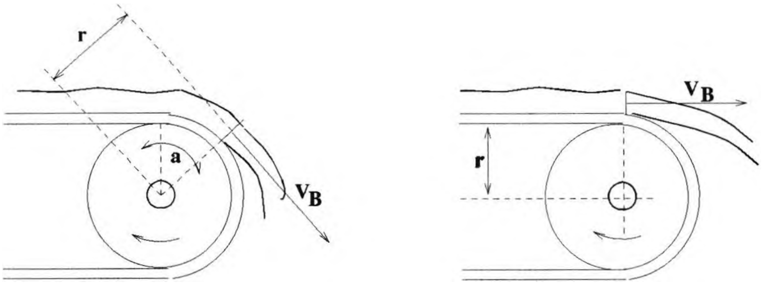


Figure 5.9: Trajectory of Material when leaving the Conveyor Belt with high and low tangential speed, respectively.

Particle Size (mm)	*Chute Width* (mm)
13—20	50
10—13	30
5—10	20*
2.4—5	10
0.0—2.4	6

Table 5.5: Minimum Chute Dimensions for Jones Riffle Divider

2. If the centrifugal force is less than the gravity weight force of the material, that means that the tangential speed is not high enough for the material to leave the belt, $v_B^2 < gr$, then the material follow the pulley in such way that $v_B^2 < gr \times cos\theta$ where θ is the angle between the vertical line to the center of pulley and the line that passes by the center of pulley and the point where the material begins its descendent trajectory.

- **Jones Riffle**:
  This typical sample divider is projected for particles beneath 5 *mm*. It is a non-mechanical sampler which splits the stream into a number of longitudinal elements, alternately either being passed into the sample or being rejected. It is the most simple and accurate non-automatic equipment. A great disadvantage is the reduction ratio: 1/2. Therefore many stages are required to get an unbiased sample. If the design is not precise any bias is multiplied. The chute dimensions depends on particle size. Smith [95] suggests chute widths according to the Table 5.5.

  Because this is not an automatic equipment its design requires some more care in manufacturing due to the interdependency in continuous flow. See also

Chapter 2, Section 2.3, 2.7 and 2.8. A more complete specification for both designs suggested is explained in Figure 5.10.

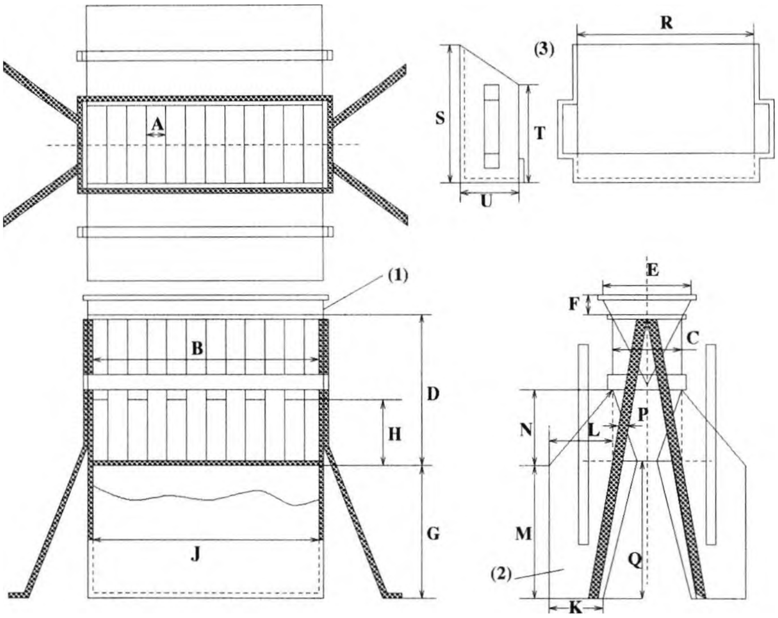


Figure 5.10: Top, Side and Front View for Jones Riffle Design.

Our proposed design is either number #20 or #10. The Table 5.6 produces their dimensions, in *mm*, according to *JIS* [62].

- **Rotary Cascade**:
  This is a laboratory unit designed for the speedy preparation of small representative samples of free flowing powders for laboratory measurements. It should have six datachable bins securely clipped with stationary hopper onto a cone mounted on a rotating turnable. Details of its design are presented in Figure 5.11. See also Chapter 2, Section 2.5 and 2.8.

Some requisites, in agreement with *BS 5309*, are vital: the particle size must be fully screened; the inner cone [*a*] must fit the feed cone; the orifice size controller [*b*] must have 5 times the diameter of the largest particle; the distributing cone [*c*] should be manufactured in stainless steel because of excessive wearing; the sample container must provide lip for pulling out samples. It must be suitable for hand and mechanical feeding. In the last case a sequence of equipment are required: crusher, chute and hopper.

What has got a great advantage over Jones Riffle Divider: the reduction rate is 1/6 and not 1/2. Usually there is no need for further subdividing before analysis takes place.

Sampler Code		*20*	*10*
N^o *of Rifles*		*16*	*16*
Body(1)	A	20±1	10±.5
	B	346	171
	C	105	55
	D	210	110
	E	135	75
	F	30	20
	G	210	110
	H	85	45
	J	360	184
	K	140	65
Receiver(2)	L	140	65
	M	210	110
	N	105	55
	P	35	20
	Q	210	110
Container(3)	R	346	171
	S	200	120
	T	135	70
	U	105	50

Table 5.6: Dimensions for Jones Riffle Divider proposed.

5.2.2 Mixing Subsystem Design

In order to homogenize powder materials industry resorts to manual and/or mechanical mixers. There are several basic mechanisms that range from small-scale random motion to large-scale random motion. They are governed by diffusion and convection principles respectively. That brings about several types of solids-mixing machines. Again the selection is a function of cost and data reliability.

We has shown in Chapter 2, Section 2.4 that mixing cannot affect directly constitution heterogeneity $[CH_L]$, the intrinsic properties of the particles. However, it affects the distribution heterogeneity $[DH_L]$ to a certain limits depending on the granulometric particle size. See also Chapter 2, Section 2.5 and 2.6. Theorically this random limit corresponds to the elimination of correlation between the physical properties — particle size, shape, surface characteristics, flowability, friability,

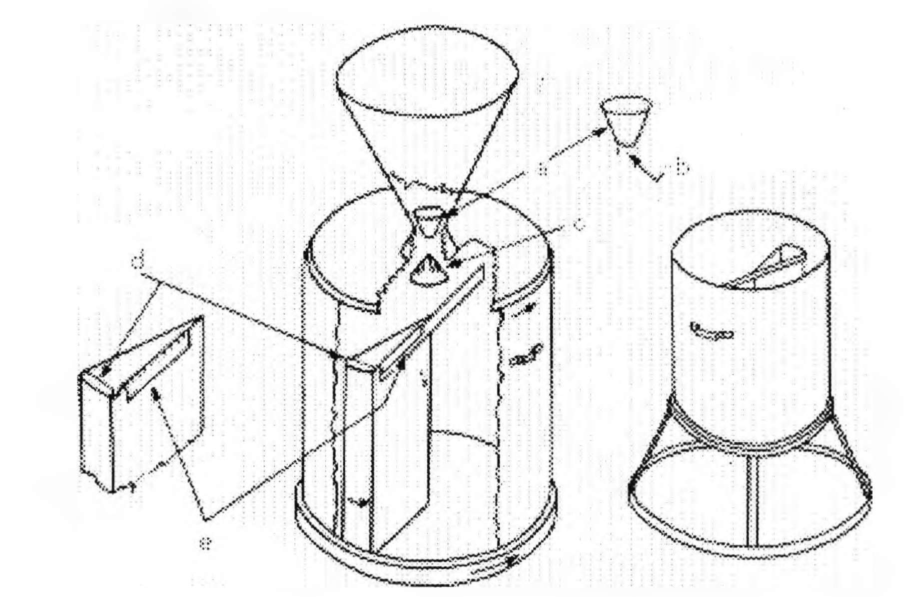


Figure 5.11: Rotary Sampler Divider with Hopper, Cone and Stand.

density, segregation — and its relative position within the bulk. Because of gravitational forces, this limit is never completely attainable. The aim of our *STS* is towards minimization of DH_L, therefore, we must include equipment whose major function is to give a thorough mixture to the particles.

Within the scope of our application — pilot experiments — two equipment are proposed:

1. Vee Mixer;
2. Cube Mixer.

- **Vee Mixer**
  It is an industrial solids-mixing machine that operates in batches. It is also called Twin Shell. The Figure 5.13 shows the sketch of a typical one where the dotted line represents agglomerate breaking device.

  Recent modification of this blender in which the two legs are of unequal length follows the Principle of Unequal Displacement. In the upright position, each blender leg holds an equal amount of material. As the blender rotates, the uneven legs force the material to shift continuously from one leg to the other. This axial-flow pattern and the radial mixing action produce a rapid, uniform blend. If the random tumbling takes place there will be a random mixture along the lines that disagree with both schemes of Figure 5.12 where distinguishable particles can be easily counted.

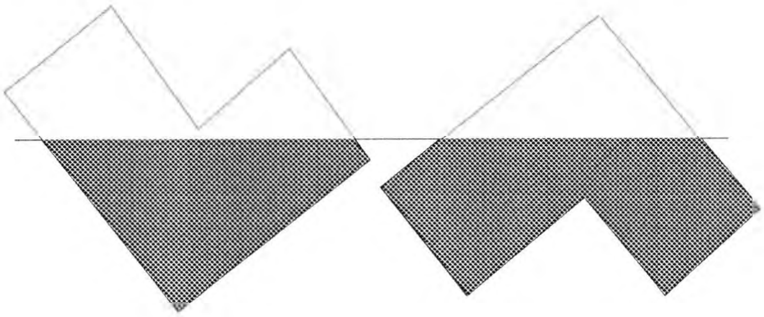


Figure 5.12: Principle of Unequal Displacement.

Where individual particles cannot be easily distinguishable and counts are not practical various type of analyses can be made on spot sample to determine mixing uniformity. In the Chapter 2, Section 2.9 some analitic methods for testing of randomness of particulate mixture are presented, apart from the modern instrumental analysis such as X-ray fluorescence, polarography, spectroscopy etc.

Evaluation of mixing power of the equipments may be made through a sampling procedure by using one of the sampling accessories in Subsection 5.2.5. The choice of the tool is important so as to remove samples without excessive disturbance of the batch. Usually the evaluation of performances depends on the preparation of material to avoid extreme differences in the properties refered before. Comminuters can strongly reduce these differences and avoid segregation.

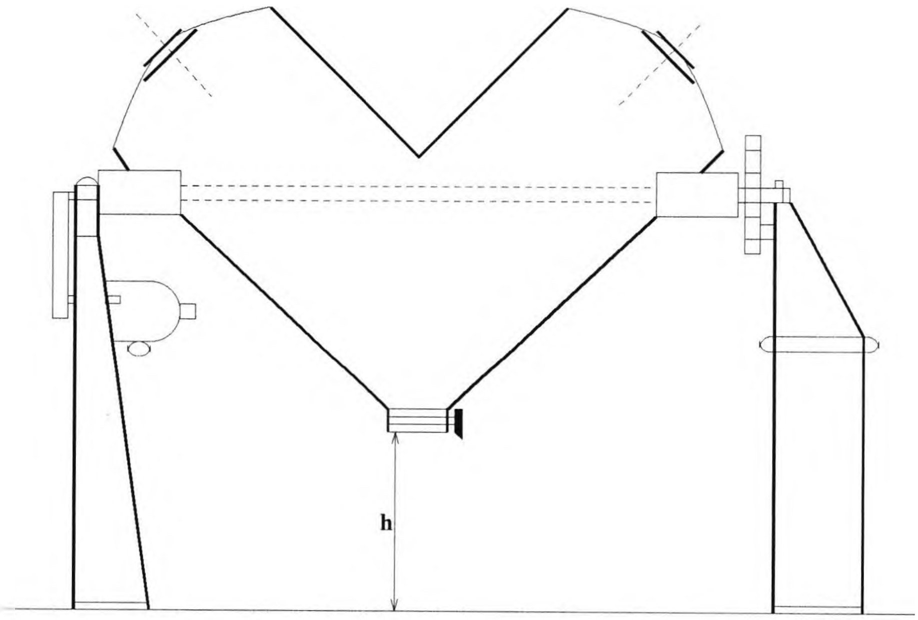


Figure 5.13: Industrial Solids-mixing Machine.

- **Cube Mixer**

  It is a simple metal cube that rotates around an axis through opposite corners diagonally. It should have room for about 10kg. That means 30cm side from corner to corner. It may be propelled manual or mechanically though manual types are more liable to bias in a long run.

  The design of a mixing system cannot be improvised, because there an optimum RPM for each machine and material. Too fast rotation introduces a centrifugal effect. Too slow mixing is incomplete. About 25RPM is suitable for tumbling. The time of residence also plays an important role. More than $15min$ it is not advisable. When using the same equipment for several different materials care must be taken in cleaning.

5.2.3 Screening Subsystem Design

To ensure that all particles have been crushed and/or pulverized to less than a certain size, to separate dissimilar materials, to classify particles when accepting consignment screening are mandatory.

Within the scope of our application — pilot experiments — two pieces of equipment are proposed:

1. Vibrating Sieve Shaker;
2. Vibrating Grizzly.

- **Vibrating Sieve Shaker**:

  It is quite difficult to indicate a Vibrating Sieve Shaker that fits a general purpose. For sampling use however, the best way is to define firstly the quantity of material (flow) to be placed in a sieve. Then concentrate on the design of sieve diameter, aperture and expected proportion of oversize.

  The larger the amount of material to pass through a screen the higher the cost of the equipment as a whole. It could be well reduced by loading a sieve lightly several times rather than treat the whole sample. That is true particularly when the sampling process is intermittent. The design in this respect can be improved by designing mesh and space cloth with bigger open area. The percentage of open area in square-mesh wire cloth [P] can be determined by the formula (Perry [82]):

$$P = \frac{O^2}{(O+D)^2} \times 100 = (OM)^2 \times 100$$

where

M is the mesh, O is the size of opening and D is the diameter of wire.

In industrial sampling efficiency of screening — degree of perfection of separation of particles into size fractions according to aperture dimensions is the underlying parameter. Knowing the screening performances it is much easier to design the whole equipment.

Let us consider a screen as in Figure 5.14, in which F stands for feed rate, C rate of material that overflows from the screen and U rate of material that underflows.

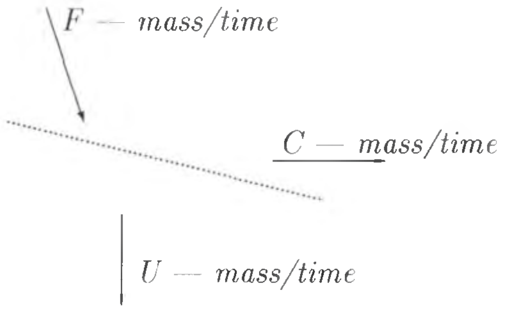


Figure 5.14: Schematization of Mass Balance for Efficiency on a Screen.

Let us call f the fraction of material (feed) above the cut point size, c the fraction of material above the cut point size in the overflow and u the fraction of material above the cut point size in the underflow (see [109]). The Efficiency of a screen is obtained by the equation below:

$$E = \frac{c(1-u)(f-u)(c-f)}{f(1-f)(c-u)^2} \tag{5.2}$$

or, if the recovery of coarse material in the overflow is 100%, which implies $u = 0$:

$$E = \frac{c-f}{c(1-f)}$$

These equations consider Figure 5.14 and the mass balance of the screen as

$$F = C + U$$

It assumes efficiency to be 100%, therefore, mass balance of undersize particles is

$$F(1-f) = C(1-c) + U(1-u)$$

and for oversize material $Ff = Cc + Uu$.

From these equalities we have:

$$\frac{C}{F} = \frac{f-u}{c-u}$$

and

$$\frac{U}{F} = \frac{c-f}{c-u}$$

The Equation 5.2, the overall efficiency $[E]$, was obtained by multiplying the recovery of oversize material in the screen overflow $[R_O]$ and undersize material in the screen underflow $[R_U]$. These recoveries are respectively:

$$R_O = \frac{Cc}{Ff} = \frac{c(f-u)}{f(c-u)}$$

and

$$R_U = \frac{U(1-u)}{F(1-f)} = \frac{(1-u)(c-f)}{(1-f)(c-u)}$$

Suppliers generally recommend and manufacture square aperture for screens and circular form for sieves. Vibrating screen, 10^o inclined, with high speed, low amplitude and static sieves is the ideal choice.

We should bear in mind some characteristics not directly depending on the material to be handled; the sieve charge $[W]$, for instance. The *JIS M8105* suggests:

$$W \leq 5A\rho D_s^{0.7}$$

where: D_s is the nominal sieve aperture, d is the coarsest particle, ρ is the bulk density of material and A is the sieve area. In order not to damage the wire cloth it is strongly recommended that the largest particle less than $10D_s^{0.7}$.

- **Vibrating Grizzly**:

  In order to eliminate oversized materials and protect comminuting system against large lumps (scalping) a Vibrating Grizzly with heavy parallel bars connected to a frame must be provided. The bars should be 30^o inclined for undesirable particles roll off. The bars themselves should be made of manganese steel to reduce wear and have a triangular cross-section to reduce jamming of powder within the spaces. A middle-sized one fits very well pilot experiments. Figure 5.1 locates it right after the Hammer Crusher and nearly at the outset of the sampling process. Such a position is standard.

5.2.4 Comminuting Subsystem Design

Comminution is generally the first stage in the quest for a representative sample. One of the major objects of this phase is the liberation, or release of the content we are interested in. If such aim is attained through coarse less expensive will be the reducing procedure. However high-grade precision for bulk materials requires good liberation and high amount of fines accordingly. See Chapter 2, Section 2.7 and 2.8.

In practice complete liberation is seldom achieved even when ground down to the desired grain size. In the Figure 5.15 it can be seen that each lump contains a proportion of *good* material and a portion of gangue. Complete liberation is only attained through further comminution.

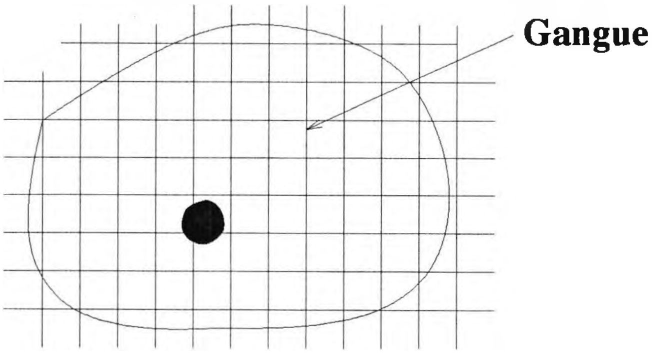


Figure 5.15: Fragment of bulk material with product and gangue.

The process of particle size reduction begins with crushing and ends up inevitably with pulverization. It passes very often through grinding operations in a sequence similar to the one in Figure 5.16.

In statistical terms, each phase is usually necessary to reduce the variability within classes because the process of comminution increases the composition heterogeneity which is synonymous with the statement that the material becomes more liberated. We are inclined to think that it would result in a higher sampling variance because of the increasing number of particles and the following formula:

$$\frac{s_2^2}{s_1^2} = (\frac{d_1}{d_2})^{-3}$$

where

s_1^2 = standard deviation before comminution;
s_2^2 = standard deviation after comminution;
d_1 = top size (5%) before comminution;
d_2 = top size (5%) after comminution.

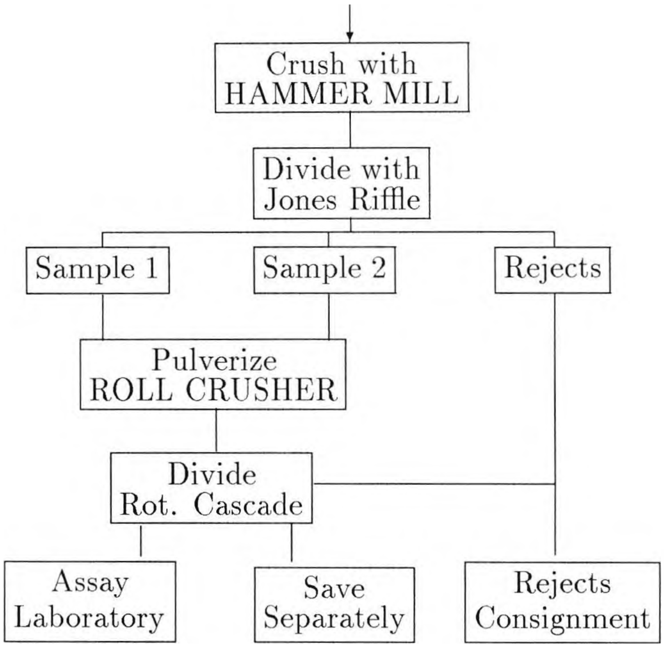


Figure 5.16: Flow sheet for Particle Size Reducing

One should bear in mind that reducing increases the liberation factor [see Chapter 2, Section 2.7] and that large lumps could seriously misrepresenting the lot if the sample unit is not relatively large. Charcoal, for instance, retained in certain screen size has low carbon content.

A rough guide to the mill sizing is the grindability coefficient — rate of grinding of material in the mill. Factors of hardness and elasticity are important to determine grindability. "*Mohn scale*" measures resistance to crushing and arranges hardness in increasing order:

Table	*Hardness*	*Type of Materials*
1 a 3	soft	gypsum, salts, charcoal, chalk, barites, etc.
4 a 7	median	phosphate, magnesite, bauxite, limestone etc.
others	hard	quartz, granite, topaz, sapphire, emery etc.

Table 5.7: Grindability of Bulk Material. Reference: Perry.

This table is related to the work required for size reduction. They are theoretical relations named after their authors. The *Kick's Law* can be written

$$E = c \times \log \frac{X_1}{X_2}$$

where X_1/X_2 is the size-reduction ratio, E is the work done and C is a constant. The *Rittinger's Law* states that the work consumed for reduction of particle size is directly proportional to the surface produced. In both cases the differential equation is

$$dE = -\frac{CdX}{X^n}$$

According to Perry [82] the solution of these equations for $n = 1$ and $n = 2$ result the equations above. For $n > 1$ the solution is

$$E = (\frac{C}{n-1})(\frac{1}{X_2^{n-1}} - \frac{1}{X_1^{n-1}})$$

It has been considered that *Kick's Law* is related to crushing while *Rittinger's Law* most closely fit fine grinding. If we consider E the work required to reduce the unit weight of feed with 80% passing the diameter X_F micron to a product with 80% passing X_P micron then,

$$E = E_i \frac{\sqrt{X_F} - \sqrt{X_P}}{\sqrt{X_F}} \sqrt{\frac{100}{X_P}}$$

where E_i, the work index to reduce a unit weight from a theoretical infinite size to 80% passing 100μ, may be found experimentally from laboratory comminution tests or from tables according to the material used.

Within the scope of our application — pilot experiments — two equipment are proposed:

1. Hammer Mill;
2. Roll Crusher.

- **Hammer Mill**

  This is equipment for fine or coarse dry grinding, mounted on a horizontal shaft and crushing taking place by impact between the hammers and breaker plates. The cylindrical grating may be positioned beneath the rotor. The number of hammer crushers should be symmetrically designed so that the direction of rotation can be reversed to distribute wear evenly on the hammers and breaker plates. Speeds must vary from 500 to 1000 *rpm*.

  The Figure 5.17 shows the distribution of both hammers and bars. The four hammers should be pivoted so that they can move out of the path of oversize material or tramp hard metal, entering the crushing chamber. The exit from the mill is perforate according to the required particle size. Material over this size is therefore retained and swept up again and again for further impacting as the feed takes place. The choice of parameter b in the figure is subordinate

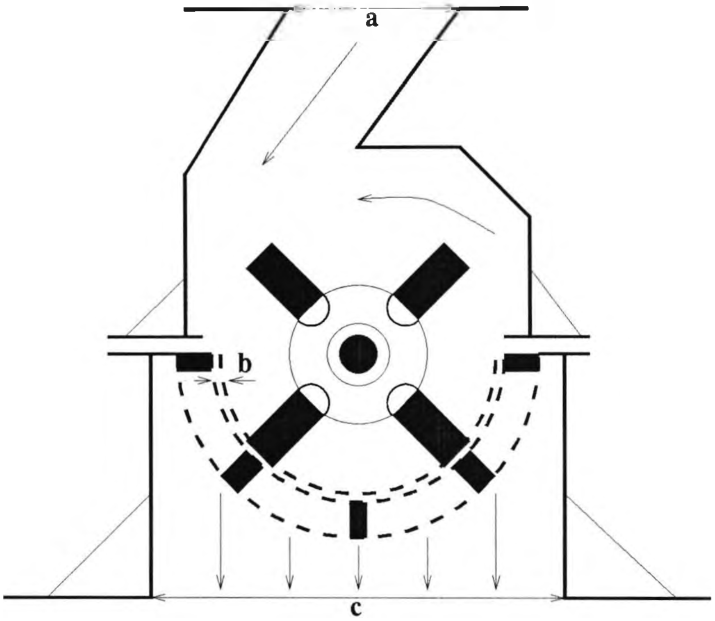


Figure 5.17: Typical Hammer Mill for Pilot Experiments. Courtesy, Pascall Engineering.

to the particle size required for the next stages of sampling. For avoiding loss of dust and moisture, it should be designed with tight filling container. That is because the proposed Hammer Mill envisages integration in the mechanical sampling system, not totally continuous but operating in batches.

- **Roll Crusher**

  This is equipment for non-abrasive materials that should be used in comminuting materials which are too fine for a hammer mill and too large for laboratory pulverizers. It is part of any industrial sampling plant. It is also used intermittently.

  Its design is shown in Figure 5.18. In accordance with Perry [82] it should be accomplished with the following specifications:

$$d = 0.048D_r \tag{5.3}$$

or

$$d = 0.02D_r + a \tag{5.4}$$

where D_r = the roll diameter;
d = the diameter of the largest feed particle;
a = the distance between roll faces.

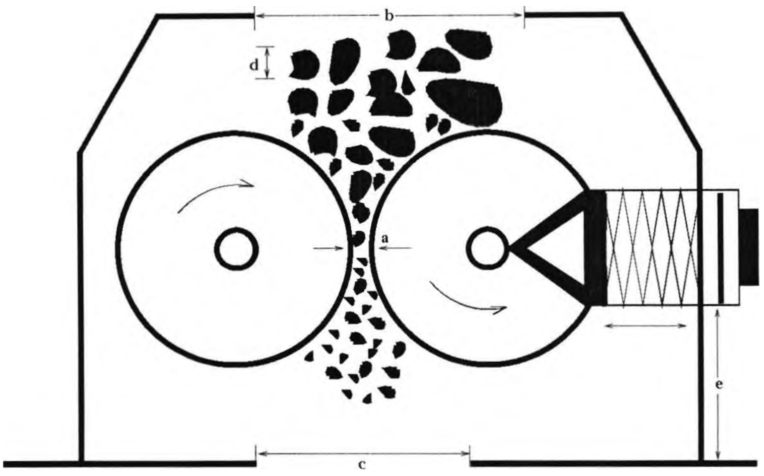


Figure 5.18: Schematic Representation of Double Roll Crusher with Spring-loaded Roller.

5.2.5 Sampling Accessories

There is a wide range of tools for a self-contained *Sampling Test Station.* The choice has been limited to those tools where the design has some importance to the result of sampling, when the *STS* cannot be operated in the same building and/or where handling of the consignment as a whole should be avoided. They are:

1. Screw Feeder;
2. Open-sided Sampling Spear;
3. Tubular Sampling Spear;
4. Shuttered Sampling Spear;
5. Shuttered Sampling Auger;
6. Sampling Frame for Checking Bias.

- **Screw Feeder**

  An accessory equipment necessary whenever it is desired to deliver a uniform and continuous stream. A typical one is shown in Figure 5.19. In the layout of *STS* in Figure 5.1 it is placed just before the moving belt. Some of required conditions to be fulfilled are presented in Chapter 3, Section 3.1 and 3.6.

  It should be used only when particle size is relatively uniform, otherwise there can be risk for the equipment itself. Segregation of coarse and fine materials brings about packing of bulk in chambers. This is worsened by dimensions of screw lodging regarding b and c.

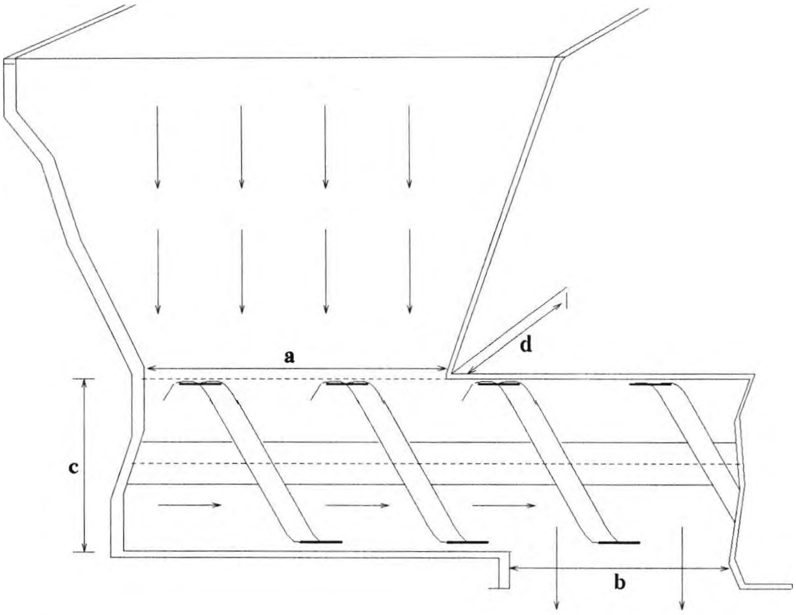


Figure 5.19: Typical Screw Feeder for Sampling Station.

- **Spears and Augers**

Spears or Thieves consist of a piece of tubular steel or aluminum alloy, fitted with a T-handle, which retains a core sample when inserted into the bulk material.

The physical texture of the material being examined governs the type of tool and the precise mode of use. It always involves withdrawal of a sample and transferring to a container. We suggest both open and closed-end sampling spears long enough to reach the bottom of package or consignment to be sampled. The Figure 5.20 shows two types of spears for dry and free running powders.

The top tool is open-sided and it is particularly important for sampling bags in storehouse. It is thrusted horizontally into the material with the tube wall uppermost then it is rotate 180° and withdrawn. Depending on the type of material typical cross sections are used. We recommend the third one with sharp edges for the same reasons considered for cutter in conveyor belt.

Other standard tool is the Tubular Sampling Spear in Figure 5.21.

It consists of a close metal tube with large holes at regular intervals along its length. It is useful for studying partitions of materials by layers when segregation is supposed to take place. When the spear is withdrawn the separate portions are tapped out into a different sampling containers.

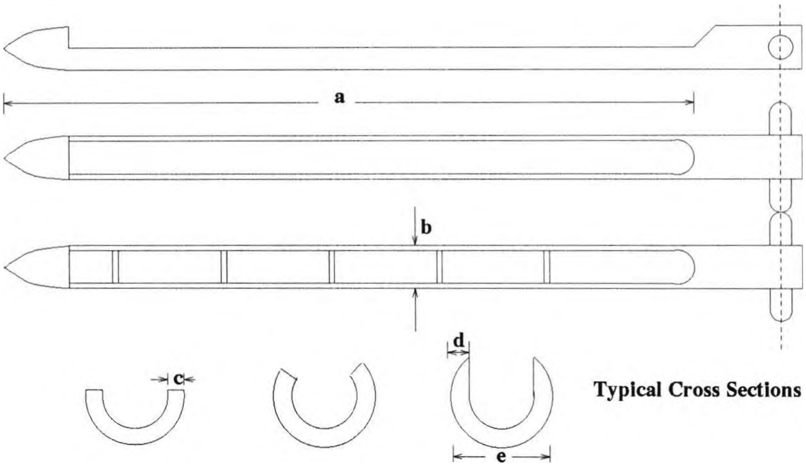


Figure 5.20: Accessories: Open-sided Sampling Spear and Divided Spear for Dry, Free-running Powders.

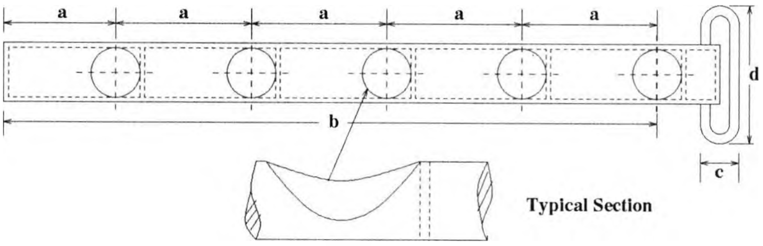


Figure 5.21: Accessories: Tubular Sampling Spear.

The Figure 5.22 shows a Shuttered Sampling Spear for pulverized and extremely free flowing materials.

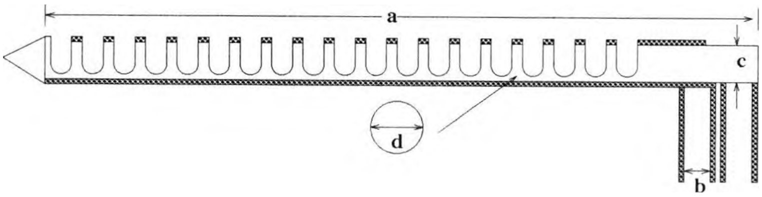


Figure 5.22: Accessories: Shuttered Sampling Spear for Dry, Free running Solids.

The Shuttered Sampling Spear is a closable tool provided with a tubular sheath outside a spear. Both are inserted into the material. When reaching the bottom of container, the tubular sheath is rotated 180° to allow particle to run into the aperture of the spear. It is designed for high precision sampling with dimensions such as its tip reaches the bottom of material, the relationship between c and d is closed to 1 and it can collect the minimum amount of sample computed for the increment. It is shown in Figure 5.22.

For sampling of bulk materials in considerably depth consignments the spear of Figure 5.23 is proposed.

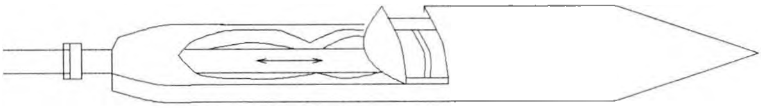


Figure 5.23: Head of a Typical Grain Spear.

The advantage of this tool is the opening as it is withdrawn.

Finally a few words about the Shuttered Sampling Auger proposed in the Figure 5.24

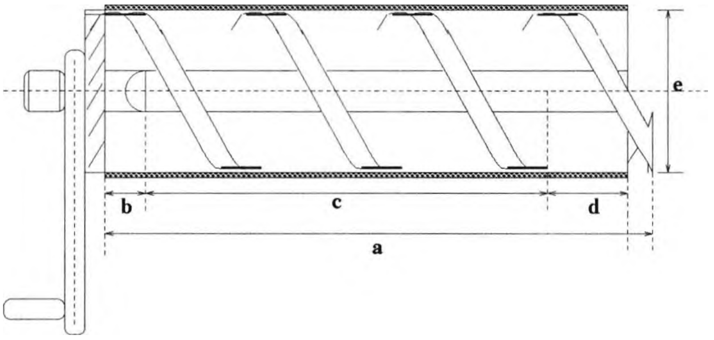


Figure 5.24: Accessories: Shuttered Sampling Auger.

It is useful tool when dealing with compacted or hardened packaged materials. It is a tube with an auger drill inside. Care must be taken when withdrawing the auger without rotating and delivering its contents into a sample container by reversing the direction of rotation of the center rod.

- **Sampling Frame for Checking Bias**

  Sampling Frame is an important portable tool for checking bias between increments particularly on a conveyor belt. The Figure 5.25 depicts the equipment consisting of two parallel plates with the same shape of the material to be checked.

  In the case of conveyor belt the plates must fit its curvature. The belt is stopped and the frame is placed in contact with the belt across its full width. Then the increment is swept out carefully as a whole. In case of large pieces obstructing the insertion of the frame, standardization of pushing to the right

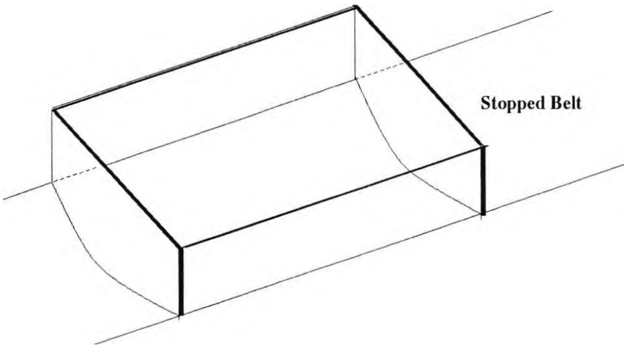


Figure 5.25: Accessories: Sampling Frame for Comparing increments.

or to the left must be kept. The height of the frame should exceed the top of material when in full capacity. The bias check program assesses how the component of interest is distributed in different increments and how big these systematic errors are when comparing the series of reference increments and the corresponding series of system increments. These systematic errors may produce positive or negative bias which must be less than the maximum permissible bias agreed between buyer and seller.

Chapter 6

Conclusion

The purpose of this thesis has been to give a comprehensive coverage of the techniques of *Bulk Sampling* with emphasis on the principles upon which the chemical engineers must base quality and productivity issues in industry. These are:

- collecting reliable data;
- isolating variability (variances);
- characterizing of fluctuation in material (space and time);
- understanding the intrinsic properties of materials.

Although there are several rules for sampling there are only two defined sets of statistical procedures which are applicable to sampling. We may use the classical one that makes use of the statistical process control tools — R and X Charts, Shewhart graphics, sequential plans — or the experimental design techniques for a more powerful insight into variability.

We have chosen the second approach and focused our attention on hierarchical designs because the tree structure is suitable for chemical processes, particularly those design where the degree of freedom are equal as we go down to the bottom of the tree structure. For these designs, where samples are not equally split, care must be taken about dividing samples in order to guard against biases.

To make this approach suitable for the continuous selection errors we include spatial statistics and regionalized variables since the Control Charts are unable to predict the real fluctuations of process. Random, long-range and periodic fluctuations are analyzed accordingly.

There are some obstacles to face when dealing with material having all three variographic terms. Firstly the there is the range of equations and parameters required to implement the method. There are two equations for each component a, A and M. One equation for long-range increments and one to access periodic terms. Five auxiliary parameters are needed for each component. Secondly the complete experiment requires three sets of data with an average number of increments:

- Short-range values: first series of at least 30 increments diverted at intervals of 2 seconds. Such series provides enough data to estimate both variance with 29 degrees of freedom and the variogram $w^*_{f1}(h1)$ with 28 degrees of freedom.
- Long-range terms: a second series of data is required at intervals of 1 minute interval and it must cover the useful domain of the variogram. For one with 30 degree we have to extract 60 increments.
- Periodic terms: third series of increments extracted at 30 minute intervals. Practice suggests about 60 though 80 would be better.

Finally there is the equipment. All the methods are based on sampling correctness without delimitation and extraction errors. A Sampling Test Station being the best alternative, although sampling in locus may be an alternative.

Some efficiency may be reached by eliminating some extra calculations. The first step has been given by Pitard [83]. His suggestion is about working through the main equation $a = A/W$ while associating the $f(t)$ function to the heterogeneity $[h]$ in the same way

$$h_m = h_{m1} + h_{m2} + h_{m3}$$

and taking the advantage of the equation:

$$h_m = \frac{a_m - a_L}{a_L} \times \frac{M_m}{M^*_m} = N_U \times \frac{a_m - a_L}{a_L} \times \frac{M_m}{M_L}$$

that involves at the same time: a_L, a_m, M_m and M_L.

As the variogram of h_m follows the same shape of a_m and the variogram of M_m does not affect the variogram of h_m, or only to the second order, we can think of eliminating a great deal of the extra work.

Regarding collection of data we have suggested a mechanical sampling plant in spite of some recommendations of international standard organizations — *BSI, AFNOR, ANSI, DIN, JIS* — which suggest the use of scoop, shovel and the techniques of coning and quartering. We do not share this view for two reasons:

1. manual sampling is responsible for the major sources of error in any chemical industry
2. mechanical sampling is the only possible way of reducing the fundamental and segregation errors represented by the constitution and distribution heterogeneity.

The protocol required for the FE is represented in the equation:

$$\sigma_{FE}^2 = Cd^3/M_S$$

By using logarithm function is possible to set up a series of stages — comminuting and dividing — to get the amount of sample with the minimum cost. For the GSE represented by the equation $\sigma_{FE}^2 = \xi\zeta\sigma_{FE}^2$ the use of mixers is mandatory for eliminating both segregation and grouping factors.

The design of a *Bulk Sampling Test Station* should be drawn on the best available statistical methodology and theory of bulk sampling to help identify a possible sources of variability and bias. Each individual piece of equipment has a role to play in the removal of variability which is not inherent to the material itself. The sophistication of the design will entirely depend on cost and allowed risks, but there will be fundamental components, common to all test station.

In addition to theoretical consideration, pilot experiments on individual component are recommended to identify real level of variation for different material and layouts.

The skeleton version of the design recommended here is implemented in Fábrica da Estrela, a branch of $IMBEL$. It is hoped that this project will grow to a full implementation and provide the *ideal* model for a cost-efficient semi-automatic station suitable for industries in developing countries.

As declared before the thesis itself has been done in a more fragmentary rather than systematic way, and there are good reasons for this: Firstly because there is not much literature about bulk sampling directed towards quality of chemicals since the first publication of *The General Sampling Theory* of J. Visman [105] in 1962. According to Bicking [8], the last paper on sampling of particulate material was written by Duncan [30] and it is found in *Technometrics.* All these approach has been presented in the text. However Gy's Theory [37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47] is applied in most of the chapter 3 because it is the only one that is suitable for one-dimensional lots and the only one that allows us to determine the moments of sampling errors (SE). Secondly because no sampling plan for chemicals can be comprehensive enough to cover all cases in a few plans as is done with indivisible materials.

Finally I should emphasize that this thesis is not an end in itself. Further research is required for a complete command of the field. For those interested in pursuing the theoretical aspects of continuous selection errors, long-range or periodic variabilitity, there are *Spatial Statistics* and *Time Series Analysis.* For those interested in pursuing the practical aspects of continuous selection errors, *Variography* and *Regionalized Variables* are powerful tools to materialize correlations. In any of these case there are plenty of references throughout, and at the end of this work a list of papers for further study.

APPENDIX I. SPSS/PC Program

There are nowadays a great number of packages available for analysis of variance. Three are particularly important: *SAS*, *Statgraphics* and *SPSS*. While they are easy to use for general purposes and factorial design, they demand some fancy operators to perform the analysis of nested balanced design.

I have been using *SPSS/PC— The Statistical Package for the Social Sciences* for balanced ones. The computations are much easier by using a new function called *MANOVA—DESIGN*. The Table below shows the imput used together with illustrations of these procedures in asterisk.

```
*PROGRAM FOR ESTIMATION OF VARIANCE COMPONENTS FROM A
*                    BALANCED NESTED DESIGN OF N FACTORS.

DATA LIST FREE / CHARCOAL ANAL SUBS SAMP.
VALUE LABELS ANAL 1 ’A1’ 2 ’A2’.
VALUE LABELS SUBS 1 ’SS1’ 2 ’SS2’.
VALUE LABELS SAMP 1 ’S1’ 2 ’S2’.
BEGIN DATA.
44 1 1 1 39 1 1 3
48 1 1 1 41 1 1 3
40 2 1 1 37 2 1 3
38 2 1 1 44 2 1 3
40 1 2 1 56 1 2 3
53 1 2 1 53 1 2 3
63 2 2 1 46 2 2 3
50 2 2 1 46 2 2 3
35 1 1 2 36 1 1 4
38 1 1 2 42 1 1 4
30 2 1 2 40 2 1 4
31 2 1 2 39 2 1 4
47 1 2 2 34 1 2 4
49 1 2 2 34 1 2 4
37 2 2 2 35 2 2 4
36 2 2 2 32 2 2 4
END DATA.
```

```
* STATISTICS OF INTEREST FOR THE MANOVA AND LEVELS

MANOVA CHARCOAL BY ANAL(1,2) SUBS(1,2) SAMP(1,4) /DESIGN ANAL
WITHIN SUBS
/DESIGN SUBS WITHIN SAMP
/DESIGN ANAL WITHIN SUBS WITHIN SAMP

* SIGNIFICANT DIFFERENCES BETWEEN SUBSAMPLING WITHIN SAM-
PLING (4 df)

/PARTITION SUBS (1,1,1,1).

* OTHER USEFUL STATISTICS LIKE RESIDUALS AND PLOTS
/RESIDUALS=CASEWISE PLOT
/ANALYSIS=CHARCOAL
/DESIGN.
```

APPENDIX II. F77 Computer Programs

The programs in this appendix have been written in standard FORTRAN, and so should be compatible with most microcomputer system with the version Fortran F77. Each program was used by a typical example, in the text, following the listing. The first program is intended for Variographic Experiment. The second one is for Variance Estimates of Staggered Design. The determination of sample size by Gy's formula in Chapter 2 was computed without any program although there are some books with such programs. For example there is a Basic program for this purpose in Wills [109].

- **Variographic Experiment:**

```
c
c  FORTRAN PROGRAM FOR VARIOGRAPHIC EXPERIMENTS
c
real*8 a(50),sum(25) c
c  TO BE READ c
open(11,file='ben.dat')
c open(11,file='b1')
c
c  TO BE WRITTEN
c
open(12,file='benur.out')
open(13,file='ben.out')
c
c  I N P U T D A T A
c
print *,'reading'
c
read(11,*)n,m
c n=number of samples, m = space/time
do 02 i=1,n
read(11,*)a(i)
02 continue
c
```

```
c C A L C U L A T I O N S
c
do 04 j=1,m
sum(j) = 0.D0
do 06 i=1,n-j
sum(j) = (a(i+j)-a(i))**2 + sum(j)
06 continue
sum(j) = sum(j)/(n-j)
04 continue
c
c O U T P U T D A T A
c
print *,'writing results '
c
write (12,800)
800 format (10x,'Variograma',/)
write (12,650)n,m
650 format (/,2x,'Number of Samples:',i2,3x,'Space/Time:',i2)
write (12,750)
750 format (//,2x,'i',3x,'Samples',/)
do 08 i=1,n
write (12,900)i,a(i)
08 continue
write (12,850)
850 format (//,2x,'j',3x,'Space/Time',/)
do 10 i=1,m
write (12,900)i,sum(i)
write (13,900)i,sum(i)
10 continue
900 format (1x,i2,3x,f11.6)
c
stop
end
```

- **Variance Estimates of Staggered Design:**

```
c
c
c  FORTRAN PROGRAM FOR VARIANCE ESTIMATES
c  FROM STAGGERED NESTED DESIGN (FACTORS 6)
c
c  NEGATIVE VARIANCE ESTIMATES SET TO ZERO
c
character A$(6)
integer A,F,H,J,Q1,K
real TO,CO
real C(11),Z(6),E(6),V(6),M(6)
real T(7,4),X(7,4)
c
c  In the next lines assign the values:
c  A = Number of levels of factor A (100)
c  A = Number of nested factors (6)
c
c
c  SET OF OBSERVATIONS FOR EACH LEVEL
c  OF FACTOR A. DIMENSION OF X INCLUDED
c  IN DECLARATION STATEMENT.
c
c
data A, F/7, 4/
data X/6.1, 8.5, 8.6, 9.3, 8.1, 8.5, 9.8,
+ 6.6, 9.6, 9.7, 7.2, 7.1, 9.0, 9.8,
6.6, 8.2, 8.0, 6.5, 2.3, 4.0, 11.7,
8.8, 8.1, 7.4, 8.0, 9.5, 9.2, 12.8/
data A/ 'F', 'E', 'D', 'C', 'B', 'A'/
c
open ( unit=7, file='result', status='unknown')
rewind (7)
c
write (7,*) 'X='
do 100 i=1,A
write (7, *) (X (i,j),j=1,F)
100 continue
```

```
c
TO=O
do 310 H=1,A
do 305 J=1,F
TO=TO+X(H,J)
c
305 continue
310 continue
c
write(7,*) 'TO=', TO
c
c  EVALUATES CALCULATION TERMS (1) TO (2*F-1) AS WELL AS
c  CORRECTION FACTOR, TOTAL AND MEAN.
c
do 380 H=1,F
do 375 J=1,A
if (H.eq.1) then
Q1=1
else
Q1=2*H-2
end if
C(Q1)=C(Q1)+ X(J,H)*X(J,H)
375 continue
380 continue
Co=TO*TO/(A*F)
do 420 K=2,F
do 415 H=1,A
do 410 J=1,K
T(H,K)=T(H,K)+X(H,J)
410 continue
415 continue
420 continue
do 445 J=2,F
do 440 H=1,A
Z(J)= Z(J)+T(H,J)*T(H,J)
440 continue
445 continue
Q=1
```

```
do 470 H=1, F-1
Q=Q+1
C(Q+H)=Z(H+1)/(H+1)
470 continue
c
c INTERMEDIATE RESULTS
c
write(7,*) ’Calc. Term Value’
write(7,*) ’————————-’
do 510 H=1, 2*F-1
write(7,*) H.C(H)
510 continue
write(7,*) ’Coo. Factor’, CO
write(7,*)
write(7,*) Number of obs.= ’,A*F
write(7,*) ’ Total of obs.= ’, TO
write(7,*) ’ Grand Mean= ’, TO/(A*F)
c
c CALCULATION OF MEAN SQUARES
c
Q=-1
do 585 K=1, F-1
Q=Q+1
E(K)=C(Q)+C(Q+1)-C(Q+2)
585 continue
E(F)=C(Q+2)-CO
do 605 H=1, F-1
E(H)=E(H)/A
605 continue
E(F)=E(F)/(A-1)
c
c COMPUTATION OF VARIANCE ESTIMATES
c
V(1)=E(1)
if (F.gt.2) then
V(2)=max(0.0,3*(E(2)-V(1))/4.0)
if (f.gt.3) then
V(3)=max(0.0,2*(E(3)-7*V(2)/6-V(1))/3)
```

```
if (F.gt.4) then
V(4)=max(0.0,5*(E(4)-13*V(3)/10-11*V(2)/10-V(1))/8)
else
V(4)=max(0.0,(E(4)-5*V(3)/2-3*V(2)/2-V(1))/4
end if
if (f.gt.5) then
V(5)=E(5)-7*V(4)/5-6*V(3)/5
V(5)=max(0.0, 3*(V(5)-16*V(2)/15-V(1))/5)
V(6)=E(6)-13*V(5) / 3-3*V(4)-2*V(3)
V(6)=max(0.0, (V(6)-4*V(2)/3-V(1))/6
else
V(5)=E(5)-17*V(4)/5-11*V(3)/5-7*V(2)/5
V(5)=max(0.0, (V(5)-V(1))/5)
end if
else
V(3)=max(0.0,(E(3)-5*V(2)/3-V(1))/3)
end if
else
V(2)=max(0.0,(E(2)-V(1))/2.0)
end if
c
c ASSIGNING DEGREES OF FREEDOM
c
do 880 H=1, F=1
M(H)=A
880 continue
M(F)=A-1
c
c PRINTING FINAL RESULTS
c
write(7,*) 'Source of Mean Square Var. Est.'
write(7,*) '——————————————'
do 930 H=F,1,-1
write(7,*) A(H+6-F), M(H), V(H)
930 continue
close(7)
stop
end
```

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