



**Workshop on Understanding and Evaluating Radioanalytical
Measurement Uncertainty**

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**An outline of methods for the estimation of uncertainty that include the
contribution from sampling**

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Workshop on
Understanding and Evaluating Radioanalytical Measurement
Uncertainty

**An outline of methods for the
estimation of uncertainty that
include the contribution from
sampling**

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Overview

@ 2 approaches for the estimation of uncertainty arising from sampling (**EURACHEM/CITAC Guide “Measurement uncertainty arising from sampling – A guide to methods and approaches - 2007)**)

@ empirical approach “top-down” (M. Ramsey)

- @ duplicate sampling
- @ estimation of uncertainty components
- @ example

@ modelling approach “bottom-up” (P. Gy)

- @ the theory of sampling of P. Gy: 7 sources of uncertainty
- @ the Fundamental Sampling Error
- @ the Grouping and Segregation Sampling Error
- @ example

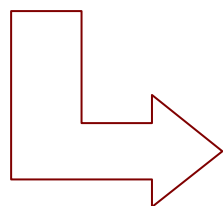
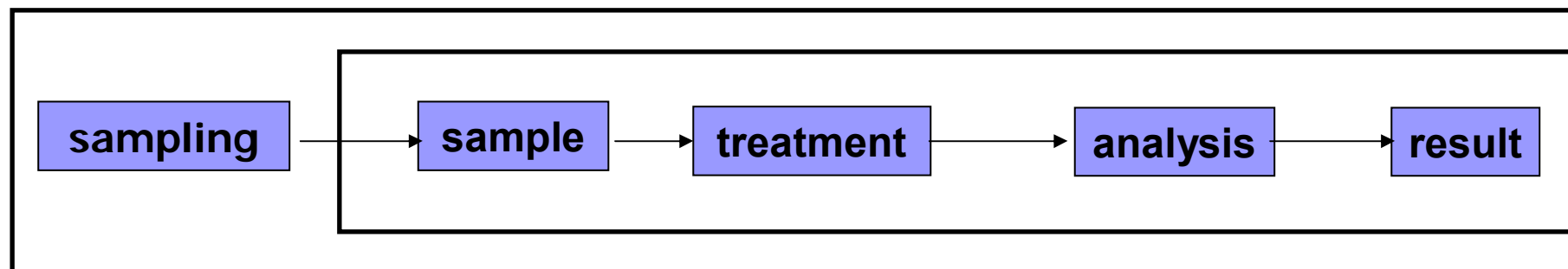




Measurement process

ISO/IEC 17025 reports sampling as a factor to be considered for total uncertainty measurement purposes

Primary sampling and chemical analysis are two parts of the same measurement process



Measurement process

Measurement uncertainty

A measurement result is characterized by its uncertainty

The uncertainty of measurement is due to:

✚ **trueness**: the closeness of agreement between the average value obtained from a large series of test results and the accepted reference value

✚ “the accepted reference value” = the true value

How close are the measurements to the true value?



Measurement uncertainty

A measurement result is characterized by its uncertainty

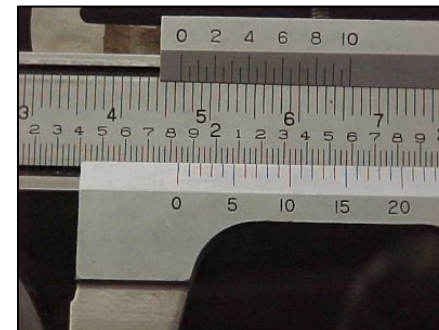
The uncertainty of a measurement is due to:

✚ precision: the closeness of agreement between independent test results obtained under stipulated conditions

✚ repeatability: precision under similar conditions

✚ reproducibility: precision under different conditions

How reproducible are measurements?

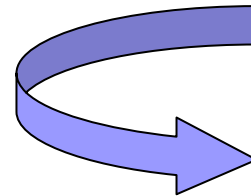


Empirical approach

- It has the widest applicability to the broadest range of measurement systems and applications (e.g. gaseous, liquid and solid)
- It is intended to obtain a reliable estimate of the uncertainty without knowing any of the individual sources

$$S_{meas} = \sqrt{S^2_{sampling} + S^2_{analytical}}$$

The measurement uncertainty has four components



- ✘ analytical precision
- ✘ sampling precision
- ✘ analytical bias
- ✘ sampling bias

Empirical approach: uncertainty sources

Estimation of uncertainty contributions in the empirical approach
4 classes of effects that contribute to the uncertainty of measurement

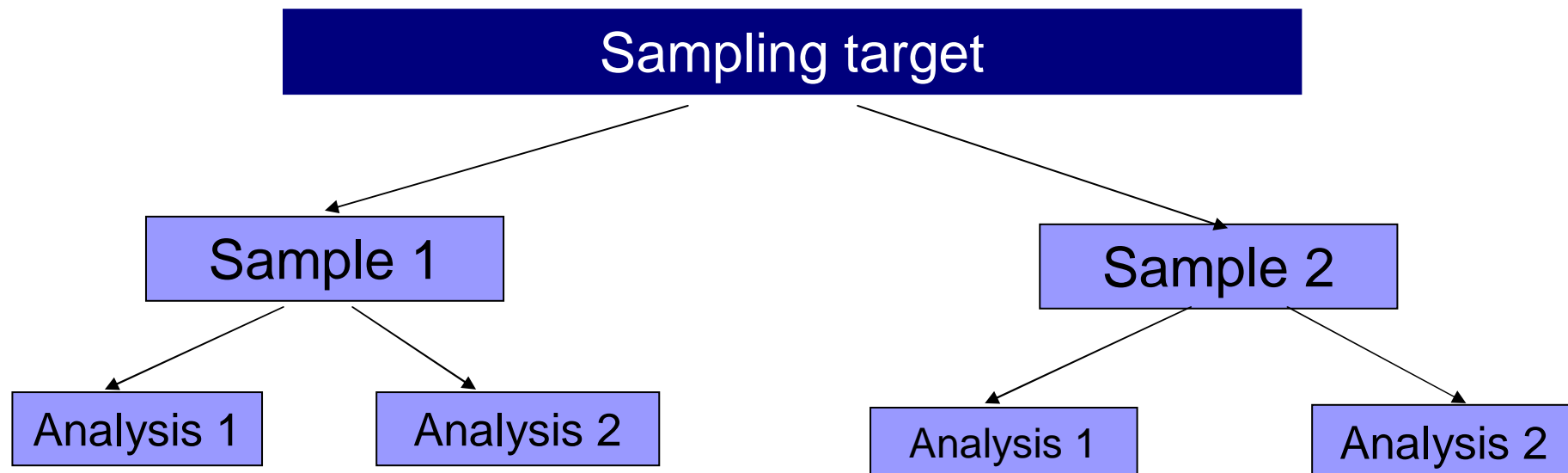
Process	Effect class	
	Random (precision)	Systematic (bias)
Analysis	e.g. duplicate analysis	e.g. certified reference materials
Sampling	Duplicate samples	Reference sampling target / Inter-organisational sampling target



Empirical approach

✘ sampling precision and analytical precision

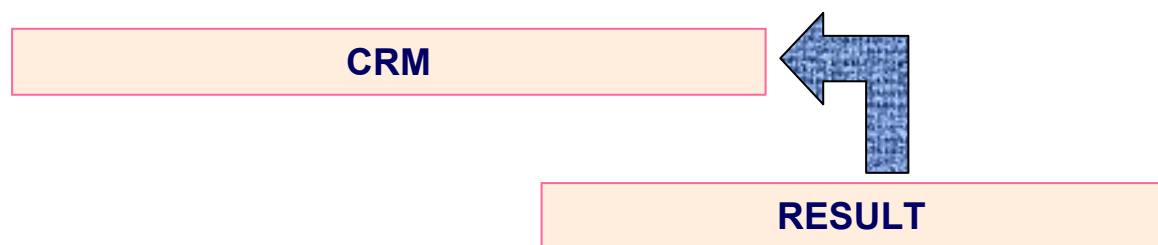
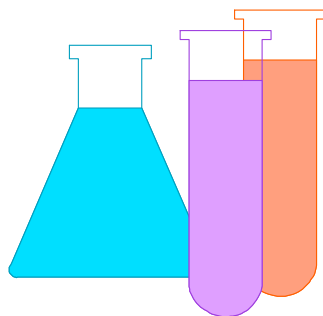
they can be estimated by replication of a proportion (e.g. 10%) of the samples and analyses respectively.



Empirical approach

✘ analytical bias

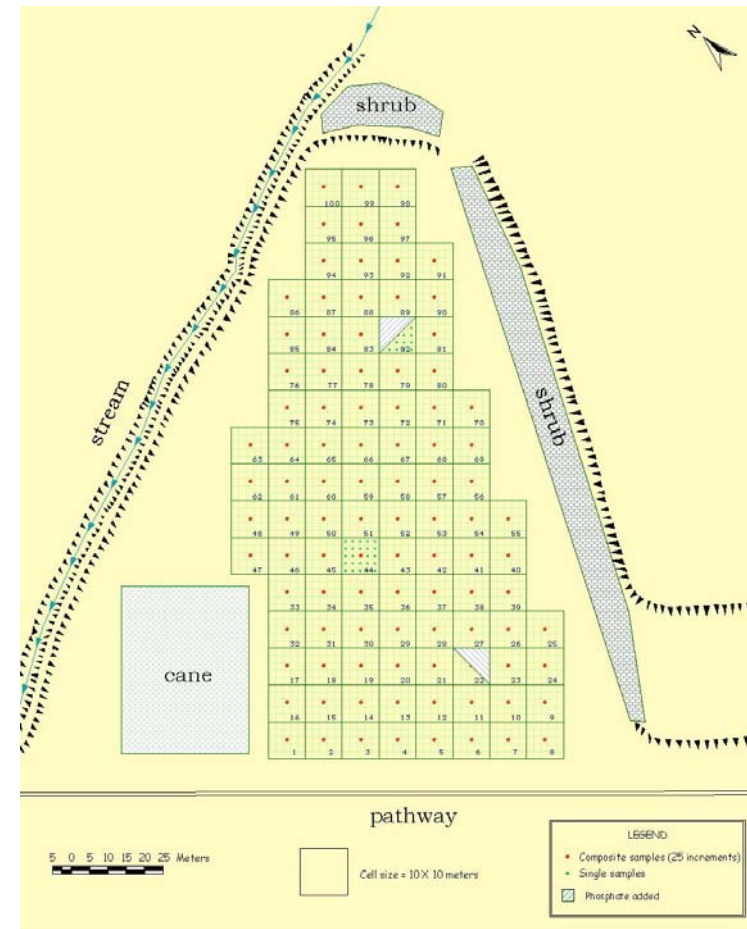
It can be estimated by measuring the bias on well-matched certified reference material



Empirical approach

✘ sampling bias

It is determined by the use of a reference sampling target (the sampling equivalent of a reference material) or by the use of measurements from inter-organizational trials, in which the sampling bias potentially introduced by each participant is included in the estimate of uncertainty based on the overall variability



Empirical approach

Four types of method are applicable to the estimation of uncertainty using the empirical approach

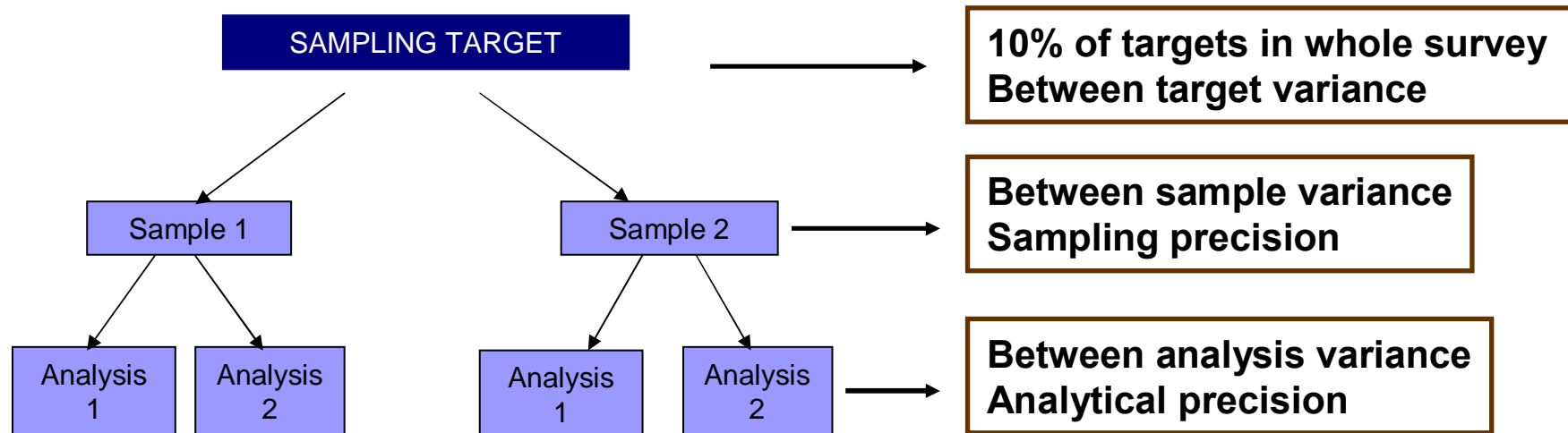
method	description	samplers	protocols	Component estimated			
				Samp. Prec.	Samp. bias	Anal. Prec.	Anal. bias
1	duplicates	single	single	yes	no	yes	yes (CRM)
2	protocol	single	multiple	between protocols		yes	yes (CRM)
3	Collaborative trial in sampling	multiple	single	between samplers		yes	yes
4	Sampling proficiency test	multiple	multiple	between protocols+ between samplers		yes	yes



Duplicate method/balanced design

✗ single sampler and single protocol

The basic principle of the replicate design is to apply the same sampling procedure two or more times on the same location to estimate the random measurement effect, preferentially taking replicate samples at some proportion of the sampling locations, typically 10% (but no less than 8 targets).

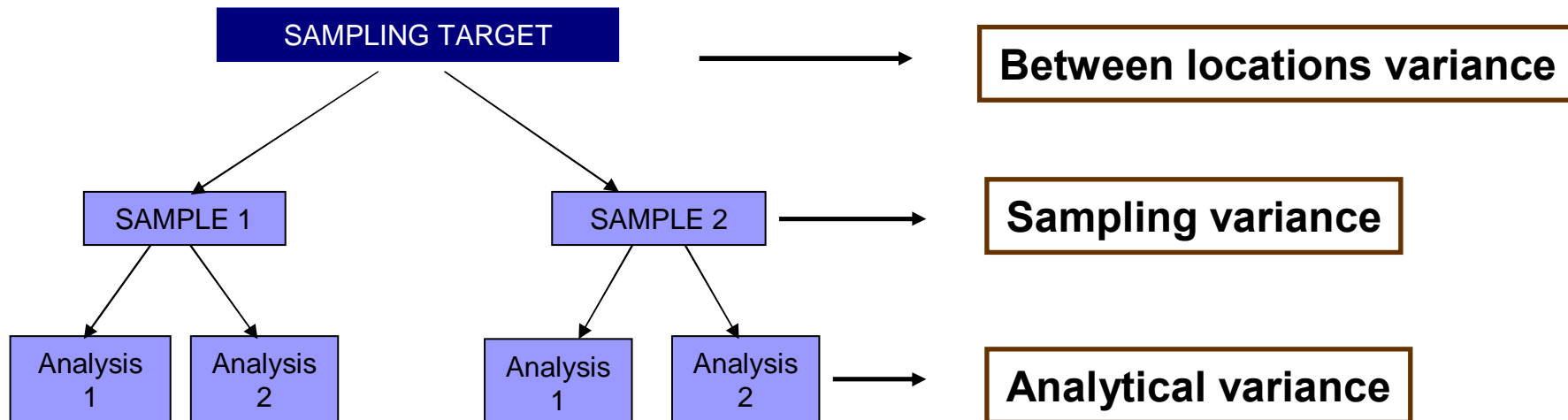


Empirical approach: the duplicate design

The random components of variation can be estimated separately using robust analysis of variance:

ROBUST ANOVA

The estimate of the bias can be done separately



Uncertainty components

Equation of the total variance

$$\mathbf{S}^2_{total} = \mathbf{S}^2_{between-target} + \mathbf{S}^2_{sampling} + \mathbf{S}^2_{analytical}$$

ESTIMATE OF COMPONENTS BY TWO WAY ROBUST ANOVA

$$U = \mathbf{S}_{meas} = \sqrt{\mathbf{S}^2_{sampling} + \mathbf{S}^2_{analytical}}$$

MEASUREMENT UNCERTAINTY

$$U = ku = 2\mathbf{s}_{meas}$$

EXPANDED UNCERTAINTY

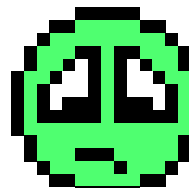
$$U\% = 200\mathbf{s}_{meas} / \bar{x}$$

RELATIVE EXPANDED UNCERTAINTY

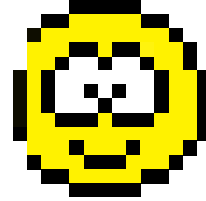




Limitations



- ✘ If there is a high proportion of outlying values, then this would be expected to lead to somewhat erroneous estimates of the component variances**
- ✘ The number of measurements used for the estimation of the uncertainty: if only few data are used then there would be large uncertainties on the estimates of the variance**
- ✘ This method estimates the random component of the uncertainty and does not estimate any systematic components in the sampling or analysis (sampling or analytical bias)**



Advantages

- ✘ The method has the widest applicability to the broadest range of measurement systems and applications (e.g. gaseous, liquid and solid)**
- ✘ The method is relatively simple to apply**
- ✘ The method uses replicated measurement and sampling to give a direct estimate of the uncertainty for the final result of the measurement without quantifying all of the sources of uncertainty individually**
- ✘ The method doesn't require previous knowledge on the matrix investigated**



Example:

Lead in contaminated top soil

Scope: estimate the measurement uncertainty , and contribution from sampling and analysis, at each of 100 different sampling targets within one site, using a common sampling protocol

MEASURAND				UNCERTAINTY ESTIMATION		
ANALYTE/ TECHNIQUE	UNIT	SECTOR /MATRIX	SAMPLING TARGET	PURPOSE	DESIGN	STATISTICS
Total lead / ICP-AES	mg/kg	Environmental / top soil	100 targets – each of area 30mx30m with depth of 0- 150mm	Uncertainty- total measurement, sampling and analytical	Empirical – duplicate method	Robust ANOVA

**EURACHEM/CITAC Guide “Measurement uncertainty arising from sampling –
A guide to methods and approaches - 2007**



Example:

Lead in contaminated top soil

Scenario and sampling target: an investigation was made of a **9 hectare site**, as part of the assessment of the land for potential housing development. The most important analyte element for human health risk assessment was found to be **lead**. In order to **compare the concentration of lead in the soil with the national regulatory threshold limit**, an estimate of the lead concentration and the measurement uncertainty was required for each of **100** sampling target.

Sampling protocol : **one hundred** samples of top soil (nominal depth 0-150mm) were taken with a **hand auger** (diameter 25 mm) at 100 locations. These locations were distributed on a **regular grid** with sample spacing of 30 m, and therefore each is intended to represent an area of 30 m by 30 m.



Example:

Lead in contaminated top soil

Study design: 10 of the samples (10% of the total number) at randomly selected locations, were sampled in duplicate using the balanced design. The duplicate samples were taken at a distance of 3 m from the original sample in a random direction. This aims to reflect the uncertainty in locating the sampling target and also the effect of small-scale heterogeneity on the measured concentration within the specified target.

Sampling and analysis : primary samples were oven dried overnight at 60°C, disaggregated, sieved to remove particles with a natural grain size greater than 2mm. The sieved samples were all ground (95%<100um) and mixed. Text portions of 0.25g were taken for dissolution with nitric and perchloric acids, prior to determination of lead by ICP-AES.

Measurement of the concentration (mg/kg) of lead on each sampling target

Row	A	B	C	D	E	F	G	H	I	J
1	474	287	250	338	212	458	713	125	77	168
2	378	3590	260	152	197	711	165	69	206	126
3	327	197	240	159	327	264	105	137	131	102
4	787	207	197	87	254	1840	78	102	71	107
5	395	165	188	344	314	302	284	89	87	83
6	453	371	155	462	258	245	237	173	152	83
7	72	470	194	82,5	162	441	199	326	290	164
8	71	101	108	521	218	327	540	132	258	246
9	72	188	104	463	482	228	135	285	181	146
10	89	366	495	779	60	206	56	135	137	149

- High degree of variability between-locations
- The **red values** higher than the threshold value 450 mg kg⁻¹ (contaminated-deterministic evaluation)
- Select 10 sampling targets as duplicate locations

Measurement of the concentration (mg/kg) of lead on 10 duplicated samples

Sample Target	S1A1	S1A2	S2A1	S2A2
A4	787	769	811	780
B7	338	327	651	563
C1	289	297	211	204
D9	662	702	238	246
E8	229	215	208	218
F7	346	374	525	520
G7	324	321	77	73
H5	56	61	116	120
I9	189	189	176	168
J5	61	61	91	119

Comments:

The low level of agreement between the concentration values from the sample duplicates is indicative of the high level of sampling uncertainty.

The agreement between the analytical duplicates (A1 and A2) is much better for most samples (<10% difference) than that between the samples duplicates. ²¹



Example: Lead in contaminated top soil

Robust ANOVA (unit mg/kg)

ROBUST ANOVA RESULTS:

Mean= 297.30884

Standard deviation (total)=218.48763

	<u>between-target</u>	<u>sampling</u>	<u>analysis</u>	<u>measurement</u>
<u>Standard deviation</u>	179.67409	123.81386	11.144044	124.31436
<u>Percentage variance</u>	67.62655	32.113293	0.26015487	32.373447
<u>Relative uncertainty</u> (% at 95%confidence)	-	<u>83.289726</u>	<u>7.4966113</u>	<u>83.626415</u>

Software ROBAN



Example:

Lead in contaminated top soil

Uncertainty estimation

$$U = S_{meas} = \sqrt{S^2_{sampling} + S^2_{analytical}} = 124.3 \text{ mg / kg}$$

$$U_{meas} \% = 200 s_{meas} / \bar{x} = 200 * 124.3 / 297.3 = 83.63\%$$

$$U_{samp} \% = 200 s_{samp} / \bar{x} = 200 * 123.8 / 297.3 = 83.29\%$$

$$U_{anal} \% = 200 s_{anal} / \bar{x} = 200 * 11.1 / 297.3 = 7.5\%$$

Example:

Lead in contaminated top soil

Summary

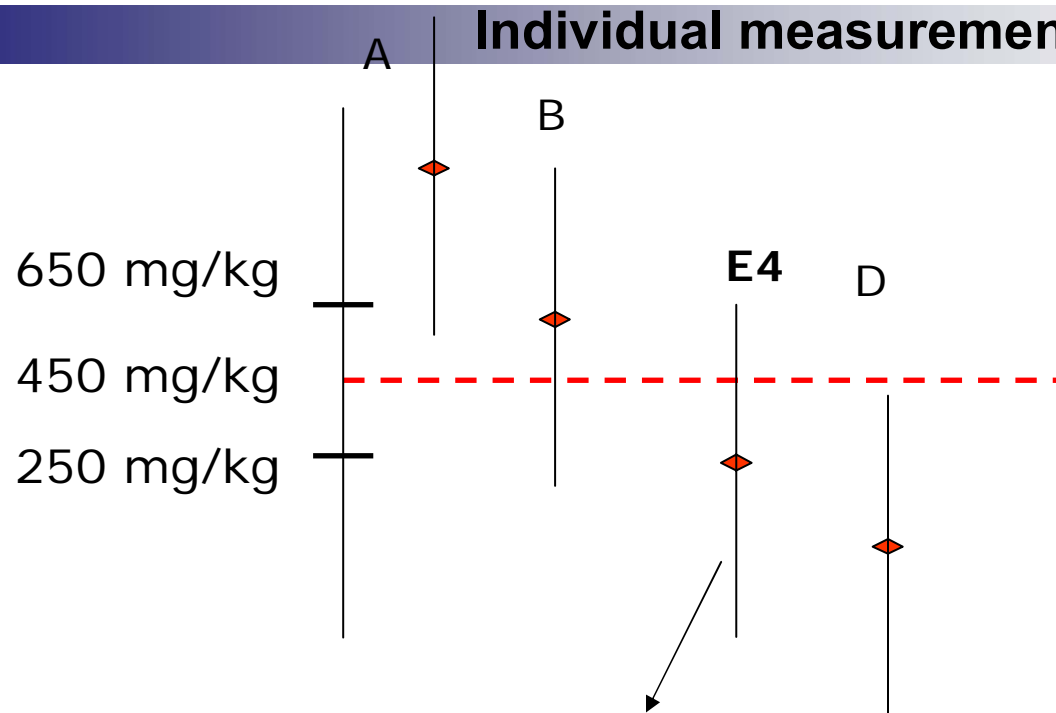
Measurement uncertainty		
SAMPLING	ANALYSIS	TOTAL
83.3%	7.5%	83.6%

WITH COVERAGE FACTOR OF 2, (95% CONFIDENCE)

Individual measurements of lead concentration reported for these targets should have attached uncertainty values equal to 83.6% of the concentration value.

Furthermore, the uncertainty on the mean measurements taken at the 10 targets where duplicate samples were taken will have reduced uncertainty estimates of 59% ($83.6/\sqrt{2}$)

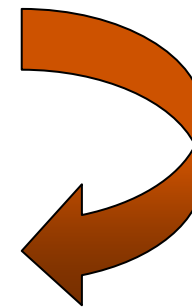
Individual measurement of lead concentration



For example:
E4 = 254 mg/kg \pm U_{meas} = 254 \pm 212.3 mg/kg

Uncontaminated
deterministic evaluation

possibly contaminated
probabilistic evaluation





Example:

Lead in contaminated top soil

COMMENTS

- The contribution from random components is calculated
- No bias (systematic) effects are considered both for sampling and analysis
- By using CRM we can estimate analytical bias adding its contribution (the whole measurement uncertainty increases)
- The relative uncertainty, calculated on a mean value (10 duplicates) is applicable within the same range of concentration
- Heterogeneity between-sampling targets is dominant element (typical in most environmental matrix)

Modelling approach

In 1951, Gy wrote, for the company employing him at that time, an internal report containing an original sampling theory to cover population of objects having different physical masses and hence different statistical weights, namely a set of mineral fragments.



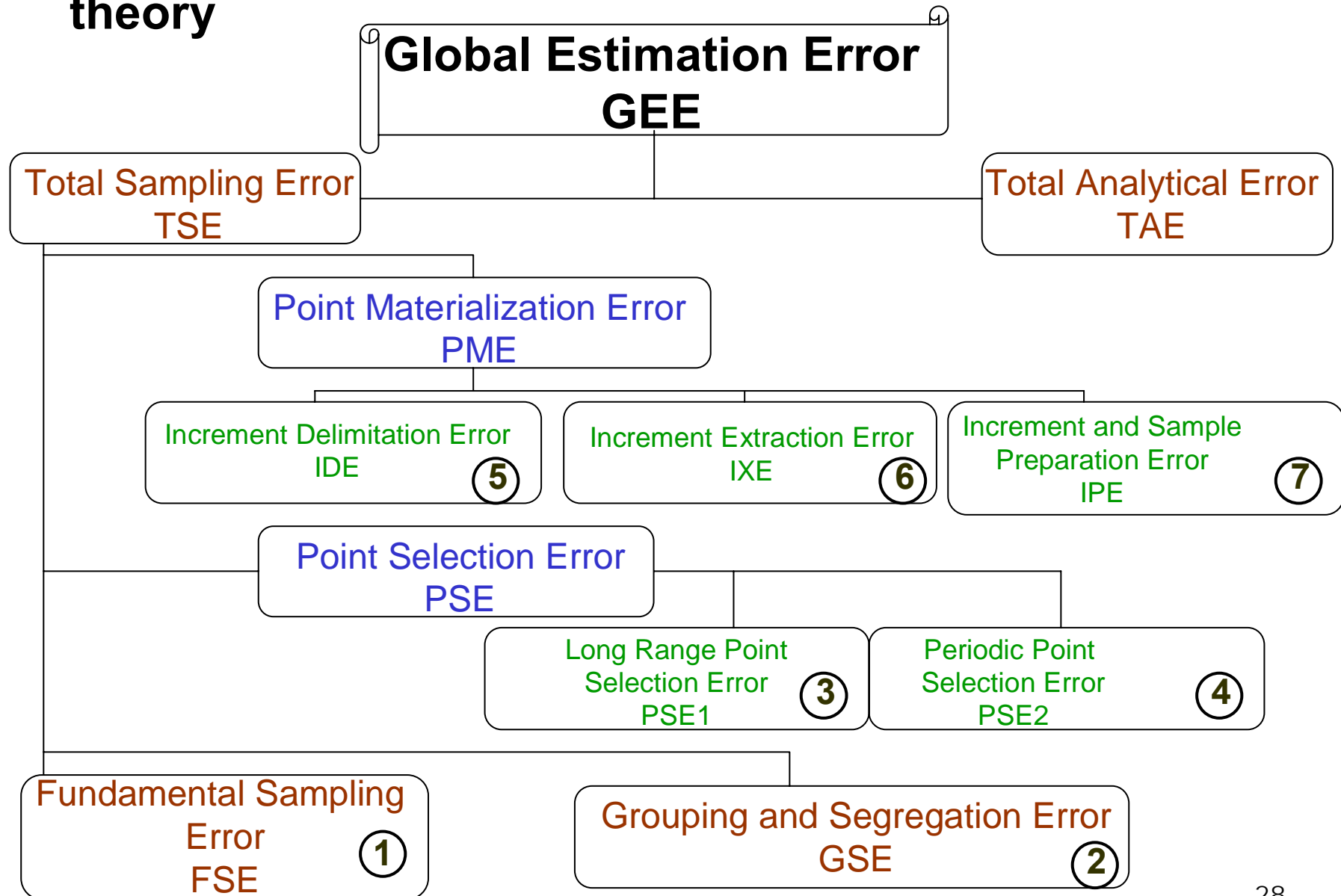
**Theory of
Sampling**

7 sampling errors

**It has a wide applicability but in particular for
particulate system**



Classification of sampling errors in Gy's sampling theory



Sampling



The primary goal of any sampling effort is to produce representative samples, defined as being accurate and precise.

Incorrect Sampling

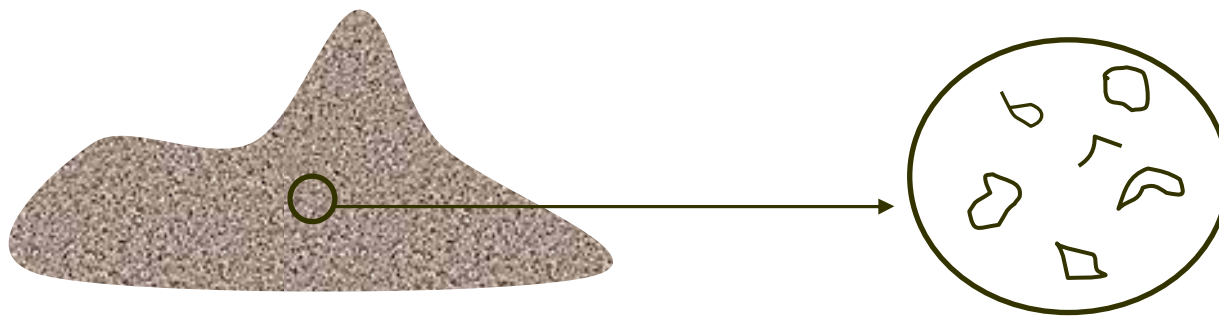
- ❑ **sampling equipment not suitable**
- ❑ **sample contamination**
- ❑ **analyte loss**
- ❑ **sample degradation**
- ❑ **gross error**

Correct Sampling

- ❑ **gives each item (particle, fragment) an equal and constant probability of being selected from the lot to be part of the sample.**
- ❑ **minimizes the errors that arise from an incorrect sampling**
- ❑ **allows a representative sample to be taken**

Heterogeneity -1

“Sampling errors arise first and last from the existence, in one form or another, of heterogeneity”!!!

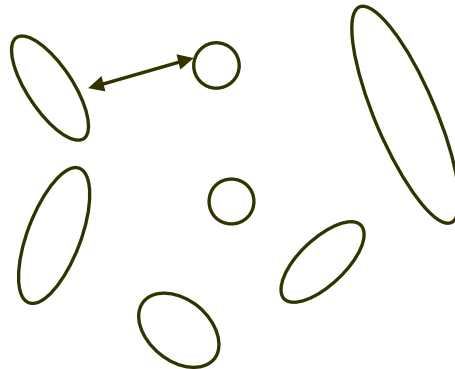


Homogeneity is an illusion

Heterogeneity -2

Constitution Heterogeneity (CH):

it refers to the fact that all natural materials are heterogeneous, that is, they consist of different types of particles (fragments, molecules, ions, grains).

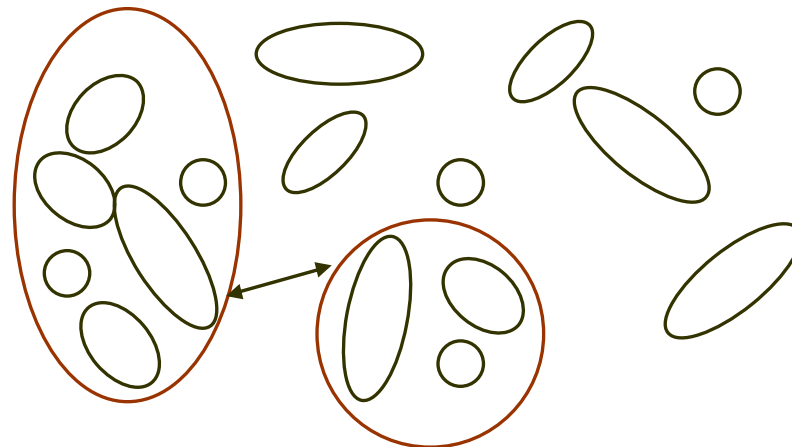


Heterogeneity -3

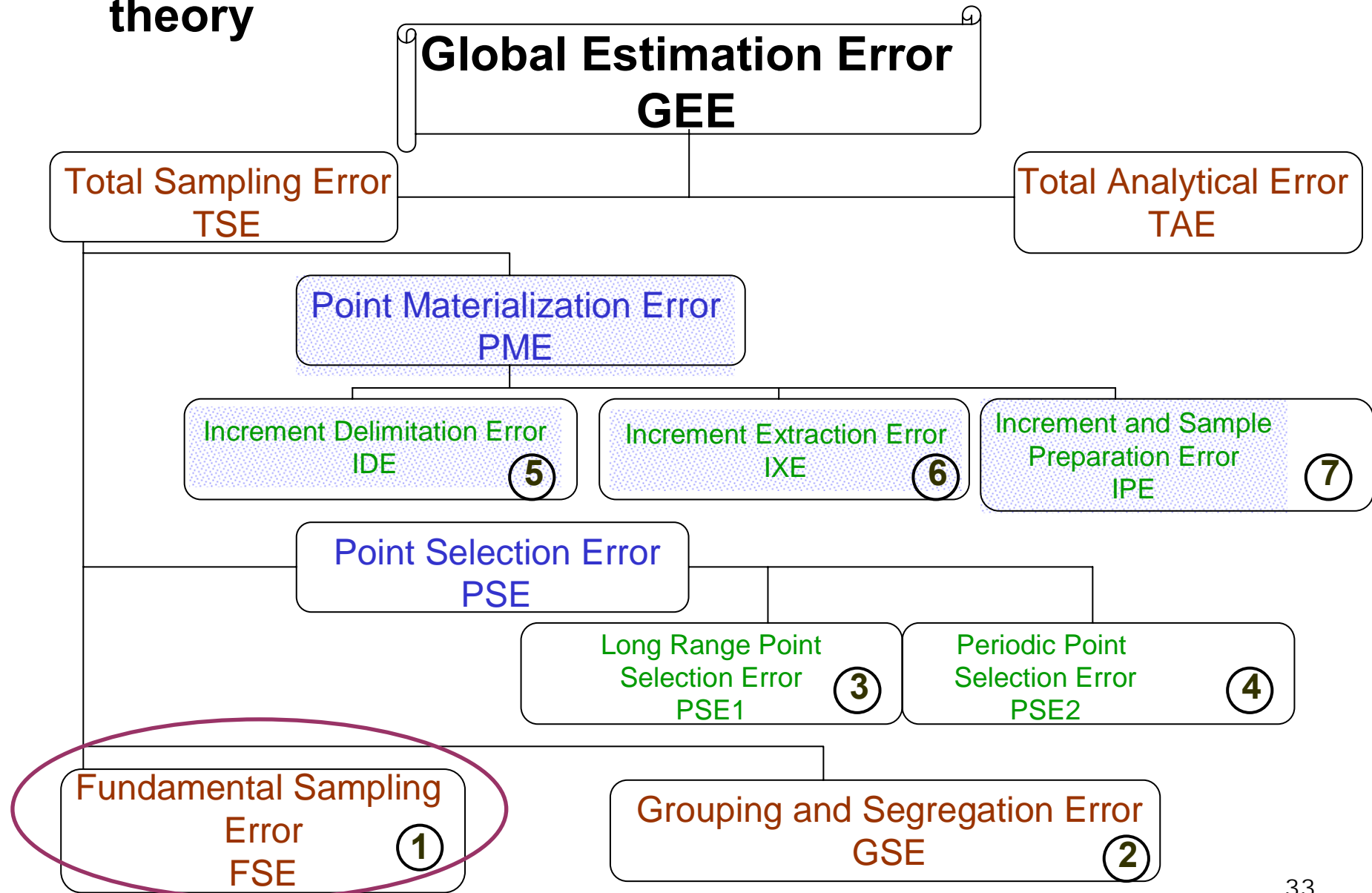
Distribution Heterogeneity (DH):

It is both a complement to and a function of the constitution heterogeneity.

It refers to the manner in which the component particles or fragments separate themselves into groups.



Classification of sampling errors in Gy's sampling theory





1

Fundamental Sampling Error (FSE)

- ④ The magnitude of this error is specifically related to the constitution heterogeneity.
- ④ It is the error that remains when a sampling operation is perfect
- ④ It occurs when a sample S is selected from a lot L
- ④ It continues to grow at each subsampling stage unless proper measures are employed
- ④ It is the only sampling error that can be estimated beforehand
- ④ It can be reduced by crushing and grinding.

$$S^2_{FSE} = \left(\frac{1}{M_S} - \frac{1}{M_L} \right) \underbrace{clfgd^3}_{\text{Sampling constant}}$$

Sampling constant ³⁴

Fundamental Sampling Error (FSE)

1

$$S^2_{FSE} = \left(\frac{1}{M_S} - \frac{1}{M_L} \right) clfgd^3$$

c = constitution factor (expressed in g/cm³)

l = liberation factor (dimensionless)

f = shape factor (dimensionless)

d = 95% upper limit of the size distribution (expressed in cm)

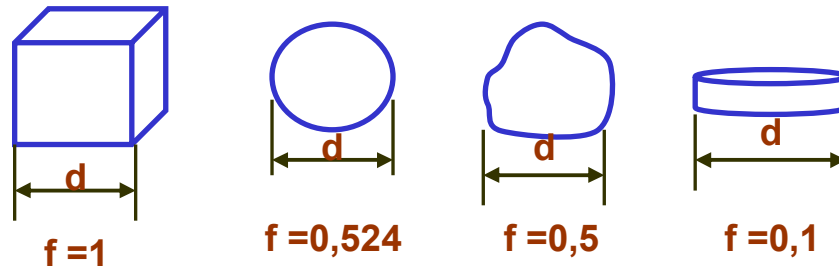
g = size distribution factor (dimensionless, it accounts for the fact that all fragments in the material are not identical in size d)



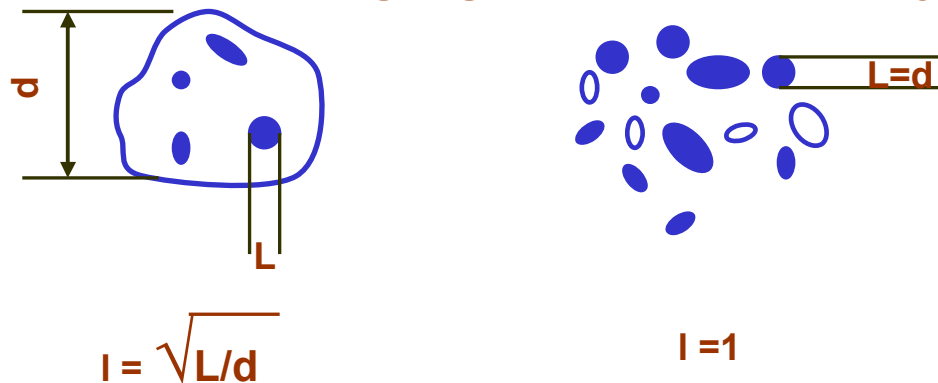
Fundamental Sampling Error (FSE)

1

Shape factor: coefficient of cubicity, it gives an idea of how different the shape of a particle is from the ideal cube whose side has the same length



Liberation factor: it takes into account that the constituent of interest and the matrix (gangue) are not perfectly separated from one another



- $l = 0,8$ for very heterogeneous material
- $l = 0,4$ for heterogeneous material
- $l = 0,2$ for average material
- $l = 0,1$ for homogeneous material
- $l = 0,05$ for very homogeneous material

Fundamental Sampling Error (FSE)

1

c = constitution factor or mineralogical factor =

the maximum degree of heterogeneity that the analyte can produce and is attained when the analyte is completely liberated

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

a_L = average concentration of the lot

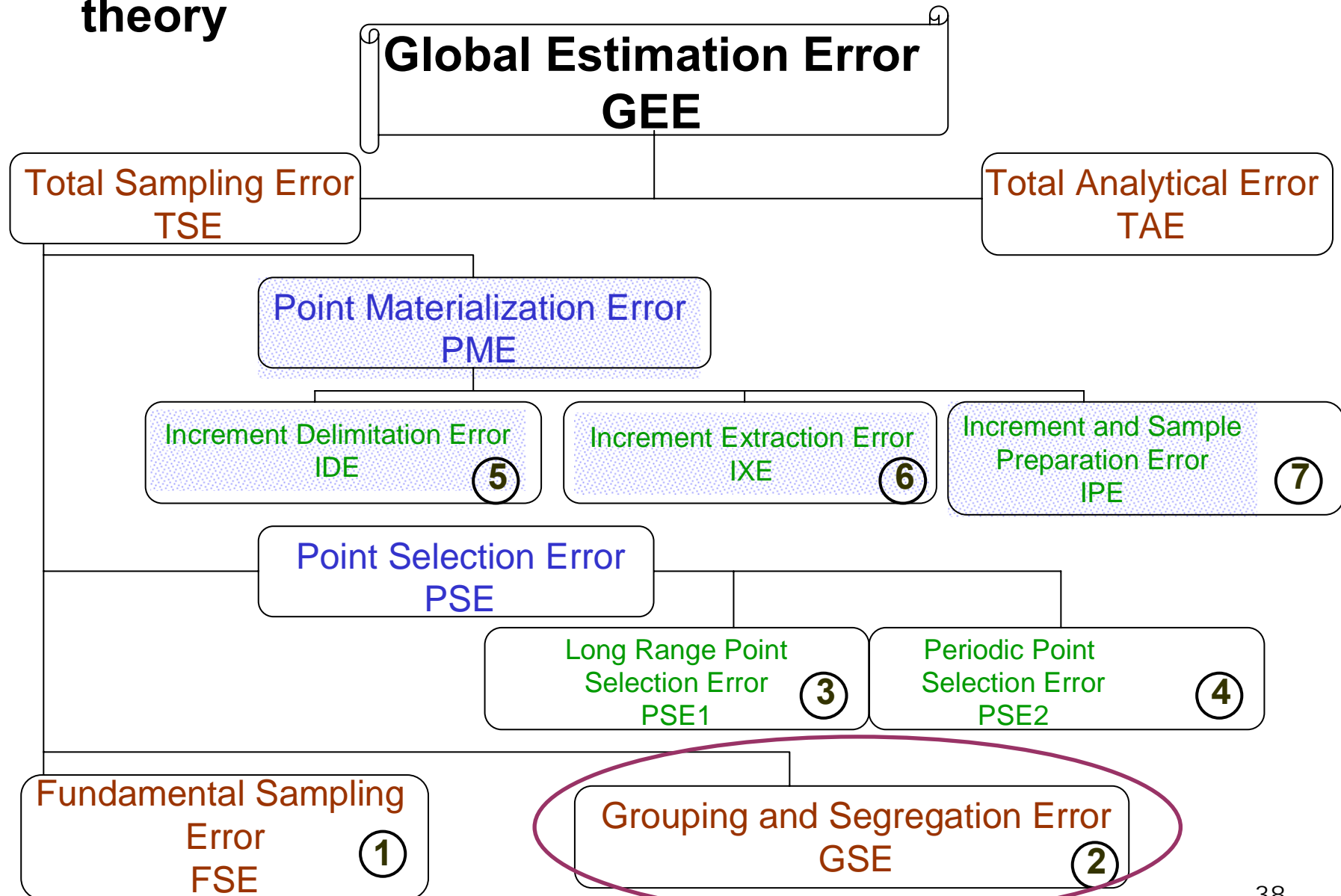
α = concentration of the analyte in the critical particles

ρ_c = density of the critical particles containing the analyte

ρ_m = density of the matrix



Classification of sampling errors in Gy's sampling theory



2

Grouping and Segregation Error (GSE)

The grouping and segregation error results from the distribution heterogeneity of the sampled material

$$S^2_{GSE} = \gamma_s \xi S^2_{FSE}$$

γ_s = grouping factor

ξ = segregation factor



segregation factor

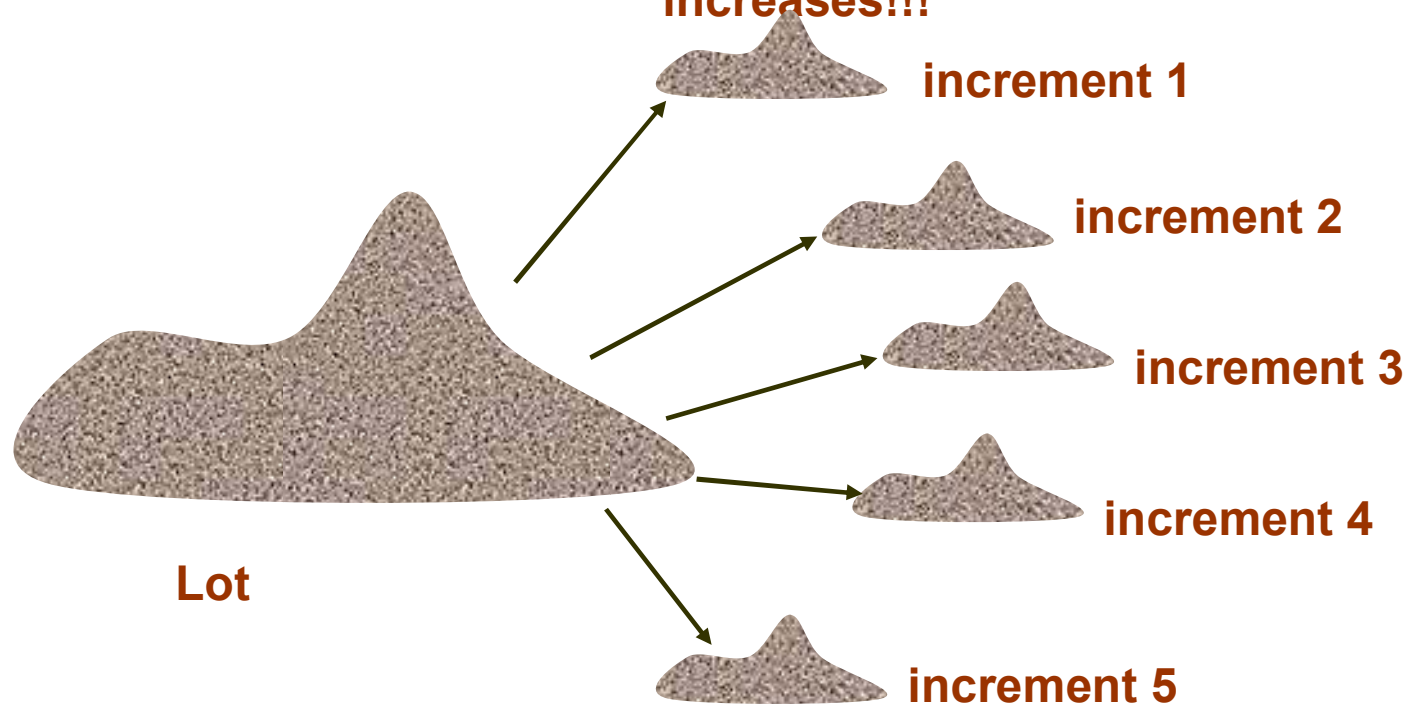
ξ = it localizes the degree of distribution of heterogeneity of a critical constituent in a given material between a natural minimum ($\xi=0$) and a maximum ($\xi=1$) equal to the constitution heterogeneity of the material



γ_s = it gives an indication of the probability that a particular fragments will be selected in a sample increment ,that is, it is a measure of random selectivity

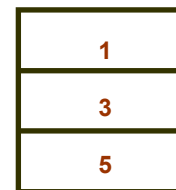
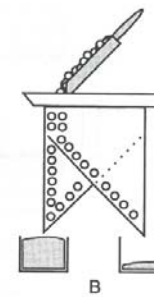
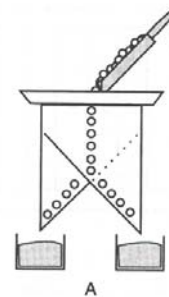
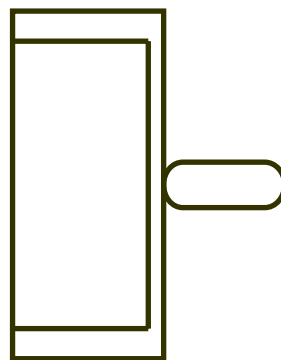
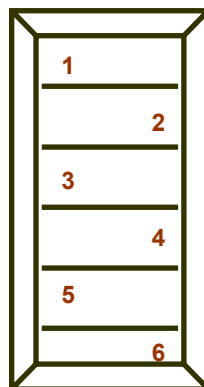
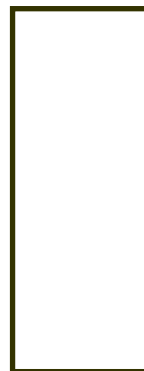
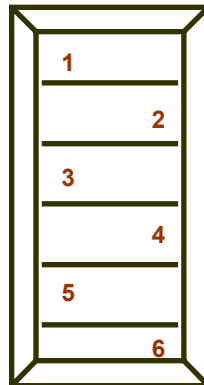
grouping factor

As the number of fragments in the increment increases, the grouping factor also increases!!!

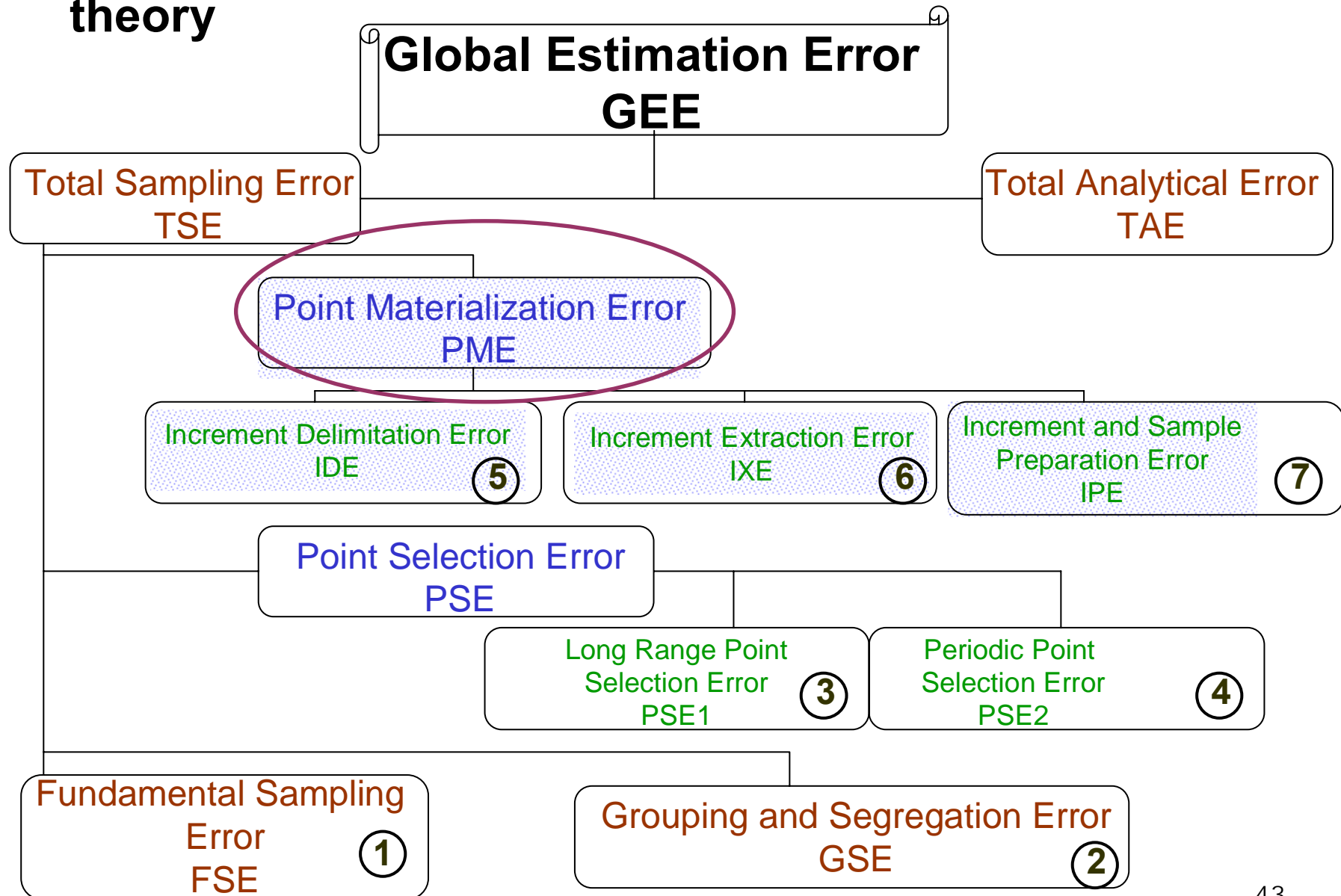


grouping factor

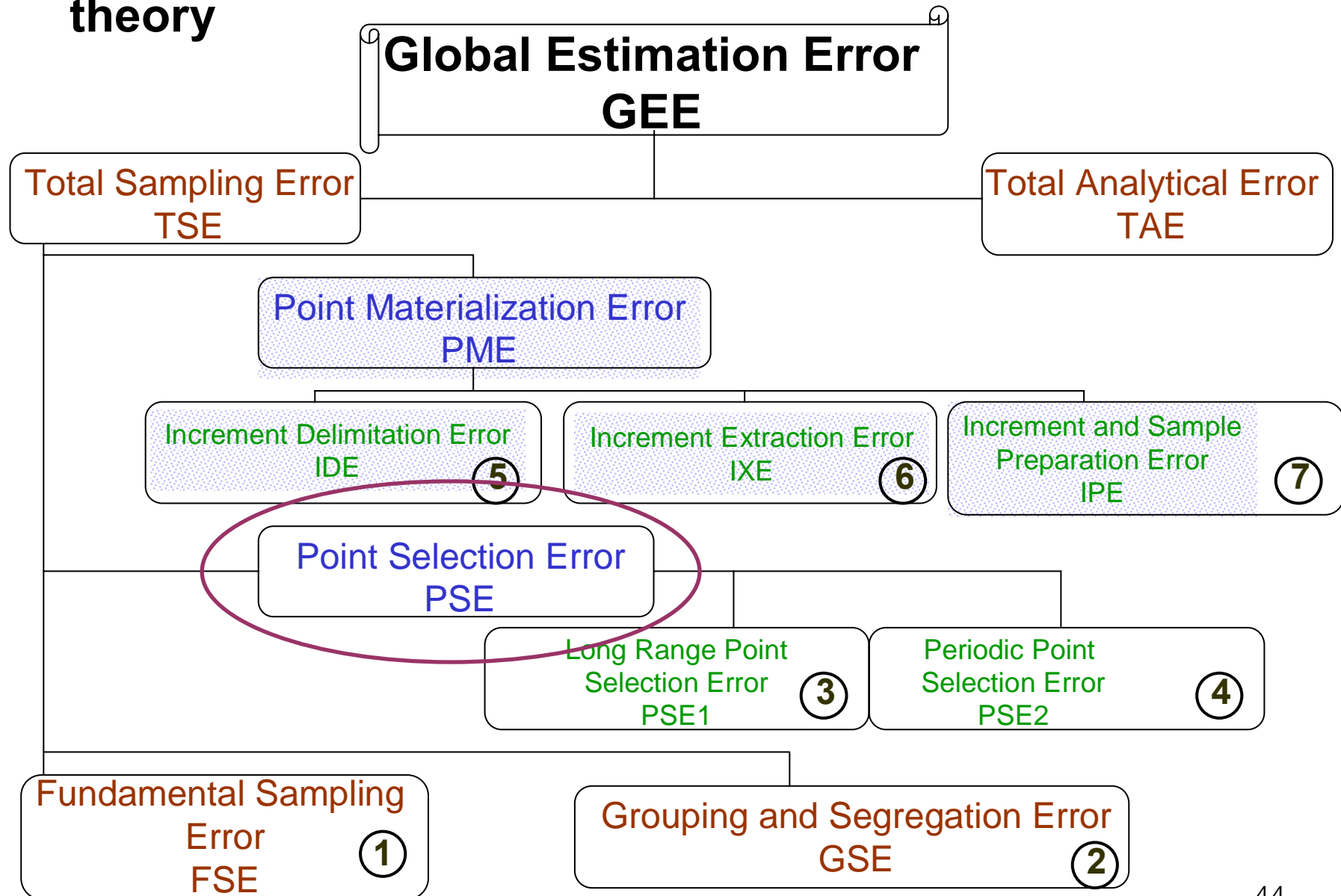
Fractional shoveling and riffling are two ways to achieve large number of increments to be collected, reducing the grouping factor



Classification of sampling errors in Gy's sampling theory

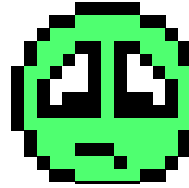


Classification of sampling errors in Gy's sampling theory

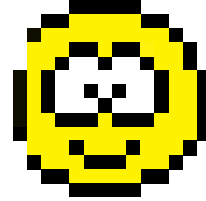




Limitations



- ✘ Requires a detailed knowledge of the matrix to be sampled (mineralogy, grain size, analyte speciation...)**
- ✘ Makes idealized assumptions about the make up of the material**
- ✘ Generic estimates may be general and not reflect the specific circumstances at the site**
- ✘ Systematic components in the sampling (sampling bias) is considered negligible by applying a correct sampling protocol**
- ✘ Not all of the sources of uncertainty might be identified, leading to an underestimate of the total uncertainty**



Advantages

- ✘ Has a wide applicability in particular for particulate system**
- ✘ Is the most complete and dated theory on sampling**
- ✘ The FSE can be estimated beforehand**
- ✘ It is possible to determine beforehand the sample size (mass) required to attain a desired relative precision**



Example: enzyme in chicken feed

SCOPE: to estimate the sampling uncertainty, applying Gy's sampling theory, of the protocol used for estimating the average content in each 25 kg bag employed to ship the product to customers. The analyte is an added enzyme ingredient in the feed. It is assumed in this example that no gross errors are present and that "incorrect sampling errors" are negligible.

MEASURAND				UNCERTAINTY ESTIMATION		
ANALYTE/ TECHNIQ UE	UNIT	SECTOR /MATRIX	SAMPLING TARGET	PURPOSE	DESIGN	STATISTICS
Enzyme / HPLC	% m/m	Food & Feed / Chicken	25 kg bag	Total uncertainty	Modelling with sampling theory of Gy	Summation of component variances



Example: enzyme in chicken feed

Scenario and sampling target: An enzyme product is used as an additive in chicken feed (density=0.67g/cm³)

Nominal concentration of the enzyme = 0.05% m/m

Density of the enzyme= 1.08 g/cm³

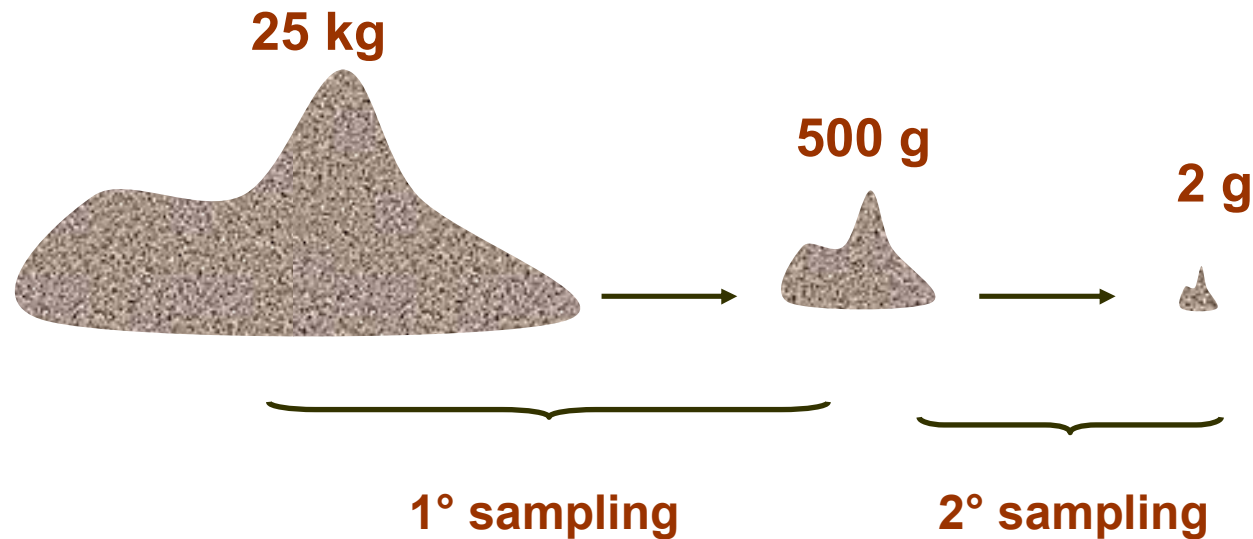
Characteristic particle size d=1.00 mm

Particle size distribution factor g=0.5

Sampling target = 25 kg bag employed to ship the product to customers

Example: enzyme in chicken feed

Sampling and analysis in the laboratory : the actual concentration of the enzyme in the sampling target (25 kg) is estimated by taking a 500 g primary sample from it. The material from the primary sample is ground to a particle size <0.5 mm. Then the enzyme is extracted from 2 g test portion by a suitable solvent and the concentration is determined by using liquid chromatography.



Example: enzyme in chicken feed

INPUT VALUES

1° SAMPLING

$M_1 = 500\text{g}$
 $M_{L1} = 25000\text{g}$
 $d_1 = 0,1\text{cm}$
 $g_1 = 0,5$

2° SAMPLING

$M_2 = 2\text{g}$
 $M_{L2} = 500\text{g}$
 $d_2 = 0,05\text{cm}$
 $g_2 = 0,25$

PARAMETERS

Sample size
Lot (sampling target) size
Particle size
Estimated size distribution
factor

$$S^2_{FSE} = \left(\frac{1}{M_S} - \frac{1}{M_L} \right) clfgd^3$$



Example: enzyme in chicken feed

INPUT VALUES

1° SAMPLING and 2° SAMPLING

$$f = 0,5$$

$$l = 1$$

PARAMETERS

Shape factor: default value for spheroidal particles

Liberation factor: the particles are liberated

$$S^2_{FSE} = \left(\frac{1}{M_S} - \frac{1}{M_L} \right) c l f g d^3$$



Example: enzyme in chicken feed

INPUT VALUES

1° SAMPLING and 2° SAMPLING

PARAMETERS

$$c = \frac{\left(1 - \frac{a_L}{\alpha}\right)}{\frac{a_L}{\alpha}} \rho_c + \left(1 - \frac{a_L}{\alpha}\right) \rho_m = 2160 \text{ g cm}^{-3}$$

Mineralogical factor



a_L = mean concentration of enzyme in the lot = 0,05%

α = enzyme concentration in enzyme particles = 100%

ρ_c = density of the enzyme particles = 1,08 g/cm³

ρ_m = density of matrix particles = 0,67 g/cm³



Example: enzyme in chicken feed

$$S_{FSE1} = 3,3\%$$

$$S_{FSE2} = 13\%$$

$$S_{\text{sampling}} = \sqrt{\sum S_{FSE_i}^2}$$

$$S_{\text{sampling}} = 13,4\%$$

Measurement uncertainty		
SAMPLING	ANALYSIS	TOTAL
26.8%	10.0%	28.6%



WITH COVERAGE FACTOR OF 2 (95% CONFIDENCE)

**Uncertainties associated with systematic effects are excluded,
such as analytical bias**



Example:

enzyme in chicken feed COMMENTS

- The largest source of uncertainty in the whole measurement process is identified as that generated in preparing the test portion (2g) for the extraction of the enzyme
- No additional allowance has been made for uncertainties associated with the systematic effects during analysis
- Incorrect sampling errors (and sampling bias) have been assumed to be negligible
- Measurement of the enzyme concentration reported for each 25 kg bag should have an attached uncertainty of 28.6% of the concentration value.

EMPIRICAL APPROACH (Duplicate method) VS MODELLING APPROACH (Gy's theory)

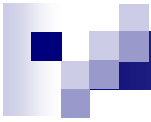


Sampling theory of Gy

- ❖ Has a wide applicability in particular for particulate system
- ❖ Requires a limited number of samples to be collected from the lot
- ❖ Requires a detailed knowledge of the matrix to be sampled (mineralogy, grain size, analyte speciation...)
- ❖ The FSE can be estimated beforehand
- ❖ It is possible to determine beforehand the sample size (mass) required to attain a desired relative precision

Duplicate method

- ❖ Has the widest applicability to the broadest range of measurement systems and applications (e.g. gaseous, liquid and solid)
- ❖ Requires a large number of samples to be collected from the lot
- ❖ Doesn't require previous knowledge of the matrix investigated



Thank you

