KHE Consulting

Theory and Practice of Representative Sampling

Why is sampling the critical success factor before analysis and decision making?

- for the company; for the customer; for the scientist; for the technician?
- in science, technology, industry; in the analytical laboratory
- for compliance; for safety; for society?
- for the seller; for the buyer; for the middleman, for the arbiter ?

Workshop documentation and further background literature - a primer syllabus

1) **DS3077 (2013) Representative sampling – Horizontal Standard**

2) Esbensen, K.H, Wagner, C. (2014) **Why we need the Theory of Sampling**. *The Analytical Scientist*

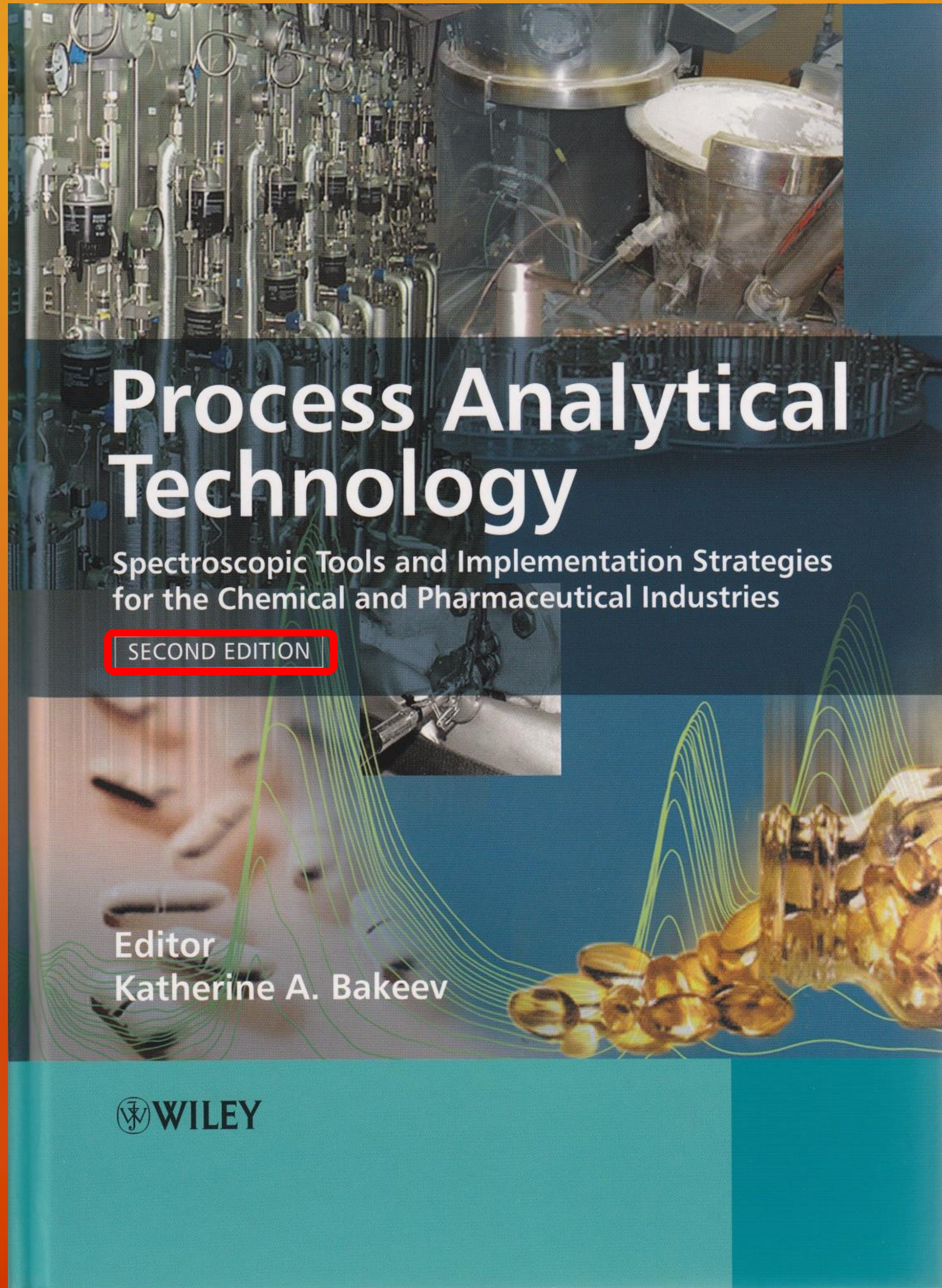
3) Esbensen, K.H, Wagner, C. (2014) **Theory of Sampling (TOS) versus Measurement Uncertainty (MU) – a call for integration**. *Trends in Analytical Chemistry (TrAC)*

4) Esbensen, K. H. Romañach, R. J. Román-Ospino, A. D.(2018) **Theory of Sampling (TOS): A Necessary and Sufficient Guarantee for Reliable Multivariate Data Analysis in Pharma ceutical Manufacturing** in *Multivariate Analysis in the Pharmaceutical Industry*, Ferreira, Menezes, Tobyn, M., (Eds.) pp 53-91. Academic Press ISBN 978-0-12-811065-2

5) Minnitt, R.C.A. & Esbensen, K.H. (2017) **Pierre Gy's development of the Theory of Sampling: a retrospective summary with a didactic tutorial on quantitative sampling of one-dimensional lots.** TOS Forum **7,** p. 7-19. doi: 10.1255/tosf.96

6) Esbensen, K.H, Román-Ospino, A,D, Sanchez, A, Romañach, R.J. (2016). **Adequacy and verifiability of pharmaceutical mixtures and dose units by variographic analysis – A call for a regulatory paradigm shift.** Intl. Jour. Pharmaceutics, vol. 499, p. 156-174.

7) Esbensen, K.H, Paoletti, C, Theix, N. (2015) (Eds) Journal AOAC International, Special Guest Editor Section (SGE): pp. 249-320 **Sampling for Food and Feed Materials (Open Access)**


Process Analytical Technology
Spectroscopic Tools and Implementation Strategies for the Chemical and Pharmaceutical Industries
SECOND EDITION
Editor
Katherine A. Bakeev
WILEY

"PROCESS SAMPLING (TOS) – the missing link in PAT"

Kim H. Esbensen & P. Paasch-Mortensen

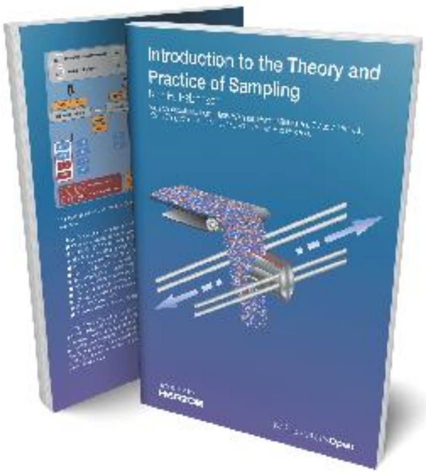
Bakeev, K. (Ed.)
PROCESS ANALYTICAL TECHNOLOGY, 2.nd Ed.(*2009*)
(chapter 3)

Introduction to the Theory and Practice of Sampling

NEW BOOK

Kim H. Esbensen

with contributions from Claas Wagner, Pentti Minkkinen, Claudia Paoletti, Karin Engström, Martin Lischka and Jørgen Riis Pedersen



This book presents the Theory of Sampling (TOS) for all readers and audiences starting from level zero. The TOS is presented in a novel didactic framework without excessive background mathematics and statistics that often scare newcomers away. The overall objective is to present a unifying conceptual framework within which all the TOS' principles, unit operations and sampling error management rules can be understood in the easiest manner possible. This book will make the reader able to start sampling in an effective manner right away, but is also intended to inspire to further skills building and self-study. It contains a wealth of key references.

Bibliographic detail
Publication: summer 2019
ISBN: 978-1-906715-29-8
Pages: approximately 280 pp.
Publisher: IM Publications Open

Workshop att.s - a signed copy ;-)

Find out more and pre-order now from

https://www.impopen.com/sampling

Sampling - most common understandings

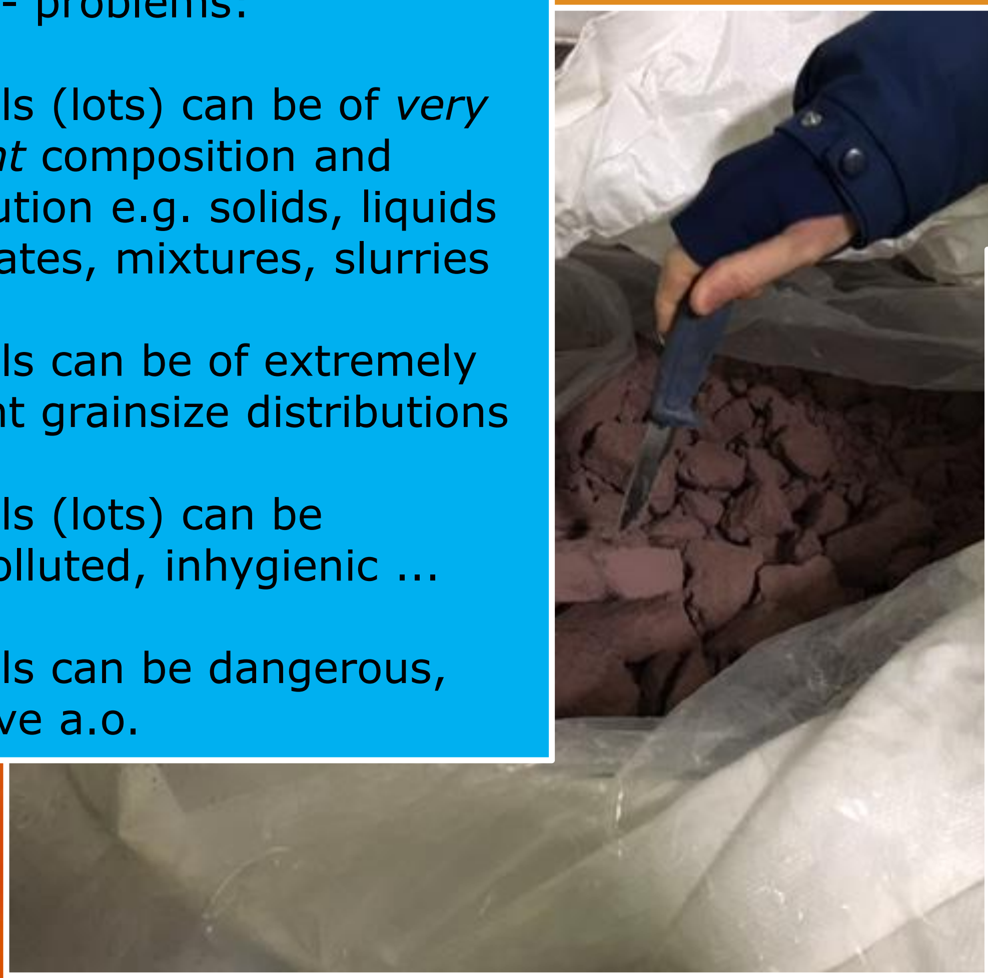
Sampling - priorities:

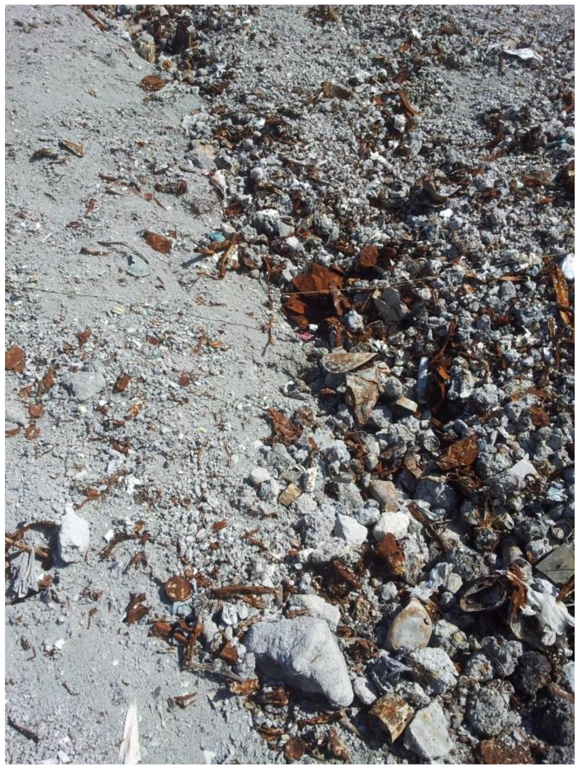
1. Sampling method, -plan
2. Equipment, containers, ID-tags, logbook, time
3. Economics, effectivity, logistics, ergonomics ...

Sampling ... there are always "problems"

Sampling - problems:

4. Materials (lots) can be of *very different* composition and constitution e.g. solids, liquids aggregates, mixtures, slurries
5. Materials can be of extremely different grainsize distributions
6. Materials (lots) can be toxic,polluted, inhygienic ...
7. Materials can be dangerous, explosive a.o.





Sampling – more problems:

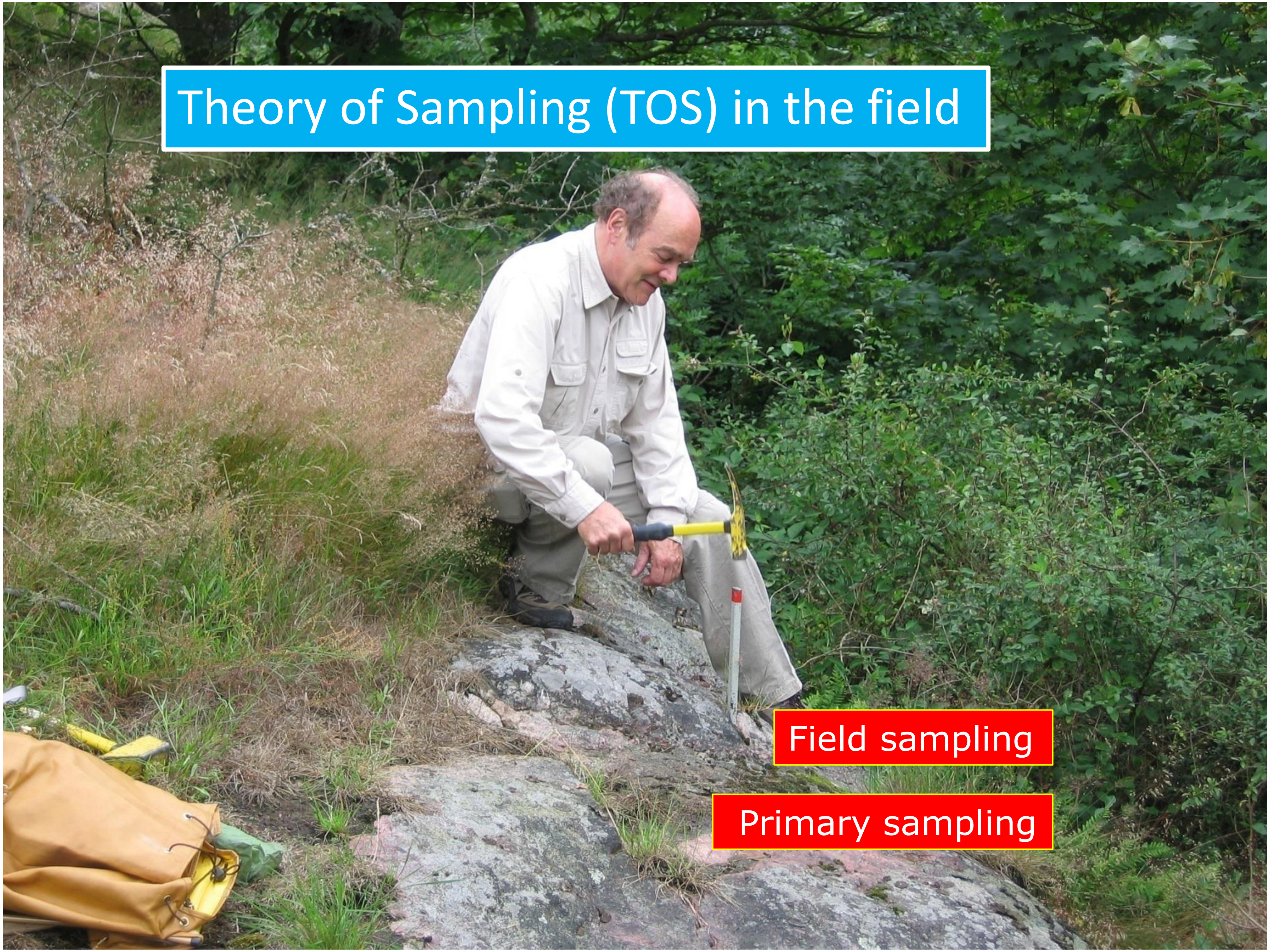
8. Lots are of vastly different sizes ...

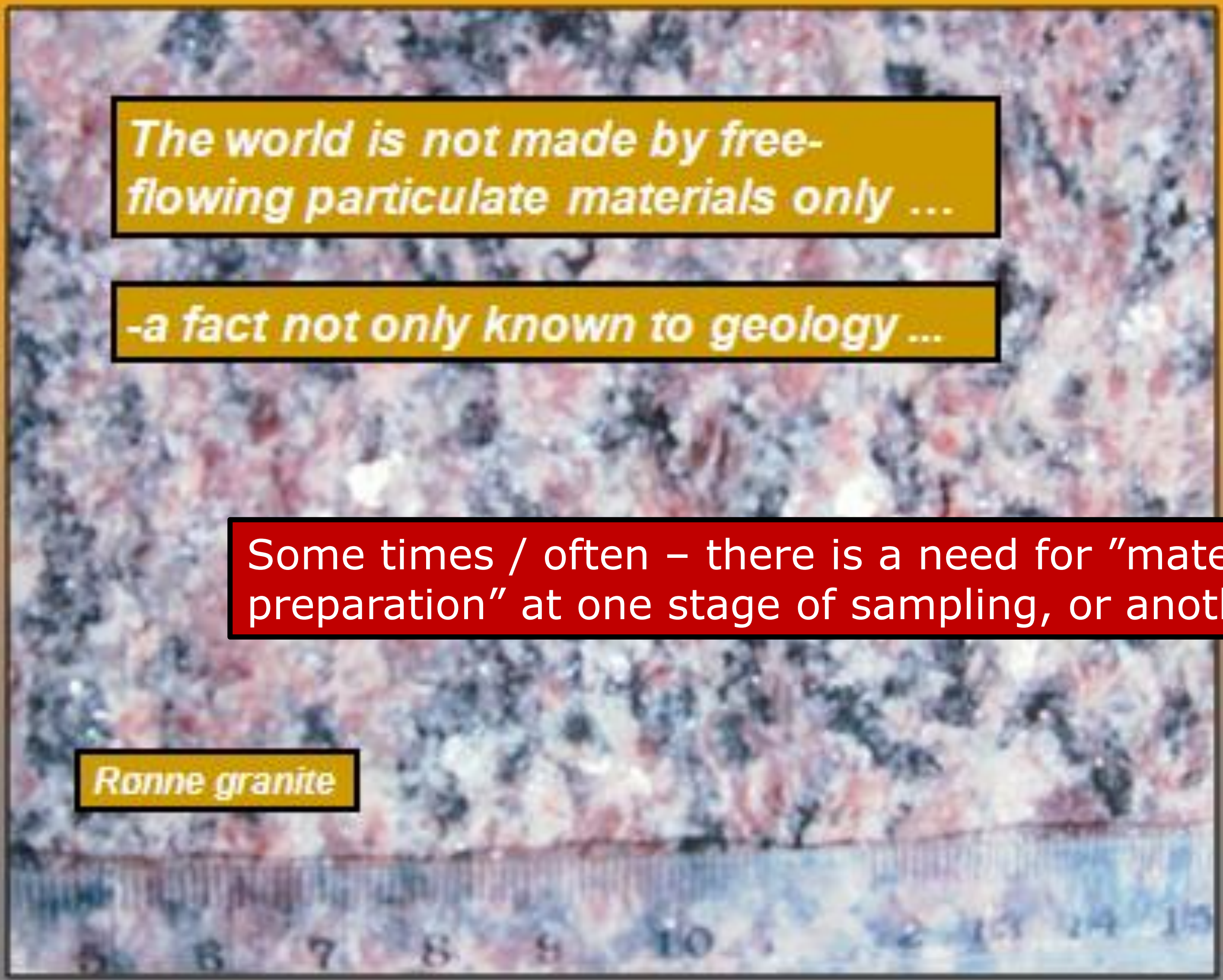
9. Lots can be of extremely different accessibility ...

Still - everybody's looking for <u>simplicity</u> (because this is complex (enough)
- but what kind of simplicity?

i) One / a few sampling procedure fits all (cases)?
ii) One / a few types of equipment fits all (cases)?
iii) Rely on the Original Equipment Manufacturers (OEMs)?

Theory of Sampling (TOS) in the field





Some times / often – there is a need for ”material preparation” at one stage of sampling, or another

Sampling (TOS) - *unifying* principles & procedures

Sampling priorities (TOS)

1. **Representativity** (1)
2. **Appropriate procedures and equipment** (2)
3. Economics, effectivity, logistics, ergonomics (3)

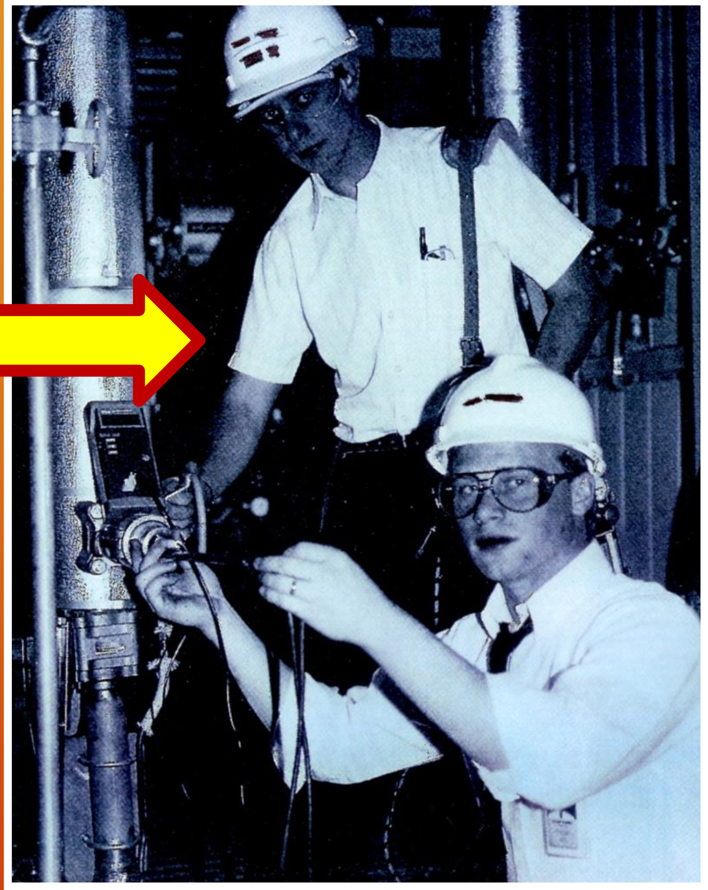
TOS – main elements …

- H terogeneity (compositional *vs.* distributional het.)
- Lot sionality & Lot size (lot mass)
- Stationar oving lots (process sampling)
- A million differe erial systems – to be sampled under a million differ nditions – Que Faire?
- Systematics of sampling:
- Unifying principles, unit Operation & 4SUO)
- & Sampling Error Management Rules (SE

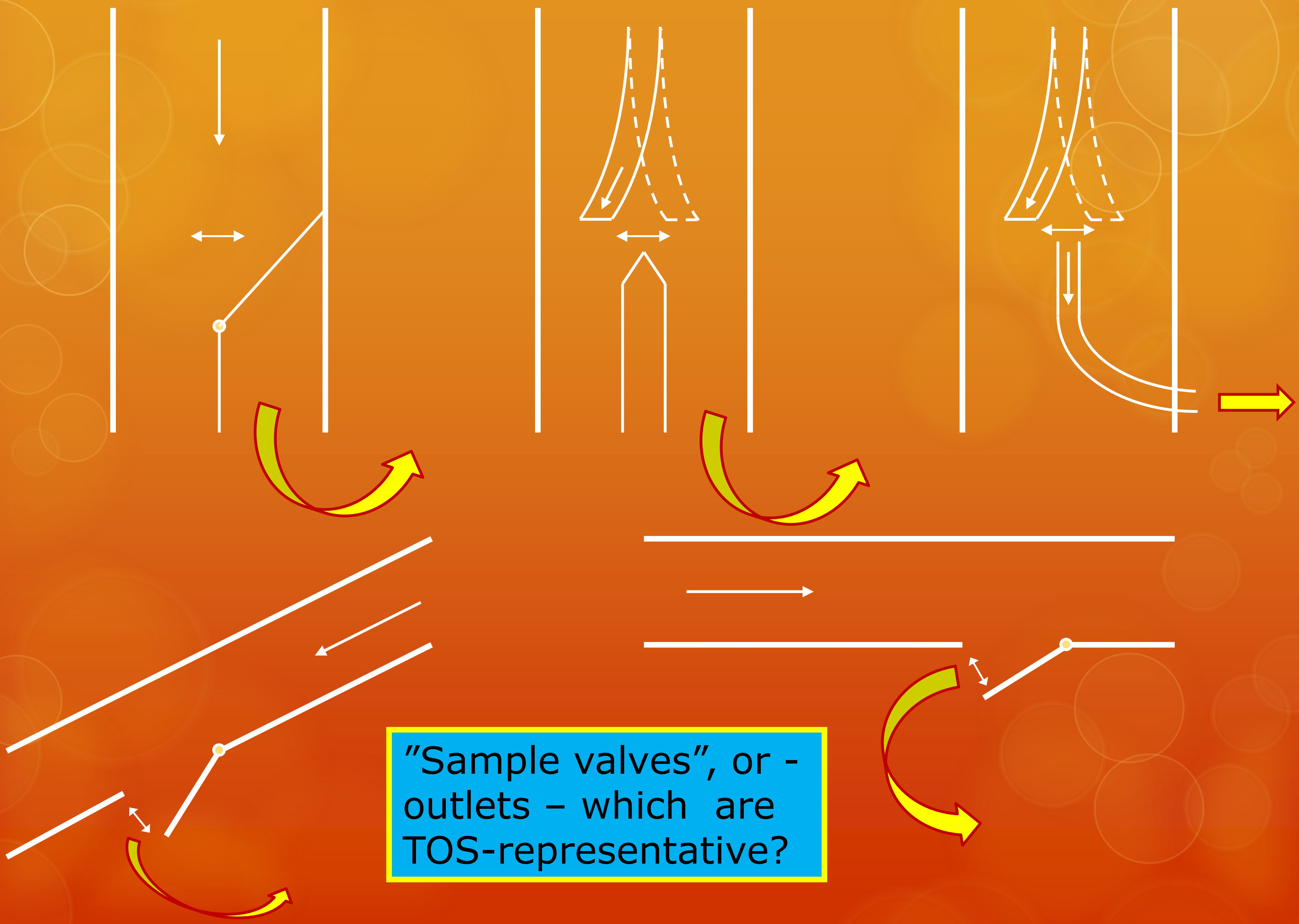
- Sampling Hall of Fame (Sampling Hall of Shame)

Please leave all preconcieved notions by the door step!

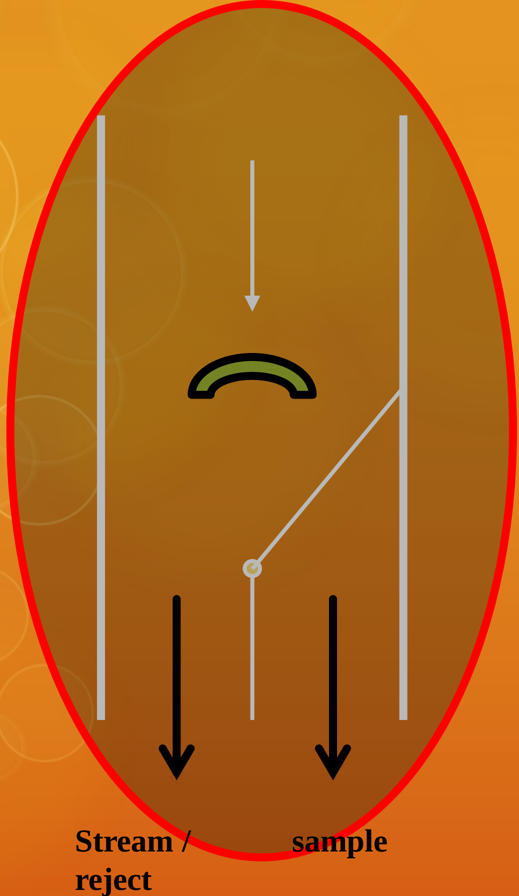
TOS agenda: complete DUALITY



Identical "sampling problems" with or without sensor technologies (PAT) ..

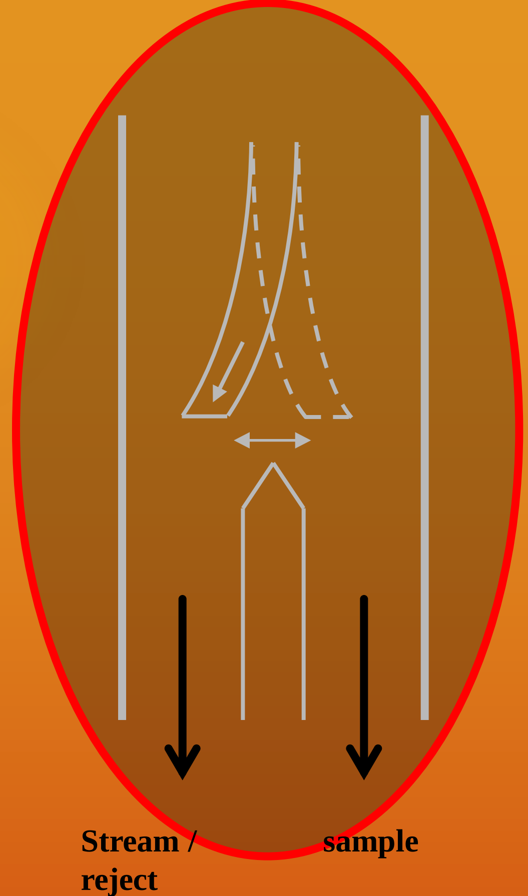


”Sample valves”, or -outlets – which are TOS-representative?



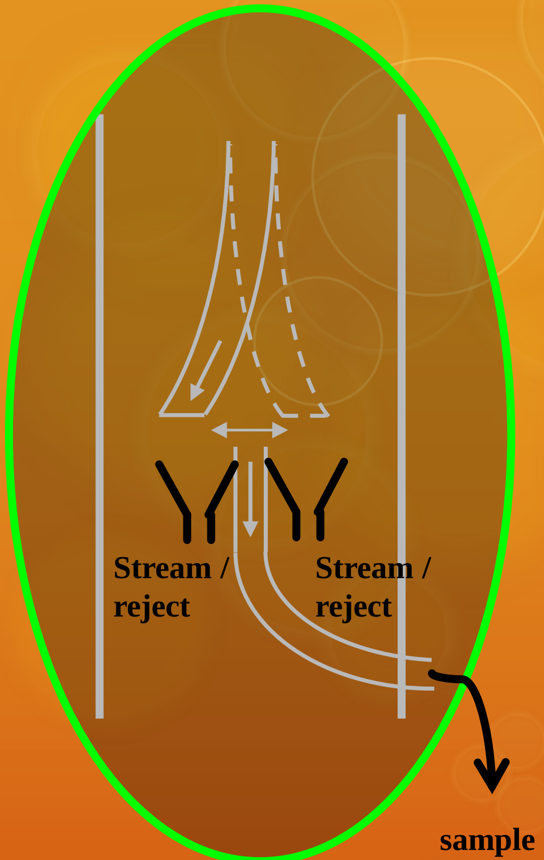
Flap valve design

1.



”Inversed” flap valve

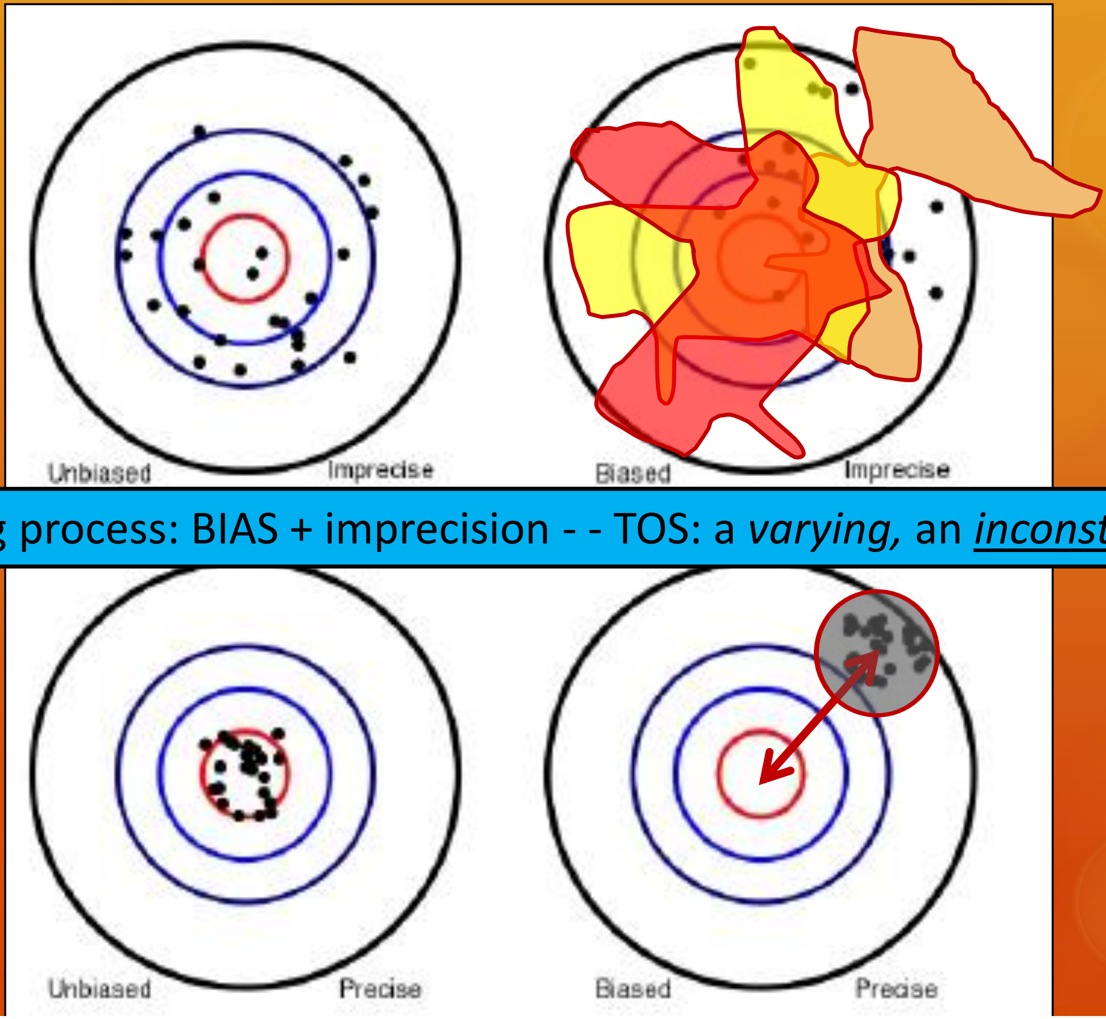
2.



In-line outtake valve

3.

Critical distinction between analysis (*sensu strictu*) – and sampling_plus_analysis! CRITICAL ISSUE !

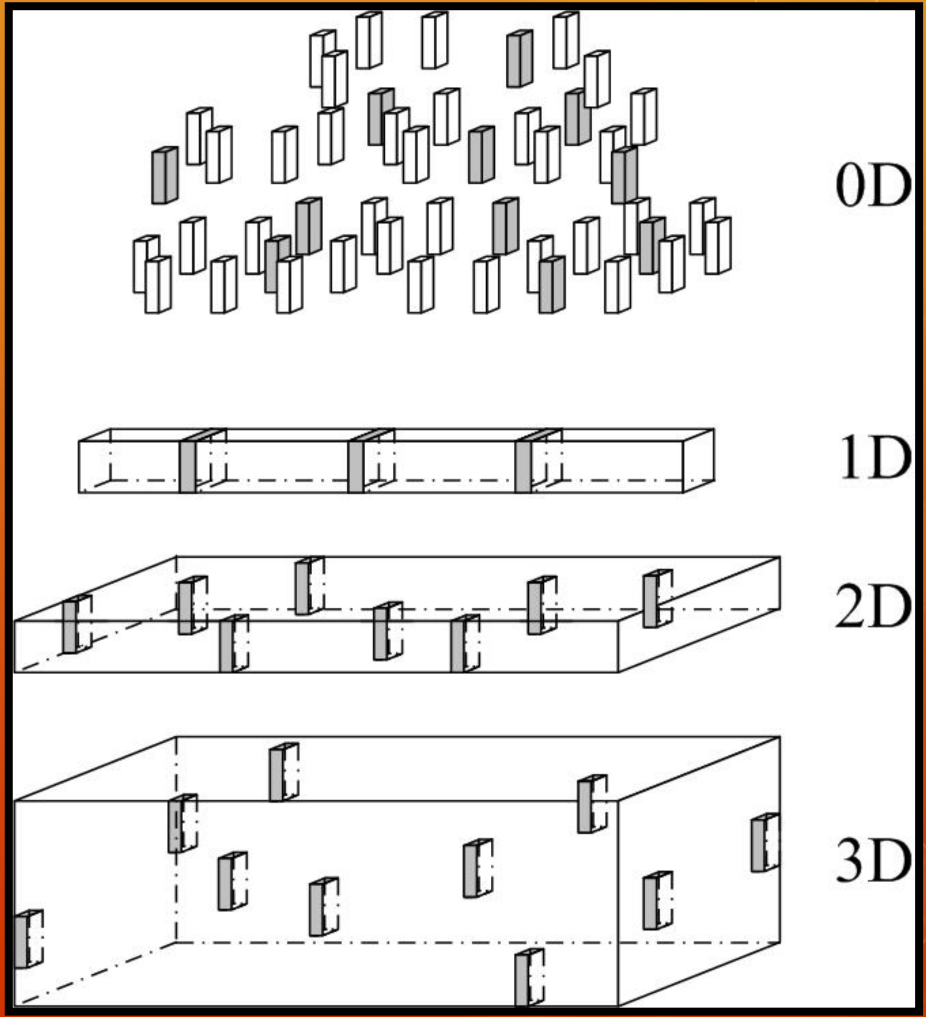


Sampling process: BIAS + imprecision - - TOS: a *varying,* an *inconstant* bias!

Analytical process: bias + imprecision (statistical concept: a constant bias)

Sampling (TOS) - *unifying* principles & procedures

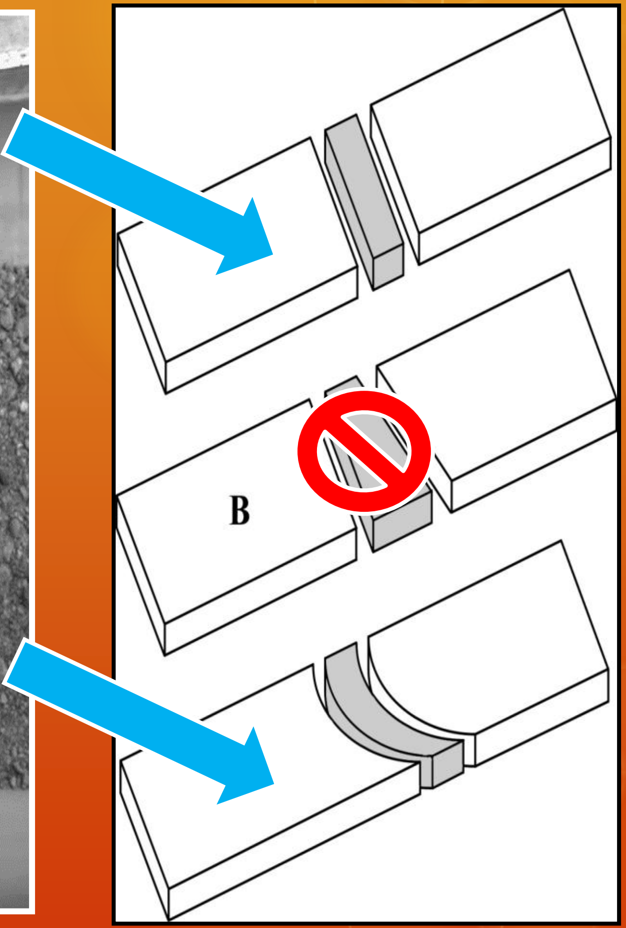
Lot Dimensionality

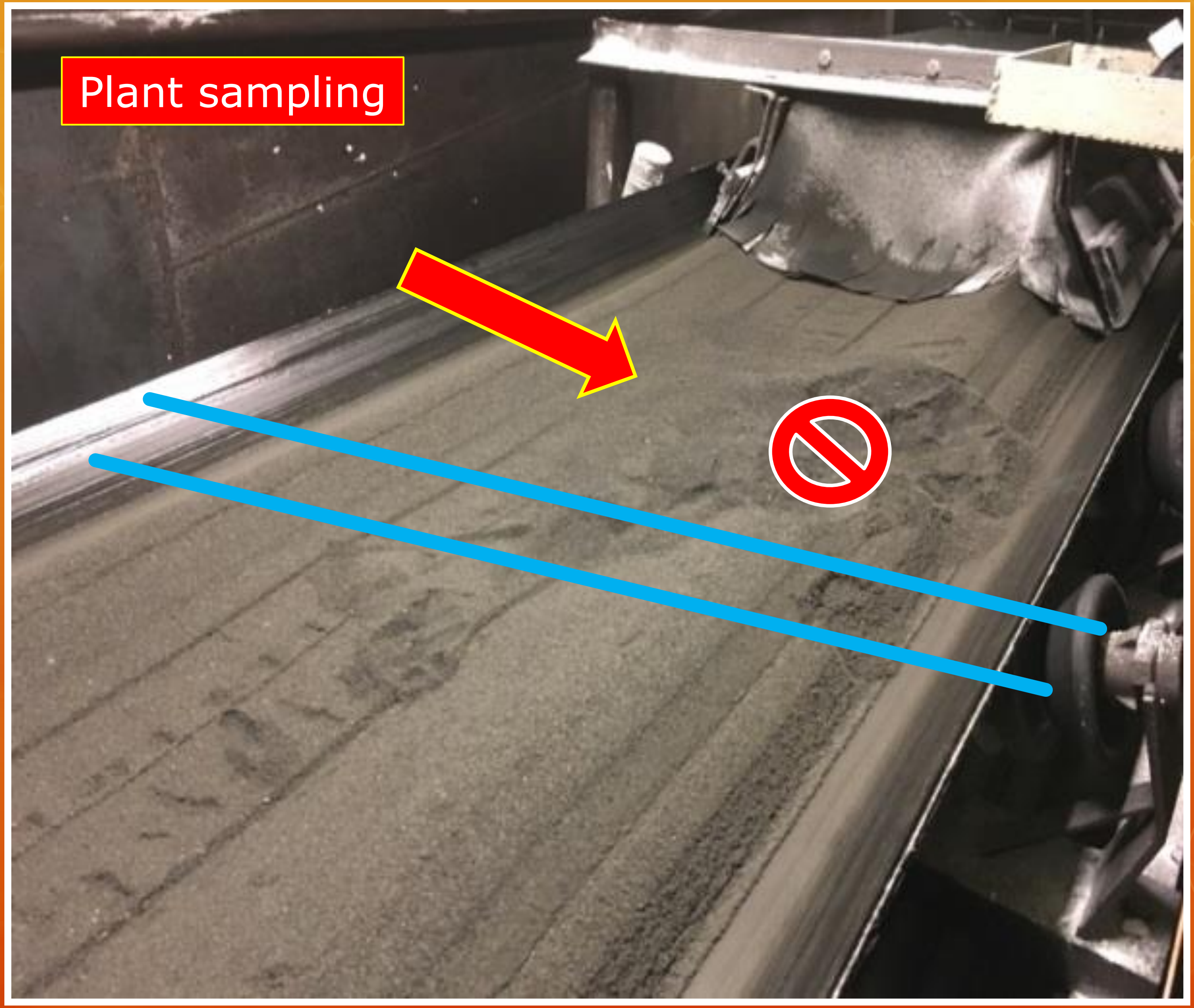


Primary sampling

Process sampling

Plant sampling




Plant sampling

doi: 10.1255/tosf.103

WHAT is wrong with this sampler?

A photographic "drive-by shooting"

It is quite some time this column was featured last—not for want of suitable "items", but rather due to a too-busy schedule. Recently, however, the following item was brought to the attention of the Editor. The photographic documentation below is the result of a photographic "drive-by shooting" from a public road.

Much can be said about this accidental sighting. The positive aspect always comes first. This *could* very well be the most inexpensive, fully automated "sampling solution" on record; so a big A+ for these aspects ;-)

But this is not all, of course. This also *could be* the most *unlucky* amateur sampler design ever (but one can never be sure). As always, what is important here is not *where* the photos were taken, or *which* company is currently making use of this unfortunate sampler, but only: "WHAT is wrong with this sampler?" Please remember, this column is published exclusively for TOS educational purposes.

The Editor presented these photos to a series of international sampling experts, asking for immediate comments, which follow:

- "My heartfelt response would be unpublishable. This reminds me of a night at the Crown Casino—pure gambling."
- "Wheel of Fortune"—there could not be a more apt name for this contraption.
- "Fascinating... but is it a children's toy?"
- "I count at least three Incorrect Sampling Errors (ISE)—most impressive."
- "A thoroughly biased primary sampling, or rather 'specimenting'."
- "...and also: what about the sub-sampling of the primary material cone?"
- "As the consultant said to the client: what number do you want, pick a number any number you'd like."
- "This is one of the worst samplers I have seen. It's a joke, sadly."
- "The managers get a result, possible with high analytical precision, but they do not get accuracy."
- "This is yet another example showing the critical need for education on correct sampling."
- "This sampler performs every possible INCREMENT MATERIALISATION ERROR instead of proper sampling."

Q.E.D.

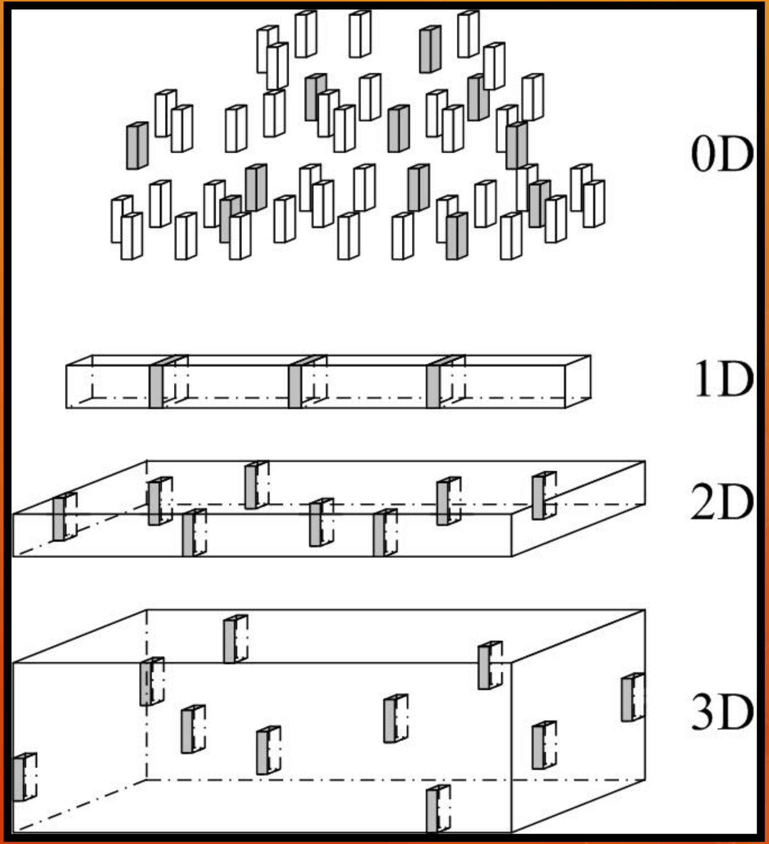
Figure 1. What caught the eye... (Photo: the Editor).

Figure 2. Upon closer inspection... The TOS-mind boggles... One is reminded of a Monty Python sketch, in which an erstwhile architect declares: "... passing by the *rotating knives*" (Photo: the Editor).

Figure 3. A-ha, the full picture—a two-step sampling solution. Sub-sampling of the primary "sample cone" is also needed (Photo: the Editor).

Lot Dimensionality (definition via practical *increments*)

Increments (high-lighted in grey)

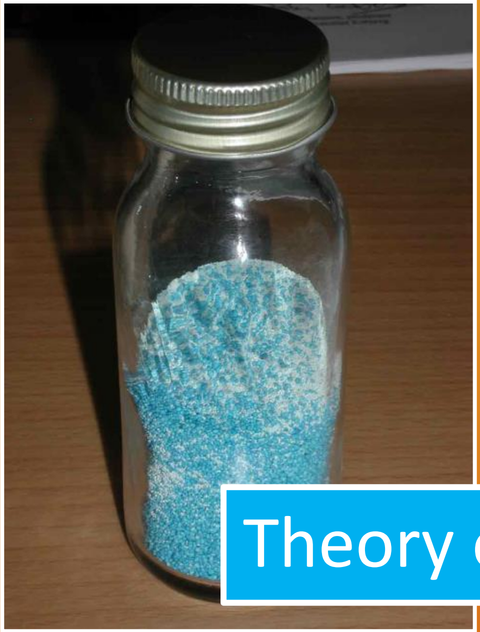


No correlation exists between increments. Total access to the complete lot volume. Increments can be picked at will without untoward effort or difficulty (practical def.)

Increments cover *two* lot dimensions, e.g. a cross-stream planar-parallel “slice”

Increments cover *one* lot dimension, e.g. a drill-core; a depth-profile

Increments do <u>not</u> cover <u>any</u> of the lot dimensions, e.g. a “depth sample”

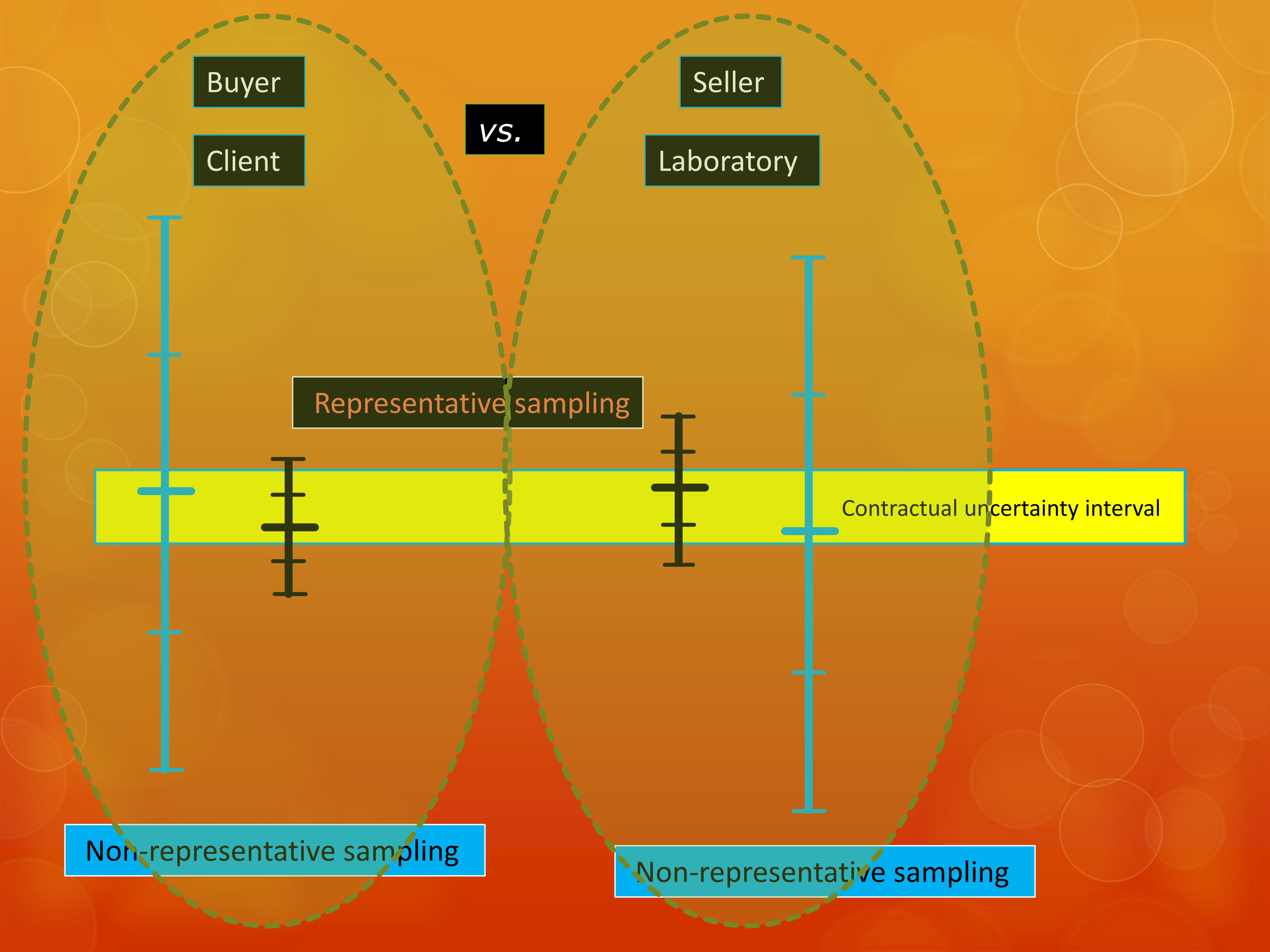


Theory of Sampling (TOS) in the laboratory

Theory of Sampling (TOS) in the laboratory
Not just sampling – but HOW TO sample??

TOS in the analytical laboratory

The ”Ingamells splitter”



Buyer
Client
vs.
Seller
Laboratory
Representative sampling
Contractual uncertainty interval
Non-representative sampling
Non-representative sampling

“TOS - difficult to understand?”

Heterogeneity

Homogeneity

Variography

INE

IDE

FSE

IEE

GSE

IPE

PIE1

PIE2

PIE3

IWE

Poisson Process(es)

KHE Consulting

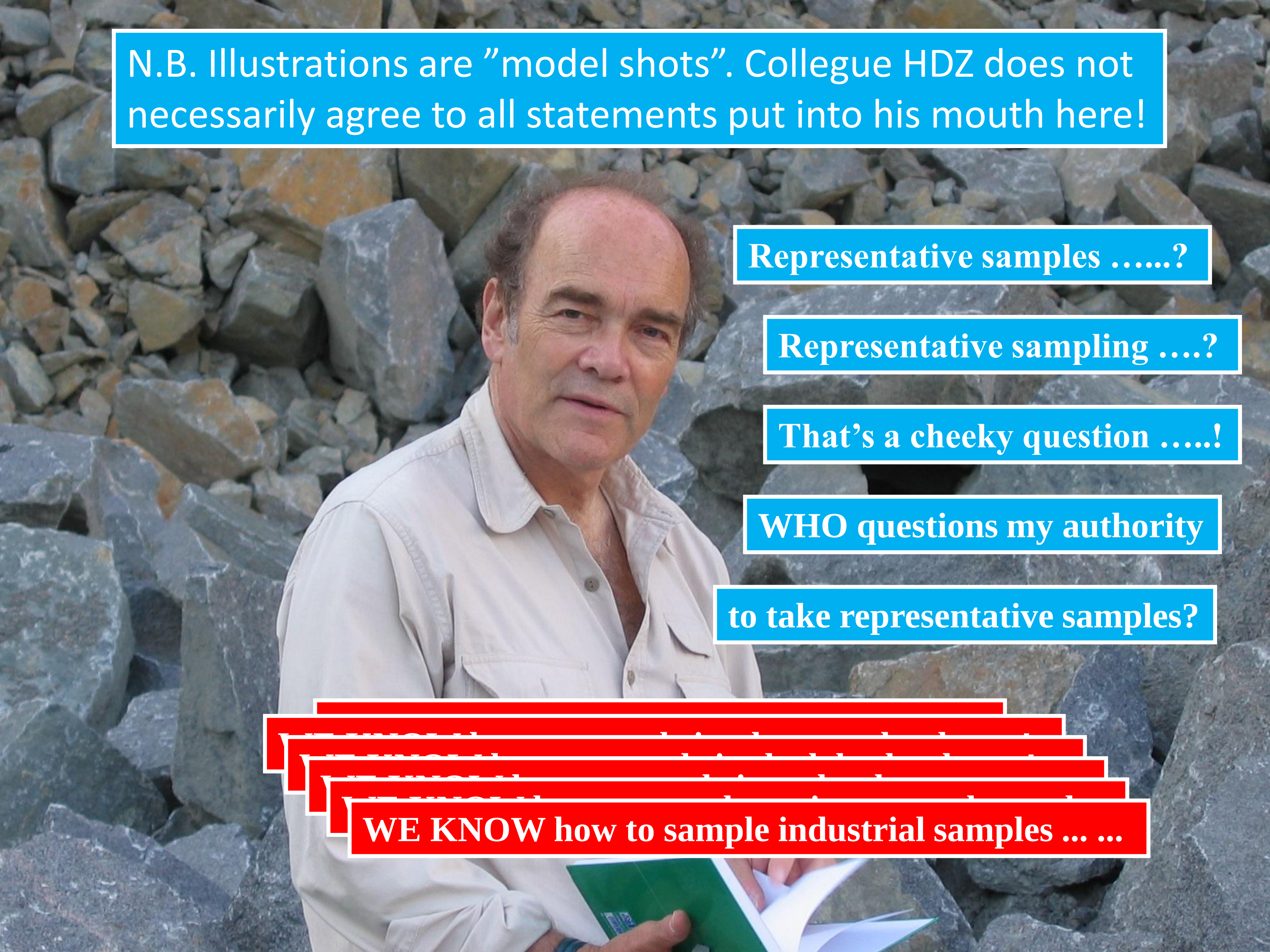
Theory and Practice of Representative Sampling

Governing principles, unit operations and sampling error management rules: Theory of Sampling (TOS)

This is a representative sample ;-)

What are the criteria for representativity?

TOS


N.B. Illustrations are ”model shots”. Collegue HDZ does not necessarily agree to all statements put into his mouth here!
Representative samples ……?
Representative sampling ….?
That’s a cheeky question …..!
WHO questions my authority
to take representative samples?
WE KNOW how to sample industrial samples … …

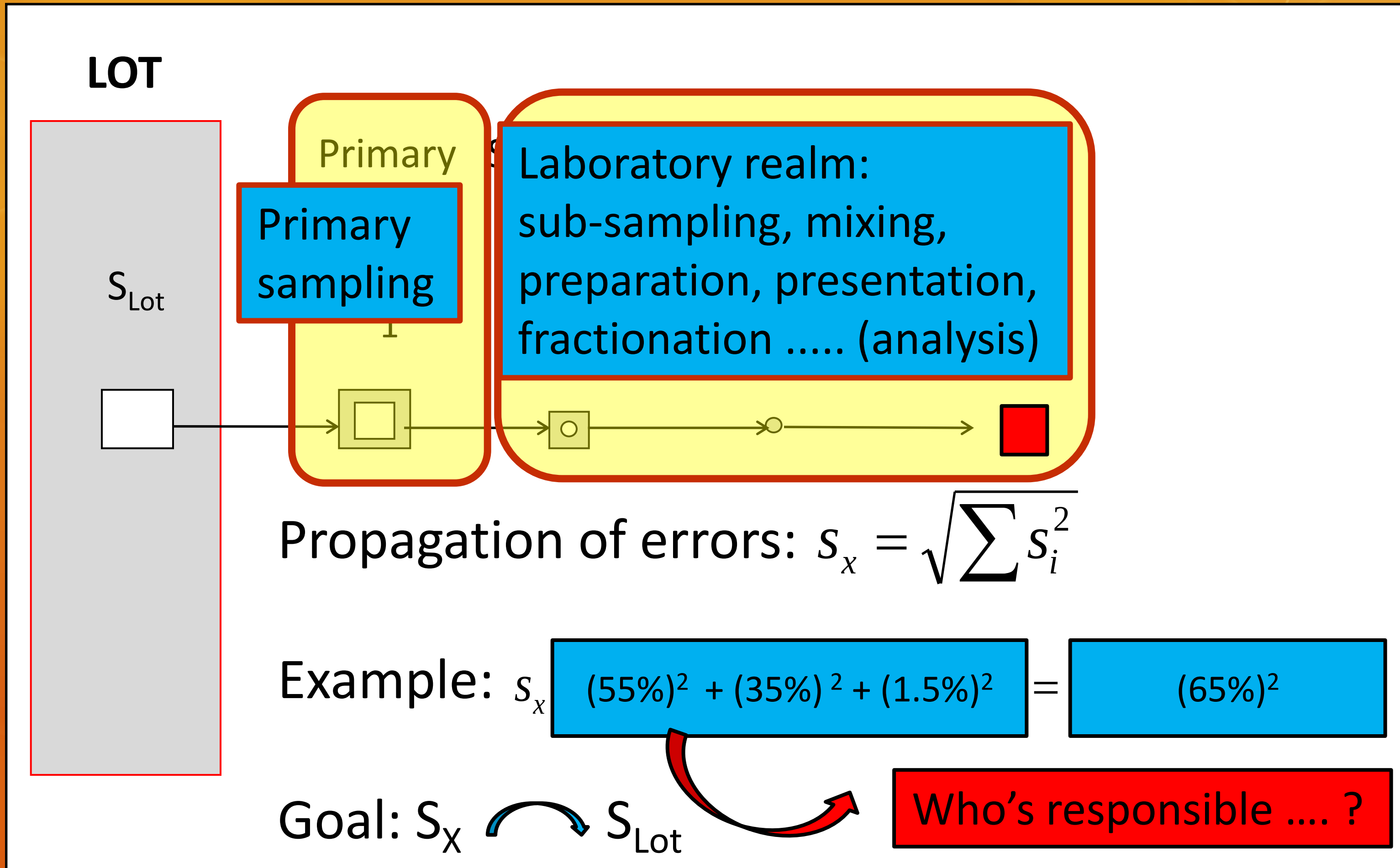
"SAMPLING – should not be gambling!"

Attributed to: **Pierre Gy**, founder of Theory of Sampling (TOS)

"TOS-sampling is not relevant for my:

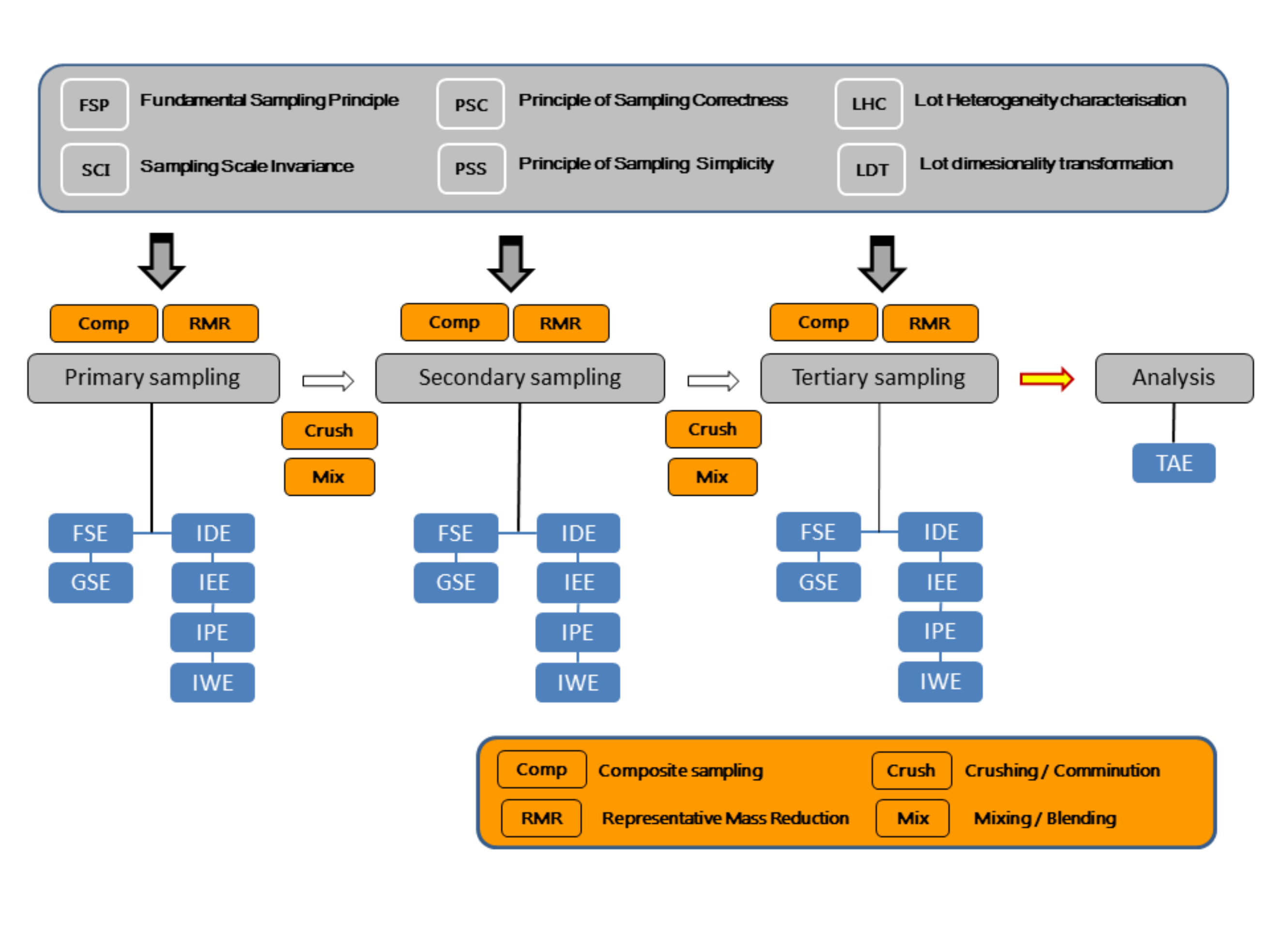
- type of material ...
- type of samples ...
- type of data ... ... "

???

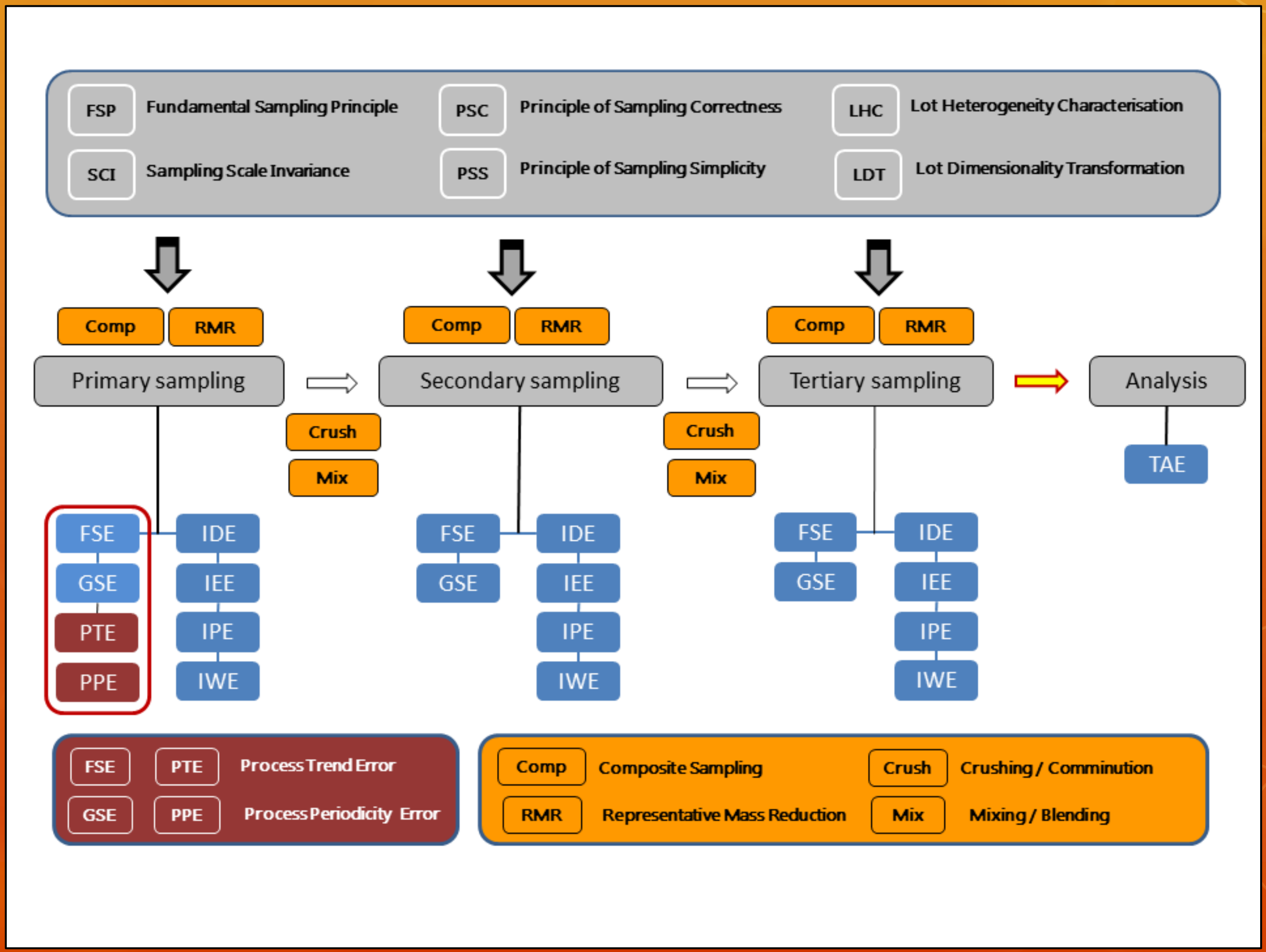


The analytical process always contains several sampling and preparation steps, but <u>usually</u> primary sampling <u>dominates</u>

TOS - basic stationary lot case



Theory of Sampling (TOS)
(both stationary as well as moving lots)
– everything in a glance



A most important insight … where all sampling starts

1. Sampling is never a one-shot operation

2. Sampling is always a multi-stage process:

   i) Primary sampling +

   ii) Representative Mass-reduction

Princple of Sampling Simplicity (PSI)

The analytical result – is but an *estimate* of a_L

Starting lot LOT (a_L)

↓

Primary sample S1 *Primary reject*

↓

Primary preparation S'1

↓

Secondary sample S2

↓

Secondary preparation S'2

↓

Laboratory sample S3 *Tertiary reject*

↓

3' preparation/presentation S'3

↓

Analytical sub-sample S4 (Analytical aliquot) *Final reject*

↓

Analysis

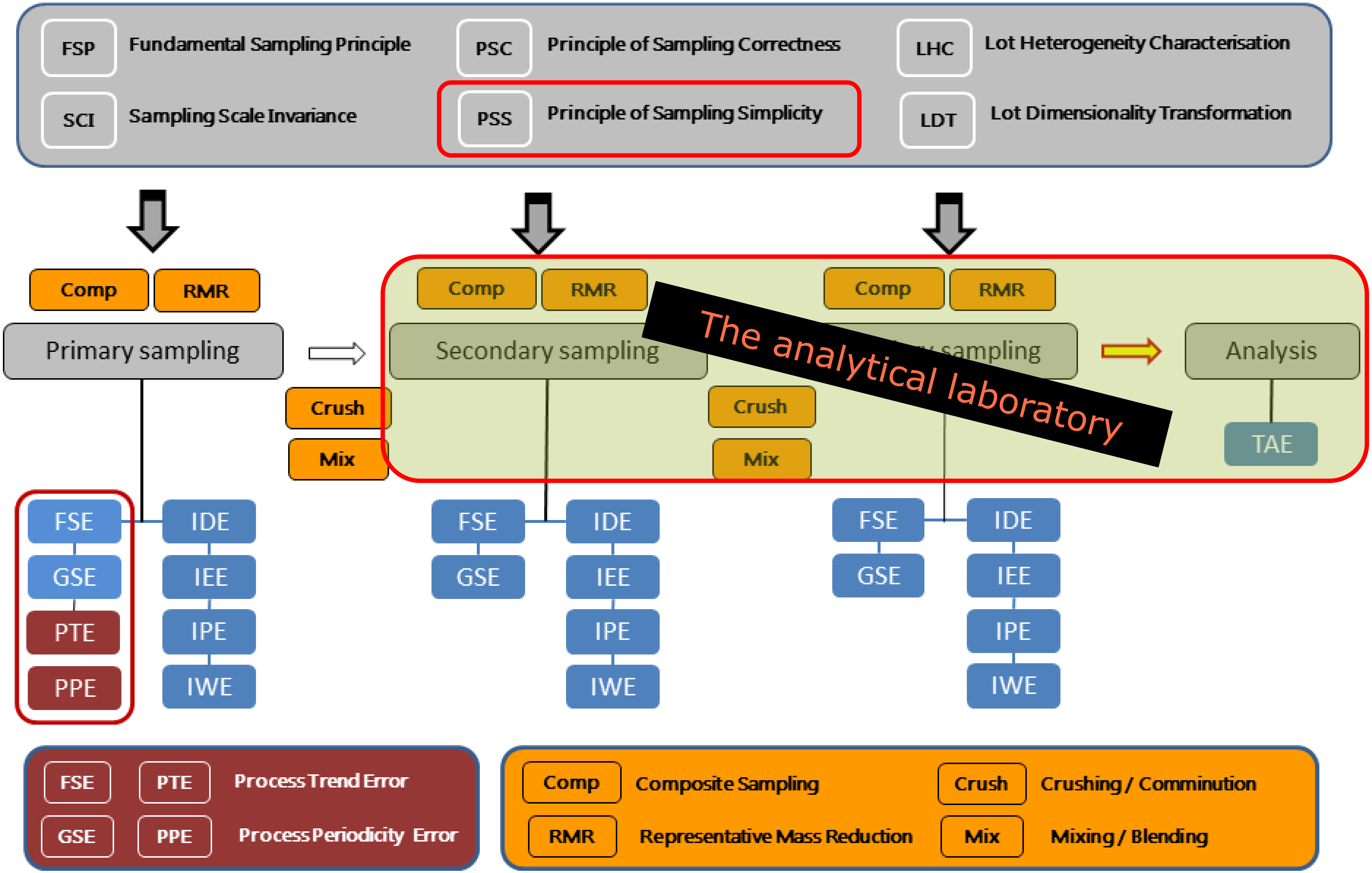
Sampling errors at all stages

Analytical result: a_S

"Decision data"

Who is responsible?

a_s 100% is not only an analytical responsibility – it is also a reflection of sampling process representativity



FSP
Fundamental Sampling Principle
PSC
Principle of Sampling Correctness
LHC
Lot Heterogeneity Characterisation
SCI
Sampling Scale Invariance
PSS
Principle of Sampling Simplicity
LDT
Lot Dimensionality Transformation
Comp
RMR
Primary sampling
Crush
Mix
Comp
RMR
Secondary sampling
Crush
Mix
Comp
RMR
sampling
Analysis
TAE
The analytical laboratory
FSE
GSE
PTE
PPE
IDE
IEE
IPE
IWE
FSE
GSE
IDE
IEE
IPE
IWE
FSE
GSE
IDE
IEE
IPE
IWE
FSE
GSE
PTE
Process Trend Error
PPE
Process Periodicity Error
Comp
Composite Sampling
RMR
Representative Mass Reduction
Crush
Crushing / Comminution
Mix
Mixing / Blending

Representative Sampling: Theory of Sampling (TOS)

TOS - Axiomatic exposé

Governing Principles (GP) – Sampling Unit Operations (SUO)

1. FSP: Fundamental Sampling Principle
2. SSI: Sampling Scale Invariance
3. PSC: Sampling Correctness (bias-free sampling)
4. PSS: Sampling Simplicity (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (Sub-sampling)

KHE Consulting

Theory and Practice of Representative Sampling TOS

Material heterogeneity – where it all begins ...

and where it sometimes / often ends as well (fatally)

Let's get started - HOW to sample?

... It all starts with HETEROGENITY, and how to counteract its effects ...

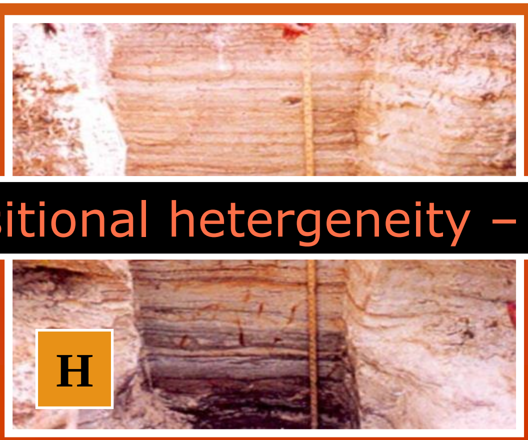
- How to sample representatively?
- How to DEFINE representativity?
- S... vs. bulk materials handling ...
- HOW BIG sh... ample be (in order to be repr... ve?)
- How to sub-sample (mass redu... (in the field? – in the laboratory?)
- How to ... ...
- WHY (all of the above)?

TOS

Three conceptual elements define HETEROGENEITY

1. Compositional Heterogeneity – CH
2. Distributional heterogeneity – DH
3. Grain-size heterogeneity – (part of CH and/or DH)

Compositional hetergeneity – CH (CH_{Lot})



Primary sampling – <u>the</u> critical success factor !!!

Compositional hetergeneity – CH (CH_{Lot})

Distrubutional hetergeneity – DH (DH_{Lot})

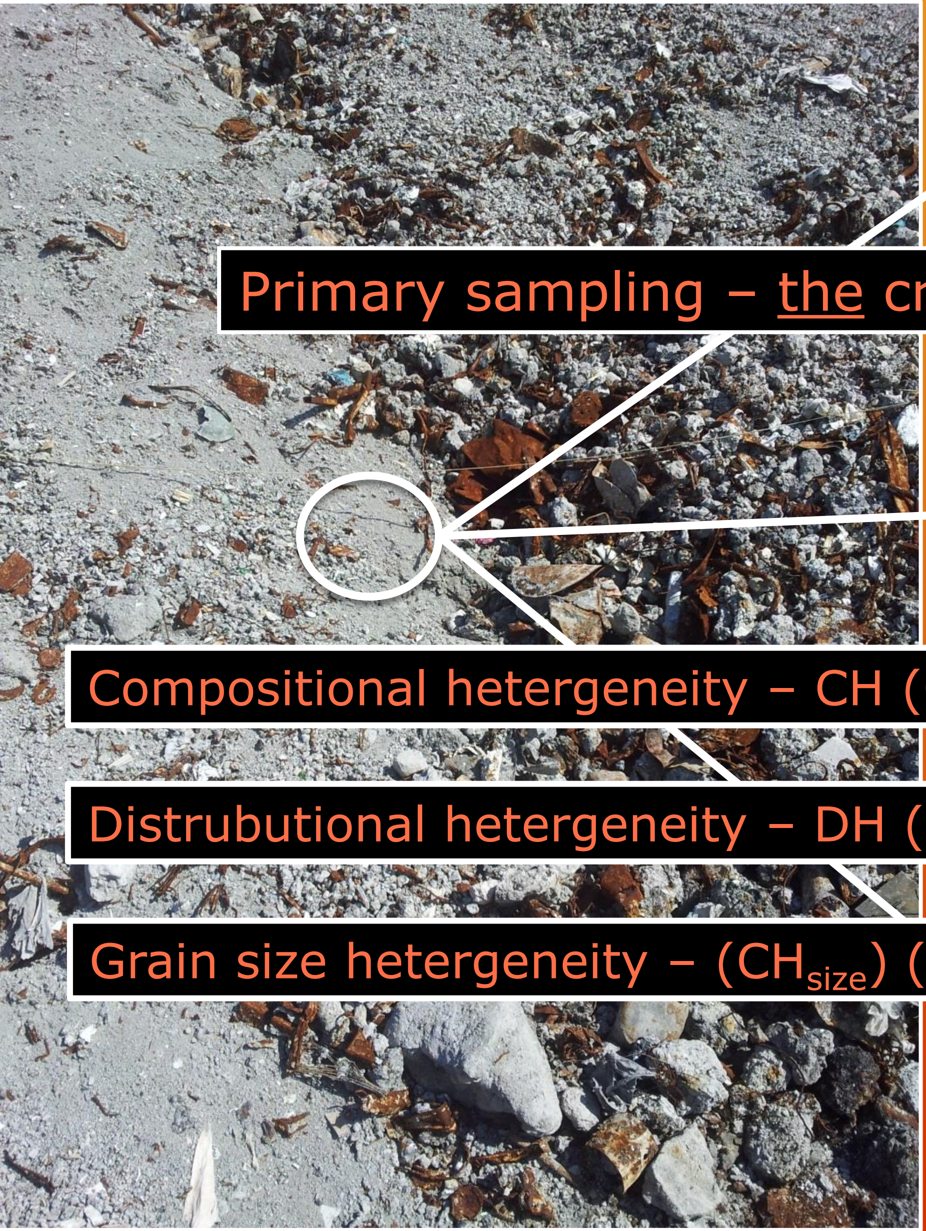
XRF-målinger på slaggen

Primary sampling – <u>the</u> critical success factor !!!

Compositional hetergeneity – CH (CH_{Lot})

Distrubutional hetergeneity – DH (DH_{Lot})

XRF-målinger på slaggen



Primary sampling – <u>the</u> critical success factor !!!

Compositional hetergeneity – CH (CH_{Lot})

Distrubutional hetergeneity – DH (DH_{Lot})

Grain size hetergeneity – (CH_{size}) (GSH_{Lot})

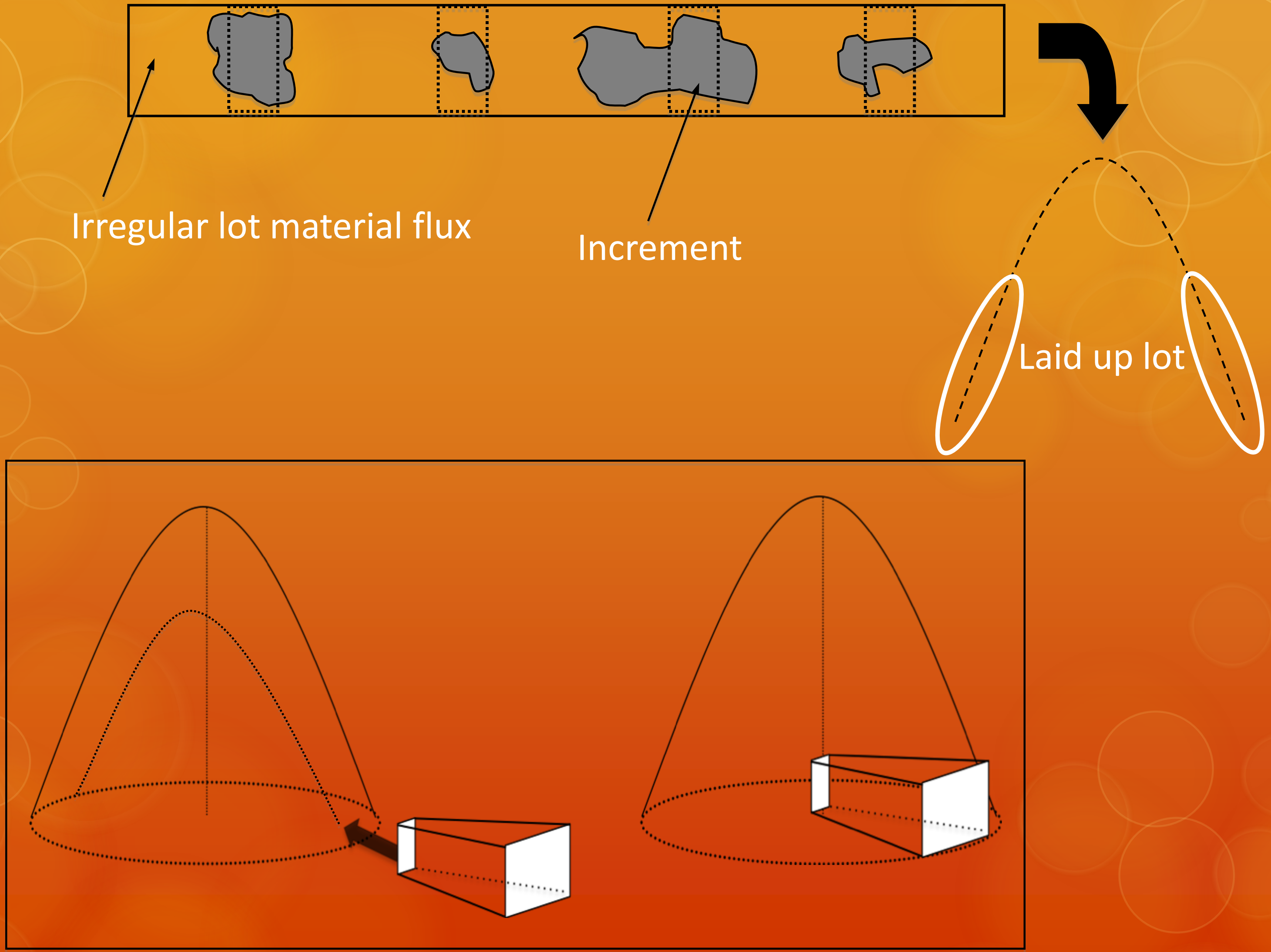
Primary sampling – counteracting heterogeneity

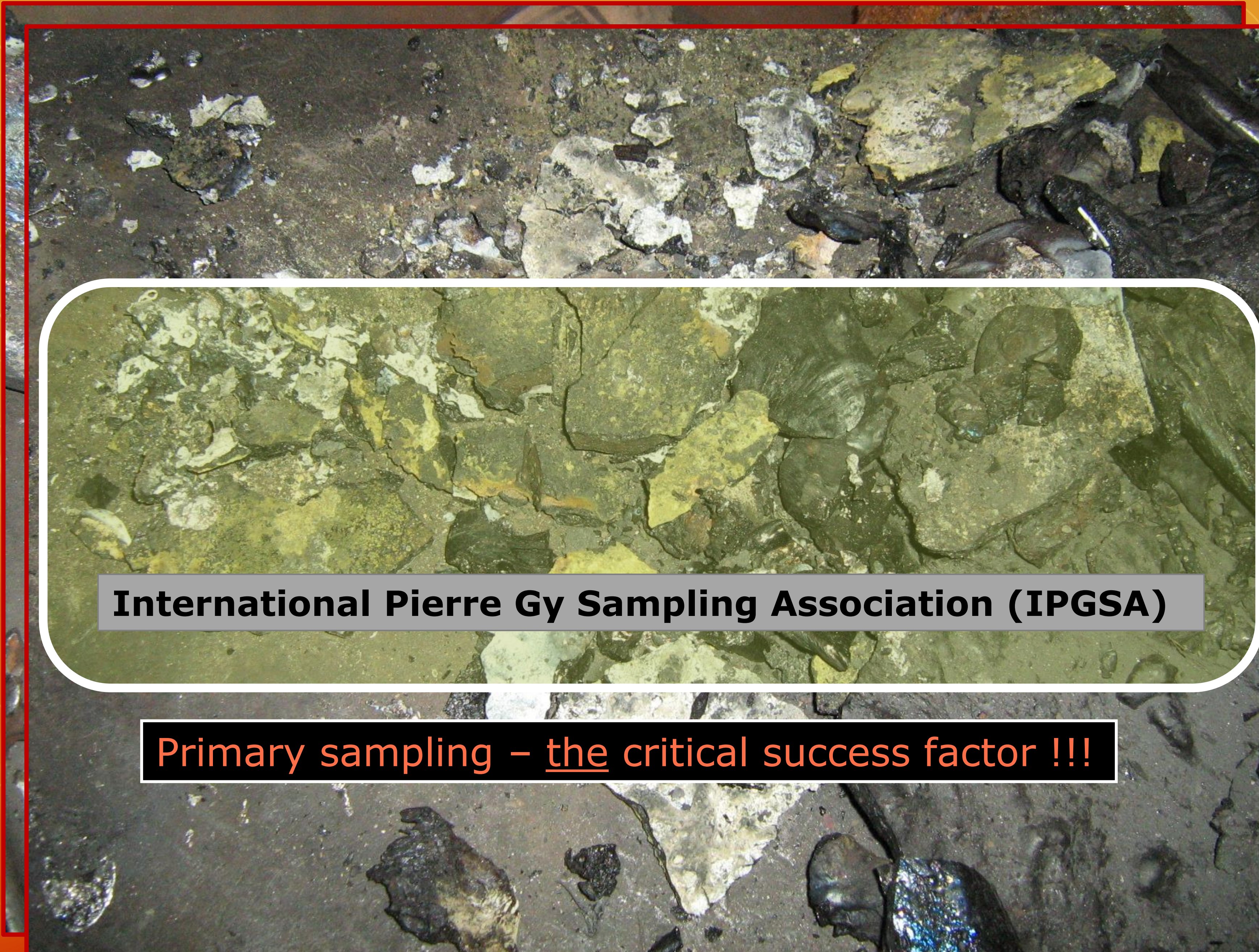
Compositional hetergeneity – CH (CH_{Lot})

Distrubutional hetergeneity – DH (DH_{Lot})

Grain-size hetergeneity → DH (DH_{Lot})

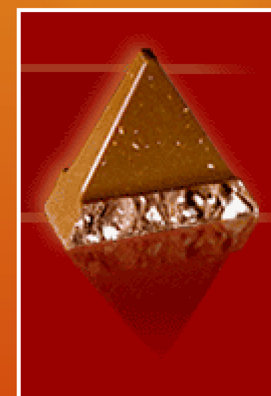
Grain size hetergeneity – (GSH_{Lot})


Irregular lot material flux
Increment
Laid up lot


International Pierre Gy Sampling Association (IPGSA)
Primary sampling – the critical success factor !!!

Large diversity of foods/feed products in this world

How to ensure representative primary sampling for <u>all</u> types of heterogeneous materials?

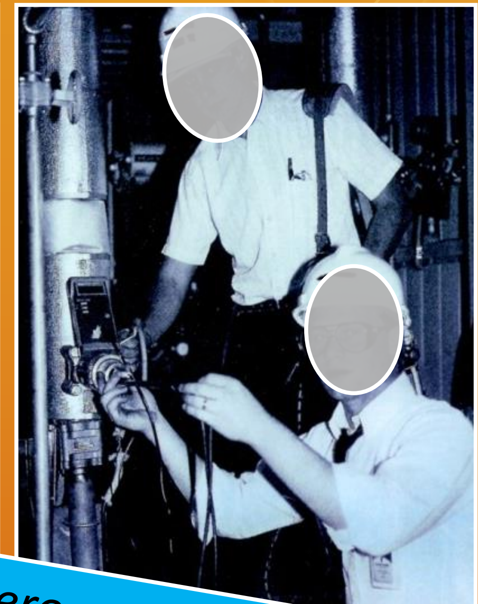


Remember him? Grab sampling!

Well. He is not alone out there in the field!

Grab sampling galore ....





A grab sample can <u>never</u> be representative of a *heterogeneous* material



There is observable heterogeneity – and there is hidden heterogeneity!
This is equally bad w.r.t. the possibility of *proper* representative sampling

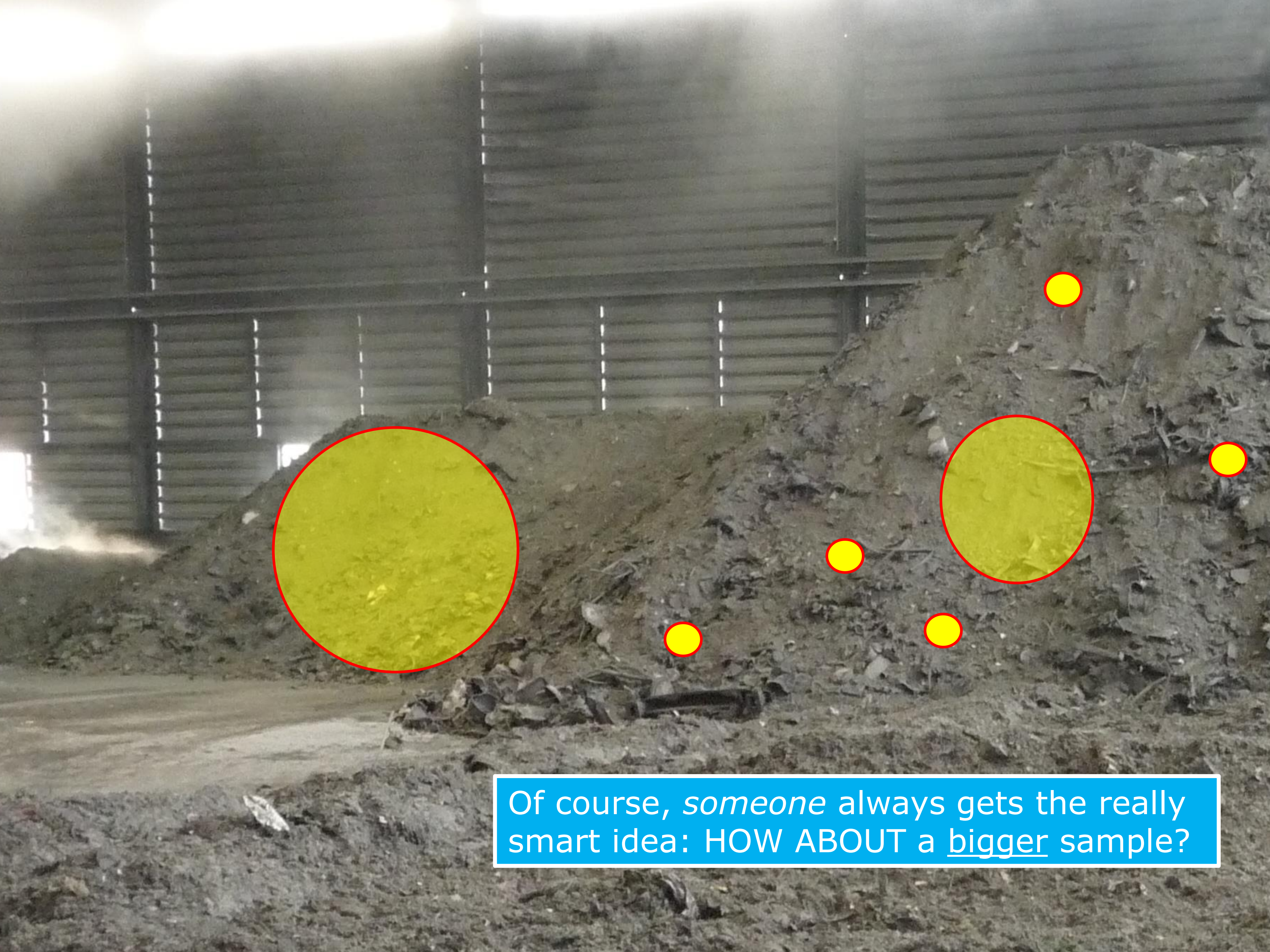
A grab sample can never be representative of a *heterogeneous* material

Materials are alwways heterogeneous (only a matter of to which degree)
It is necessary to sample all materials *as if* they were significantly het. !!


450
A grab sample can never be representative of a *heterogeneous* material


A grab sample can never be representative of a heterogeneous material
450

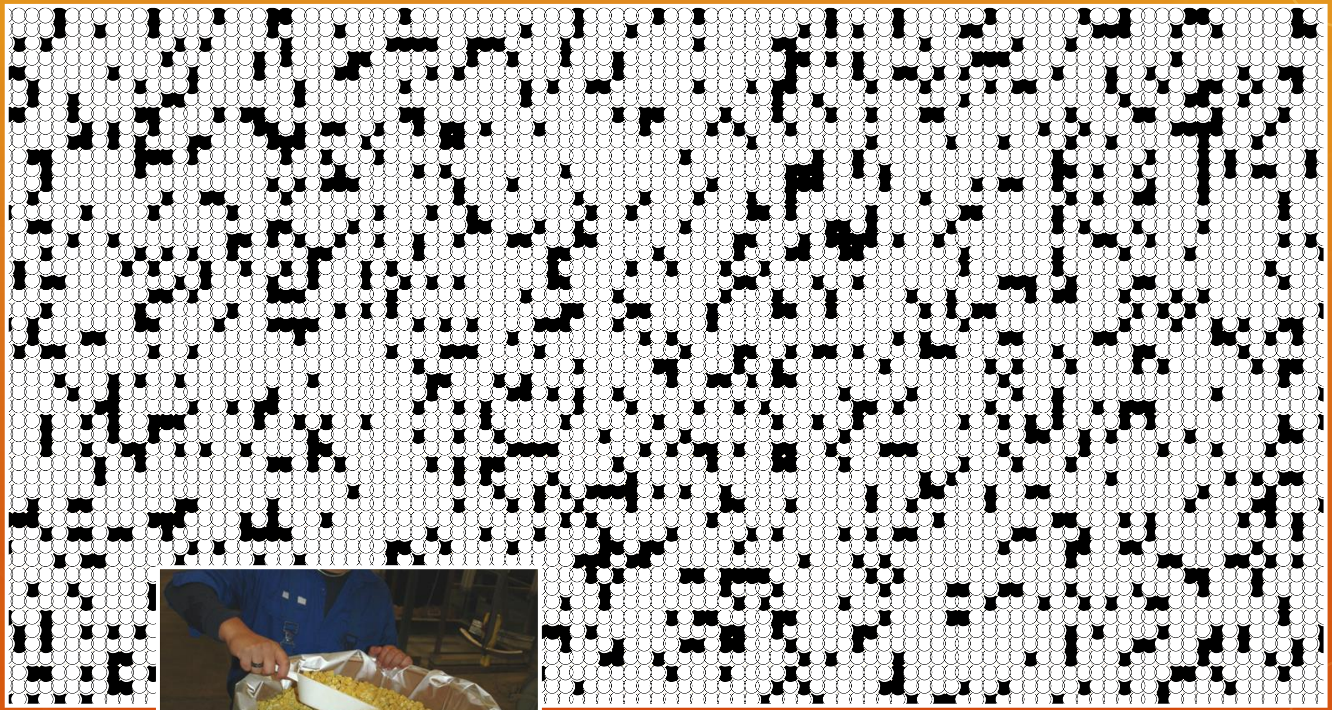

A grab sample can never be representative of a heterogeneous material


Of course, *someone* always gets the really smart idea: HOW ABOUT a bigger sample?

But there is a big surprise comming – a feature that will make sampling very, very much easier, <u>despite</u> there being so many very diffrent kinds of materials

Sampling is not really so much material dependent --
Sampling is much more up against lot *heterogeneity*

HETEROGENEITY – the arch enemy

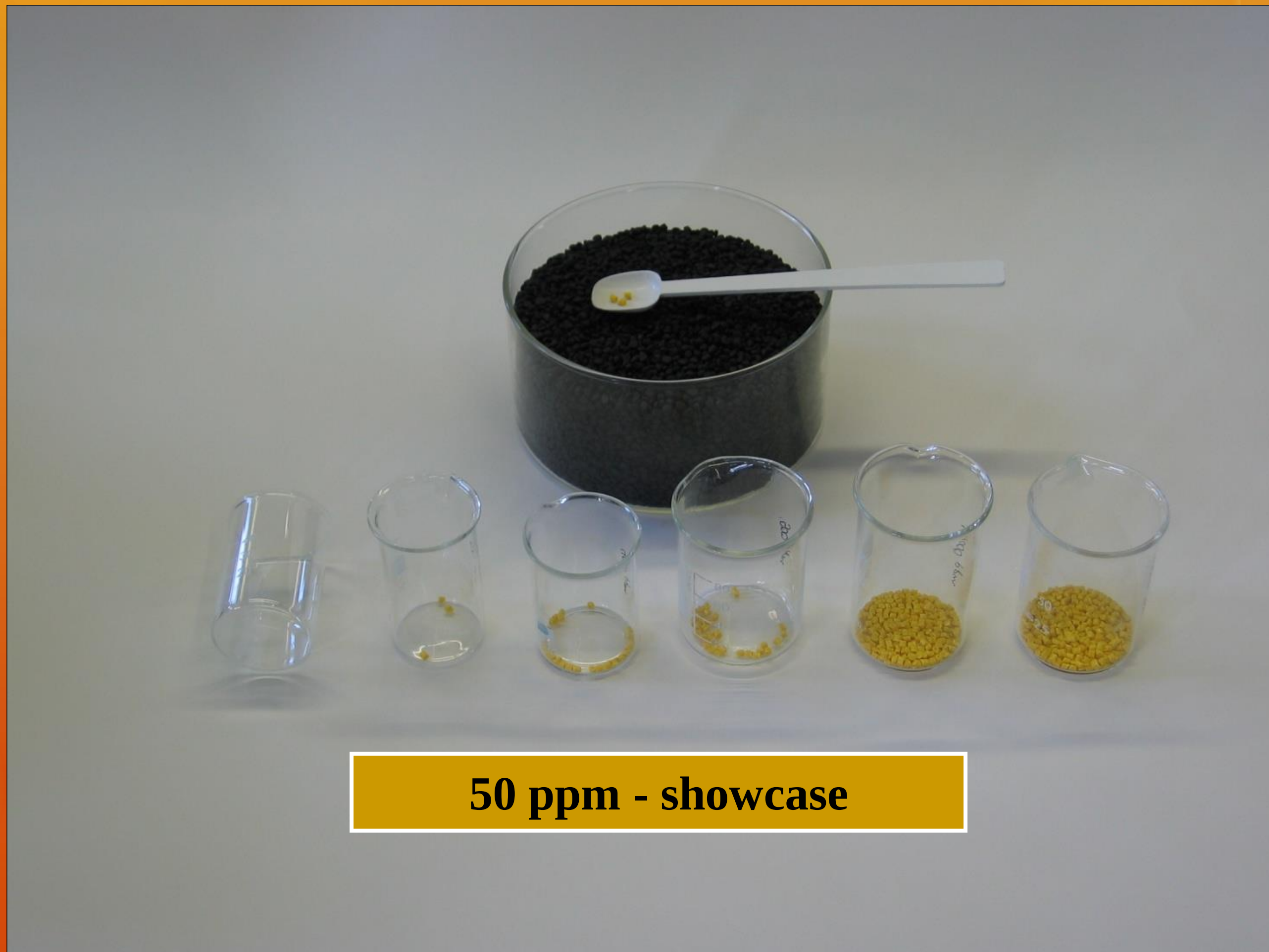


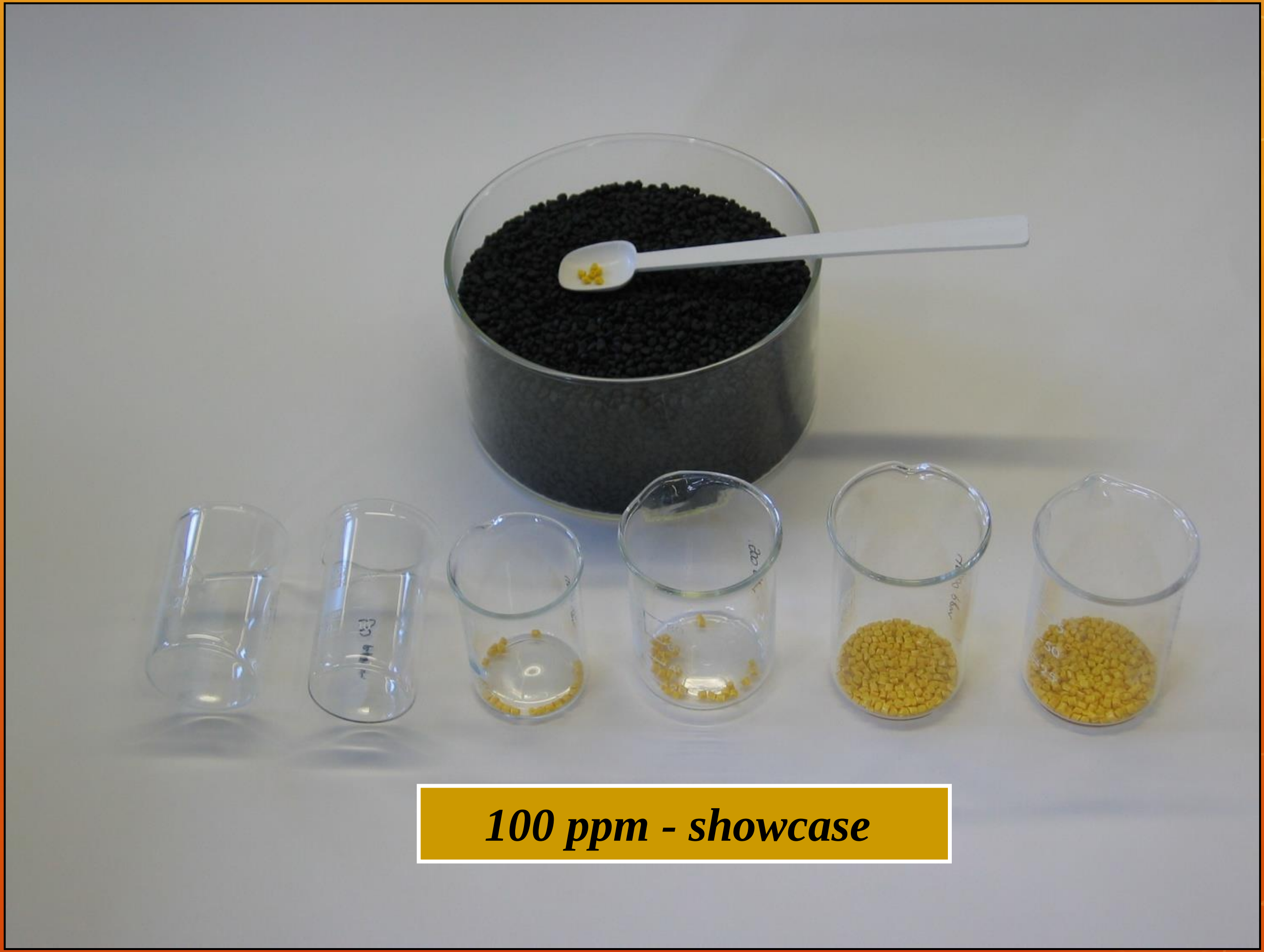
Grab sampling – the deadly sin !!!

GRAPHIC illustration (trace concentrations)

- trace concentration: below 1%

concentration: 50 - 10.000 ppm (1%)

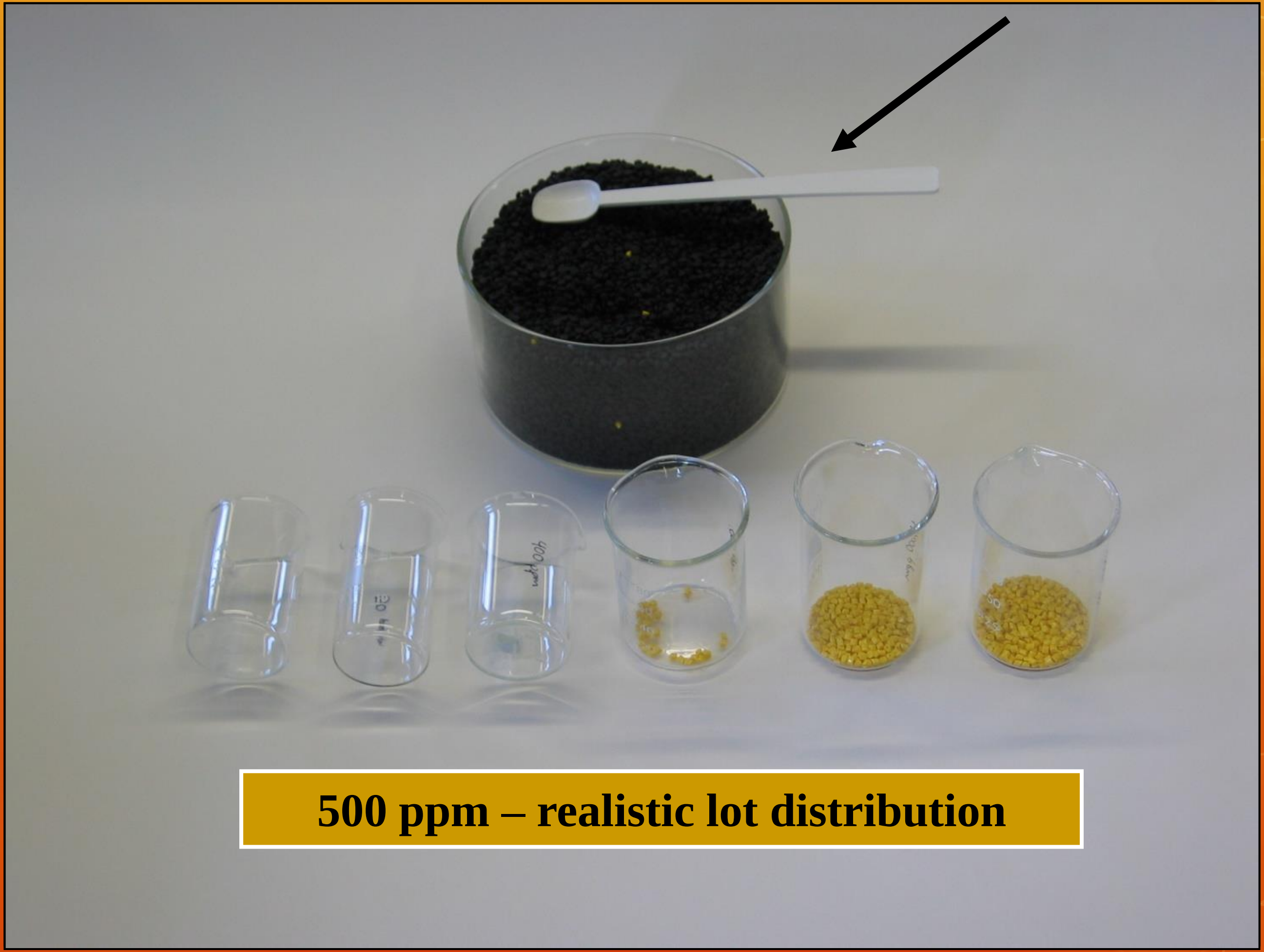

50 ppm - showcase



100 ppm - showcase

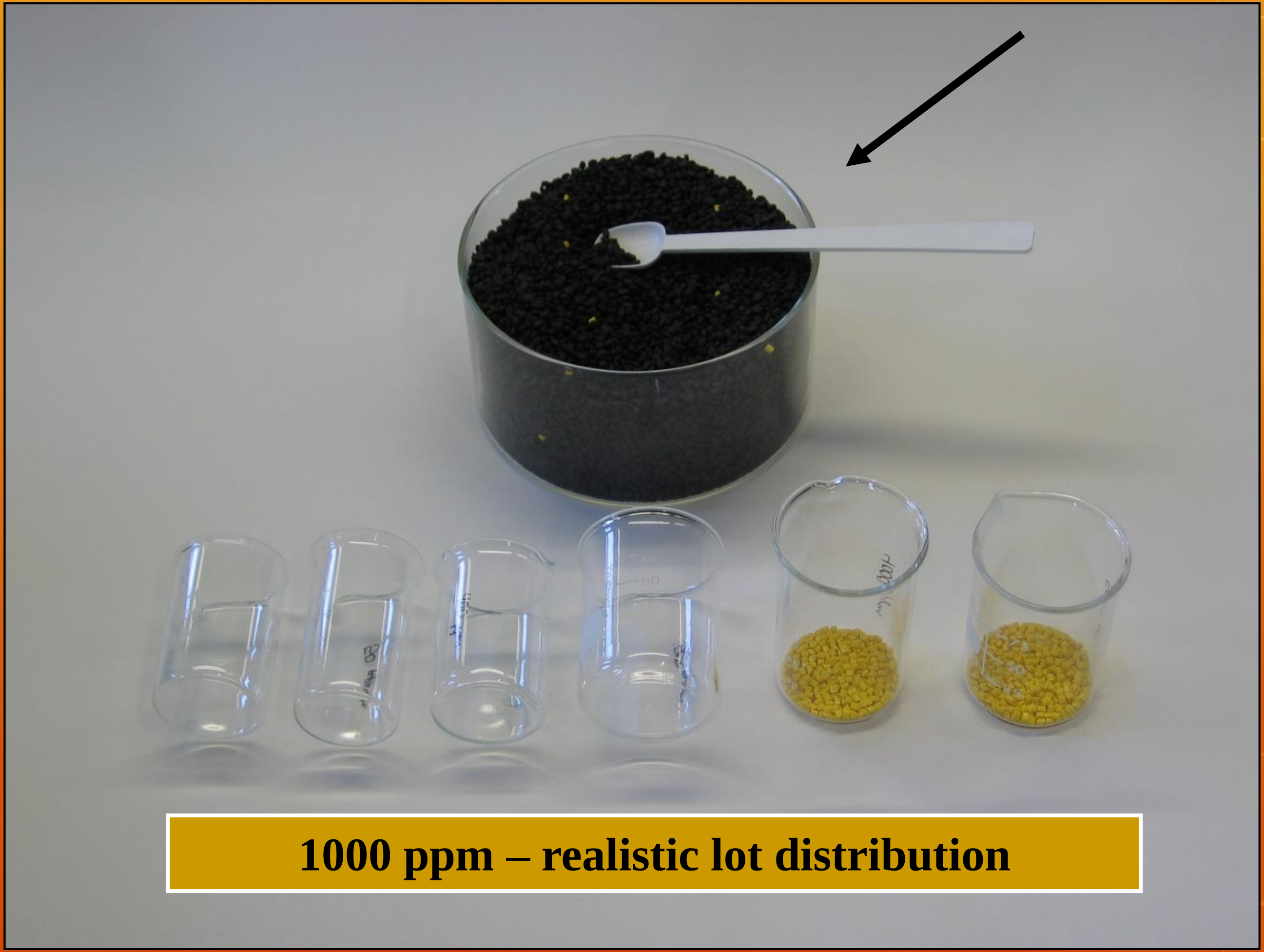
500 ppm - showcase

beware of spoon size



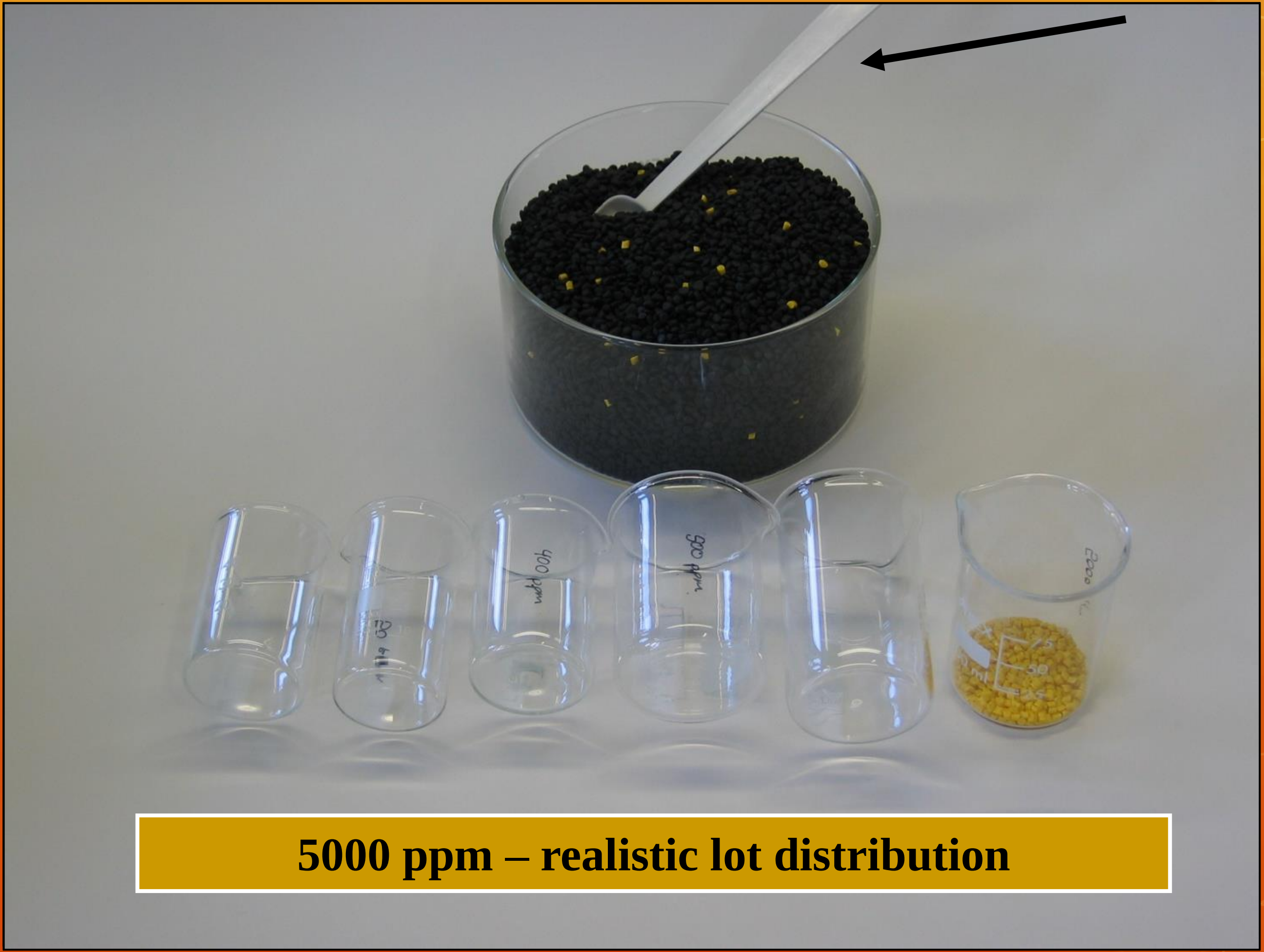
500 ppm – realistic lot distribution

beware of spoon size



1000 ppm – realistic lot distribution

beware of spoon size

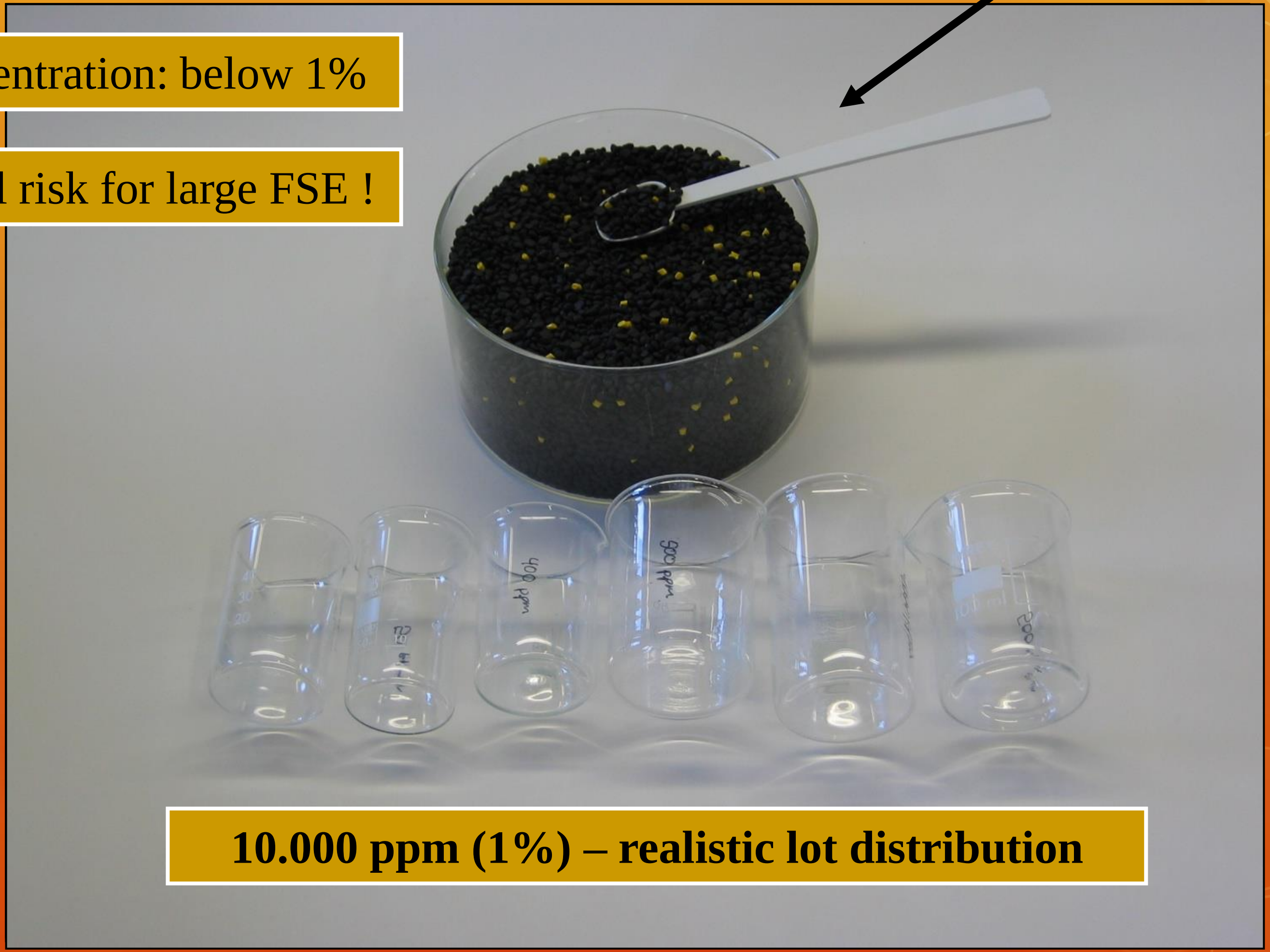


5000 ppm – realistic lot distribution

beware of spoon size

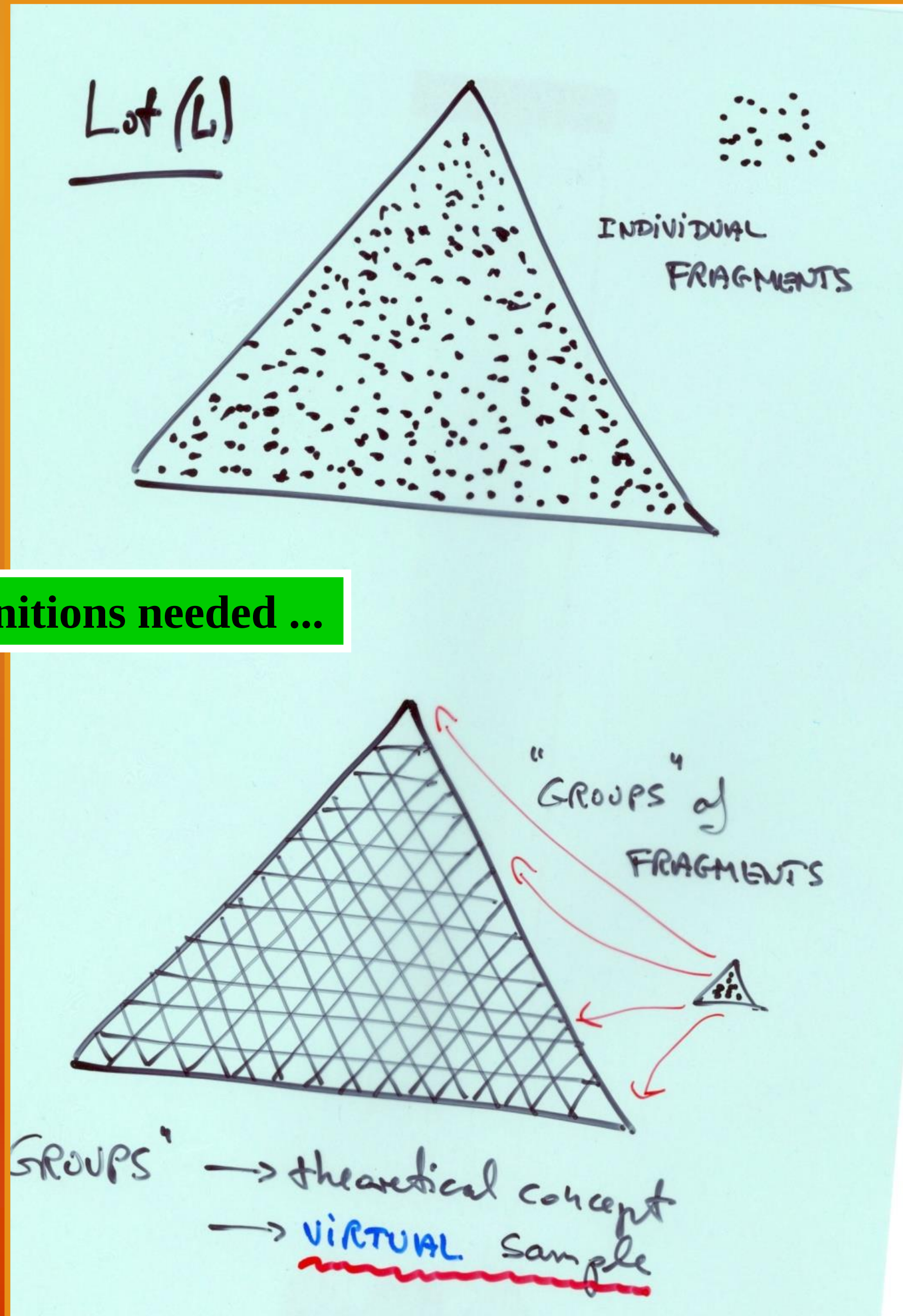
- trace concentration: below 1%

- Substabtial risk for large FSE !



10.000 ppm (1%) – realistic lot distribution

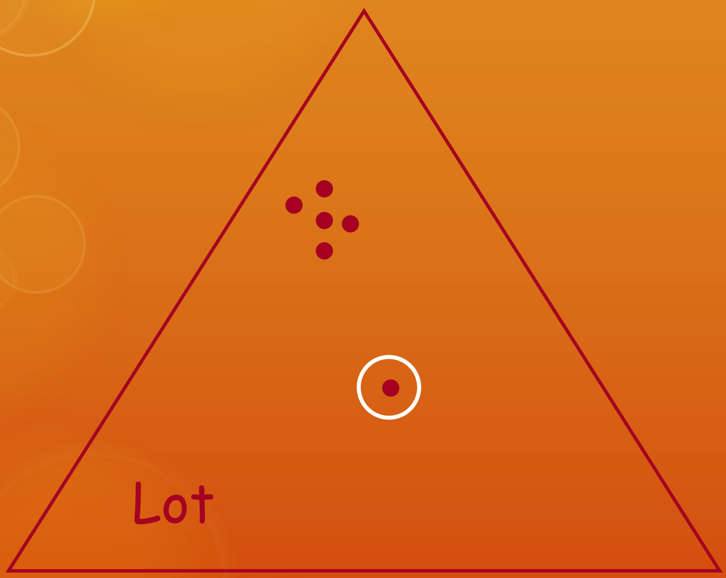
Experiment exemplum - credits: Suzanne Roy & Lars Beck



Quantitative definitions needed ...

Heterogeneity (quantitative definitions)

Constitutional heterogeneity (CH)



Sampling unit: fragment

- The lot is an ensemble of fragments.
- The contribution of each fragment to the total heterogeneity of the lot is defined individually ($\mathbf{h_i}$).
- The heterogeneity of the lot (**CH**) takes into account the contributions from all fragments.
- Since fragments are looked upon independently, CH does not depend on the spatial distribution of the fragments in the lot.
- CH only speaks about composition heterogeneity … …

Constitutional heterogeneity (CH)

Heterogeneity contribution of a fragment - to the lot (h_i)

$$h_i = \boxed{\frac{a_i - a_L}{a_L}} \times \boxed{\frac{M_i}{\overline{\overline{M_i}}}}$$

a_i: fragment grade
a_L : lot grade
M_i: fragment mass

Compositional differences fragment-lot (compositional heterogeneity)

Fragment size ('physical' heterogeneity)

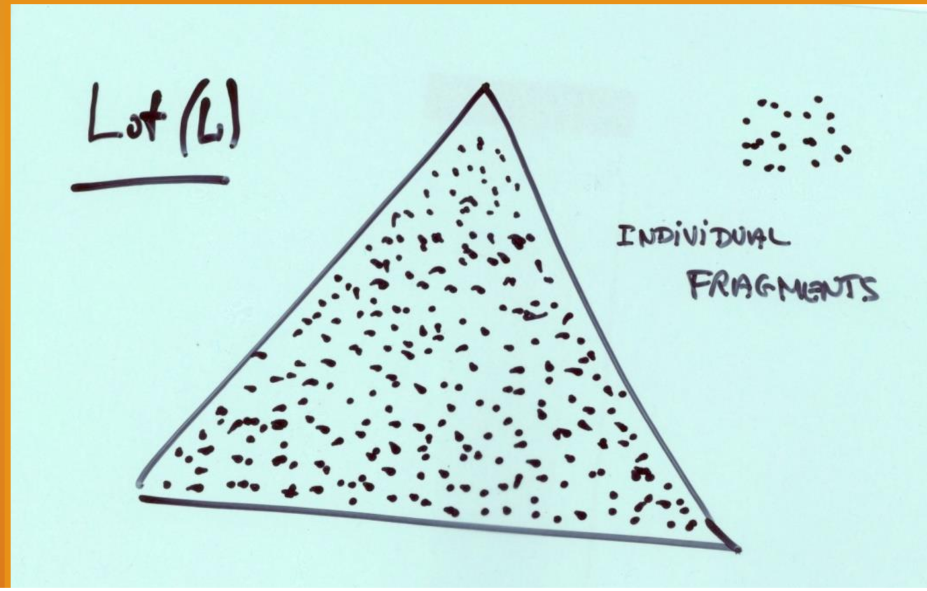
Compositional difference is weighted by fragment size.

Constitutional heterogeneity (CH)

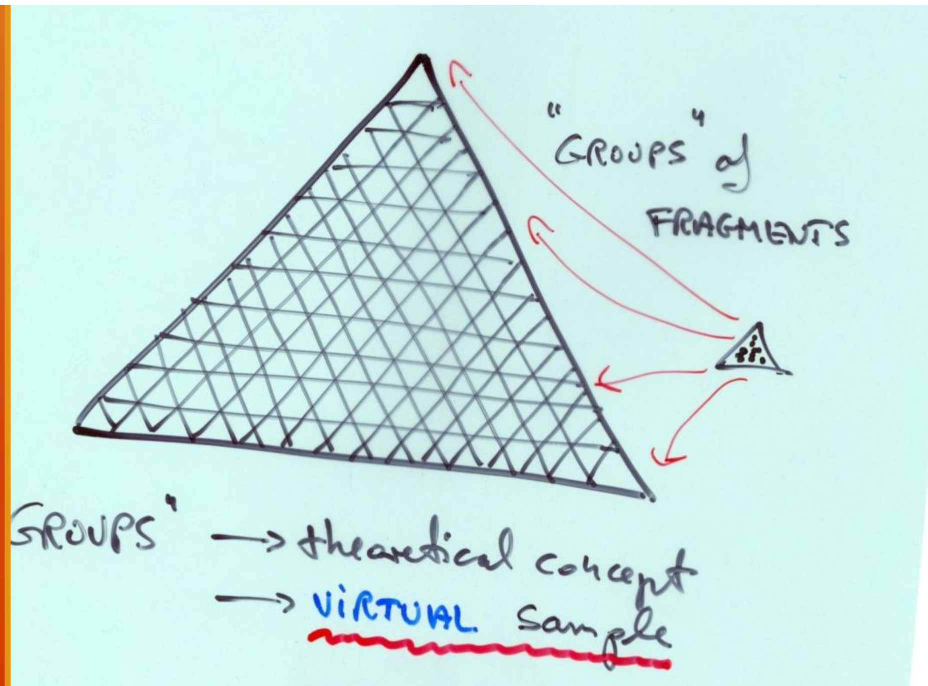
$$CH_L = s^2(h_i) = \frac{1}{N_F}\sum_i h_i^2$$

N_F: nr. of fragments

- Variance of <u>all</u> individual **fragment** heterogeneities contributing to the lot heterogeneity … (CH_L)
- Dimensionless (relative scale)



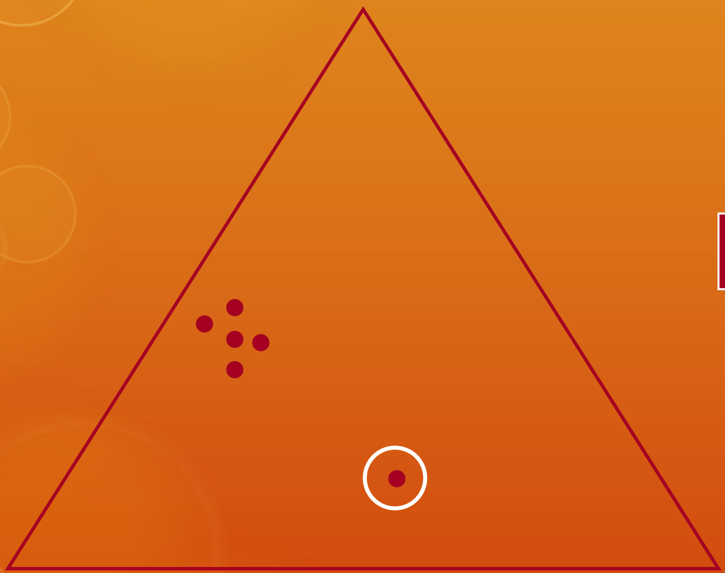
- *et voila*: Pierre Gy’s famous conceptual insight - (”the trick”)

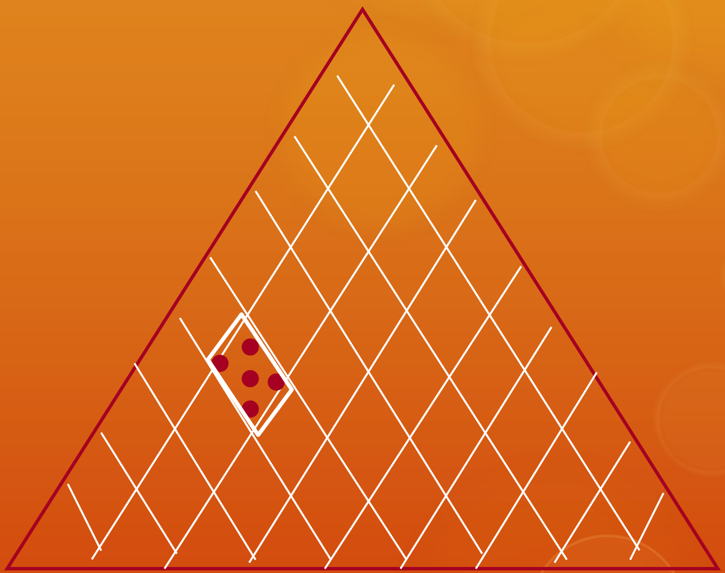


From CH to DH

Constitutional heterogeneity (CH)

Distributional heterogeneity (DH)





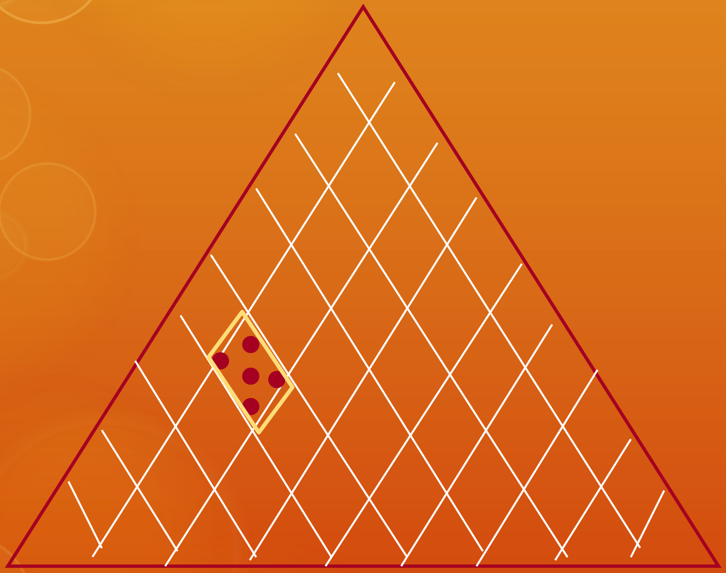
Sampling unit: fragment

Sampling unit: group

- a step up in ”observation scale”

Distributional heterogeneity (DH)

Distributional heterogeneity (DH)



Sampling unit: group

- The lot is now considered as an ensemble of groups (increments).
- The contribution of each group to the total heterogeneity of the lot is again defined individually (**h_n**).
- The heterogeneity of the lot (**DH_L**) takes into account the contributions from all groups.
- Since groups constitute a complete network of units, DH depends on the spatial distribution of the lot.
- Indeed the set of groups makes up the entire spatial disposition of the lot

Distributional heterogeneity (DH)

Heterogeneity contribution of a group to the lot (h_n):

$$h_n = \boxed{\frac{a_n - a_L}{a_L}} \times \boxed{\frac{M_n}{\overline{M_n}}}$$

a_n: group grade
a_L : lot grade
M_n: group mass

Compositional differences group-lot (compositional heterogeneity)

Group size

Compositional difference is weighted by group size

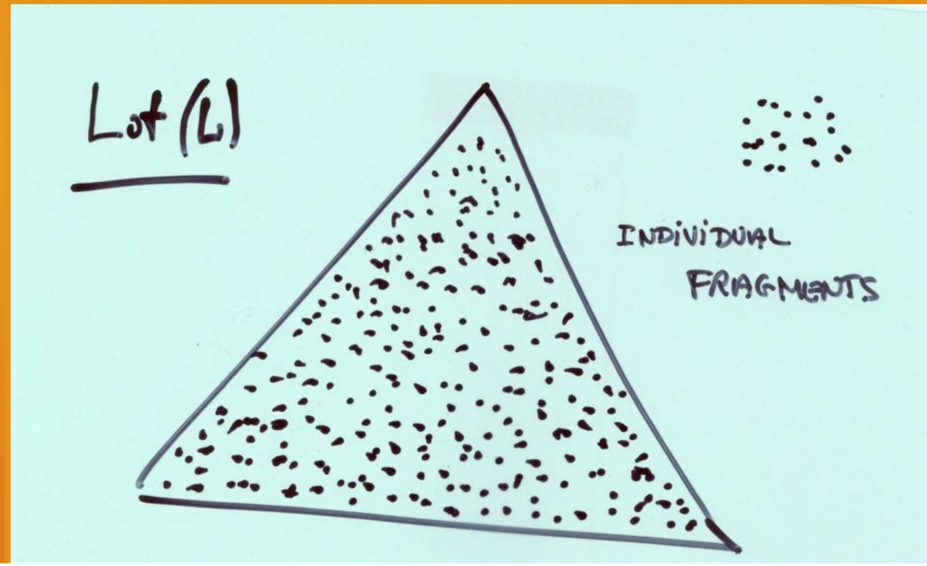
Distributional heterogeneity (DH)

$$DH_L = s^2(h_n) = \frac{1}{N_G} \sum_n h_n^2$$

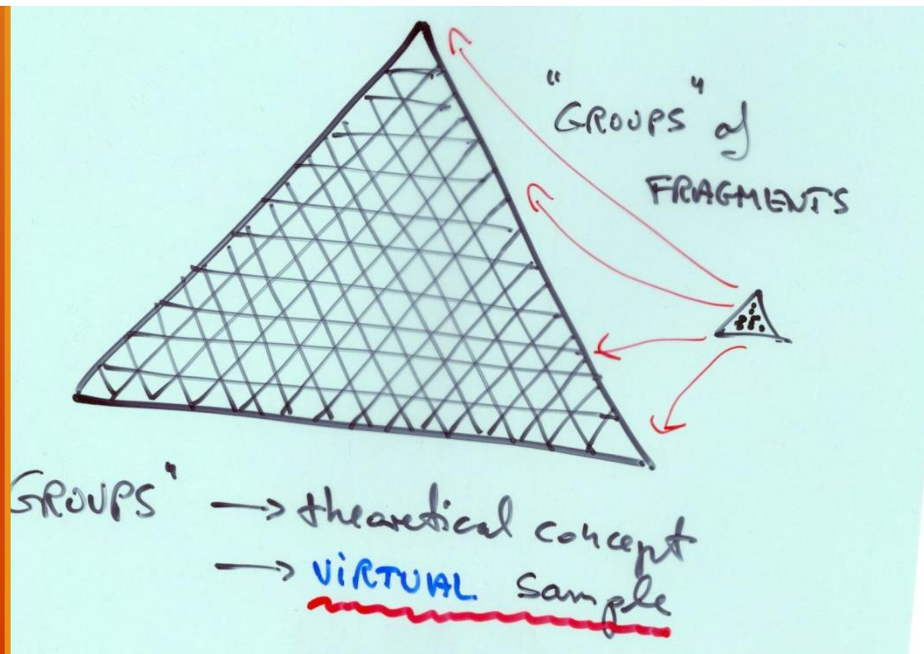
N_G: nr. of groups

- Variance of <u>all</u> **group** heterogeneity contributions
- Dimensionless (relative scale)

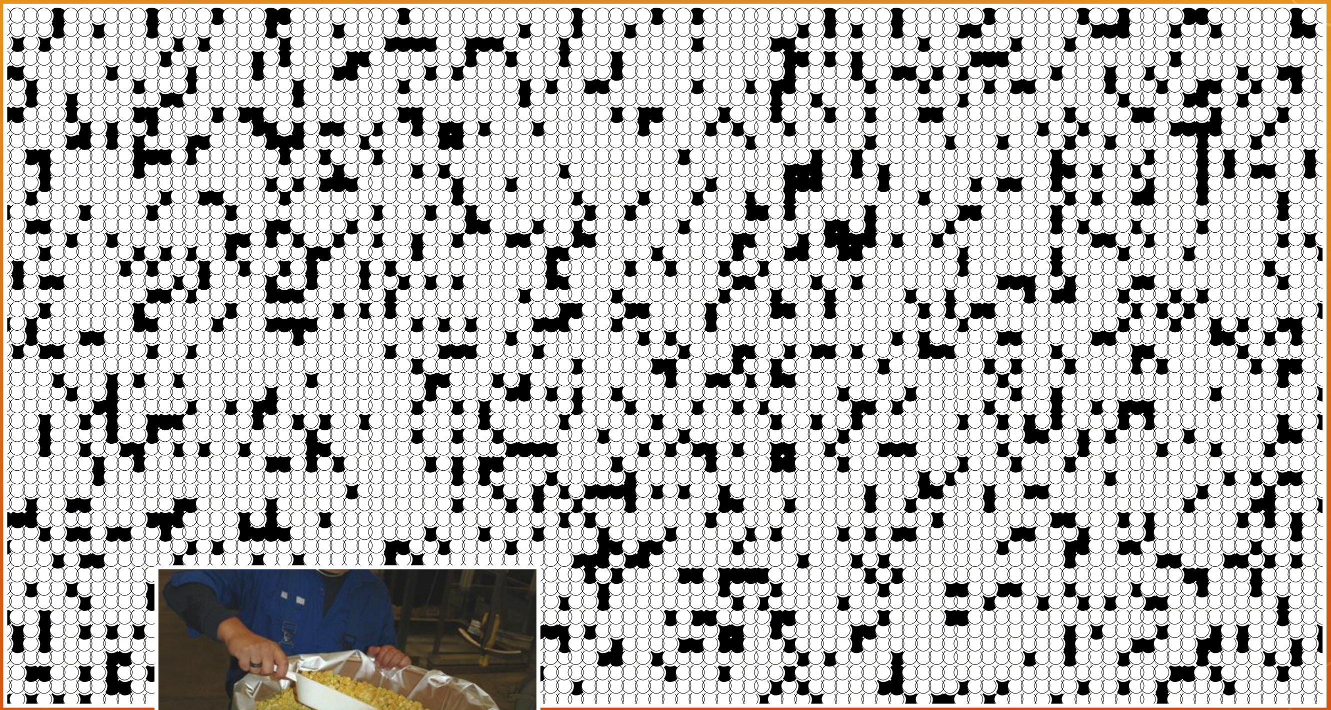
- No more steps in ”observation scale” needed – DH_L ... <u>is</u> the entire lot !!!



Pierre Gy's conceptual insight - only three observation module scales ever needed: fragment / group / lot - q.e.d.

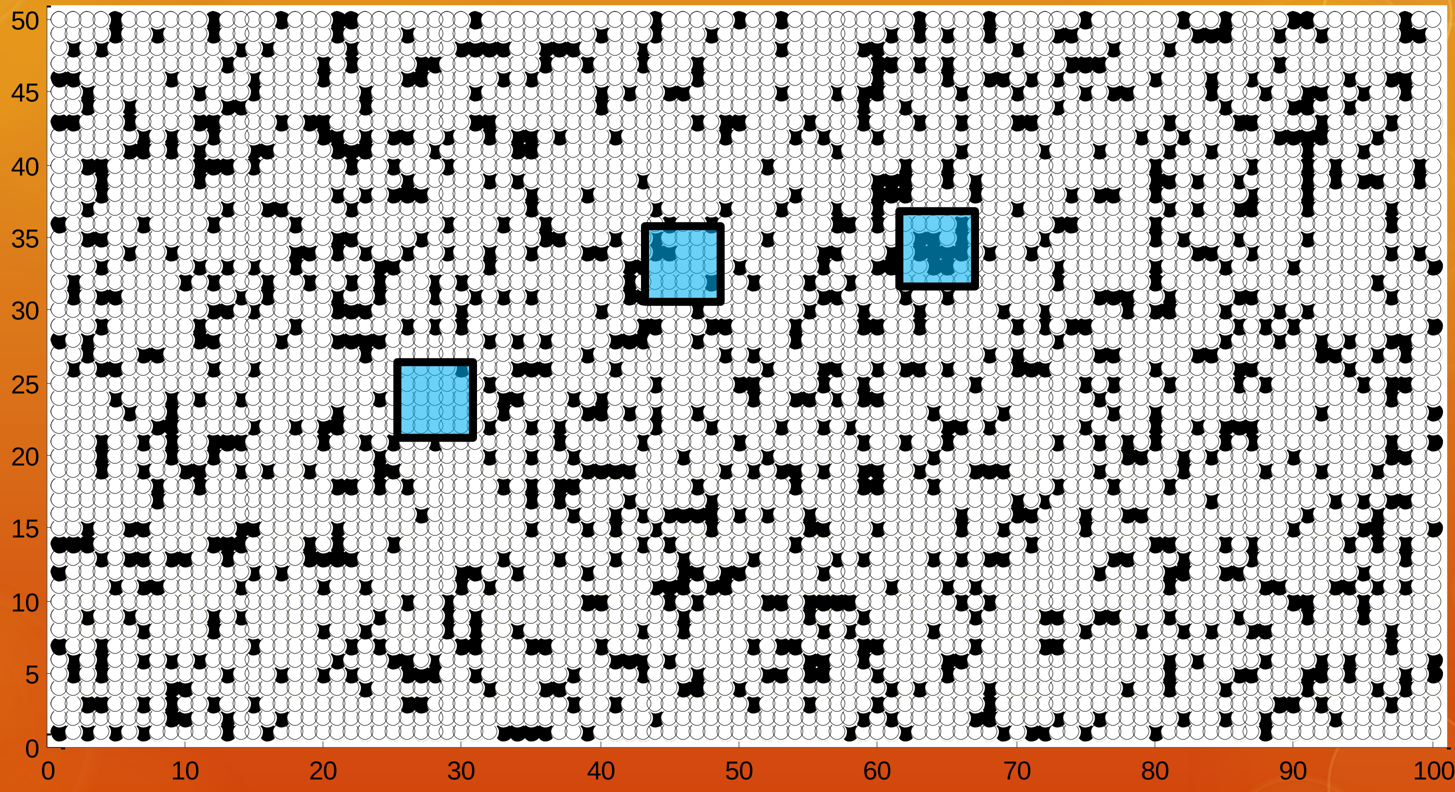


HETEROGENEITY – the arch enemy



Grab sampling – the deadly sin !!!

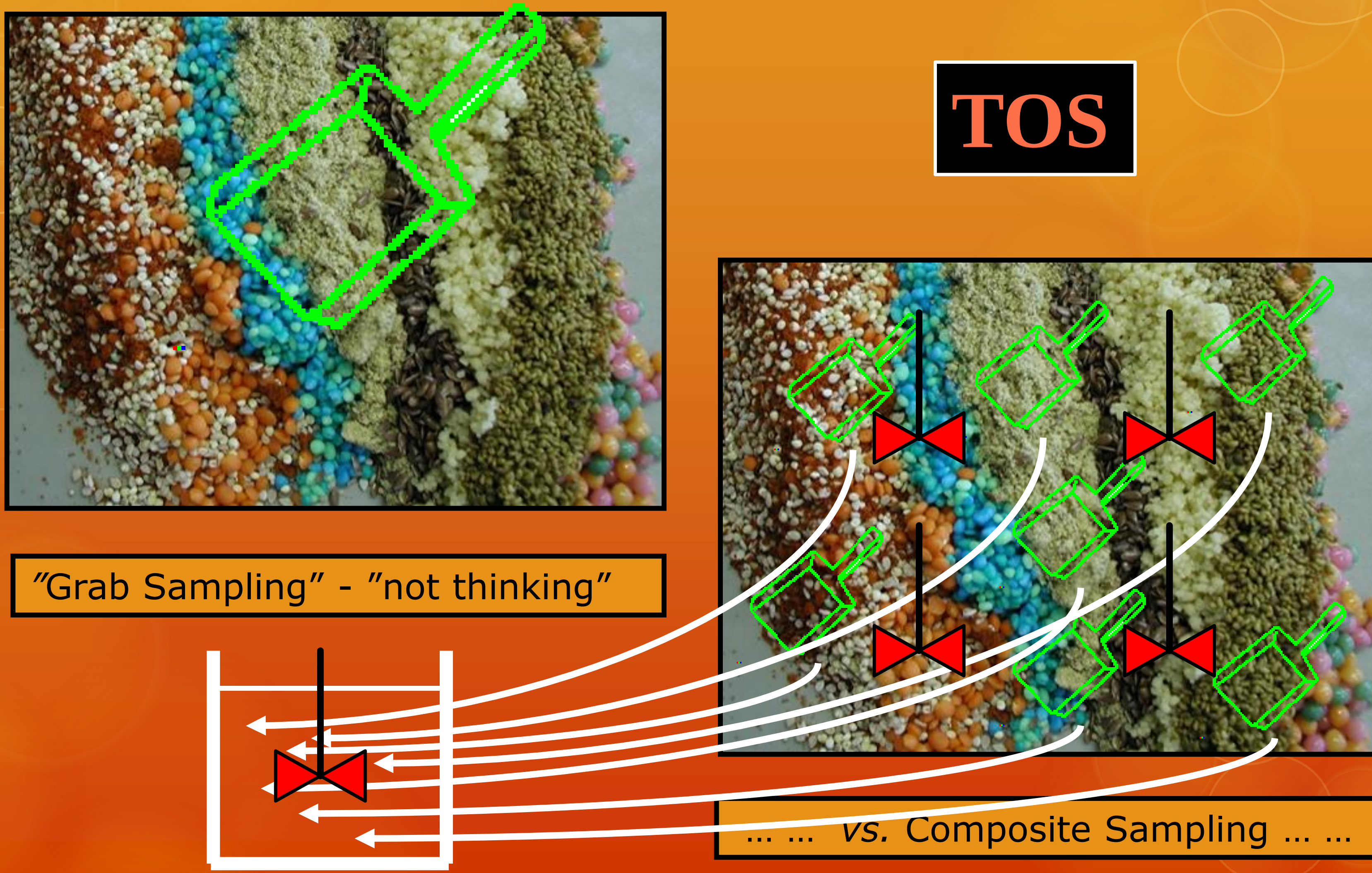
Heterogeneity - the unifying characteristic for all types of material

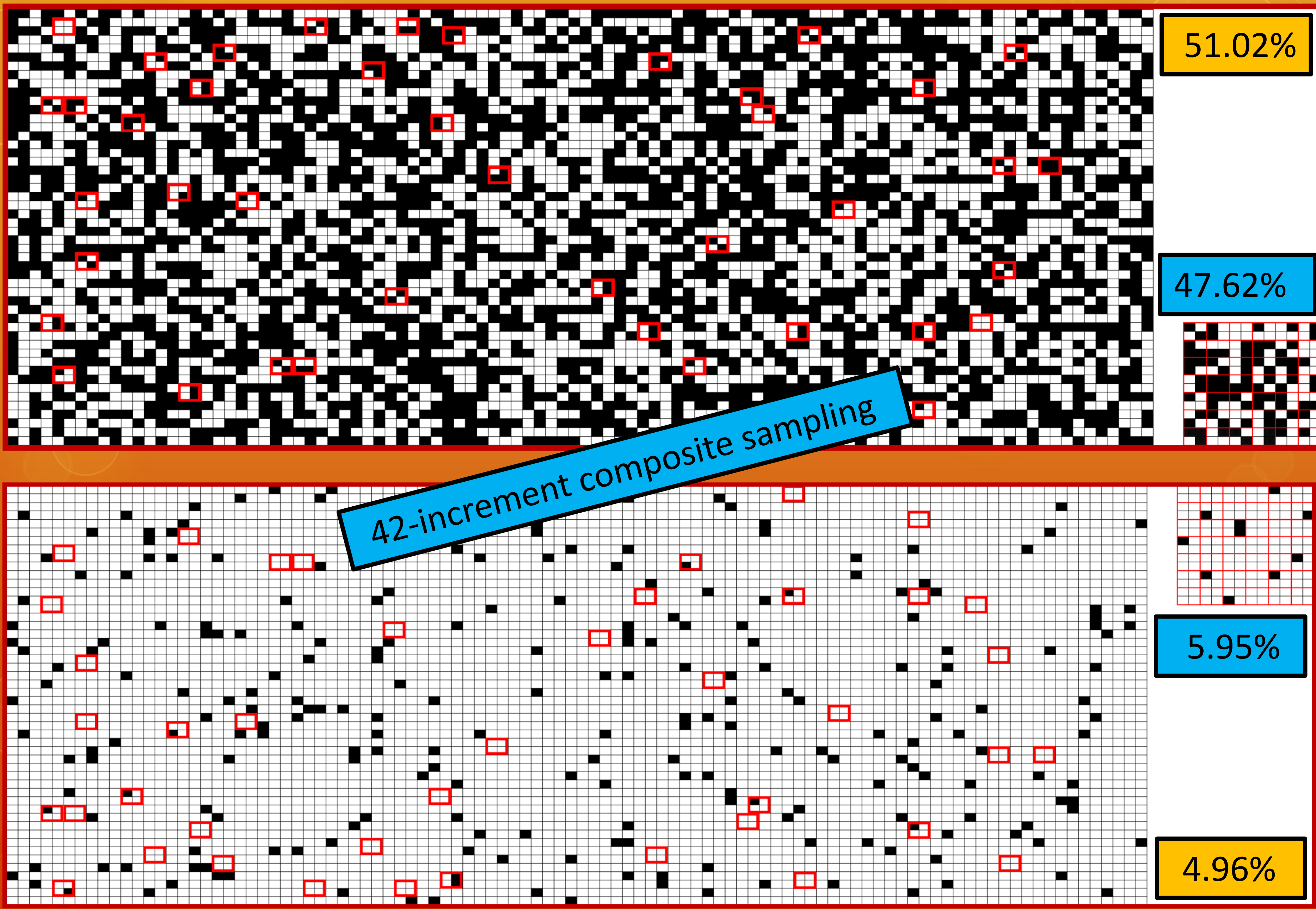


Grab sampling – not representative!!!

TOS

Sampling Unit Operations: Composite Sampling





51.02%
47.62%
42-increment composite sampling
5.95%
4.96%

It so easy to do it **WRONG!** And so easy to do it **RIGHT!**

A very smart problem-dependent composite sampling principle ;-)

Model photo: with permission

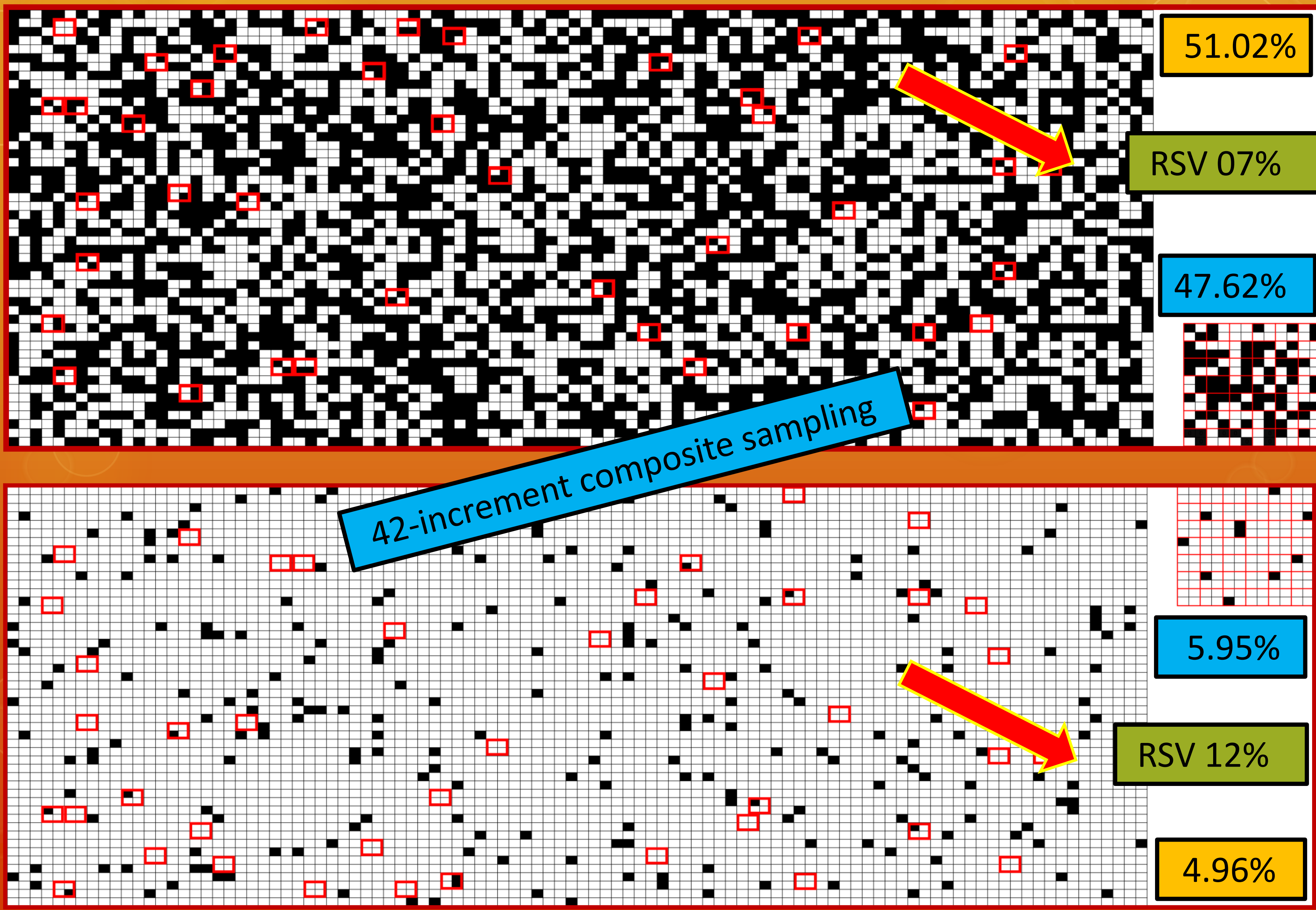

UNPASTEURISED
CHEDDAR

Grab sampling - illustration

Here we take ”random sampling” in full earnest …

”It would appear that the plant is made up of cars in a parking lot ..”

”Further mass-reduction – again by grab-sampling - shows that the lot is composed of parts of black cars only!”



51.02%
RSV 07%
47.62%
42-increment composite sampling
5.95%
RSV 12%
4.96%

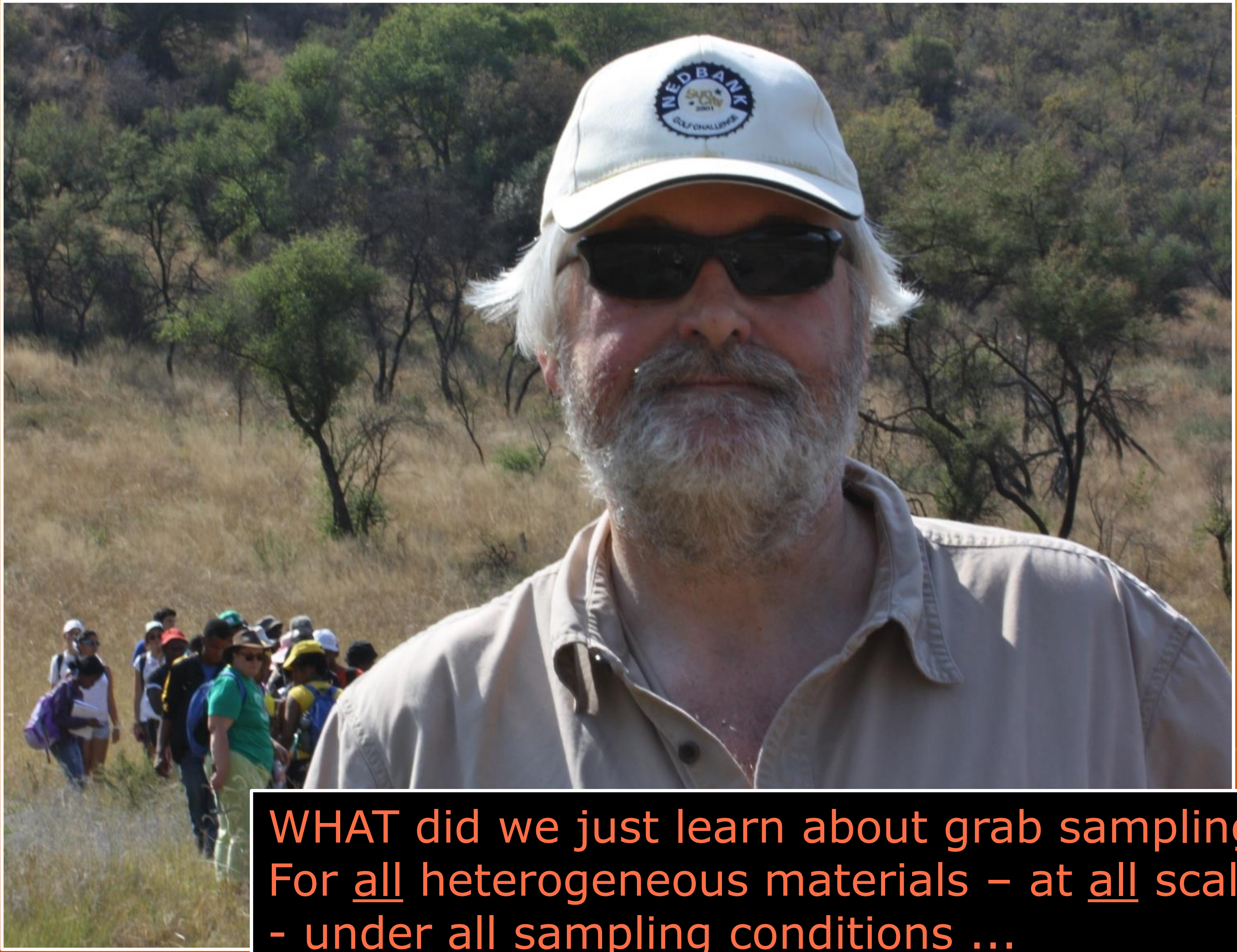
Representative Sampling: Theory of Sampling (TOS)

TOS - Axiomatic exposé

Governing principles (GP) – Sampling unit operations (SUO)

1. FSP: Fundamental Sampling Principle
2. SSI: Sampling Scale Invariance
3. PSC: Sampling Correctness (bias-free sampling)
4. PSS: Sampling Simplicity (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (Sub-sampling)

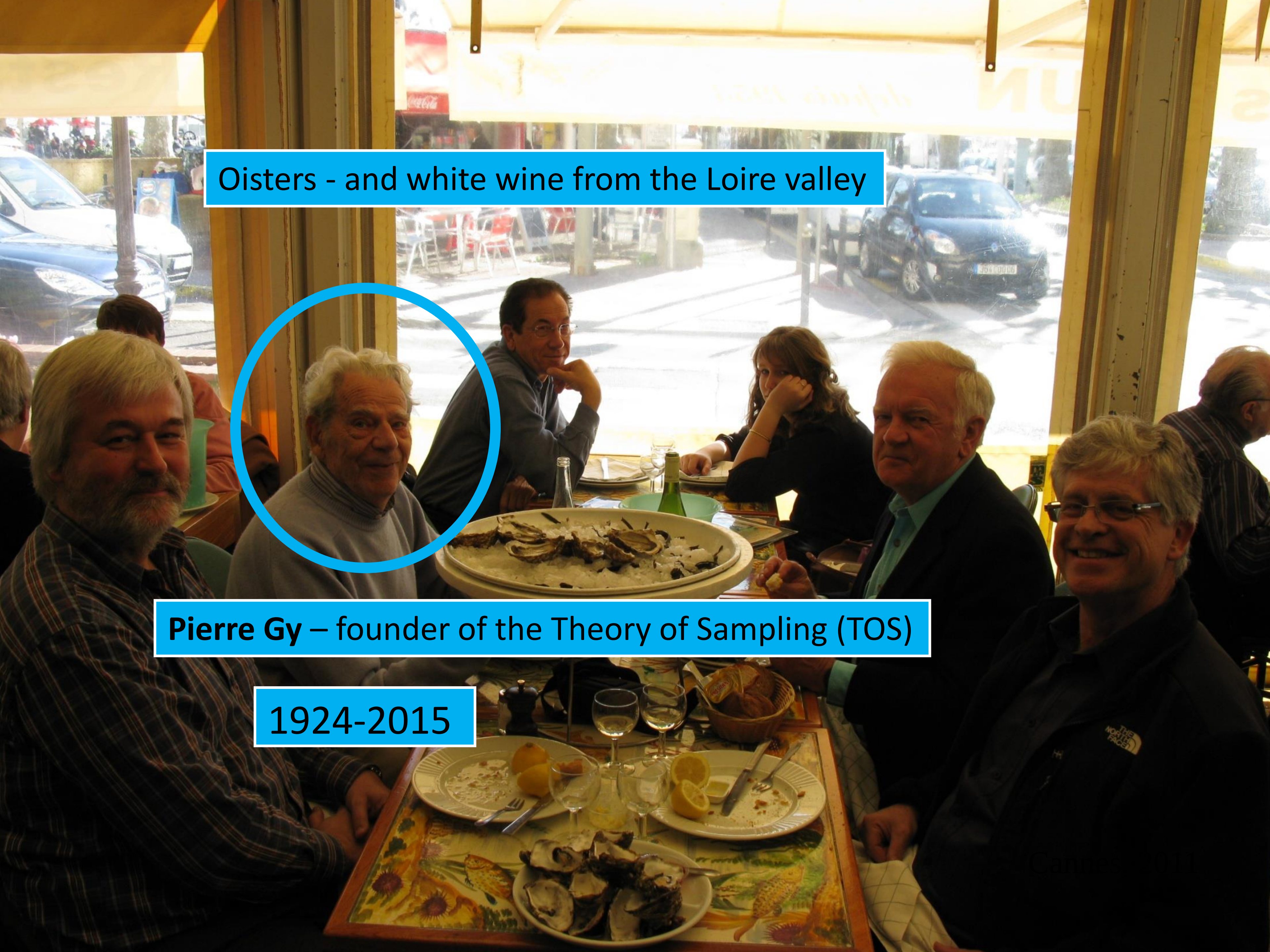
Exit grab sampling!



WHAT did we just learn about grab sampling?
For <u>all</u> heterogeneous materials – at <u>all</u> scales
- under all sampling conditions ...

The one EXCEPTION from grab sampling

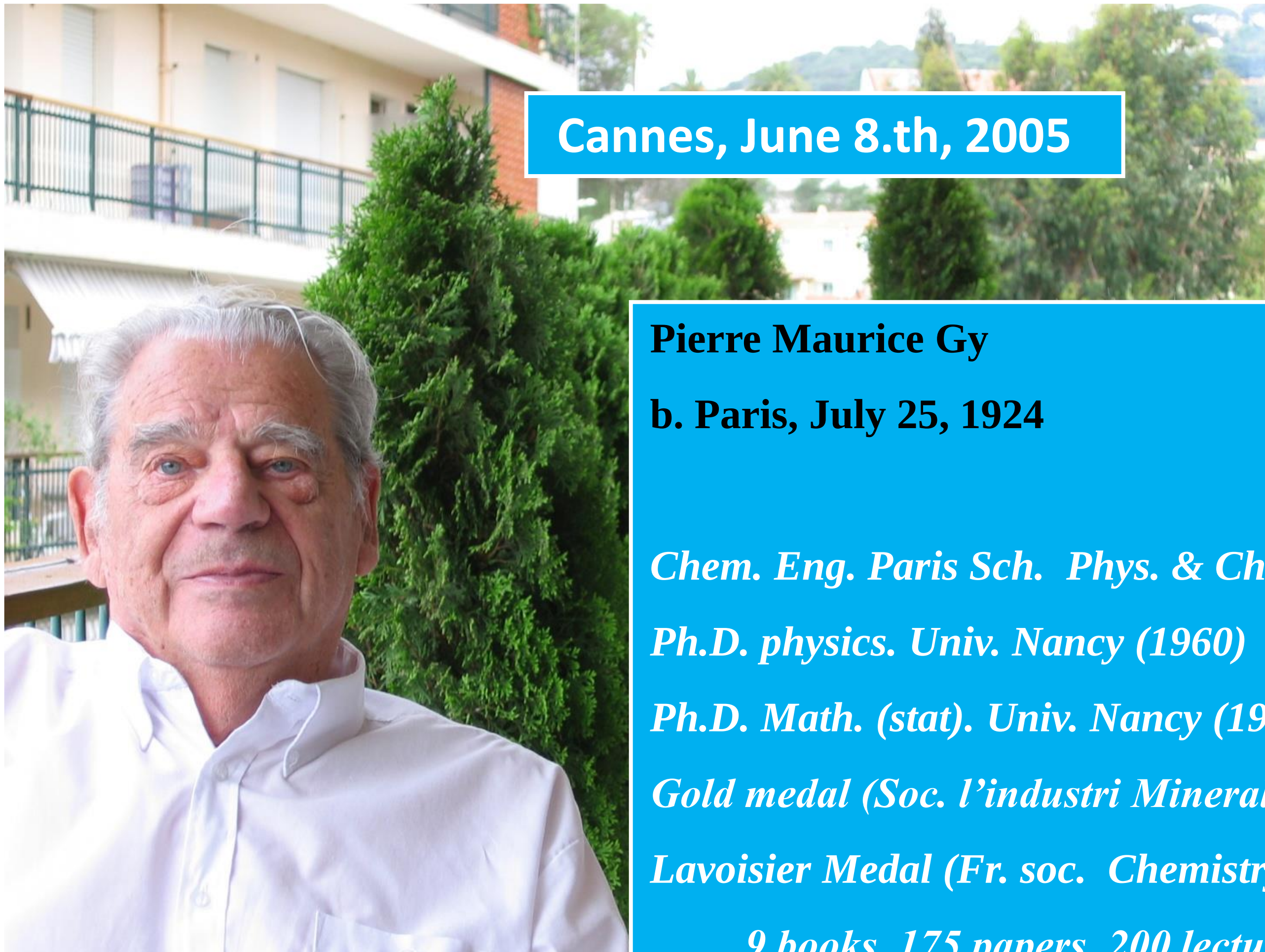
Well there are two exceptions ... ...



Oisters - and white wine from the Loire valley

Pierre Gy – founder of the Theory of Sampling (TOS)

1924-2015



Cannes, June 8.th, 2005

Pierre Maurice Gy

b. Paris, July 25, 1924

Chem. Eng. Paris Sch. Phys. & Chem. (46)

Ph.D. physics. Univ. Nancy (1960)

Ph.D. Math. (stat). Univ. Nancy (1975)

Gold medal (Soc. l'industri Minerale) (63,76)

Lavoisier Medal (Fr. soc. Chemistry) (1995)

… 9 books, 175 papers, 200 lectures …

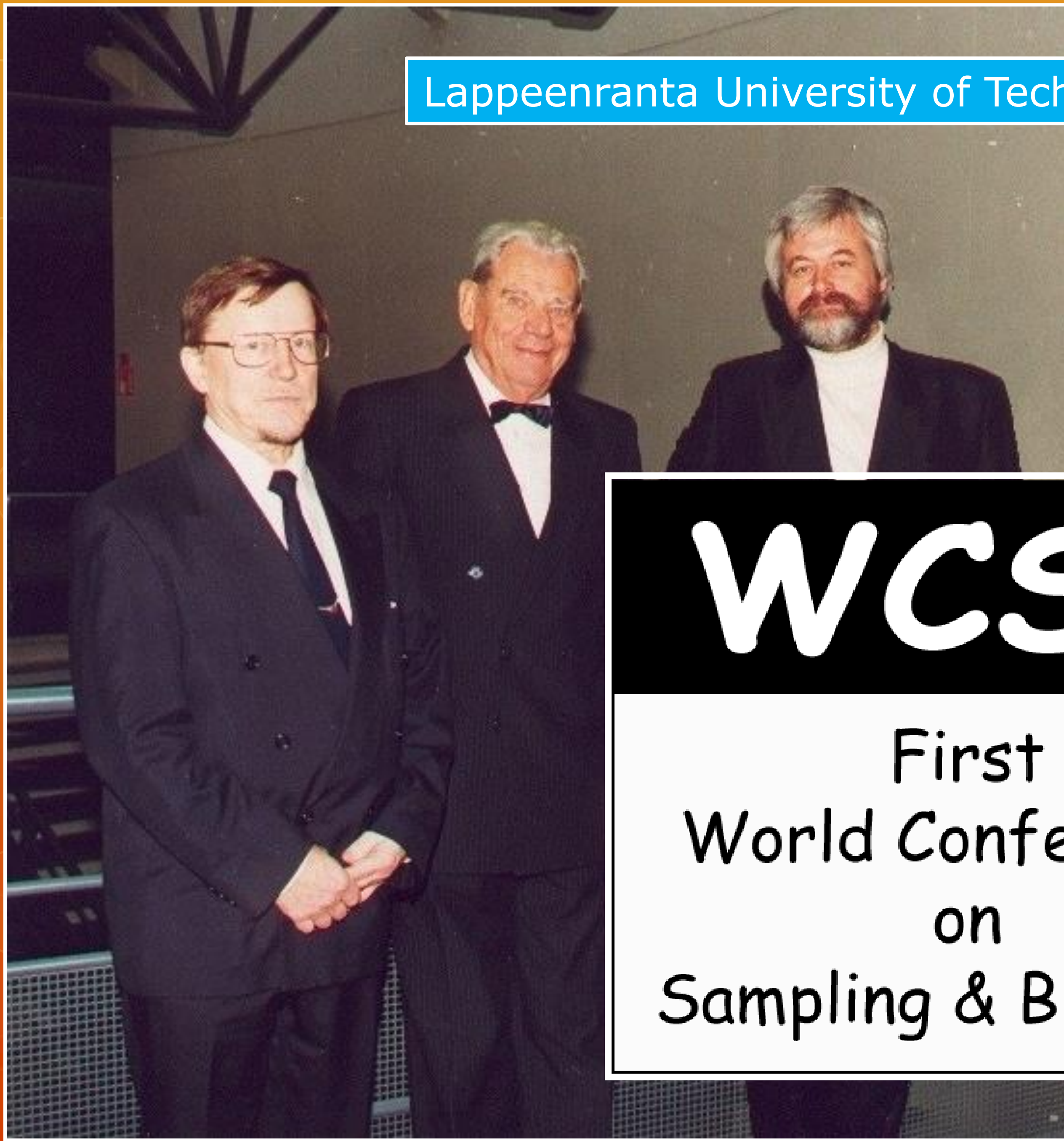
Pierre Gy: founder of TOS

A brilliant scientist – a monumental *ouevre* – a gentleman friend to all samplers

From where certain VIKINGS originated
who raided *Le Normandie* 1000 years ago
and later then setteled there:
... The family Pierre Gy ...

The estuary ”Gyland”, Flekkefjord, Norway

Lappeenranta University of Technology (LUT) - 1999



WCSB

First
World Conference
on
Sampling & Blending

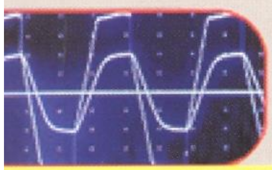
2003

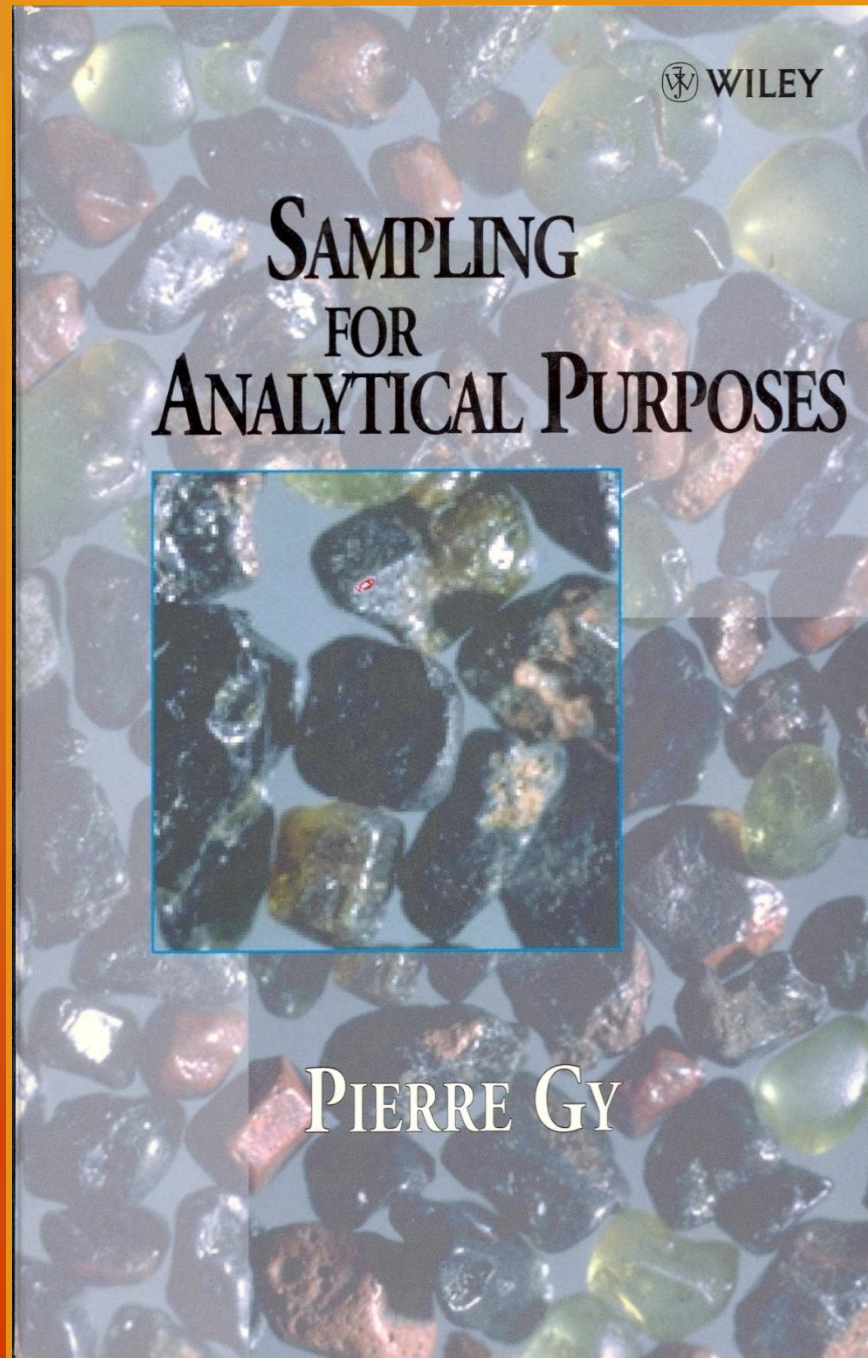
ELSEVIER

Vol. 74, issue 1, 28 November 2004

ISSN 0169-7439

CHEMOMETRICS AND INTELLIGENT LABORATORY SYSTEMS




WILEY
SAMPLING FOR ANALYTICAL PURPOSES
PIERRE GY

KHE Consulting

Theory and Practice of TOS Representative Sampling

A minimum understanding of governing principles and sampling unit operations

- for all types of materials (all degrees of heterogeneity:low / intermediate / high
- at all scales (for all lot sizes: small / intermediate / big / extreme)
- unifying principles of representative sampling: field/plant/laboratory

The THEME of today's shortcourse: WHAT comes BEFORE analysis?

Measurement Uncertainty (MU)

Theory of Sampling (TOS)

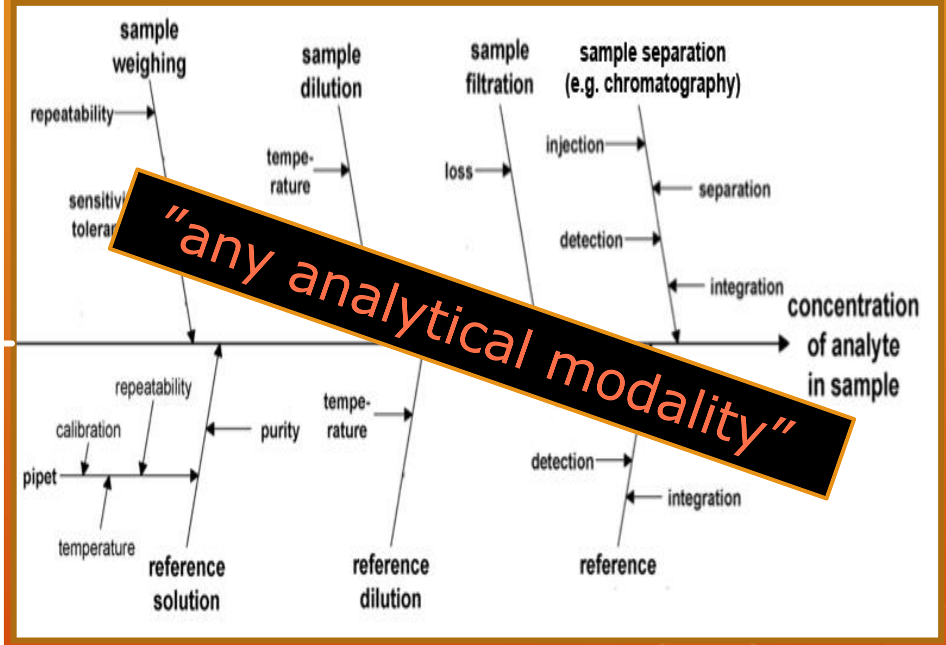
APGC + MS/MS
(single) MS
(universal) MS
LC-MS + APGC + CI + (tandem) MS
GC –GC
HPLC / HRMS .. (data independent MS/MS)
Tandem Ionization
UHPLC / QT [MS/MS libraries]
GC – TF-MS
.....
.....

Total Sampling Error (TSE)

Total Analytical Error (TAE)

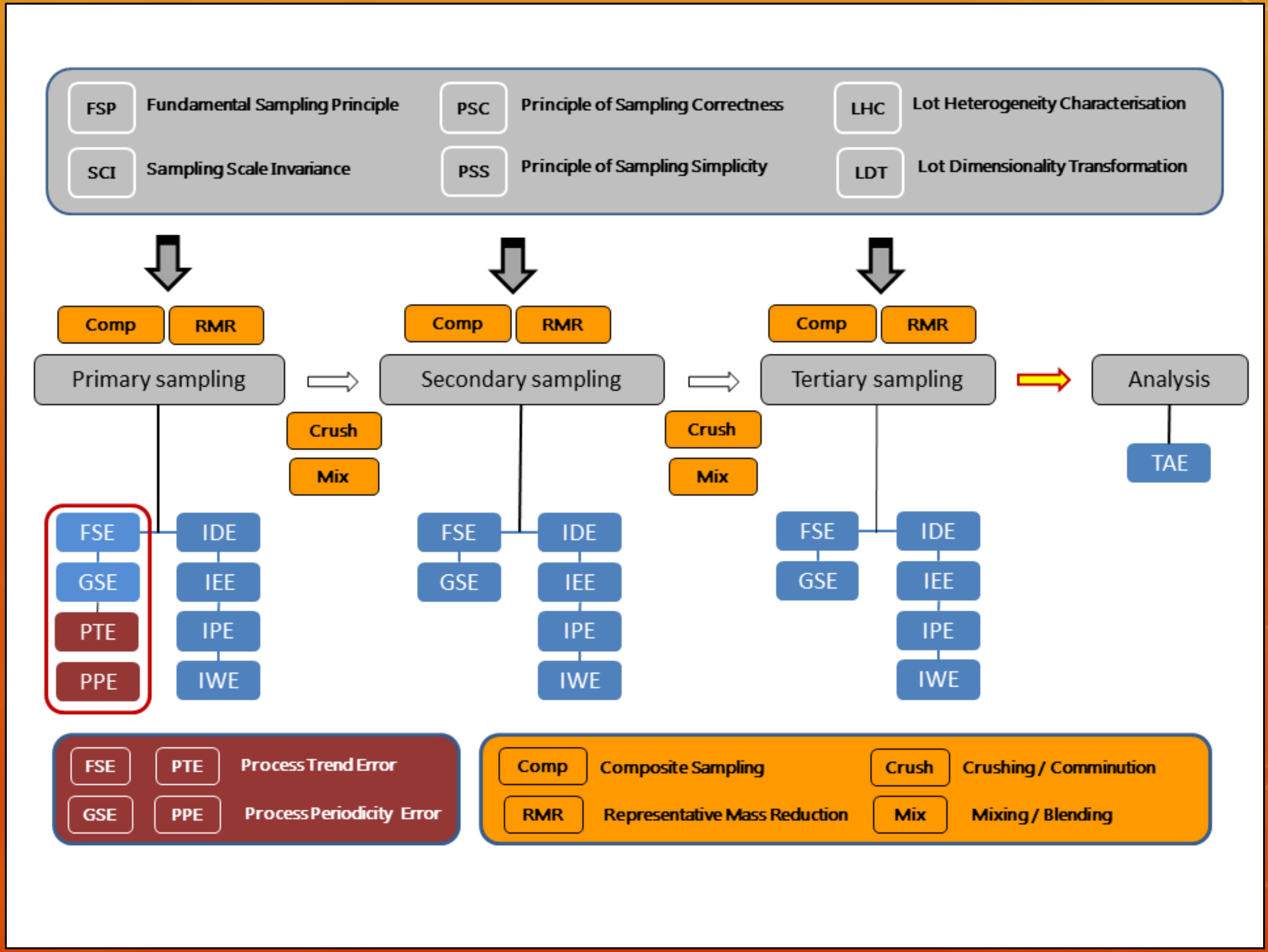
Theory of Sampling (TOS)

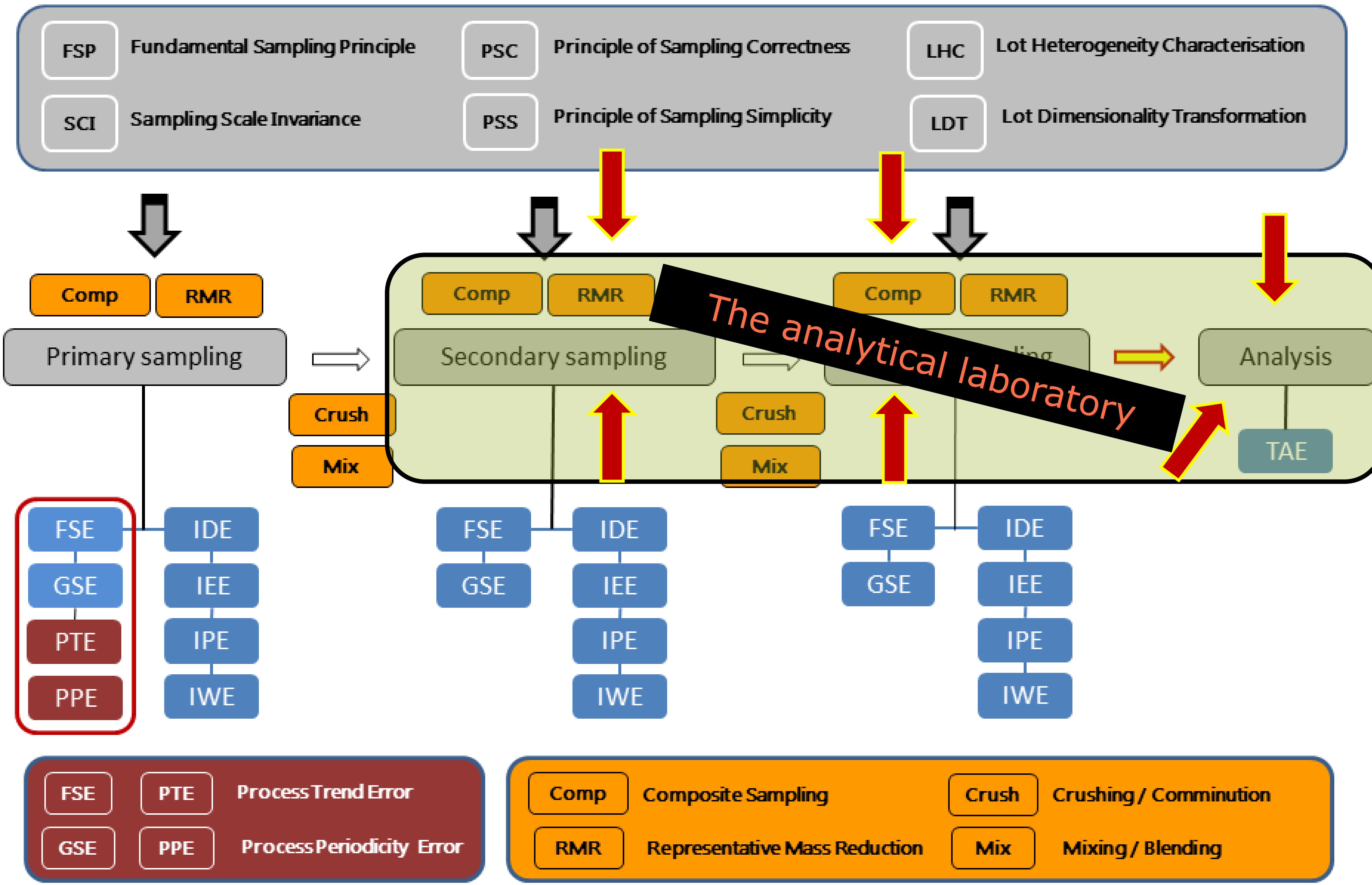
Measurement Uncertainty (MU)



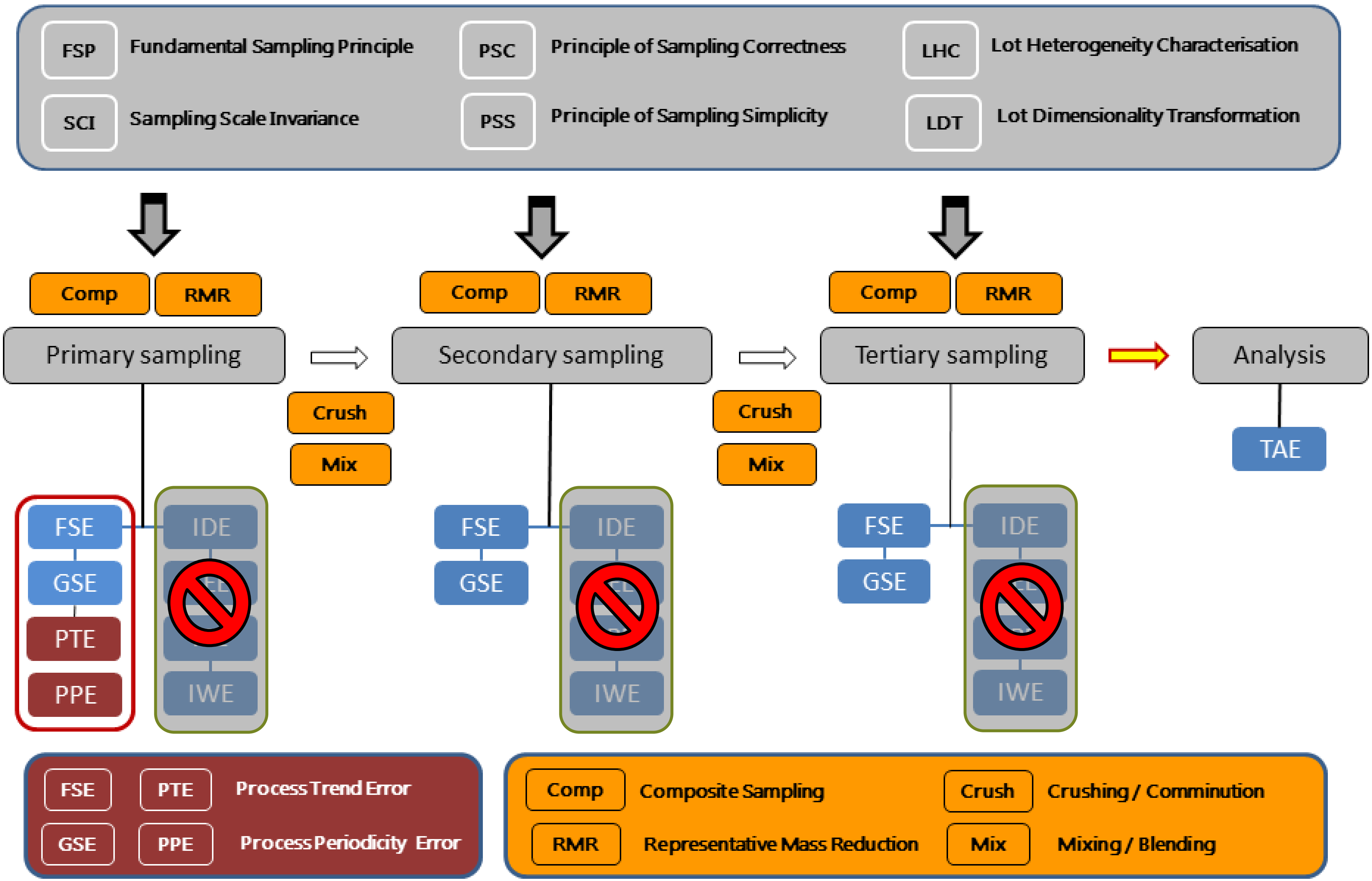
$MU_{total} = MU_{sampling} + MU_{analysis}$

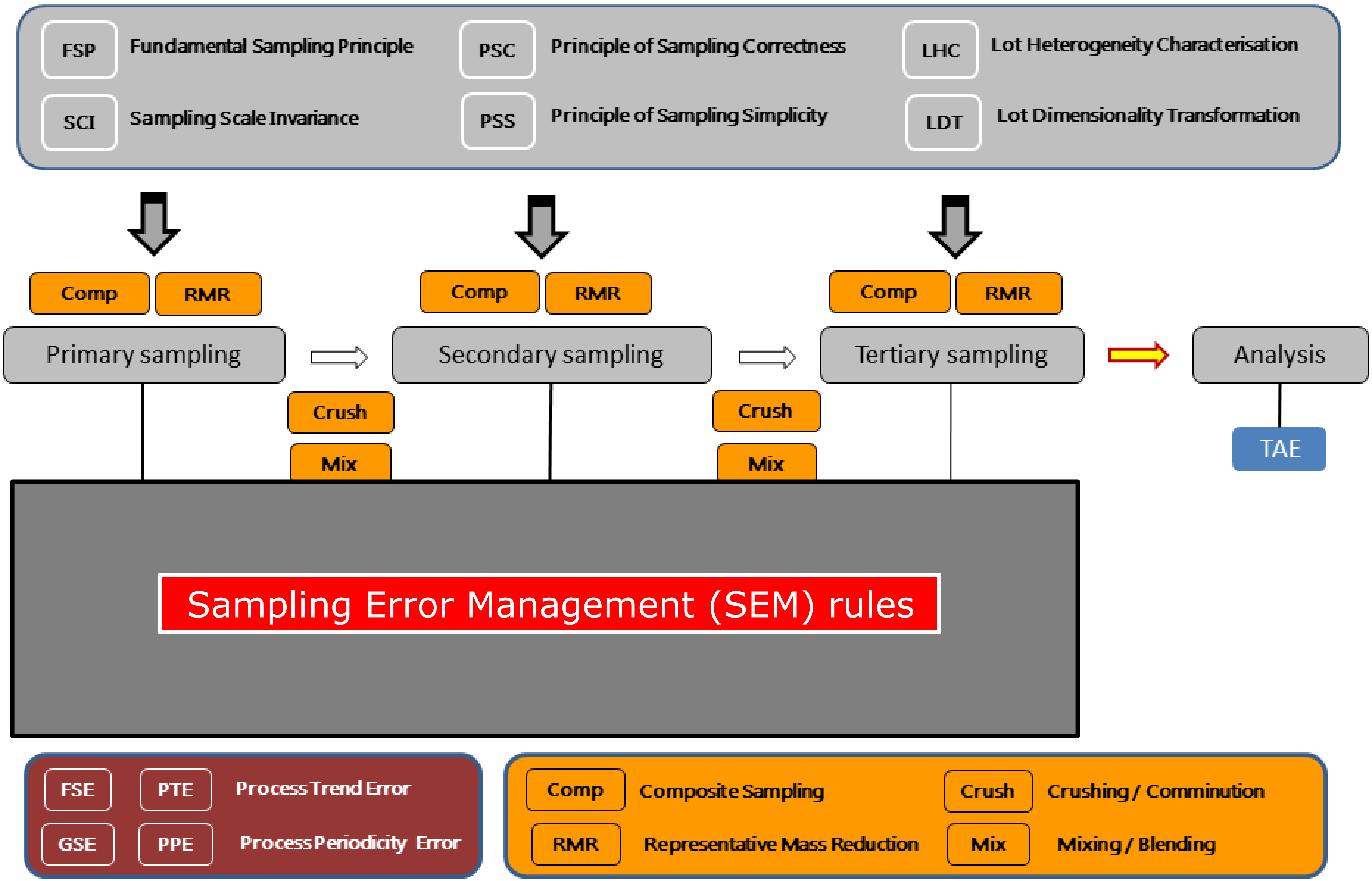
Theory of Sampling (TOS) – everything in a glance





FSP
Fundamental Sampling Principle
PSC
Principle of Sampling Correctness
LHC
Lot Heterogeneity Characterisation
SCI
Sampling Scale Invariance
PSS
Principle of Sampling Simplicity
LDT
Lot Dimensionality Transformation
Comp
RMR
Primary sampling
Crush
Mix
FSE
GSE
PTE
PPE
IDE
IEE
IPE
IWE
Comp
RMR
Secondary sampling
Crush
Mix
FSE
GSE
IDE
IEE
IPE
IWE
The analytical laboratory
Comp
RMR
Analysis
TAE
FSE
GSE
IDE
IEE
IPE
IWE
FSE
PTE
Process Trend Error
GSE
PPE
Process Periodicity Error
Comp
Composite Sampling
Crush
Crushing / Comminution
RMR
Representative Mass Reduction
Mix
Mixing / Blending


FSP
Fundamental Sampling Principle
PSC
Principle of Sampling Correctness
LHC
Lot Heterogeneity Characterisation
SCI
Sampling Scale Invariance
PSS
Principle of Sampling Simplicity
LDT
Lot Dimensionality Transformation
Comp
RMR
Primary sampling
Secondary sampling
Tertiary sampling
Analysis
Crush
Mix
TAE
FSE
GSE
PTE
PPE
IDE
IWE
FSE
PTE
Process Trend Error
GSE
PPE
Process Periodicity Error
Comp
Composite Sampling
Crush
Crushing / Comminution
RMR
Representative Mass Reduction
Mix
Mixing / Blending

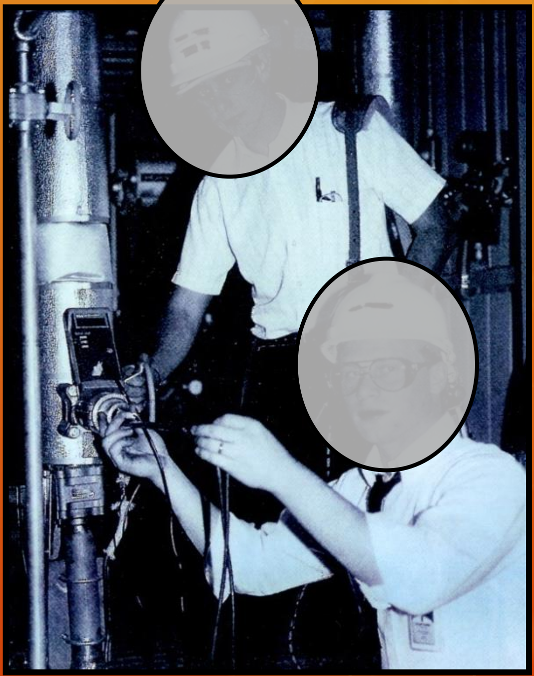

FSP
Fundamental Sampling Principle
PSC
Principle of Sampling Correctness
LHC
Lot Heterogeneity Characterisation
SCI
Sampling Scale Invariance
PSS
Principle of Sampling Simplicity
LDT
Lot Dimensionality Transformation
Comp
RMR
Primary sampling
Comp
RMR
Secondary sampling
Comp
RMR
Tertiary sampling
Analysis
Crush
Mix
Crush
Mix
TAE
Sampling Error Management (SEM) rules
FSE
PTE
Process Trend Error
GSE
PPE
Process Periodicity Error
Comp
Composite Sampling
Crush
Crushing / Comminution
RMR
Representative Mass Reduction
Mix
Mixing / Blending

Sampling *competence*

The sampling *fool*

So, let us all become *fully* TOS competent!

The sampling *fool*



Sampling is actually only dependent upon three things

Representative Sampling: Theory of Sampling (TOS)

TOS - Axiomatic exposé

Governing principles (GP) – Sampling unit operations (SUO)

1. FSP: Fundamental Sampling Principle
2. SSI: Sampling Scale Invariance
3. PSC: Sampling Correctness (bias-free sampling)
4. PSS: Sampling Simplicity (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (Sub-sampling)

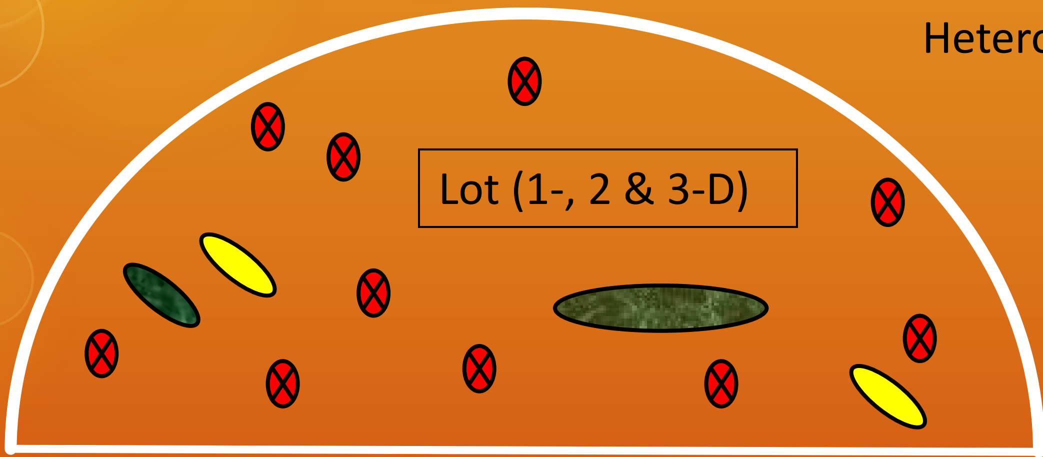
A grab sample ...

Fundamental Sampling Error (FSE) [+ GSE]

Several increments ... ...

Trying (very well) to deal with (GSE) [+ *FSE*]

Heterogeneity (hidden)



Fundamental Sampling Principle (FSP):

All increments must have the *same* (non-zero) probability of ending up in the sample (non-neg)

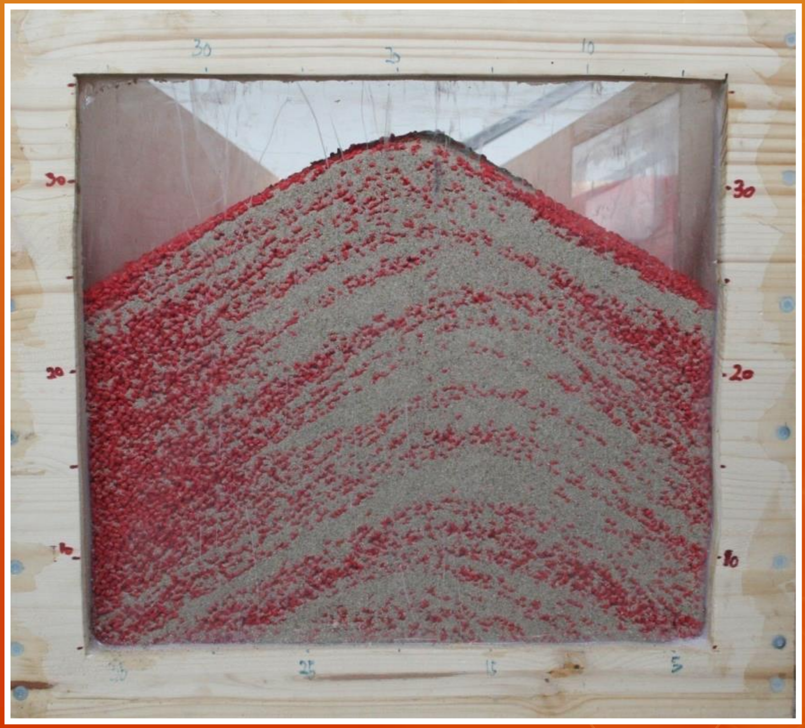
FSP

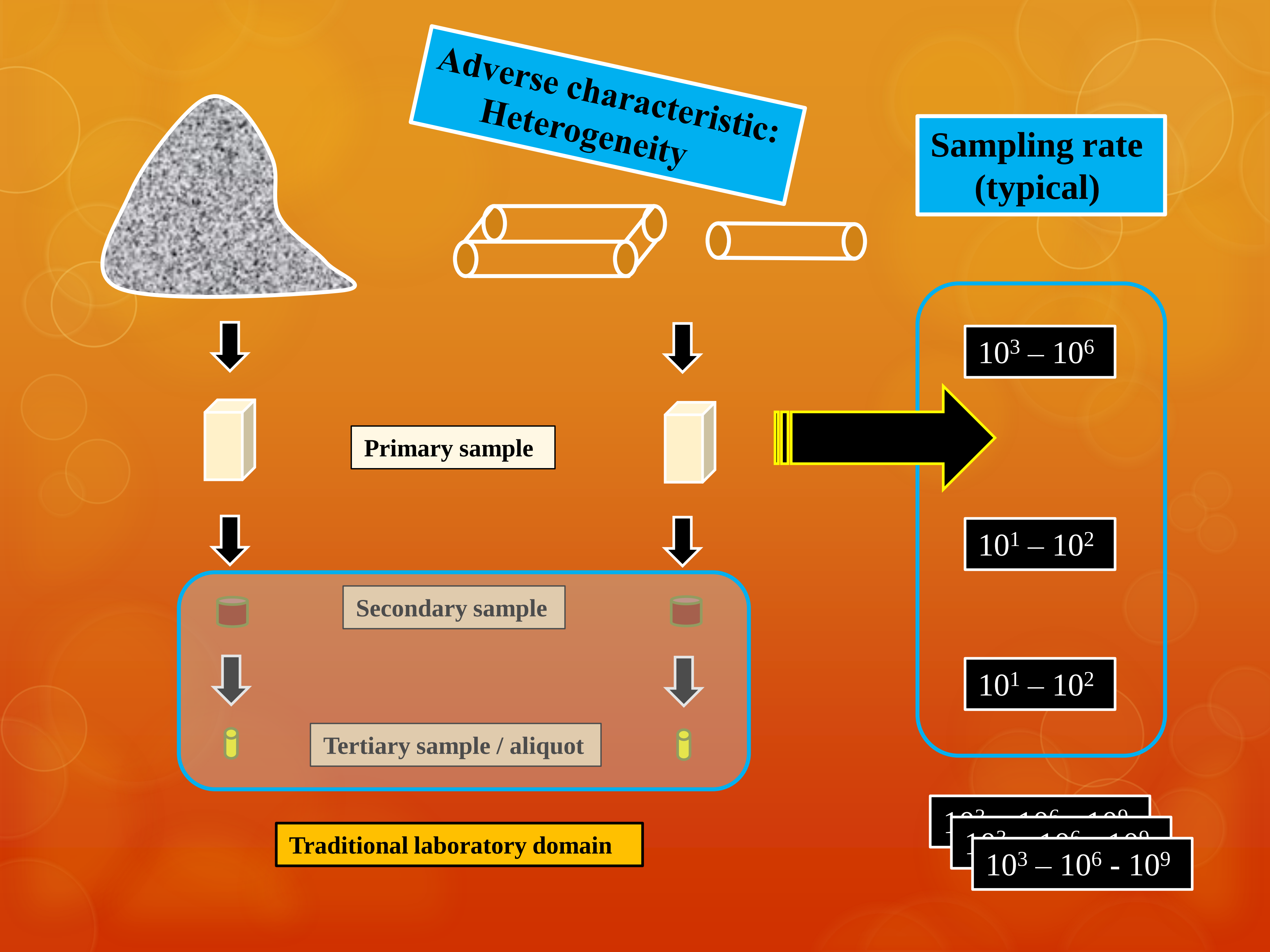
Fundamental Sampling Principle (FSP) 3-D lot

Fundamental Sampling Principle (FSP) 3-D lot

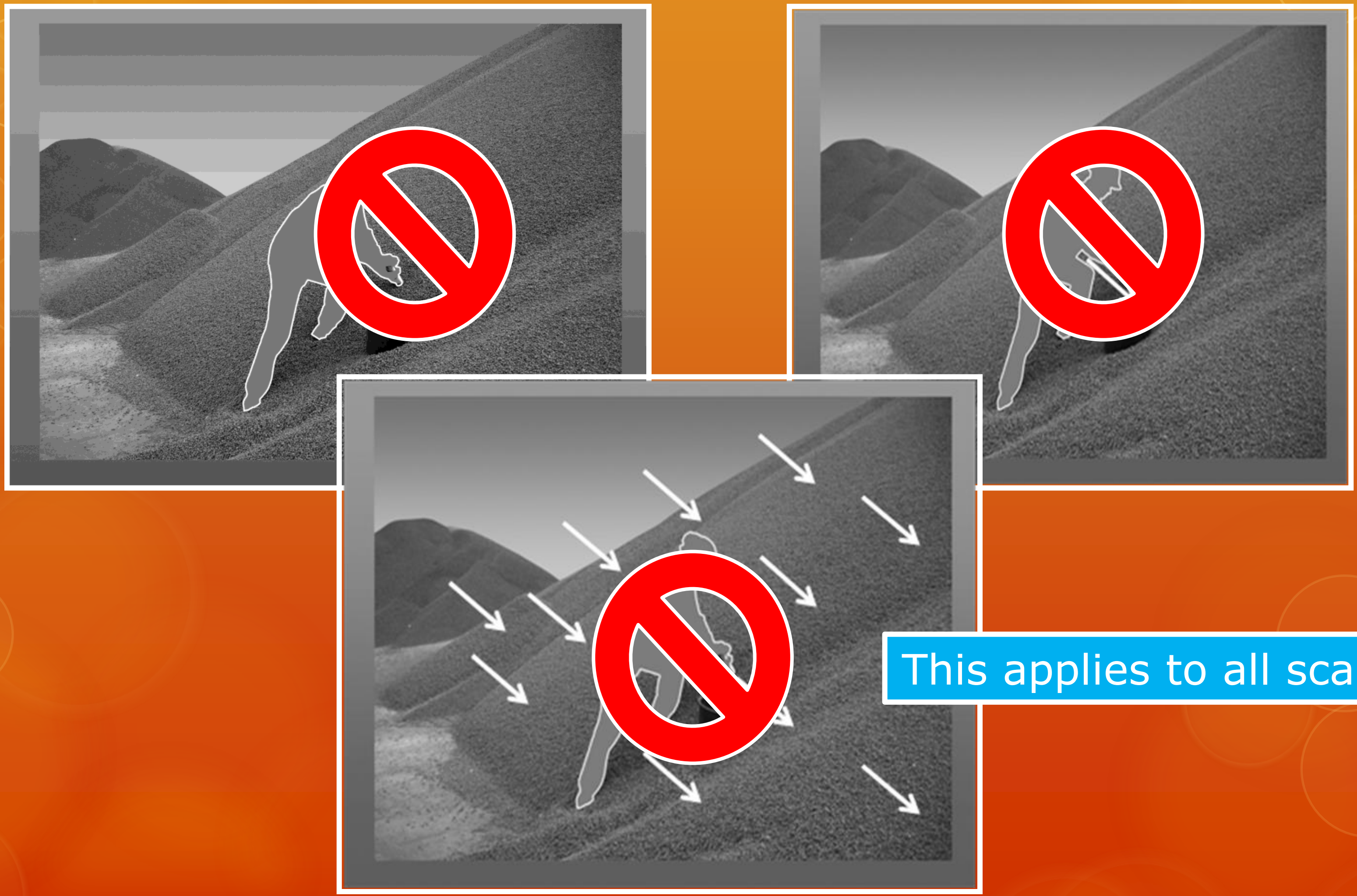
Fundamental Sampling Principle (FSP) 3-D lot

FSP



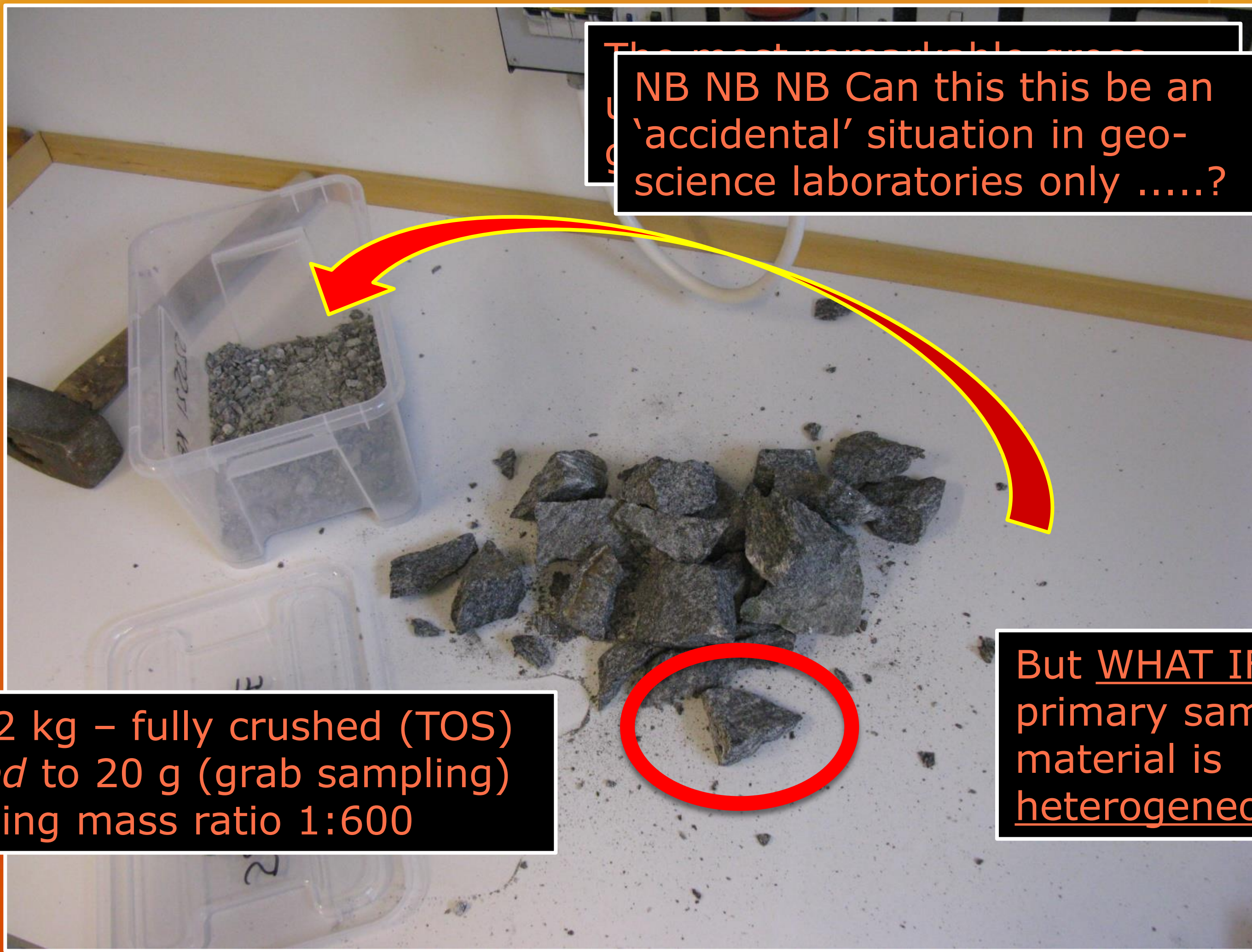

Adverse characteristic: Heterogeneity
Sampling rate (typical)
10³ – 10⁶
Primary sample
10¹ – 10²
Secondary sample
10¹ – 10²
Tertiary sample / aliquot
Traditional laboratory domain
10³ – 10⁶ - 10⁹

Fundamental Sampling Principle (FSP) 3-D lot



This applies to all scales!

- the analytical result <u>depends</u> on the sampling procedures used ....



NB NB NB Can this this be an ‘accidental’ situation in geo-science laboratories only .....?

Whole 12 kg – fully crushed (TOS) *compared* to 20 g (grab sampling) – missing mass ratio 1:600

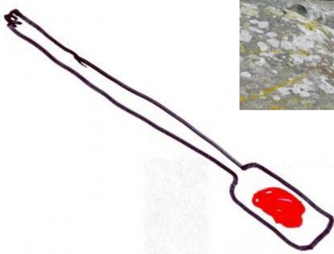
But <u>WHAT IF</u> the primary sample material is <u>heterogeneous</u>?

Representative Sampling: Theory of Sampling (TOS)

TOS - Axiomatic exposé

Governing principles (GP) – Sampling unit operations (SUO)

1. FSP: Fundamental Sampling Principle
2. SSI: Sampling Scale Invariance
3. PSC: Sampling Correctness (bias-free sampling)
4. PSS: Sampling Simplicity (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (Sub-sampling)



...... only the SCALE !!!

Sampling <u>in the laboratory</u>: What’s the difference w.r.t. the field/plant etc?

<u>Identical</u> sampling issues and problems - at all scales ..

TOS' Simplifying, Governing Principles …

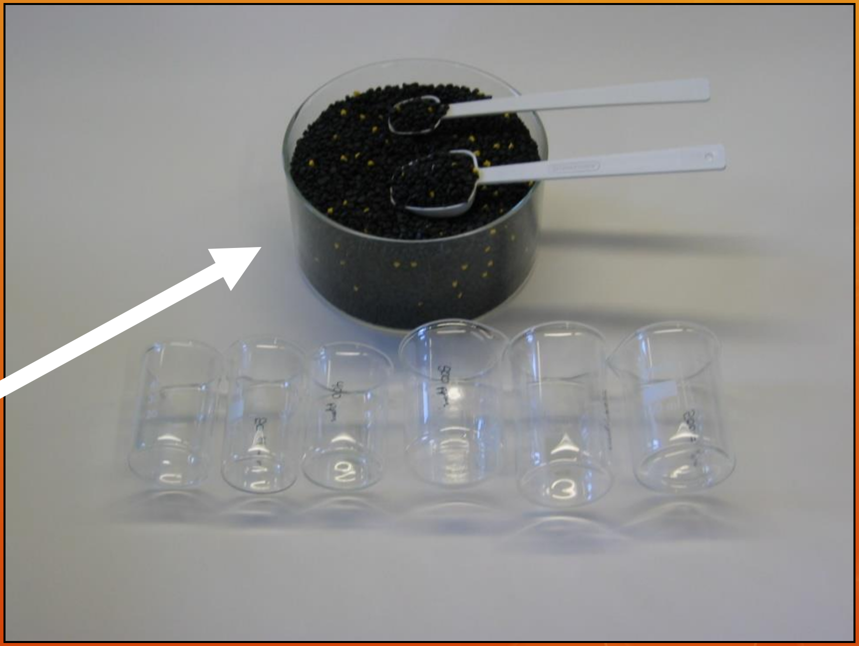
Principle of Sampling Scale Invariance (SSI)

Heterogeneity is a.o. a reflection of:

- *Concentration*
- *Spatial distribution*

Heterogeneity and its manifestation is also dependent of:

- *Sampling tool size*



Sampling rate - 1:50

These sampling tool sizes are very unrealistic w.r.t. real-life situations ...

”1 gram for analysis -----”

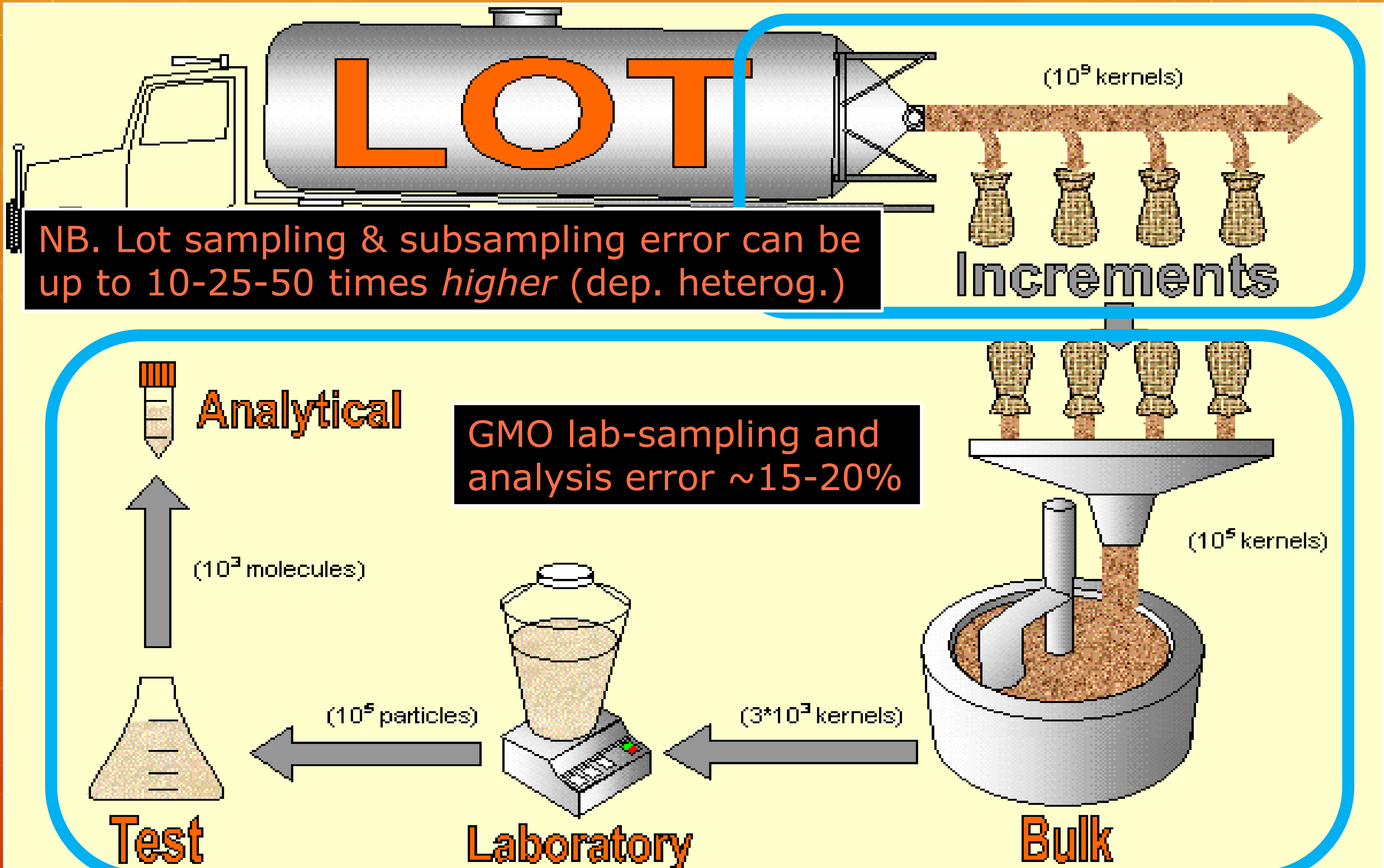
How big is the original lot, which shall be characterised by the analytical result?

	Sampling rate:
1 kg	$1 / 10^3$
10 kg	$1 / 10^4$
100 kg	$1 / 10^5$
1.000 kg (1 ton)	$1 / 10^6$
10.000 kg (5 ton)	$1 / 10^7$
......	....

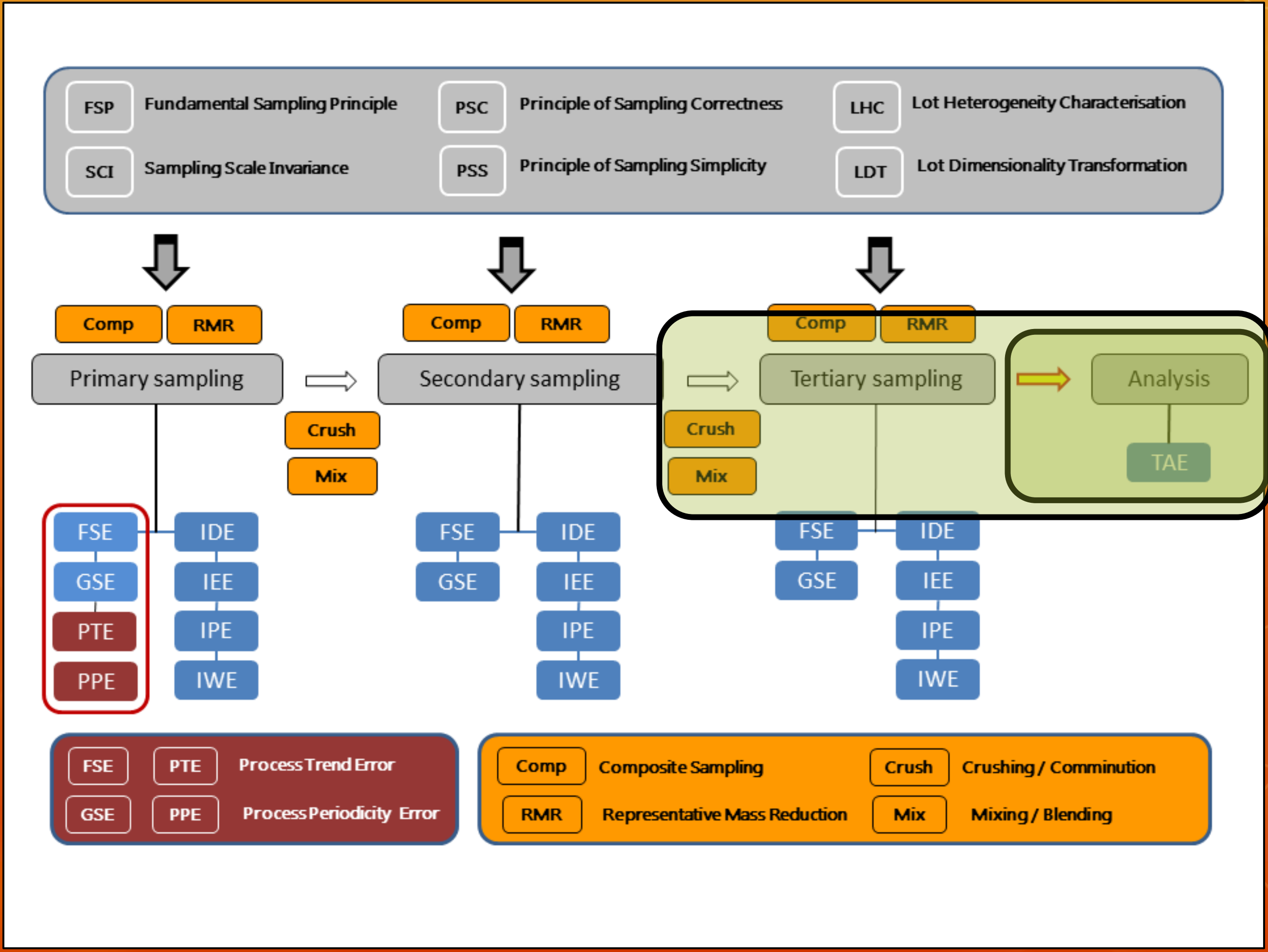
Are these weights realistic w.r.t. analytical performance?

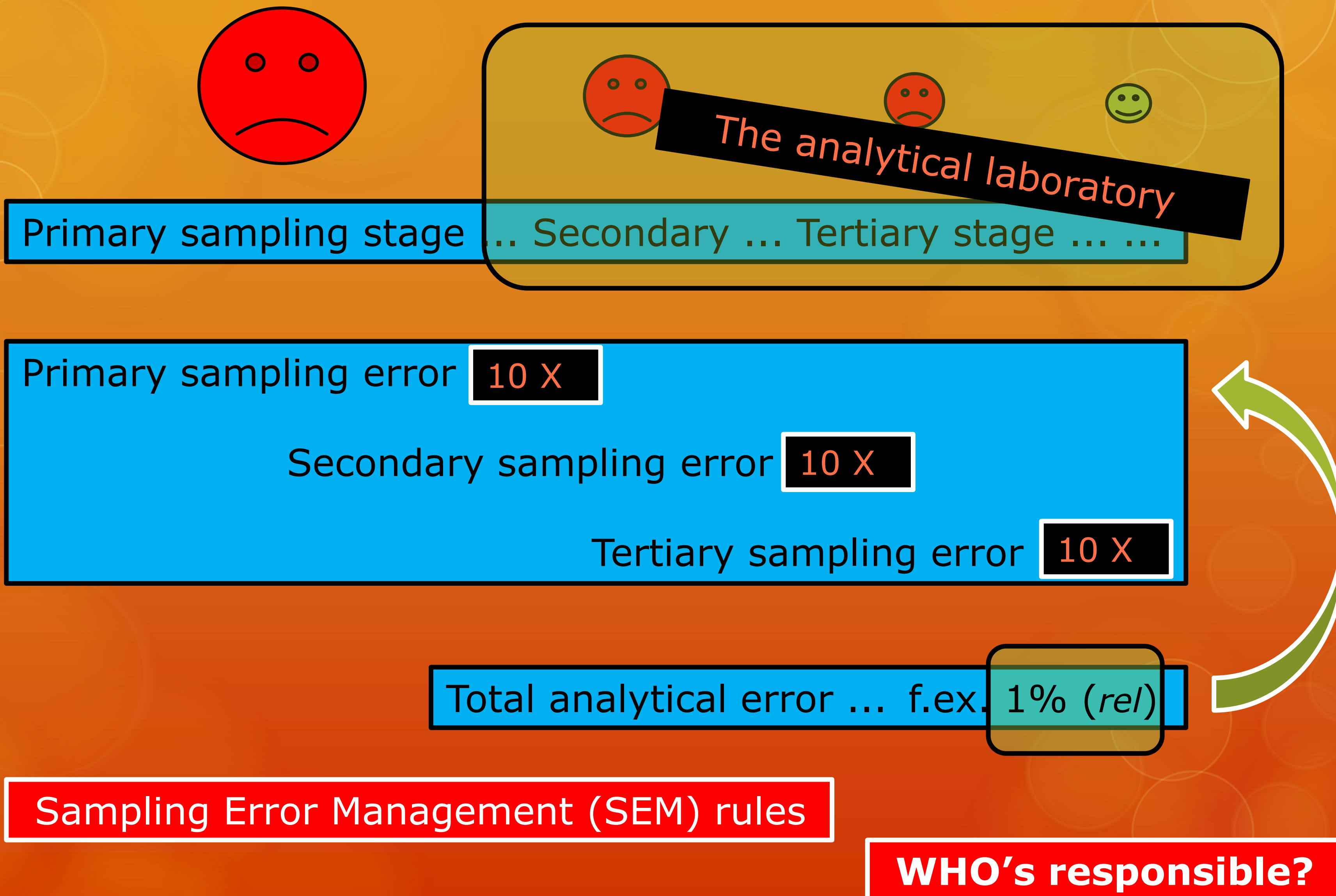
What are the *effective* analytical weights?

- the analytical result <u>depends</u> on the sampling procedures used ....



Theory of Sampling (TOS) – everything in a glance




The analytical laboratory
Primary sampling stage … Secondary … Tertiary stage … …
Primary sampling error
10 X
Secondary sampling error
10 X
Tertiary sampling error
10 X
Total analytical error … f.ex. 1% (*rel*)
Sampling Error Management (SEM) rules
WHO's responsible?

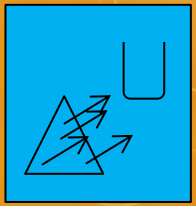
Representative Sampling: Theory of Sampling (TOS)

TOS - Axiomatic exposé

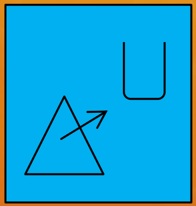
Governing principles (GP) – Sampling unit operations (SUO)

1. FSP: Fundamental Sampling Principle
2. SSI: Sampling Scale Invariance
3. PSC: Sampling Correctness (bias-free sampling)
4. PSS: Sampling Simplicity (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (Sub-sampling)

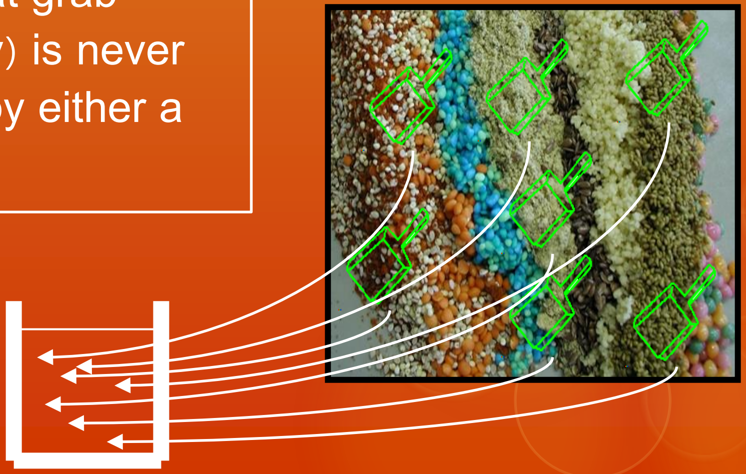
Composite sampling employs Q increment extractions with the aim to 'cover' the lot volume (only Q = 4 increments shown in this principal illustration). Proportional to the heterogeneity encountered, a higher number of increments will be required. Comp samp. must always respect FSP !!!

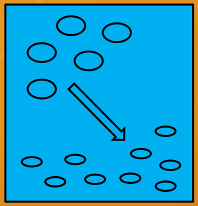


GP (6) Lot Heterogeneity Characterisation (LHC) guarantees that no sampling plan, sampling procedure nor sampling equipment is employed without a mandatory heterogeneity characterisation of the lot material.



Composite sampling is specifically demanding that grab sampling (extraction of one single increment only) is never invoked, unless thoroughly tested and accepted by either a Replication Experiment (RE) or by variographics.

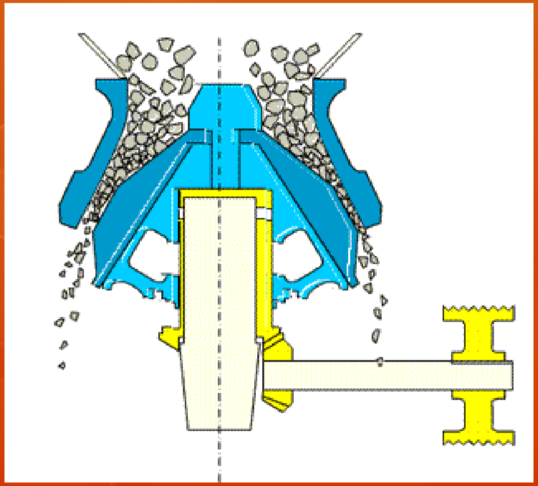


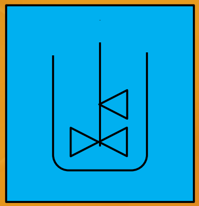


Crushing (**comminution**) is a sampling unit operation which is only brought to bear when necessary, i.e. when the top particle size is contrasting too much with respect to smaller size ranges in order for sampling to be effective and representative. Comminution is the technical process in which the top particle sizes is preferentially crushed first.

A consequence of crushing/comminution is that the majority of particle sizes tend to become more similar, with the further advantage that mixing becomes more effective.

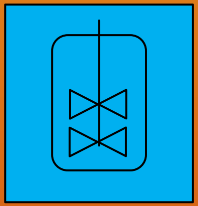
Maceration, crushing or shredding in the presense of a facilitating liquid (often used for selective extraction), as applied to biological materials also lead to reduced general particle sizes.





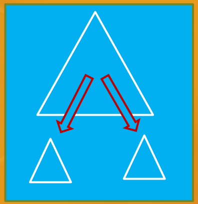
Mixing is a forced mechanical process designed to reduce the distributional heterogeneity (DH) of a material system.

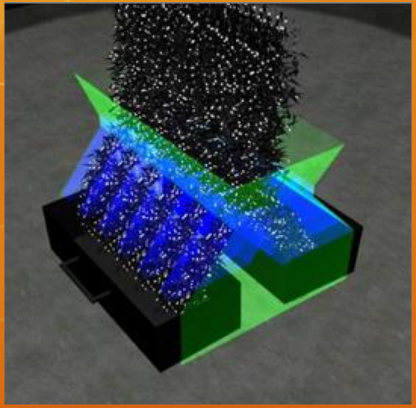
It is always advantageous to mix the results of a sampling or a sub-sampling process *before* further processing (sub-sampling or a next stage mass reduction).

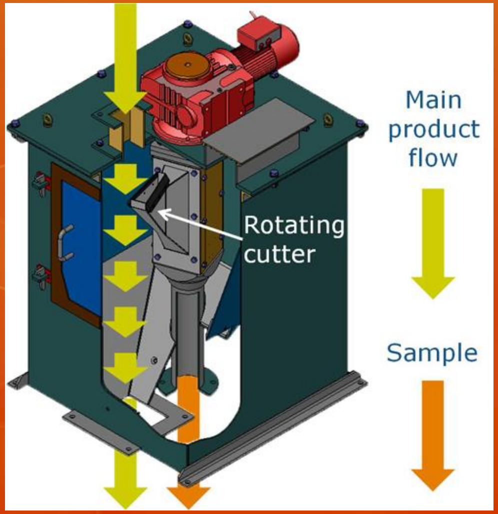


Blending is mixing under stoichiometric constraints, i.e. the final mixing product, a blend, must satisfy compositional constraints e.g. tea, tobacco, cement, pharmaceutical drugs.

Mixing / blending can be applied to both polyphase dry systems (aggregates) and to slurries (solid – liquid systems).







Representative Mass Reduction (RMR) is the key sampling unit operation connecting all sampling stages. Often the terms mass reduction and sub-sampling are used inter alia. There are very many sub-sampling procedures and types of equipment offered on the market, but far from all deliver representative solutions.

For stationary lots, the benchmark study by Petersen et al. (2004) showed conslusively that only the *riffle-splitting principle* lead to Representative Mass Reduction (RMR). Riffle splitters have different physical manifestations; both stationary and roraty solutions exist.

For dynamic lots, lots in movement, the *Vezin sampler* is by far the most effective, fully representative RMR equipment in existence. The Vezin sampler is also superior regarding slurries a.o.

Representative Sampling: Theory of Sampling (TOS)

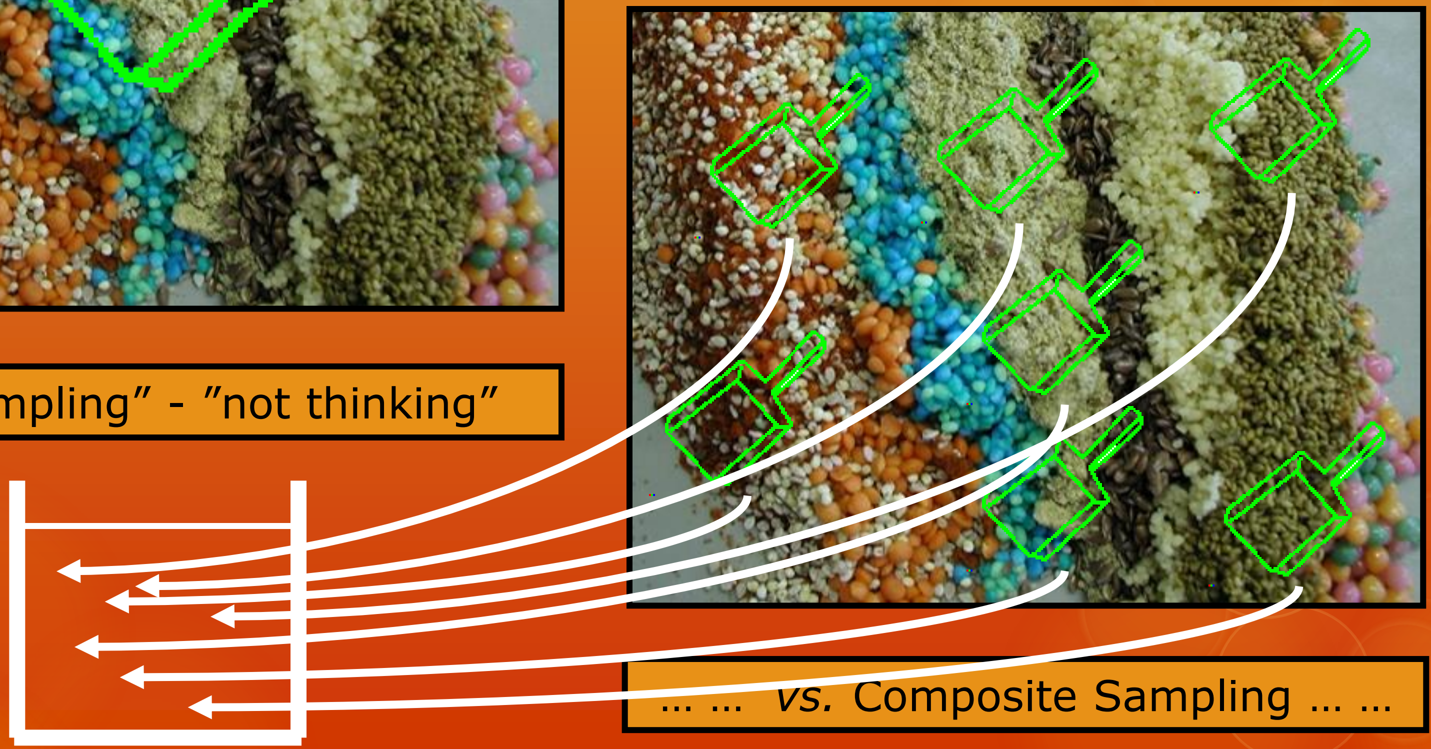
TOS - Axiomatic exposé

Governing principles (GP) – Sampling unit operations (SUO)

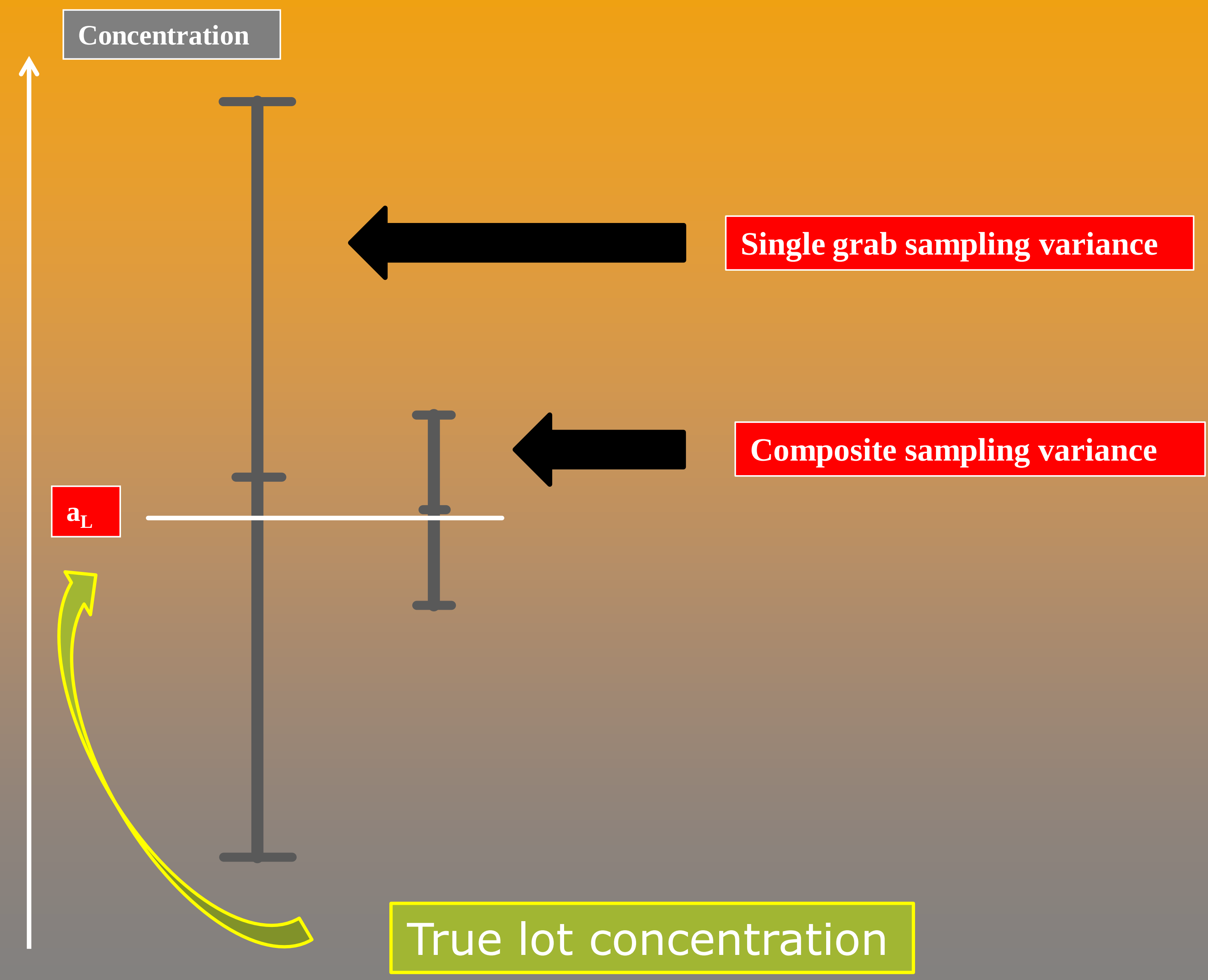
1. FSP: Fundamental Sampling Principle
2. SSI: Sampling Scale Invariance
3. PSC: Sampling Correctness (bias-free sampling)
4. PSS: Sampling Simplicity (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (Sub-sampling)

Sampling Unit Operations: Composite Sampling

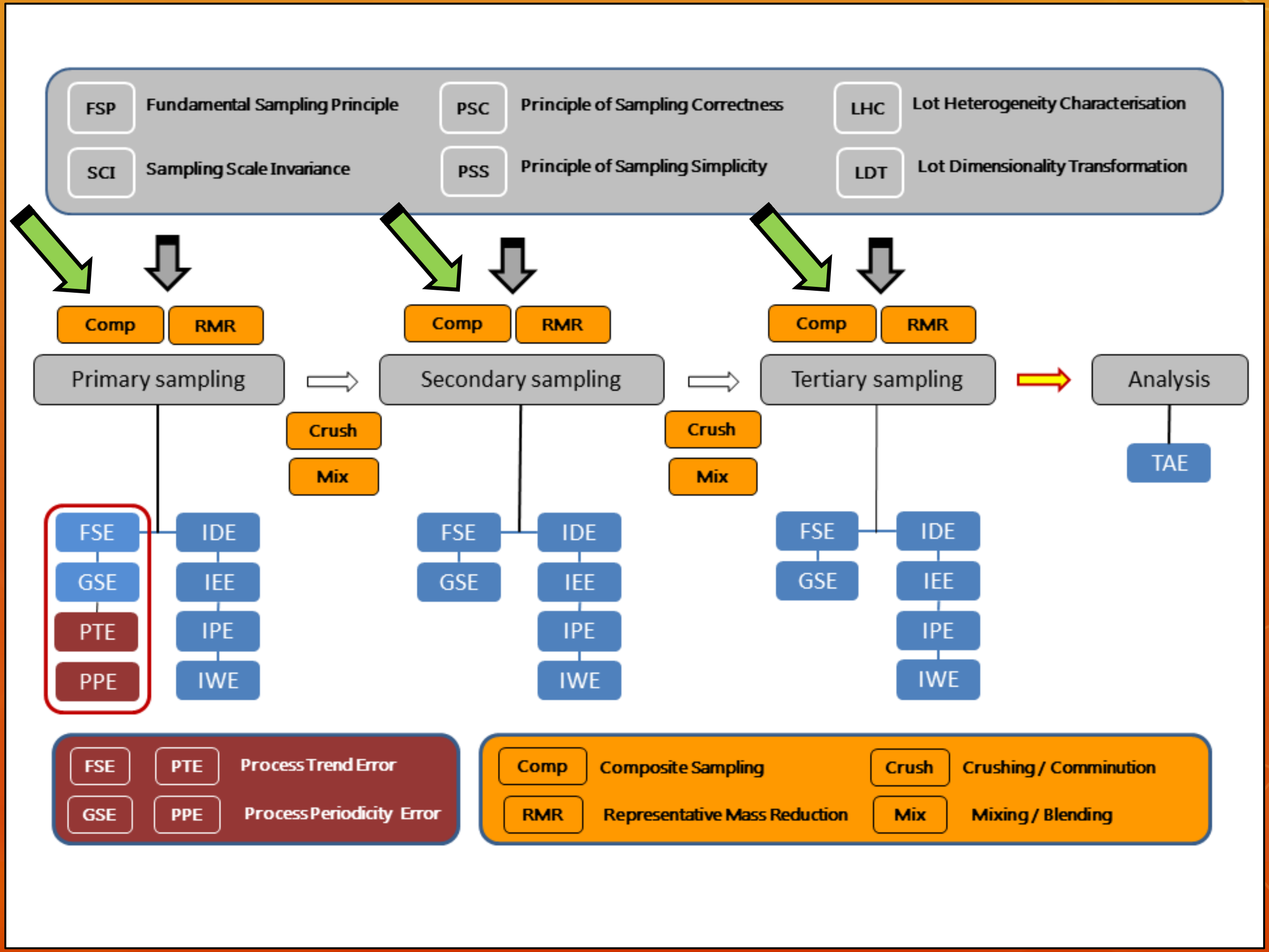
"Grab Sampling" - "not thinking"



… … *vs.* Composite Sampling … …


Concentration
Single grab sampling variance
Composite sampling variance
a_L
True lot concentration

Theory of Sampling (TOS) – everything in a glance



Representative Sampling: Theory of Sampling (TOS)

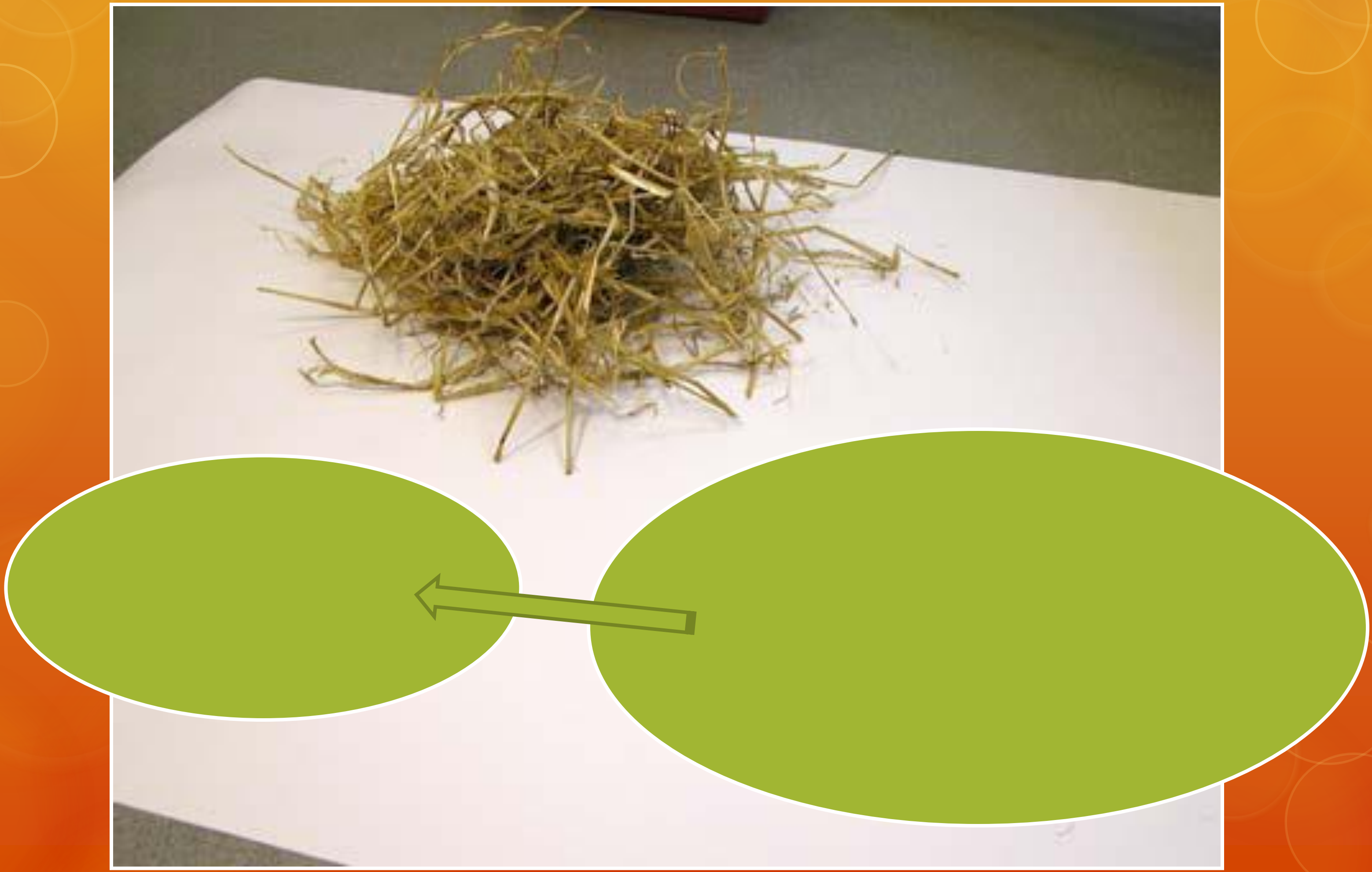
TOS - Axiomatic exposé

Governing principles (GP) – Sampling unit operations (SUO)

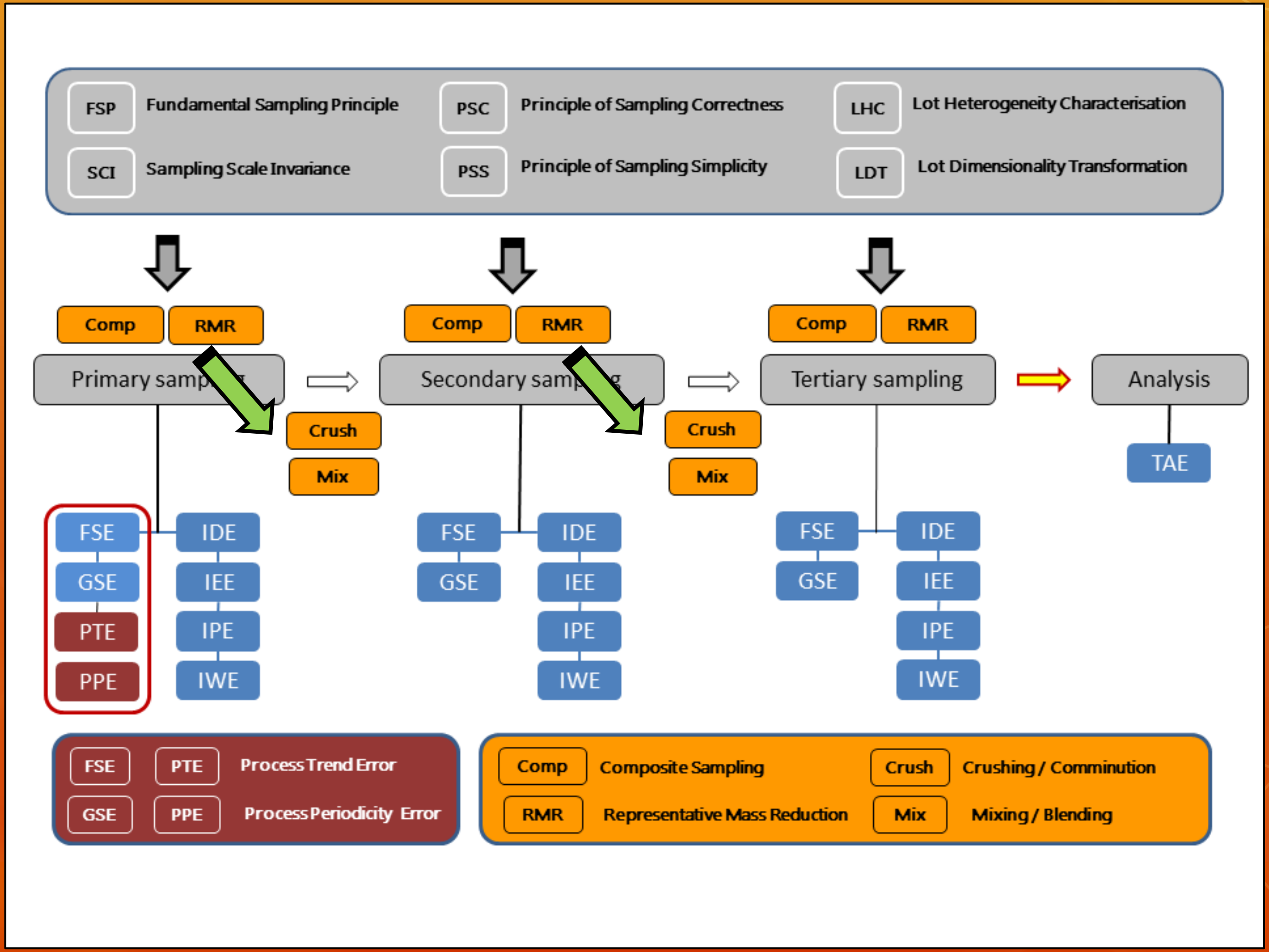
1. FSP: Fundamental Sampling Principle
2. SSI: Sampling Scale Invariance
3. PSC: Sampling Correctness (bias-free sampling)
4. PSS: Sampling Simplicity (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (Sub-sampling)

Crushing / Maceration

REALLY difficult materials ... Que faire?

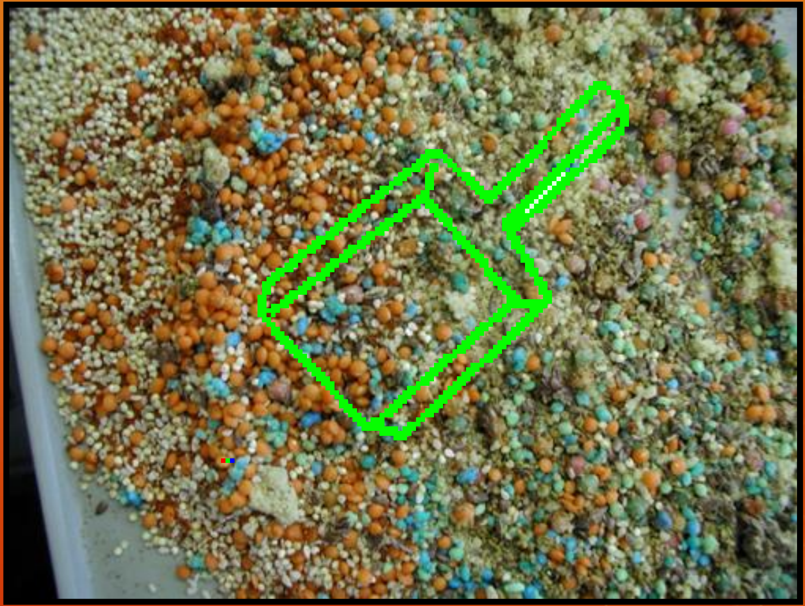


Theory of Sampling (TOS) – everything in a glance



Sampling Unit Operations: Mixing / Blending

NB: Crushing + composite sampling + mixing – Unbeatable!

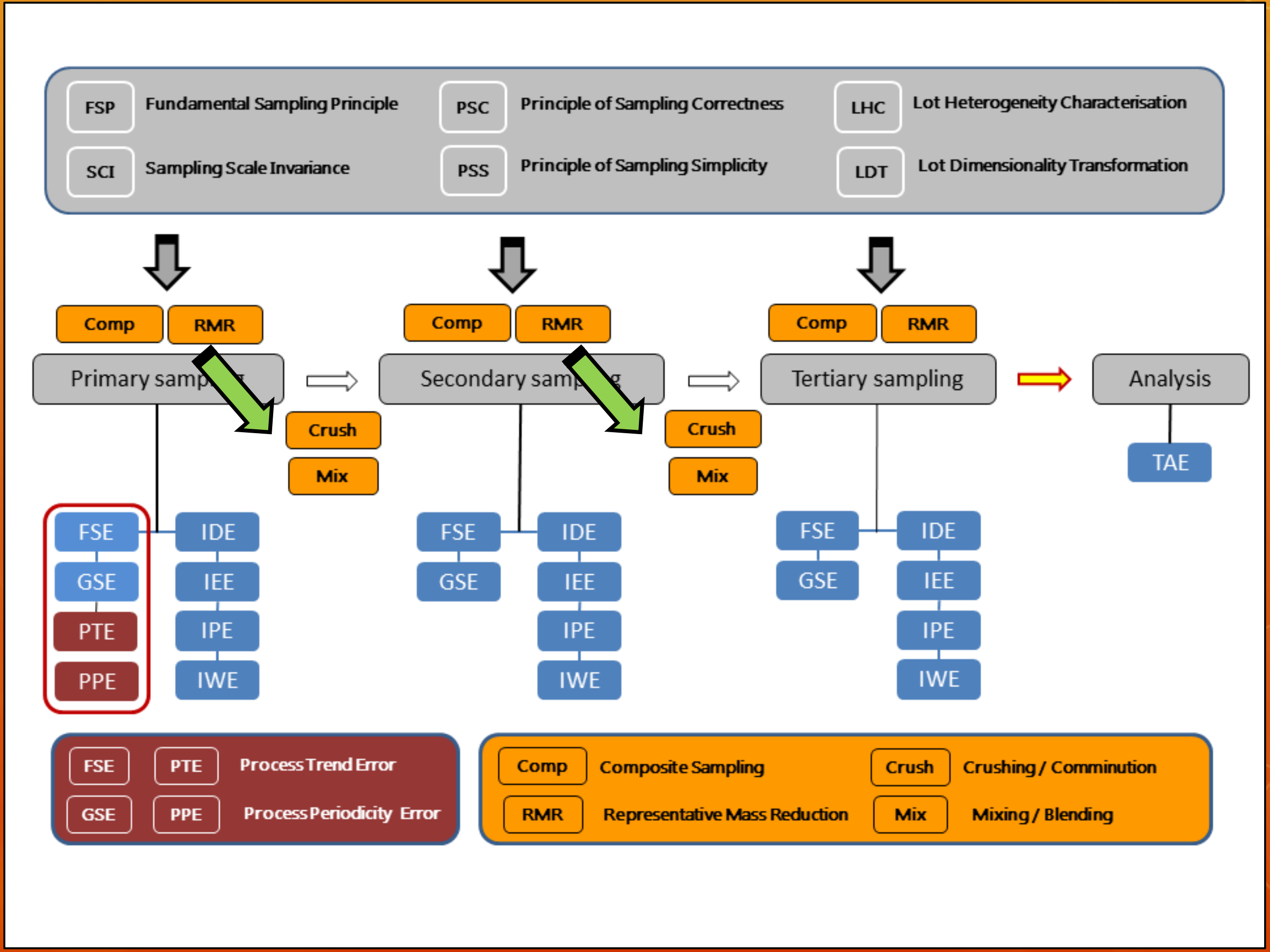



By way of contrast .... By way of CONTRAST

In general one cannot cannot crush the entire primary lot!

But *sometimes*, you do this anyway. BIG advantages ahead!

Theory of Sampling (TOS) – everything in a glance



Representative Sampling: Theory of Sampling (TOS)

TOS - Axiomatic exposé

Governing principles (GP) – Sampling unit operations (SUO)

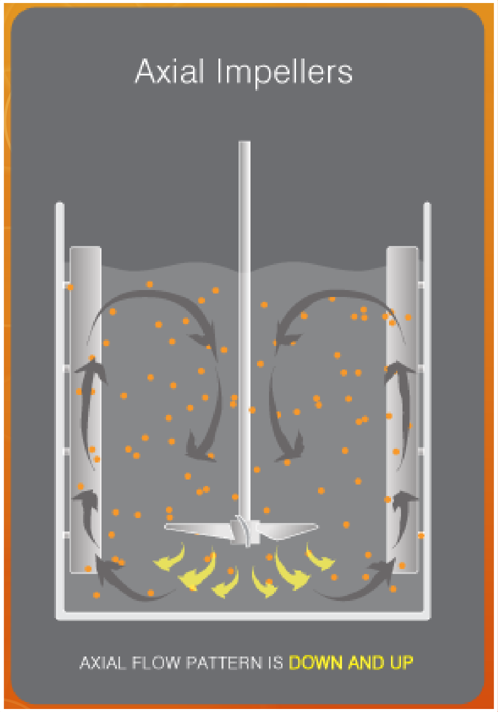
1. FSP: Fundamental Sampling Principle
2. SSI: Sampling Scale Invariance
3. PSC: Sampling Correctness (bias-free sampling)
4. PSS: Sampling Simplicity (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (Sub-sampling)

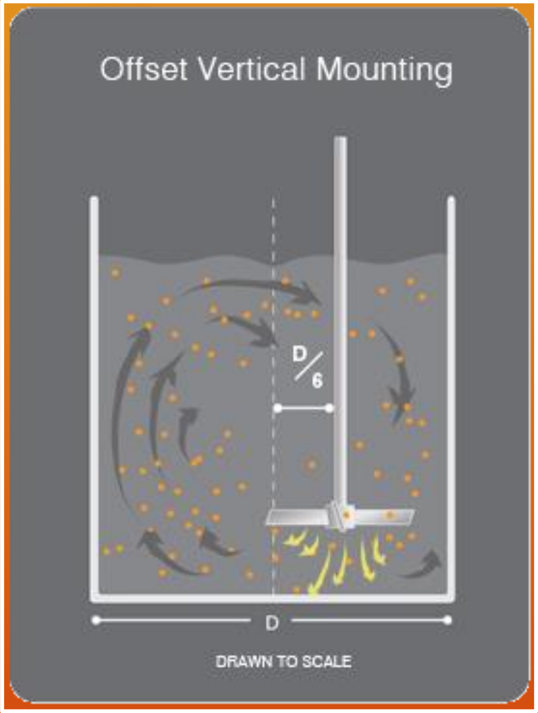
Sampling Unit Operations: Mixing / Blending

Sampling Error Management (GSE)

Mixing – intuitively clear. However, forceful mixing is a much less effective process than commonly known ...

Mixing – It is manifestly not enough just ”to mix” and then hope all is OK





Mixing – It is always necessary to conduct a baseline *validation* of the mixing/blending operation in use, e.g. A Replication Experiment (RE).

Sampling Unit Operation: Mixing / Blending

Reduces contributions to sampling variation from the Grouping and Segregation Error (GSE)

$$s^2(GSE) = \zeta \cdot \gamma \cdot s^2(FSE)$$

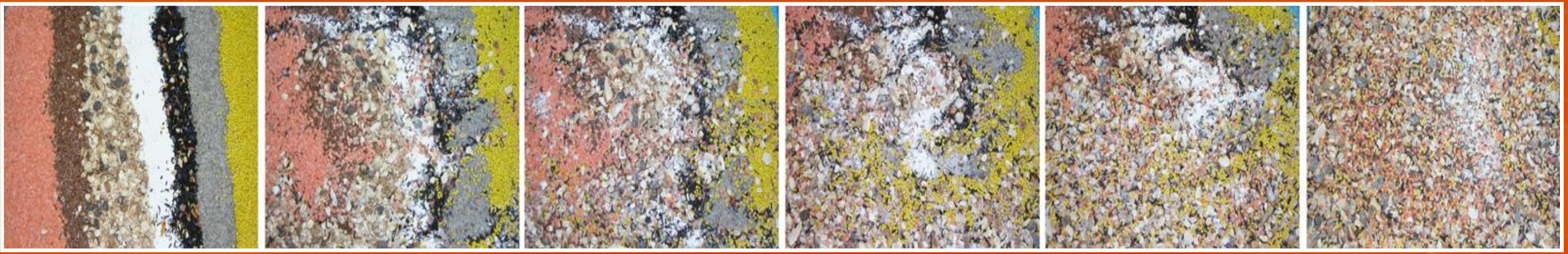
$$\gamma = \frac{N_F - N_G}{N_G - 1} \approx \boxed{\frac{N_F}{N_G}}$$

Segregation factor

Grouping factor (unaffected by mixing - reduced only by selecting smaller increments)

$\zeta \approx 1$

$\zeta \approx 0$



Four practical Sampling Unit Operations (SUO)

1. Composite Sampling
2. Particle Size Reduction (comminution)
3. Mixing / blending
4. Representative Mass Reduction (- sample preparation)

Theory & Practise of Sampling (TOS)

Practical procedures … …

Four Sampling Unit Operations (SUO)

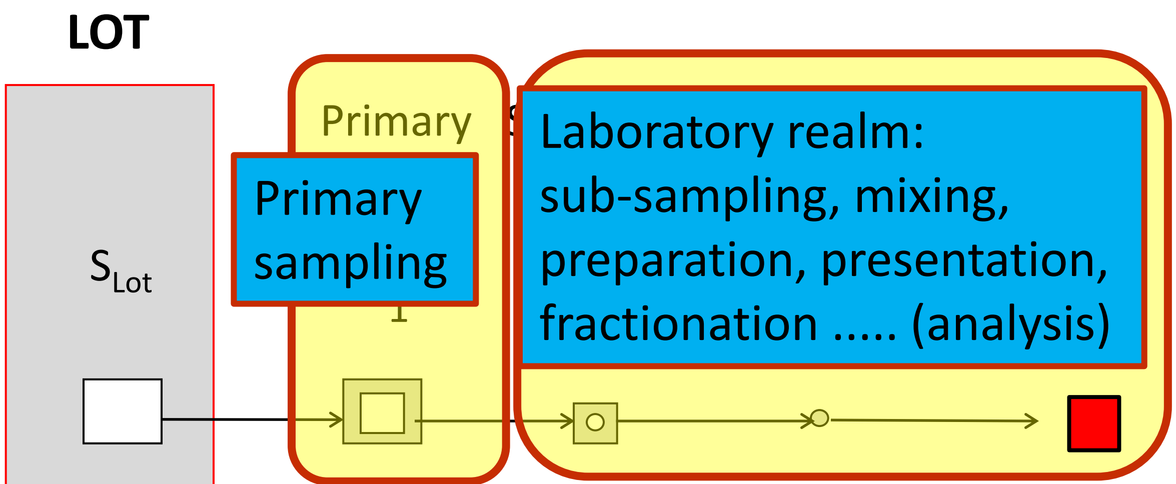
Used as active steps in the sampling process (often used several times, in combination)

Representative Sampling: Theory of Sampling (TOS)

TOS - Axiomatic exposé

Governing principles (GP) – Sampling unit operations (SUO)

1. FSP: Fundamental Sampling Principle
2. SSI: Sampling Scale Invariance
3. PSC: Sampling Correctness (bias-free sampling)
4. PSS: Sampling Simplicity (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (Sub-sampling)



Propagation of errors: $s_x = \sqrt{\sum s_i^2}$

Example: s_x $(55\%)^2 + (35\%)^2 + (1.5\%)^2 = (65\%)^2$

Goal: $S_X \curvearrowright S_{Lot}$

Who's responsible .... ?

The analytical process always contains several sampling and preparation steps, but <u>usually</u> primary sampling <u>dominates</u>

Sampling Unit [illegible]eration: Comminution

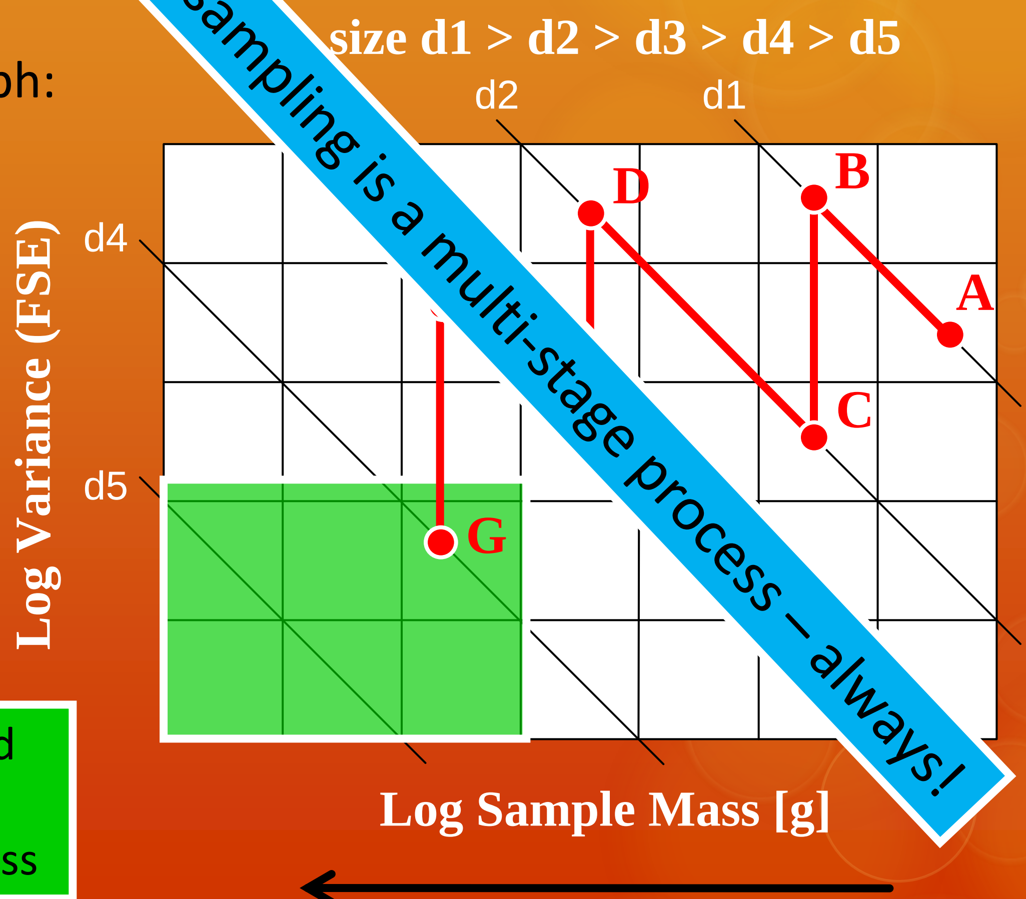
Representative sampling is a multi-stage process – always!

Particle size reduction (crushing)

Sampling nomograph:

$$var(FSE) = C \times d^3 \left(\frac{1}{M_S} - \frac{1}{M_L} \right)$$

Sampling Error Management (FSE)



Acceptable treshold region of sampling error vs sample mass

Fundamental insights - I

- The empowering role of ***universal*** principles:

- Six Governing Principles (GP)
- Four Sampling Unit Operations (SUO)
- Sampling Error Management (SEM) rules ....


مقام معظم رهبری:
دهه
فجر
والفجر و لیال عشر

An important analogy (for *some* ..)

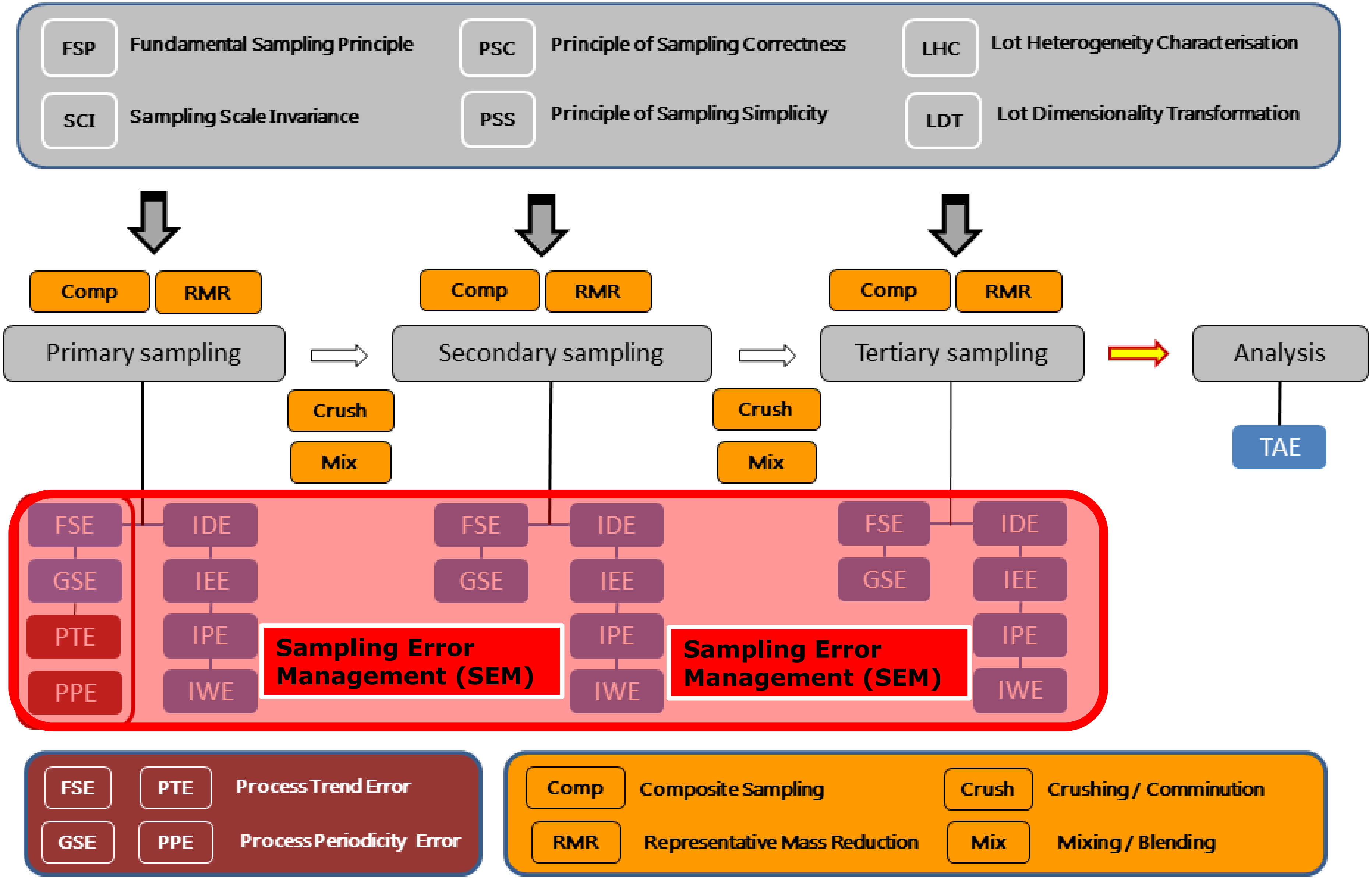
1. $\nabla \cdot \mathbf{D} = \rho_V$
2. $\nabla \cdot \mathbf{B} = 0$
3. $\nabla \times \mathbf{E} = -\dfrac{\partial \mathbf{B}}{\partial t}$
4. $\nabla \times \mathbf{H} = \dfrac{\partial \mathbf{D}}{\partial t} + \mathbf{J}$

Maxwell's Equations describe the world of electromagnetics. The four equations describe how electric and magnetic fields *propagate*, *interact*, and how they are *influenced* by objects

Governing principles (GP) & Sampling Unit Operations (SUO)

1. FSP: Fundamental Se Invariance
2. PSC: Sampling Correctness (bias-free sampling)
3. PSS: Sampling Simplicityampling Principle
4. SSI: Sampling Scal (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (sub-sampling/splitting)

All GP's & SUO's are not involved in all sampling tasks. The analysis & the sampling objective determines which GP's and SUO's to use. The Theory of Sampling (TOS) to the fore ... DS 3077: First horisontal standard (2013)


FSP
Fundamental Sampling Principle
PSC
Principle of Sampling Correctness
LHC
Lot Heterogeneity Characterisation
SCI
Sampling Scale Invariance
PSS
Principle of Sampling Simplicity
LDT
Lot Dimensionality Transformation
Comp
RMR
Primary sampling
Crush
Mix
Comp
RMR
Secondary sampling
Crush
Mix
Comp
RMR
Tertiary sampling
Analysis
TAE
FSE
GSE
PTE
PPE
IDE
IEE
IPE
IWE
Sampling Error Management (SEM)
FSE
GSE
IDE
IEE
IPE
IWE
Sampling Error Management (SEM)
FSE
GSE
IDE
IEE
IPE
IWE
FSE
PTE
Process Trend Error
GSE
PPE
Process Periodicity Error
Comp
Composite Sampling
Crush
Crushing / Comminution
RMR
Representative Mass Reduction
Mix
Mixing / Blending

Elimination of (all) Incorrect Sampling Errors (ISE)

TOS' Preventive Paradigm (TPP)

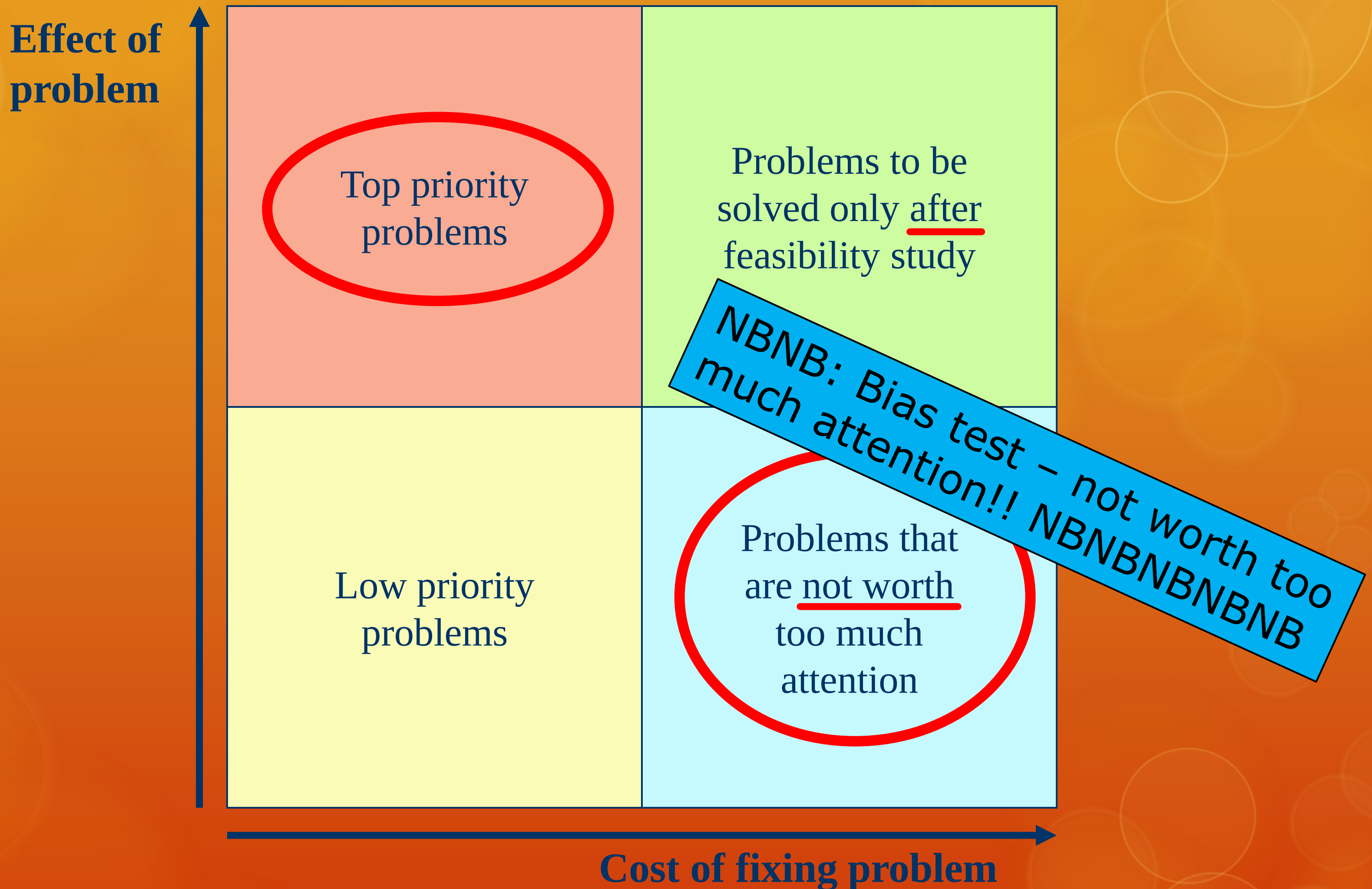
Principle of Sampling Correctness (PSC)

Effect of problem

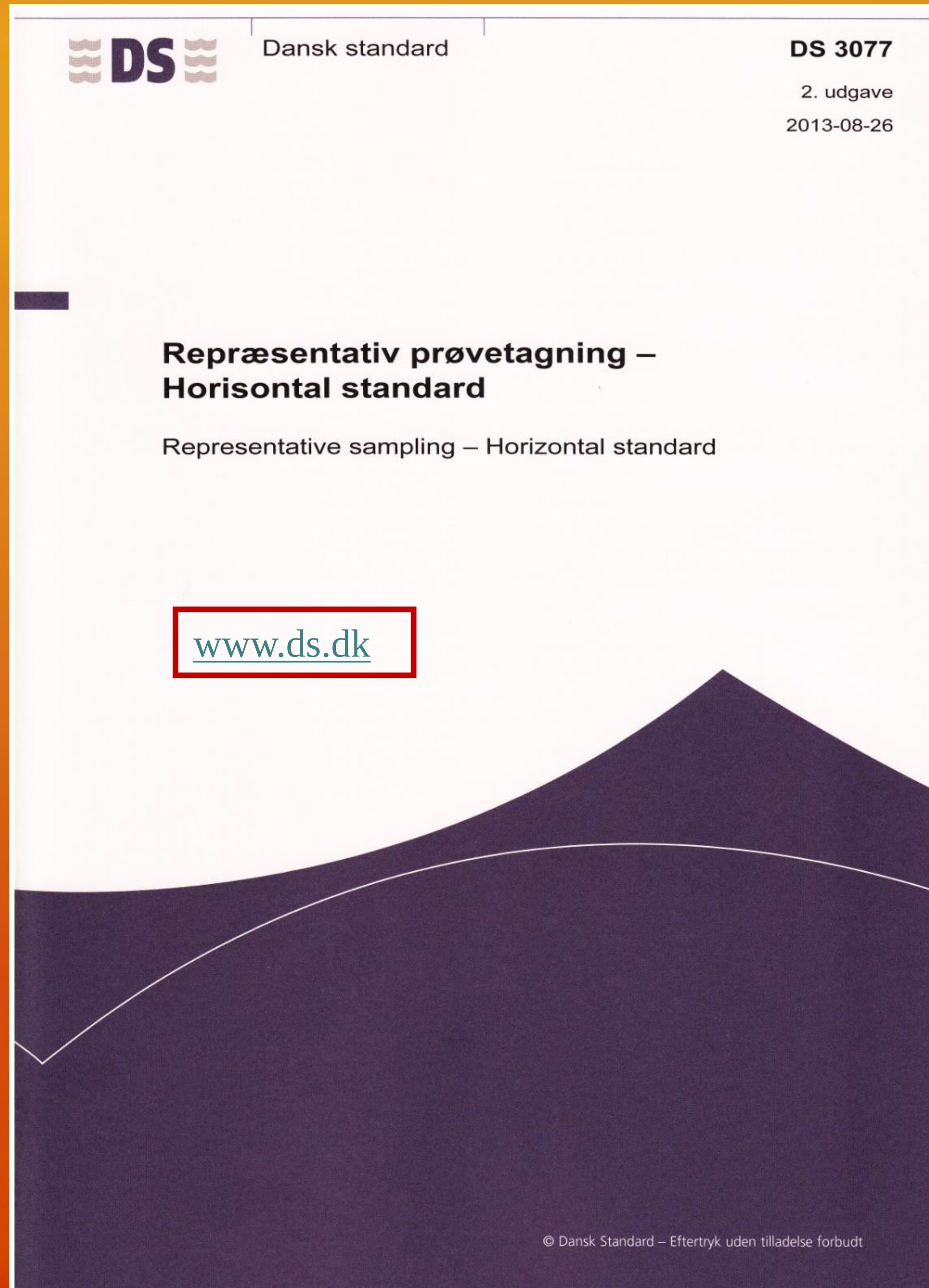
Sampling variation, due to inferior SEM: **FSE GSE** **IDE IEE IPE IWE** **TAE**	**IDE** *(cyclicity)* (process sampling) **PPE**
PTE *(trends)* *(process sampling)*	**"Effects estimation"** **Bias Test(s)** **Round Robin test(s)** **"Correction factors"**

Cost of fixing problem

Courtesy: Francis Pitard Sampling Consultants



Courtesy: Francis Pitard Sampling Consultants



Dansk standard

DS 3077

2. udgave

2013-08-26

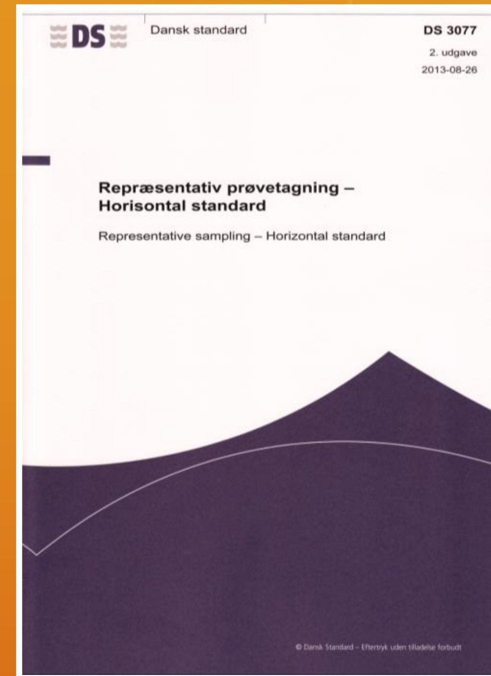
Repræsentativ prøvetagning – Horisontal standard

Representative sampling – Horizontal standard

www.ds.dk

Horizontal – Representative Sampling

DS-3077


Dansk standard

DS 3077

2. udgave

2013-08-26

Repræsentativ prøvetagning –
Horisontal standard

Representative sampling – Horizontal standard

This standard outlines a practical, iterative, self-controlling approach with minimal complexity, based on the Theory of Sampling (TOS). The generic sampling process described and all elements involved are sufficient and necessary for the stated objective, with the consequence that no exceptions can be allowed in order to be able to document the intended sampling representativity. It is necessary to consider the full pathway from primary sampling to analytical results in order to be able to guarantee a reliable and valid analytical outcome. This standard, including normative references, annexes (and further, optional references) constitute a complete and sufficient competence basis for this purpose. The present approach will ensure appropriate levels of accuracy and precision for both primary sampling as well as for all sub-sampling procedures and mass-reduction systems at the subsequent laboratory stages before analysis.

DS3077 (2013) ... ... First publication

5+ years in use ... ... (hundreds in use)

2019 ... ... time for revision

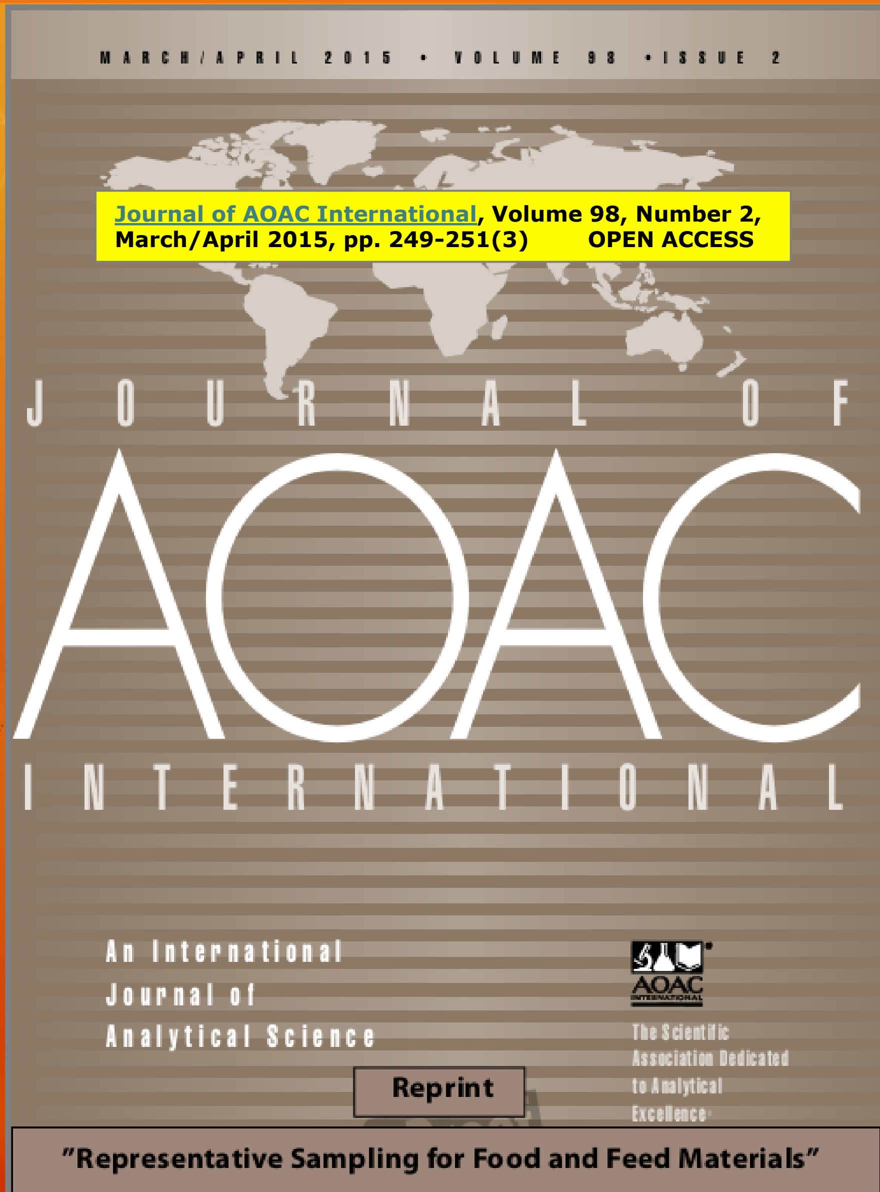
2019 ... ... and for induction as an ISO standard

Need for support from all stakeholders ... ...

1. Individuals
2. Companies
3. Corporations
4. Organisations
5. Public and regulating agencies
6. ISO ... ...

YOU may be called upon – are you ready?

2015: SPECIAL SESSION ON J. AOAC



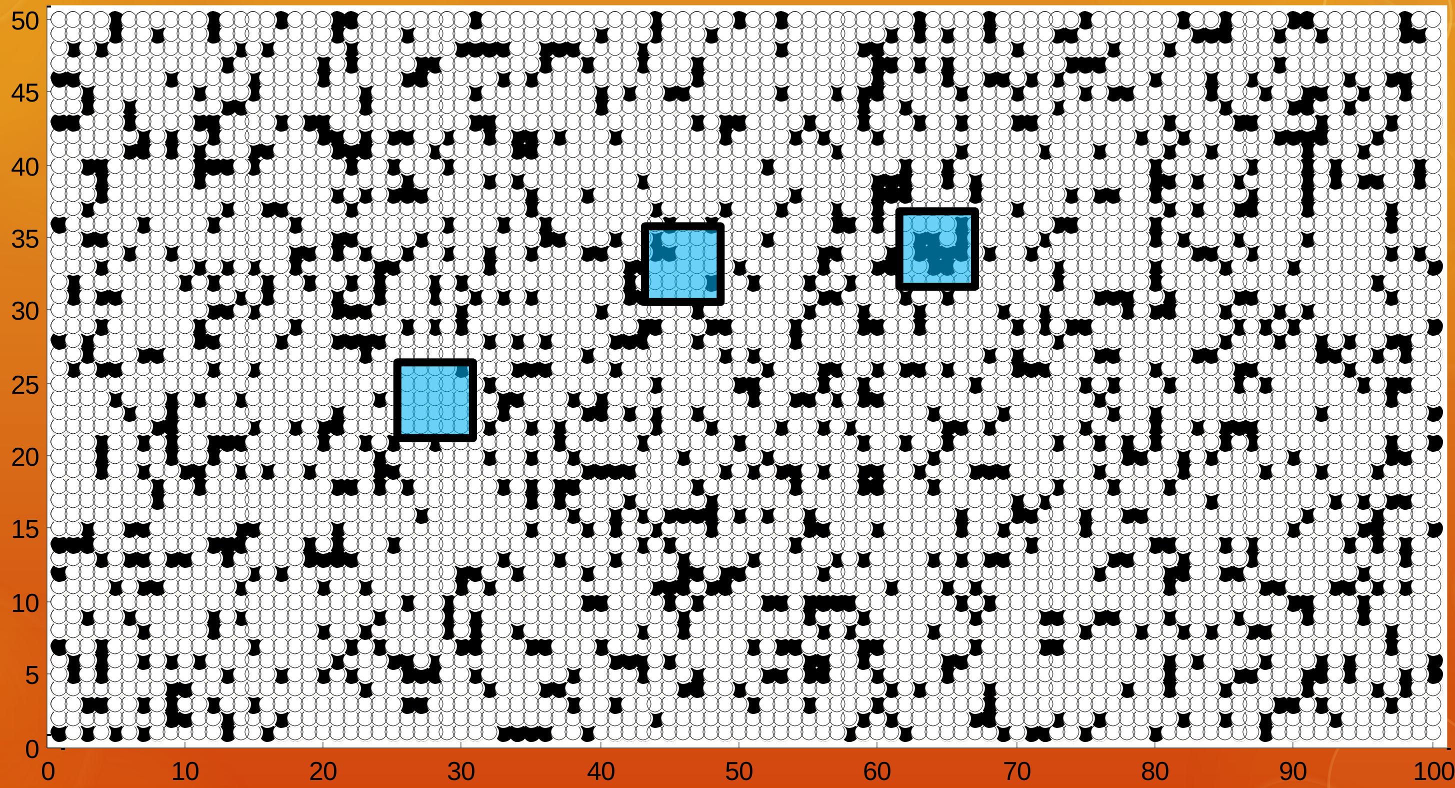
A World's first! Merging the Theory of Sampling (TOS) and foods/feed safety assessment

Transatlantic Special Section taskforce, Oct. 2014, Windsor, CO:
Nancy Thiex, Kim H. Esbensen, Charles A. Ramsey, Claas Wagner, Claudia Paoletti.

Fundamental insights - II

- The role of *statistics* – in sampling and analysis

Heterogeneity - the unifying characteristic for all types of material



These 3 grab samples will obviously not give rise to identical analytical results

TOS

A (most) surprising, critical distinction

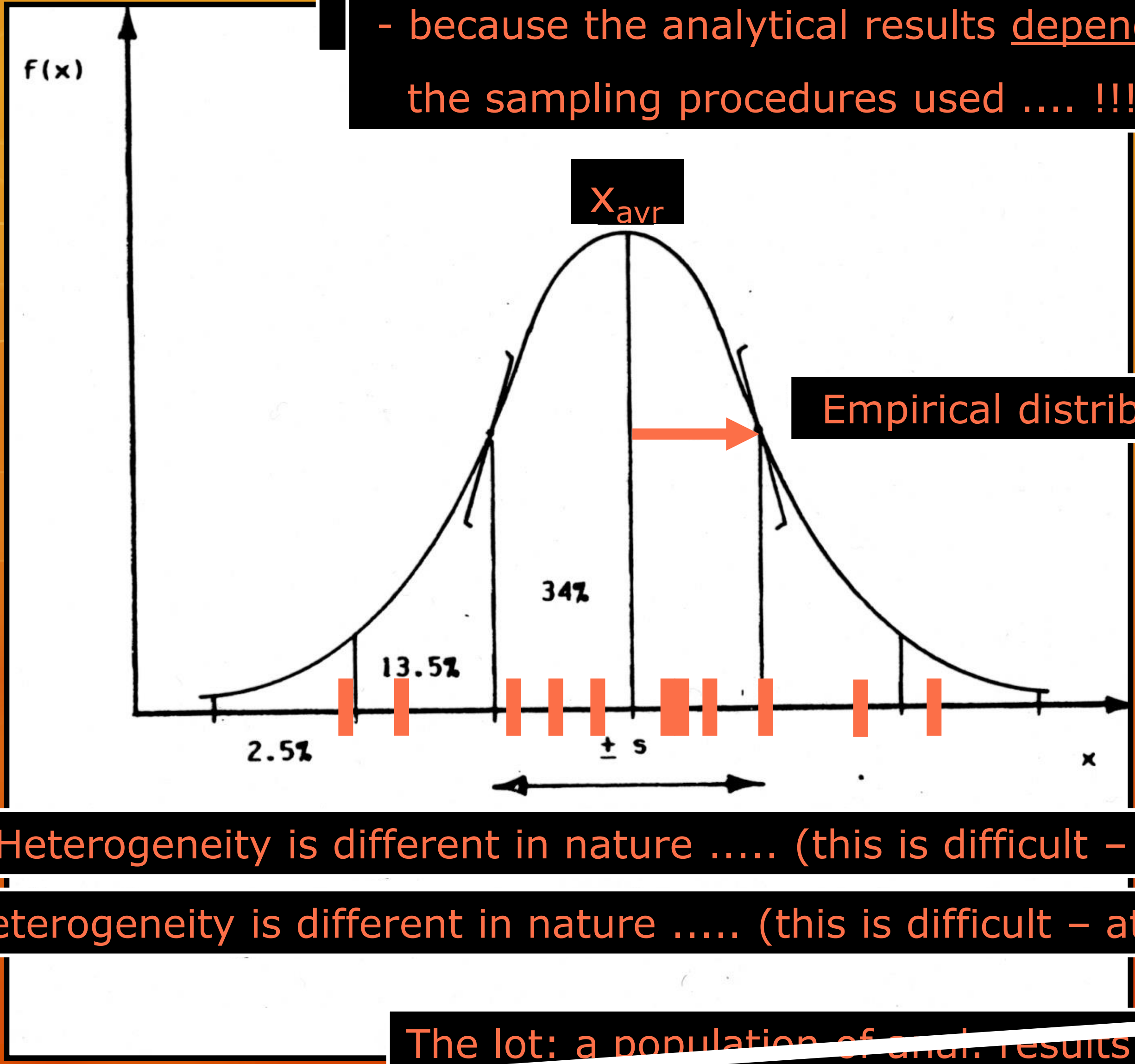
Because the sampler is free to choose between alternative sampling procedures, - equipment and – conditions ....

- based, or <u>not</u> based, on a competent understading and accept of the adverse role of heterogeneity when ***<u>interacting</u>*** with a specific sampling process ....

- the analytical result will <u>depend</u> on these choices!

All analytical result will <u>depend</u> on the specific sampling procedure(s) used to deliver the analytical aliquot!

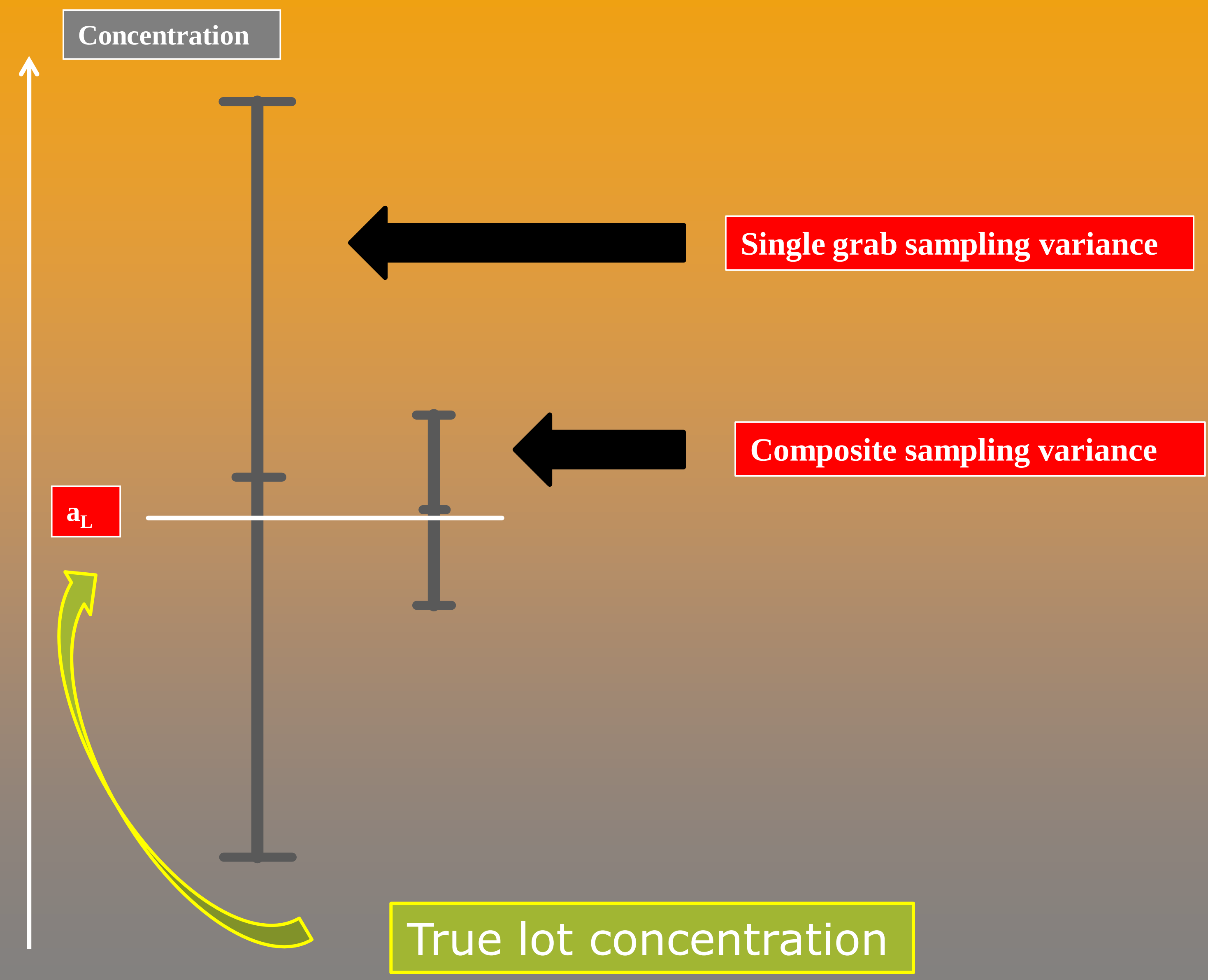
- very difficult to avoid conventional
- because the analytical results <u>depend</u> on the sampling procedures used .... !!! !!!



Heterogeneity is different in nature ..... (this is difficult – at first)

Heterogeneity is different in nature ..... (this is difficult – at first)

~~The lot: a population of anal. results~~


Concentration
Single grab sampling variance
Composite sampling variance
a_L
True lot concentration

There is in fact a lot more use of statistics in TOS –

But that is for another day / month / year ... ...

The present INTRODUCTION to TOS will provide a sufficient conseptual framework to be able to start sampling in an efficient manner right away ... ...

But it is also meant to inspire to continued skills building and further self studies (comsult course documentation and other TOS literature platforms)

Representative Sampling: Theory of Sampling (TOS)

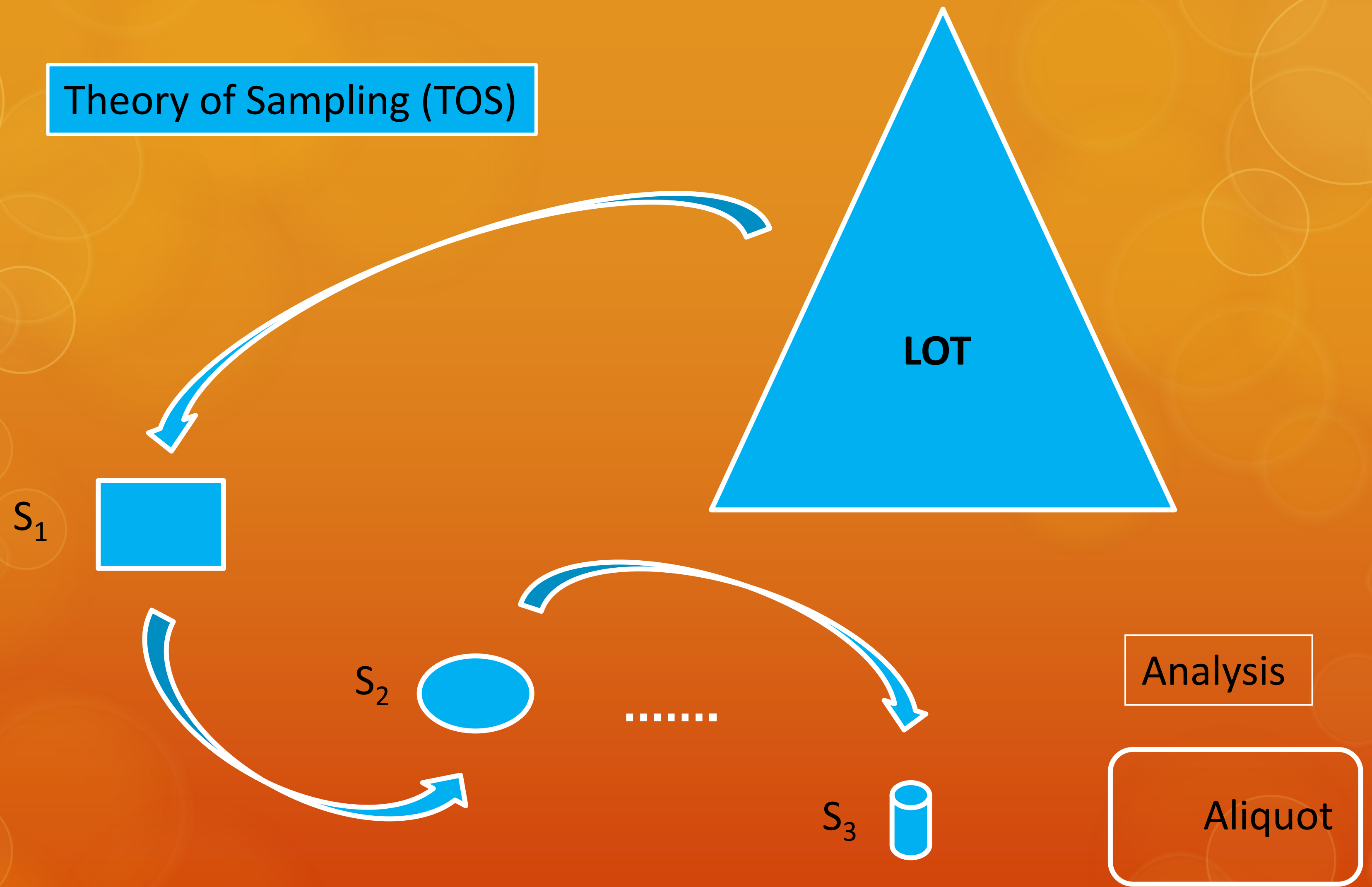
TOS - Axiomatic exposé

Governing principles (GP) – Sampling unit operations (SUO)

1. FSP: Fundamental Sampling Principle
2. SSI: Sampling Scale Invariance
3. PSC: Sampling Correctness (bias-free sampling)
4. PSS: Sampling Simplicity (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. The Replication Experiment, RE(**r**)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (Sub-sampling)


The Replication Experiment, RE(r)
HOW TO? - What you can do one time:
-you can replicate, f.eks. 10 times
Replication Experiments need only to be carried out for each principal type of material as sampled by a specific sampling procedure ... NB NB NB NB

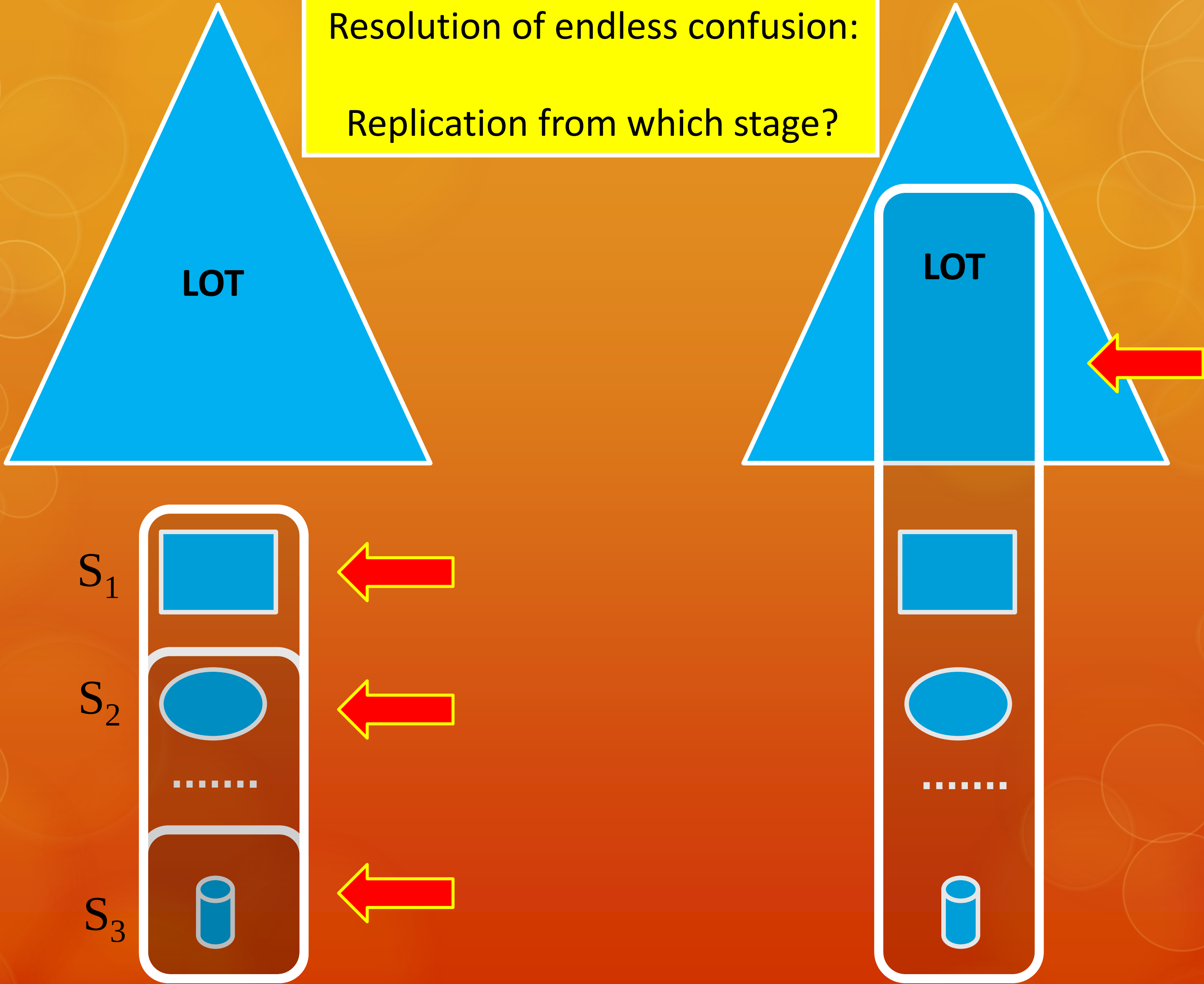
Theory of Sampling (TOS)

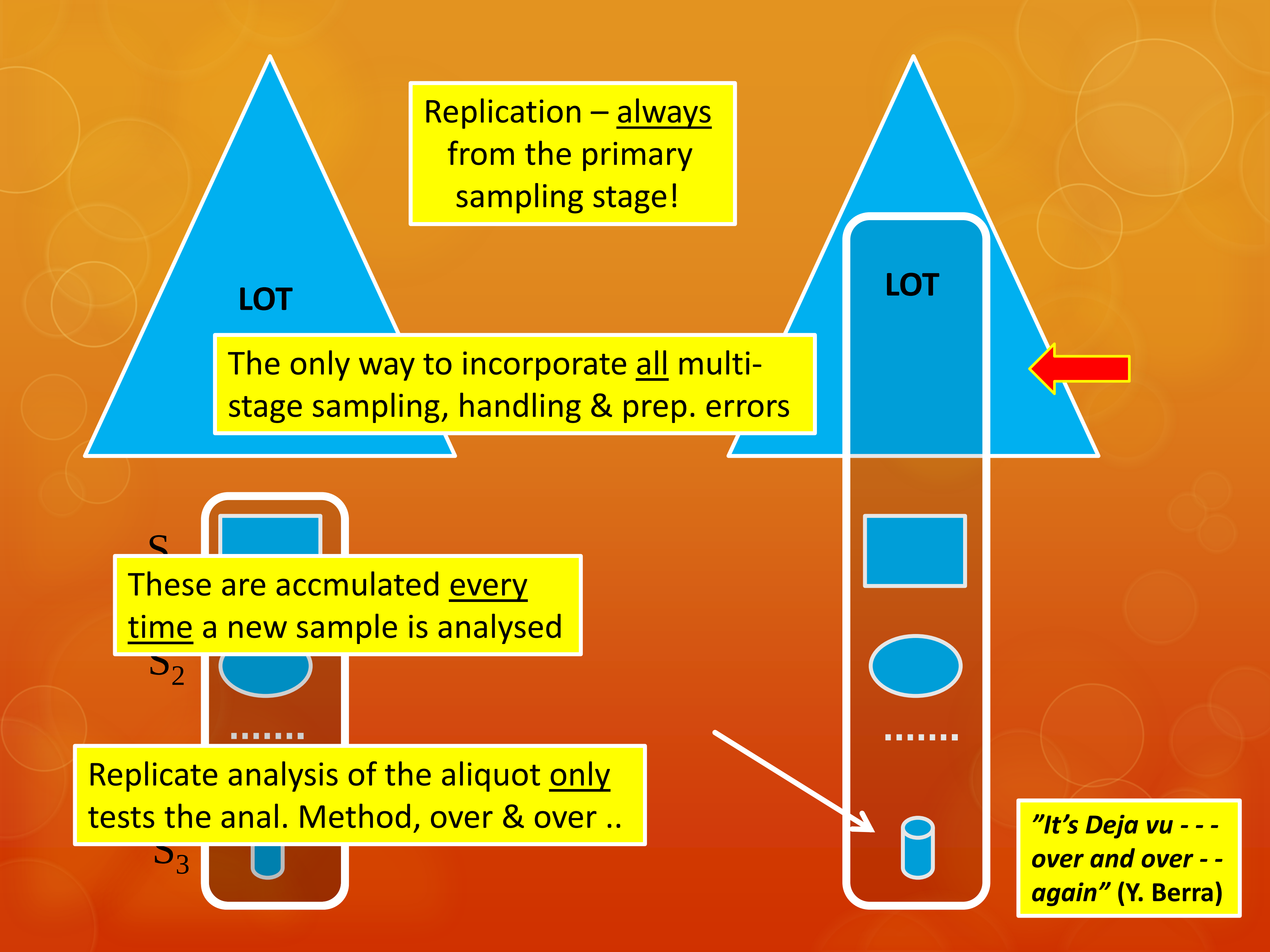


Framework for understanding sampling + analysis variability ... TOS

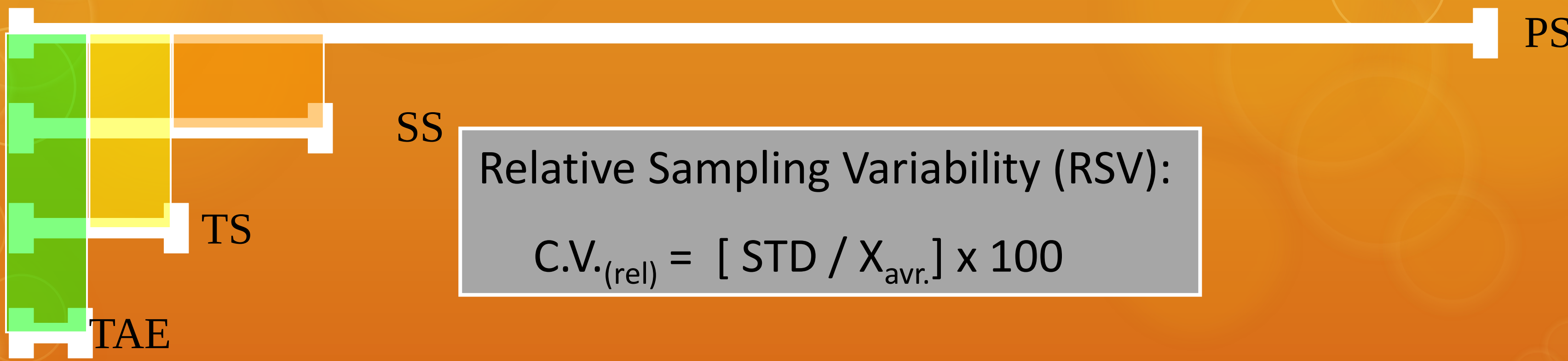
Resolution of endless confusion:

Replication from which stage?




Replication – always from the primary sampling stage!
LOT
LOT
The only way to incorporate all multi-stage sampling, handling & prep. errors
S
These are accmulated every time a new sample is analysed
S_2
Replicate analysis of the aliquot only tests the anal. Method, over & over ..
S_3
"It's Deja vu - - - over and over - - again" (Y. Berra)

Relative Sampling Variance (RSV) – C.V.$_{(rel)}$



Relative Sampling Variability (RSV):

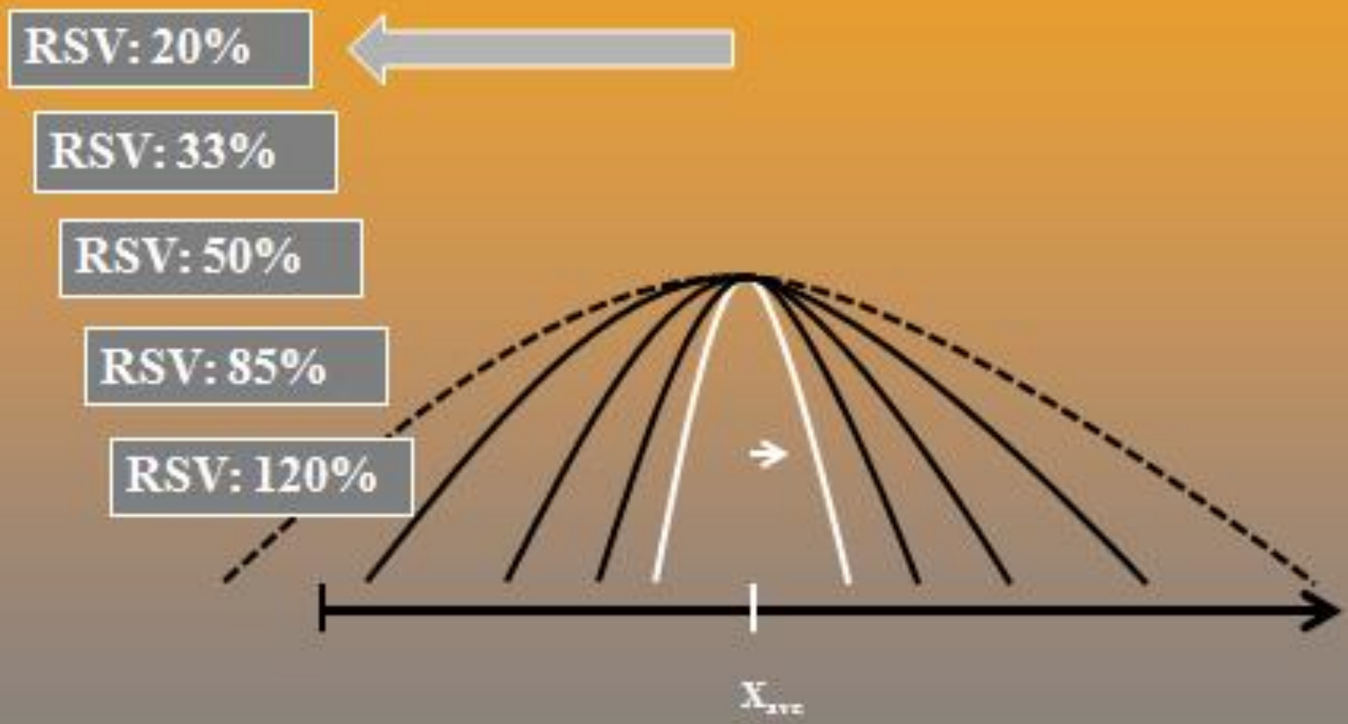
$$C.V._{(rel)} = [\ STD / X_{avr.}] \times 100$$

Relative Sampling Variability (RSV), aka relative Coefficient of Variation, C.V.$_{(rel)}$

at all scales

Replication Experiment: RSV[%] characterises all sampling + analysis operations – for all types of equipment and all types of materials !!!

RSV threshold(s)



CV_1 - Variability among analytical replicates = analytical uncertainty

CV_2 - Variability among increments = analytical + sampling uncertainty

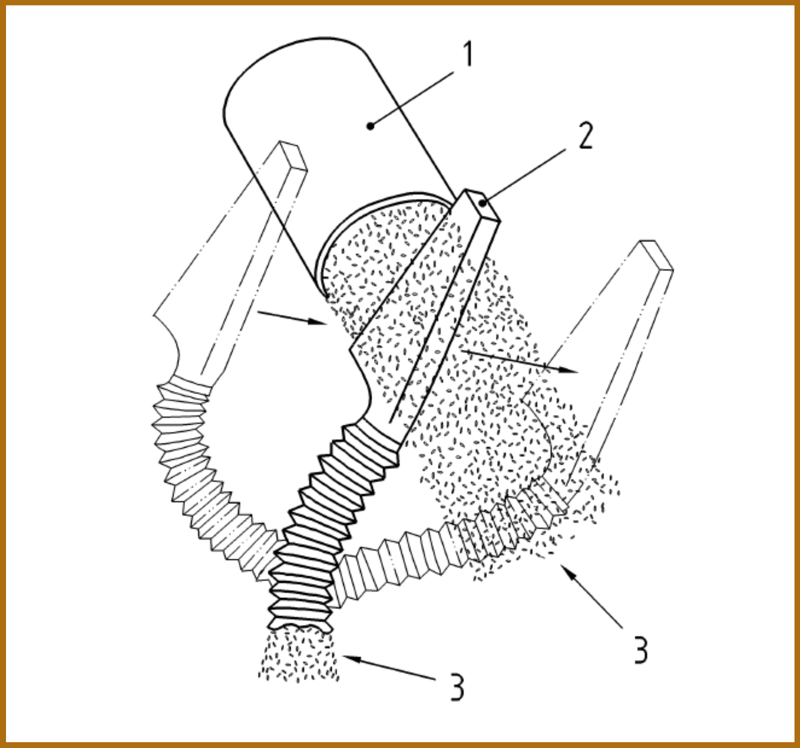
Lot	CV_1 ⟷	CV_2
1	10,18	116,85
2	7,77	44,5
3	6,85	40,8
4	6,52	51,59
5	22,34	249,88
6	30,96	133,64
7	20,12	60,63
8	19,65	57,54
9	5,06	39,74
10	6,52	62,13
11	5,68	52,88
12	6,25	38,04
13	4,69	35,03
14	15,48	218,12
15	34,09	171,81

There never was an analytical result – without preceding sampling

The specific analytical mesurement uncertainty CV_1 .... should not be used as a measure of the total measurement uncertainty CV_2.

What would be the consequence(s)?

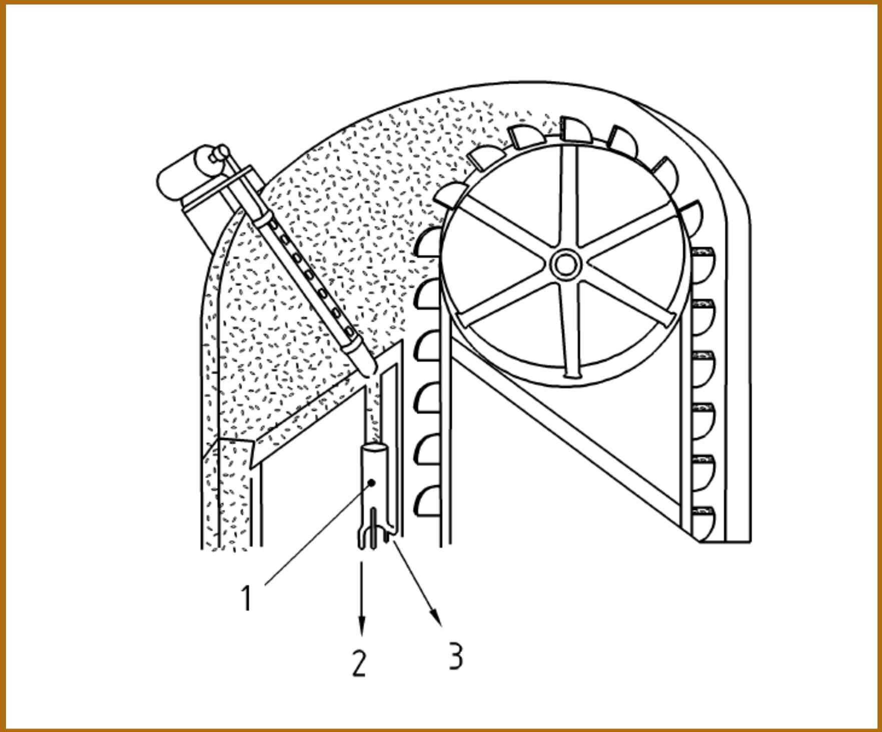
Who is responsible?



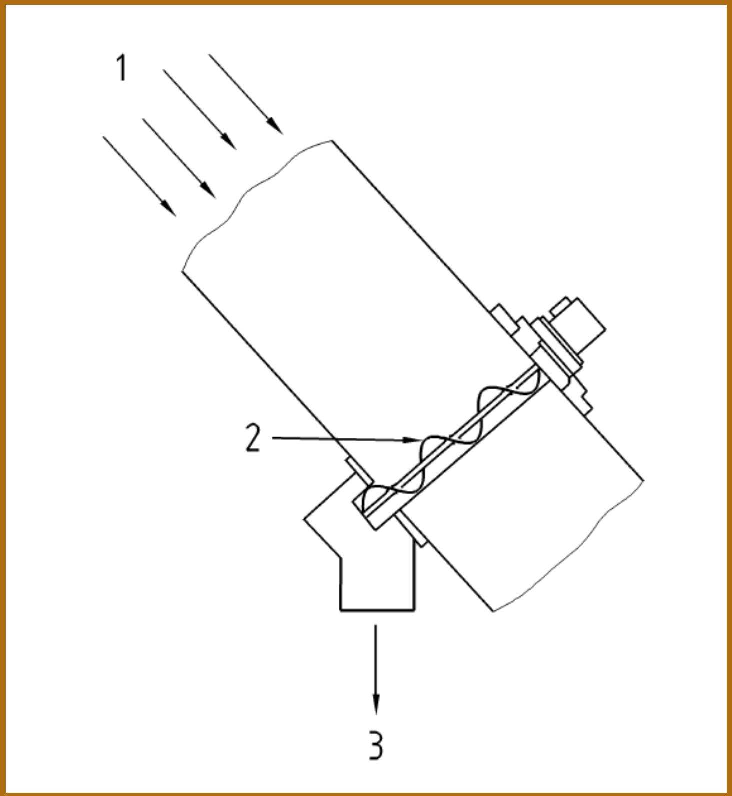
RSV: 08% Material 1

RSV: 18% Material 2

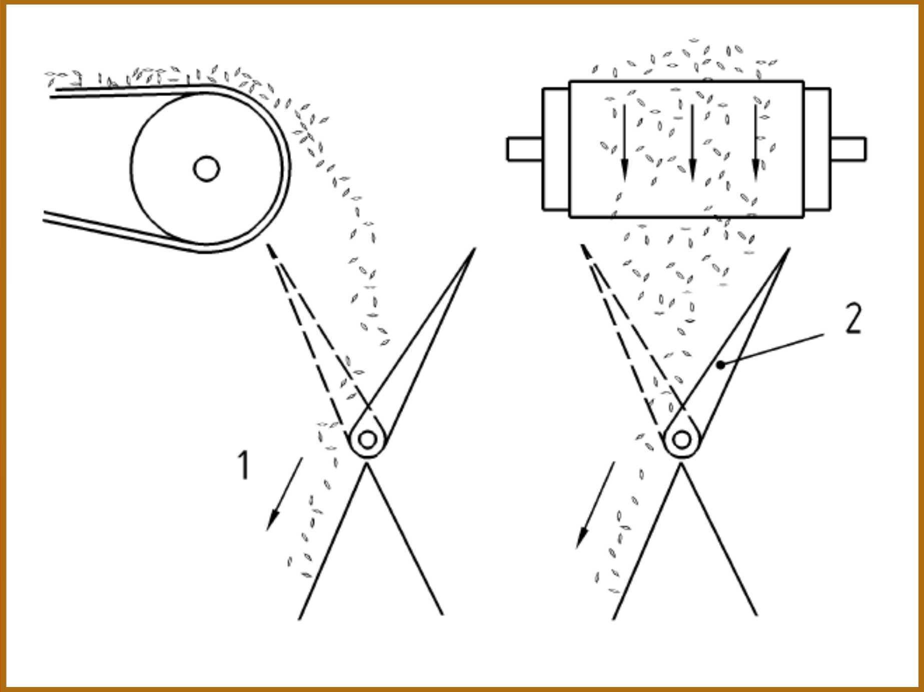
RSV: 78% Material 3



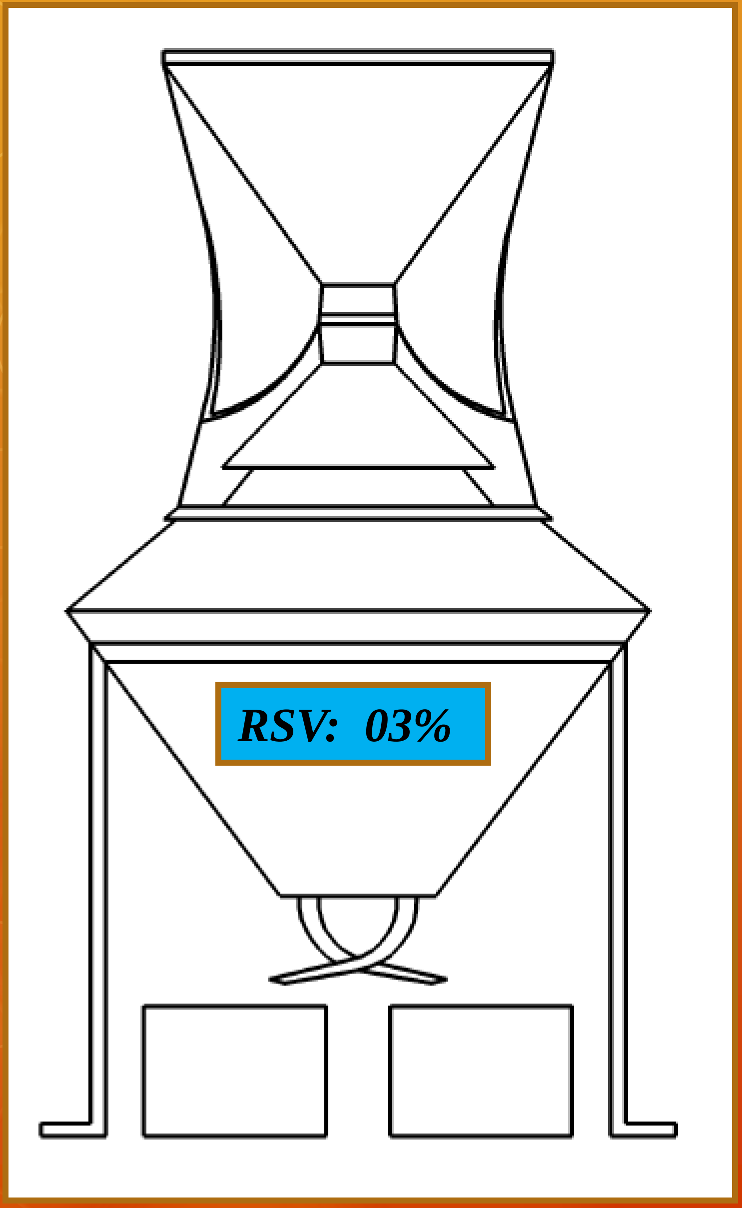
RSV: 158%

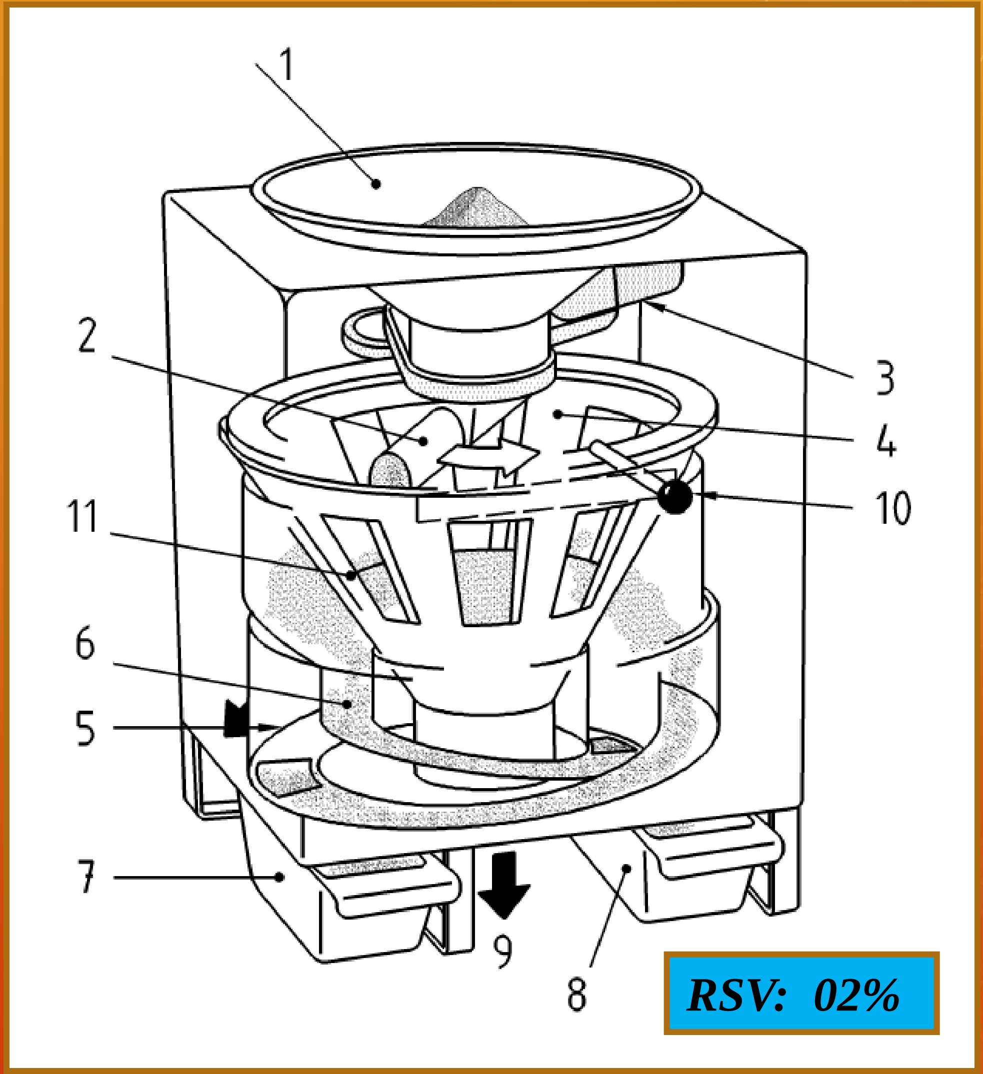


RSV: 57%

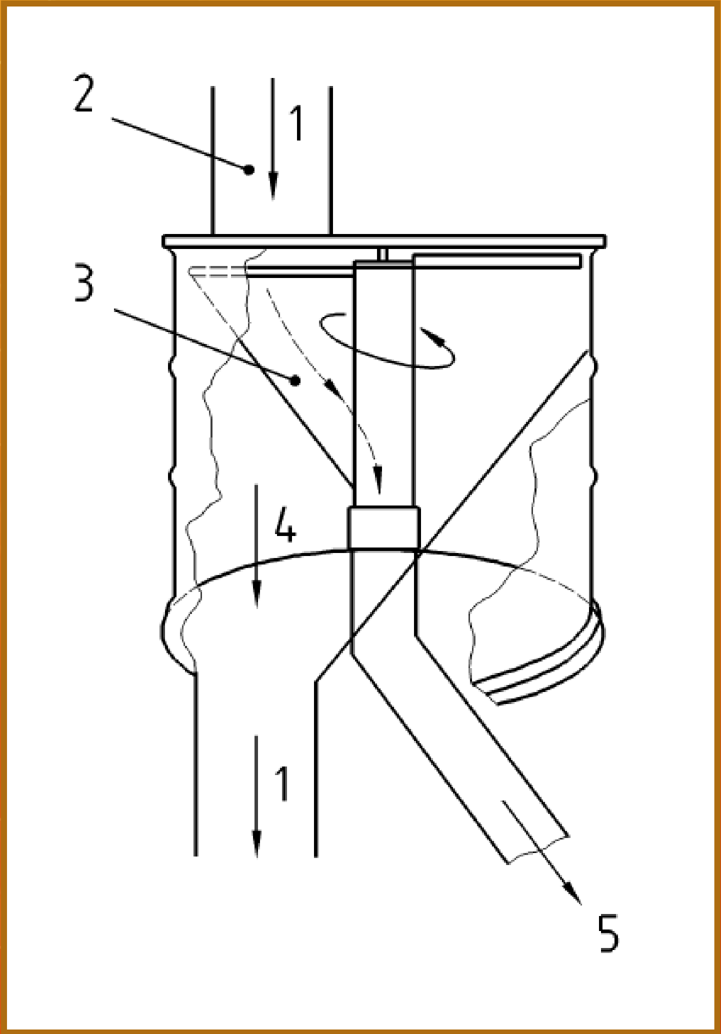


RSV: 380%

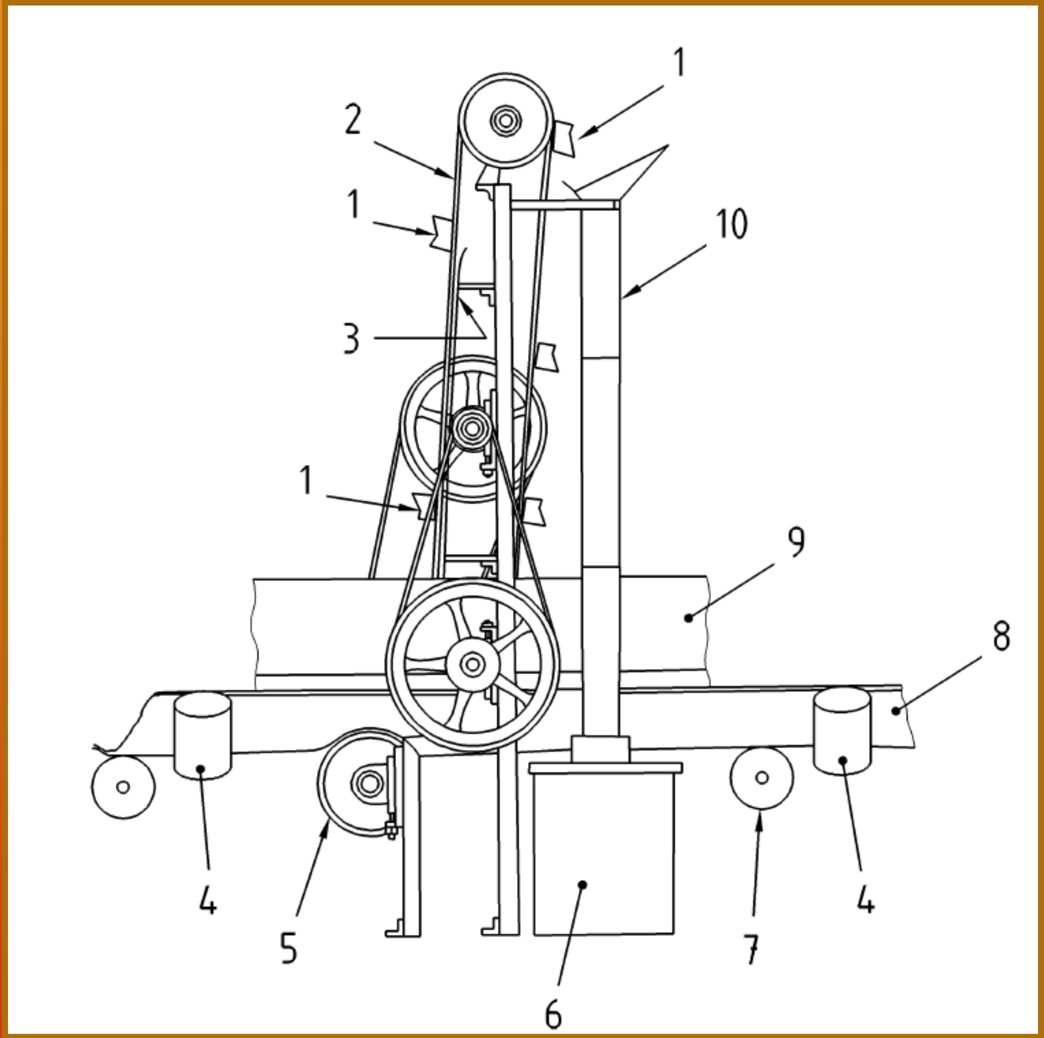

RSV: 03%


1
2
3
4
10
11
6
5
7
9
8
RSV: 02%

The Good



The .. I don't know WHAT?




RSV: 375%


RSV: 75%


RSV: 133%

A word of caution – re. RSV [%]

RSV [%] is a measure of the total (effective) sampling variance, estimated on the condition that a possible <u>sampling bias</u> has been <u>eliminated</u>.

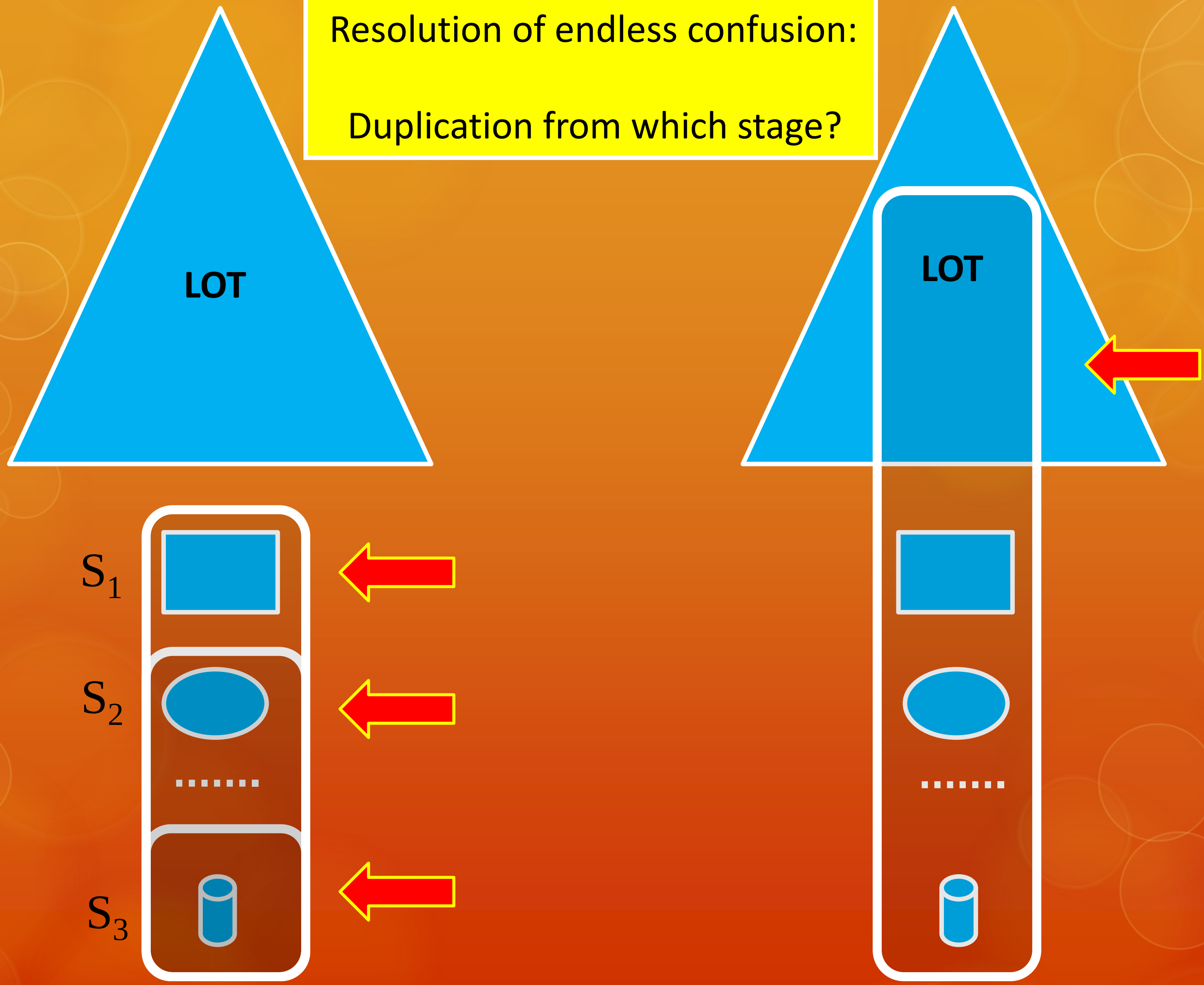
If this is not the case, RSV [%] will fluctuate for each estimation attempt (due to the uncontrollable sampling bias inconstancy) ... ...

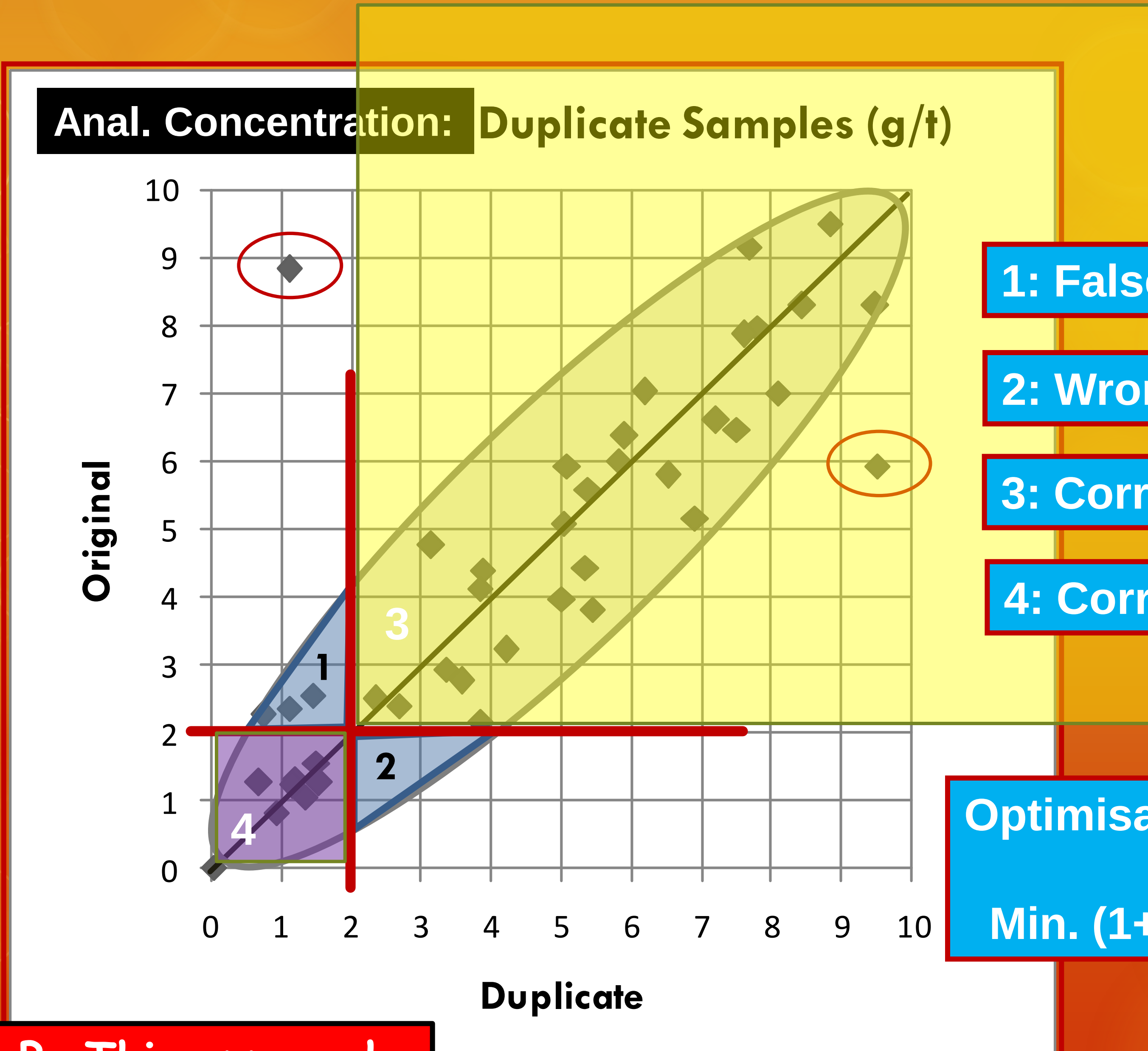
MUCH CONFUSION WILL FOLLOW .... VERY MUCH ....
if TOS' framework is not fully understanding (GP; SUO, SEM)

A word (or two) on the issue of "Duplicate samples"

Resolution of endless confusion:

Duplication from which stage?





1: False acceptance

2: Wrong rejectance

3: Correct acceptance

4: Correct rejectance

Optimisation criterion:

Min. (1+2) / (3+4) [%]

N.B. This approach <u>cannot</u> detect bias !!

Duplicate "precision ellipse"

Representative Sampling: Theory of Sampling (TOS)

TOS - Axiomatic exposé

Governing principles (GP) – Sampling unit operations (SUO)

1. FSP: Fundamental Sampling Principle
2. SSI: Sampling Scale Invariance
3. PSC: Sampling Correctness (bias-free sampling)
4. PSS: Sampling Simplicity (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (Sub-sampling)

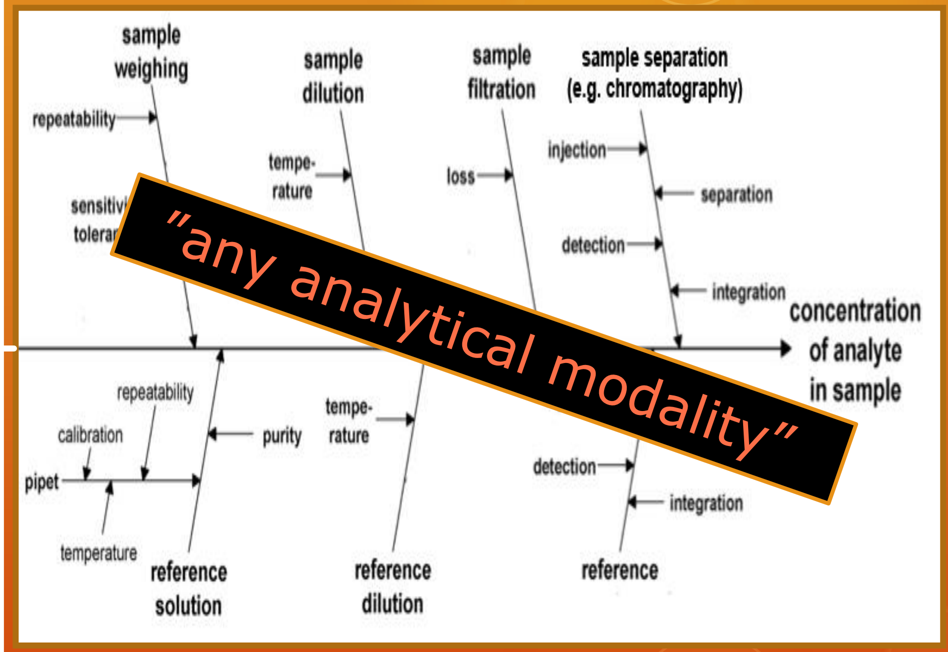
Sampling bias

Fundamental insights - IV

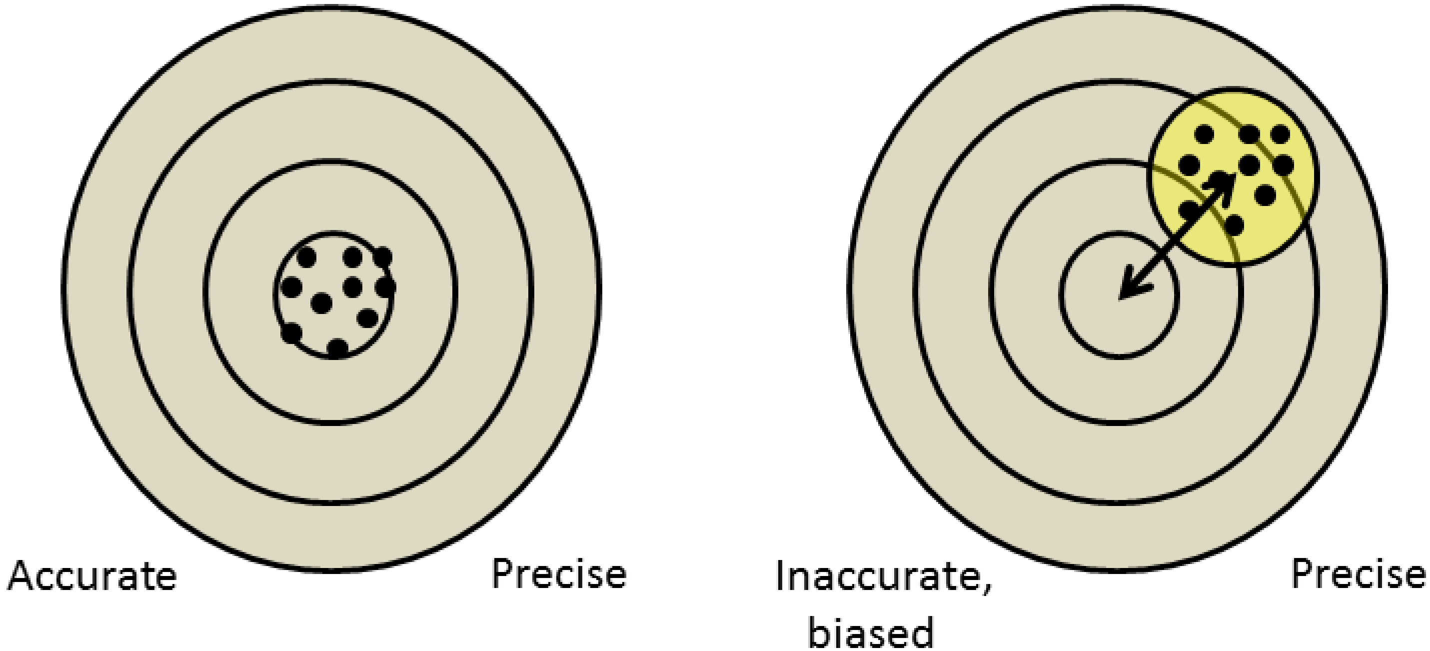
- The most important distinction in sampling:
- Analytical bias vs. sampling bias
- Sampling bias vs. sampling variance
-
- Real world: → (Sampling + analysis) bias
- → (Sampling + sub-sampling + + anal.) bias

Theory of Sampling (TOS)

Measurement Uncertainty (MU)

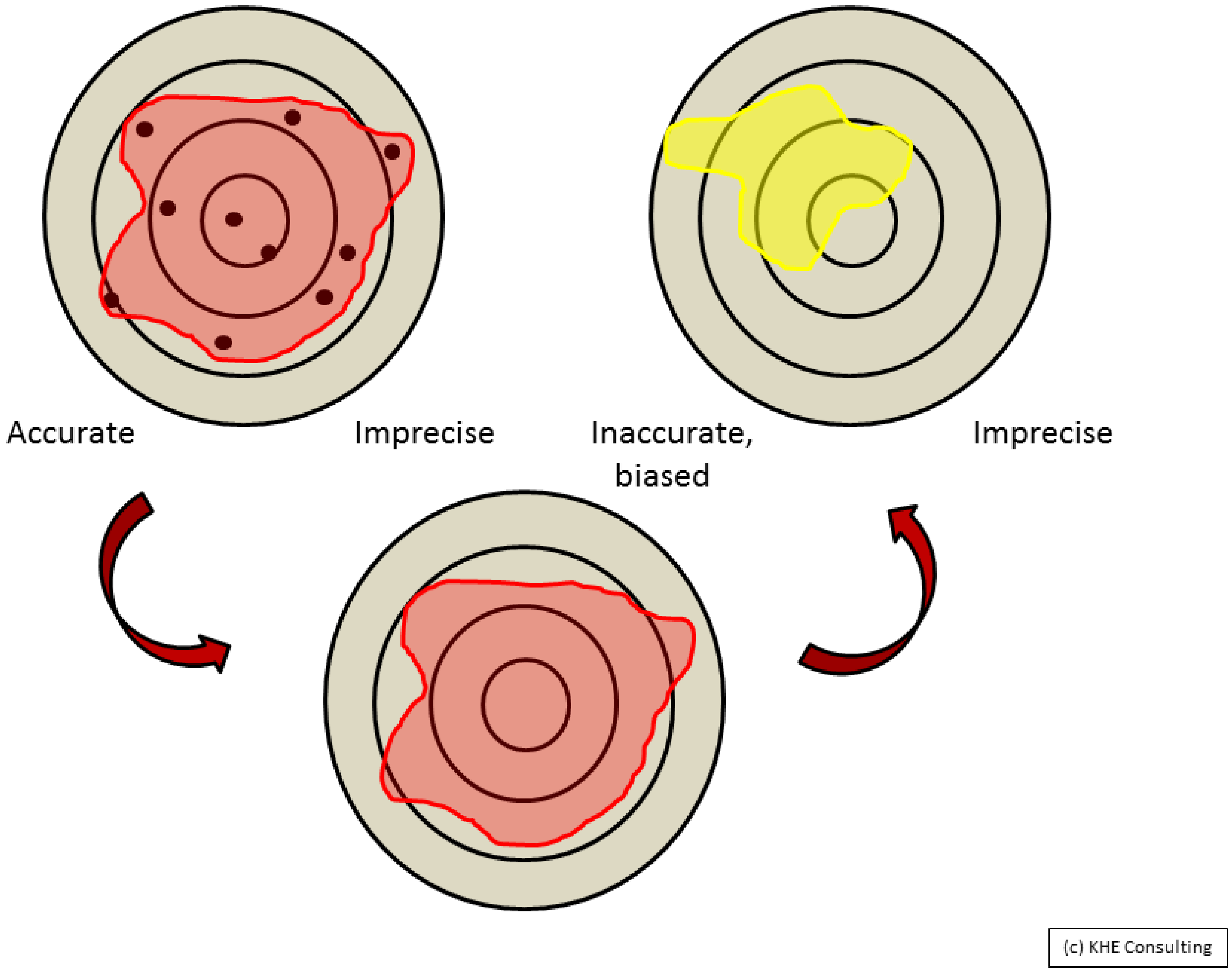


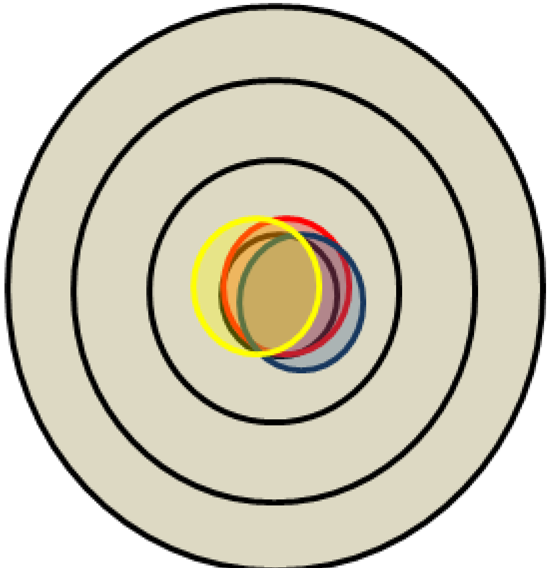
$MU_{total} = MU_{sampling} + MU_{analysis}$

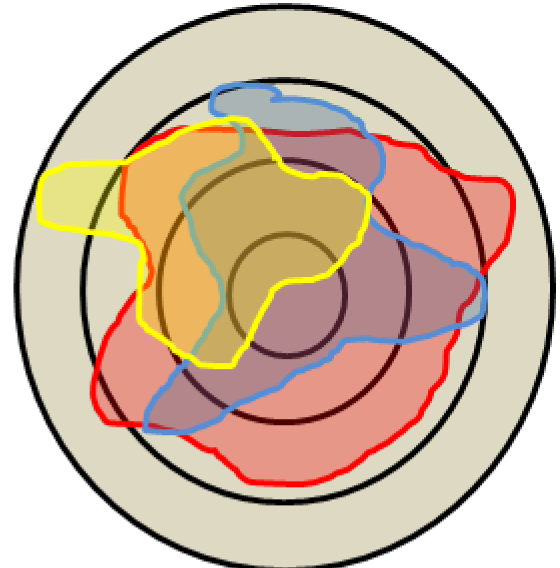


Replication Experiment, RE(10) delineating *ideal* characteristics: ***unbiased*** analytical process

Replication Experiment, RE(10) delineating *realistic* characteristics: ***constant*** analytical bias


Accurate
Imprecise
Inaccurate, biased
Imprecise
(c) KHE Consulting





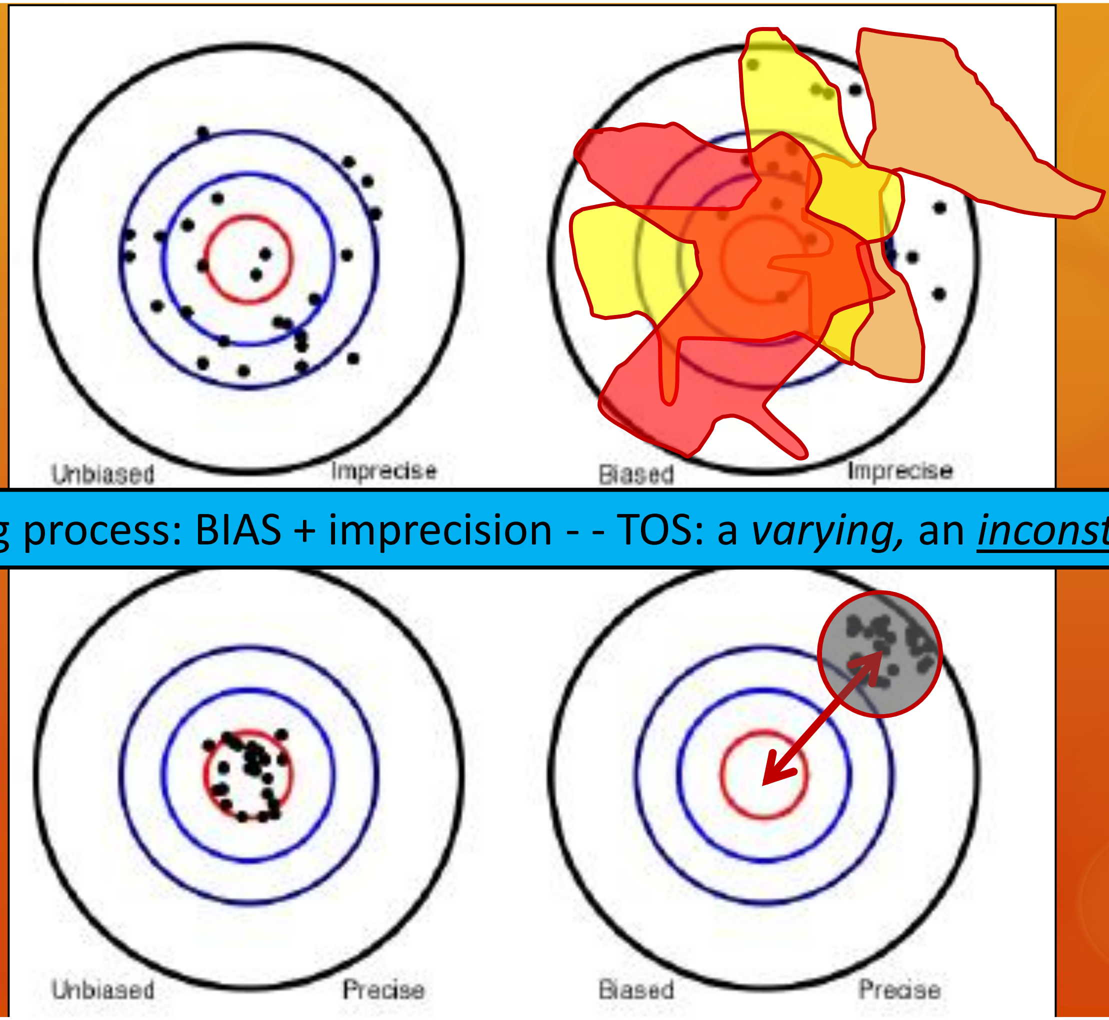
Accurate Precise

Inaccurate, biased Imprecise

3 X Replication Experiment, RE(10) delineating *unrealistic* expectations: ***constant***, vanishing sampling bias

3 X Replication Experiment, RE(10) delineating *realistic* characteristics: ***inconstant*** sampling bias

Critical distinction between analysis (*sensu strictu*) – and sampling_plus_analysis! MUST be understood!



Sampling process: BIAS + imprecision - - TOS: a *varying,* an *inconstant* bias!

Analytical process: bias + imprecision (statistical concept: a constant bias)

Fundamental insights - V

- INTRODUCTION to PROCESS SAMPLING

Representative Sampling: Theory of Sampling (TOS)

TOS - Axiomatic exposé

Governing principles (GP) – Sampling unit operations (SUO)

1. FSP: Fundamental Sampling Principle
2. SSI: Sampling Scale Invariance
3. PSC: Sampling Correctness (bias-free sampling)
4. PSS: Sampling Simplicity (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (Sub-sampling)

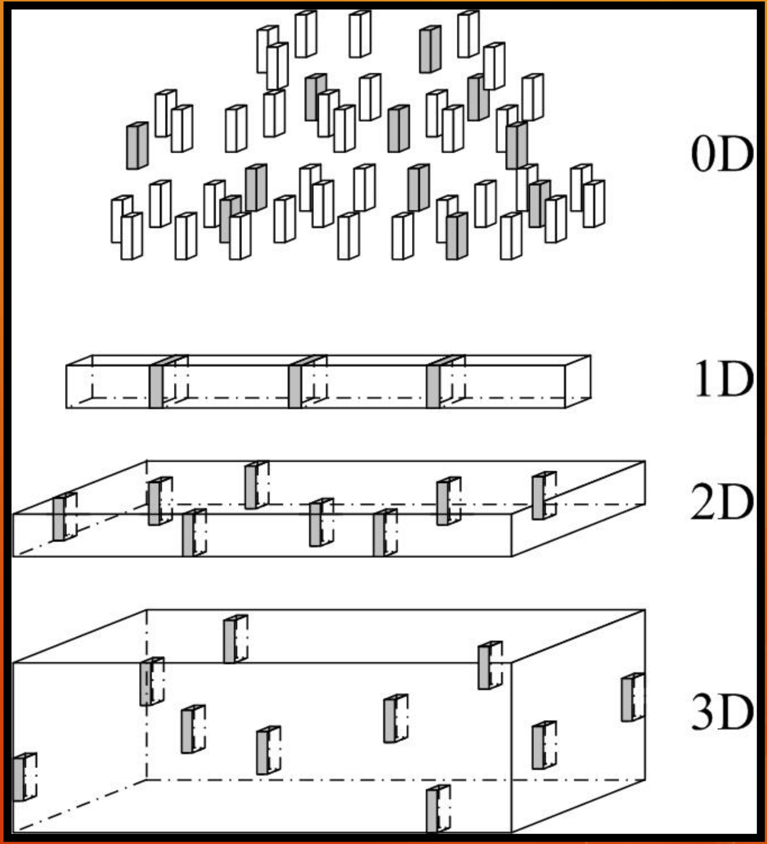
Lot Dimensionality (definition via practical *increments*)

No correlation exists between increments. Total access to the complete lot volume. Increments can be picked at will without untoward effort or difficulty (practical def)

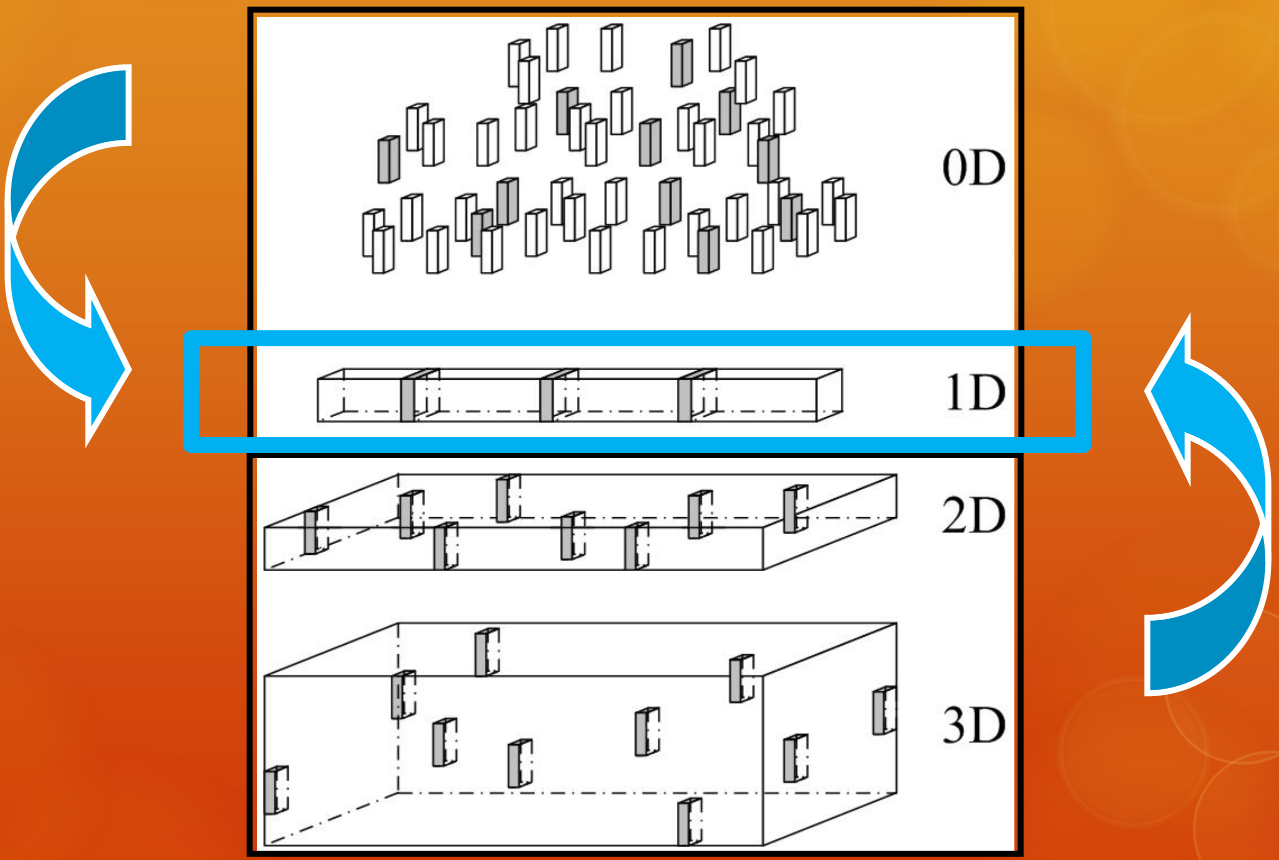
Increments only cover *two* lot dimensions (e.g. a cross-wise planar-parallel “slice”)

Increments only cover *one* lot dimension (e.g. a drill-core; a profile)

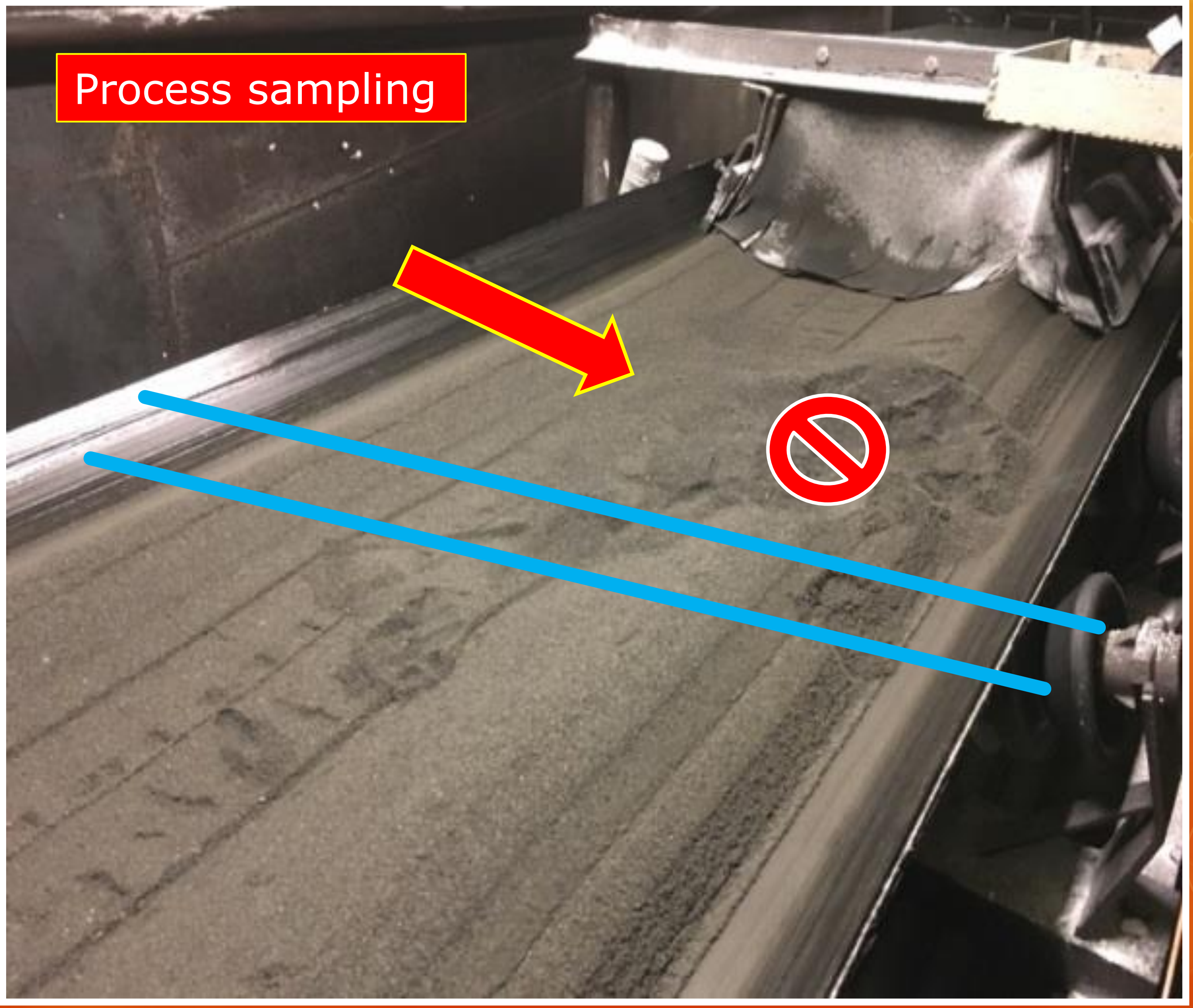
Increments do not fully cover any of the lot dimensions (e.g. a “depth sample”)

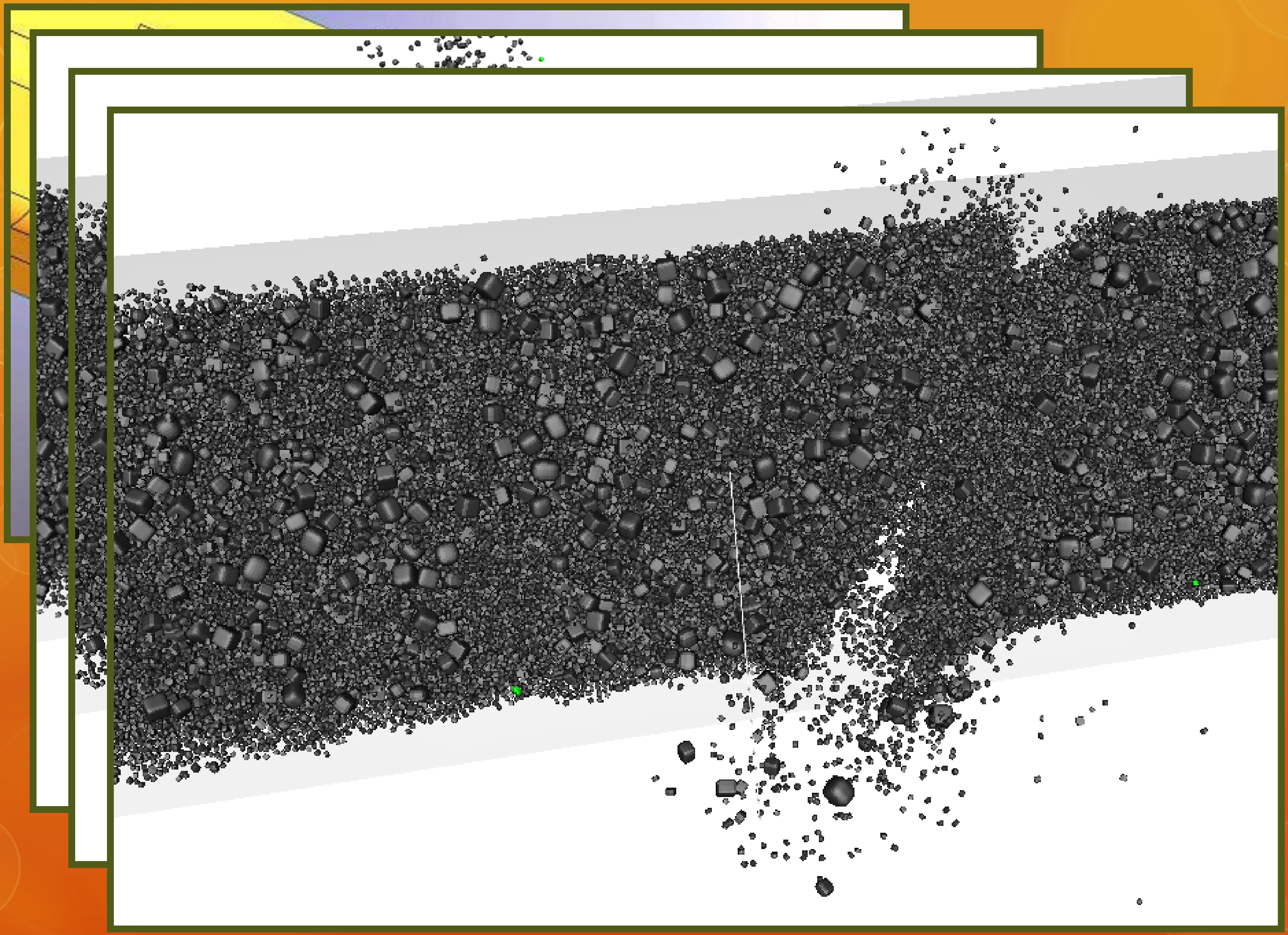


LDT: Lot Dimensionality Transformation

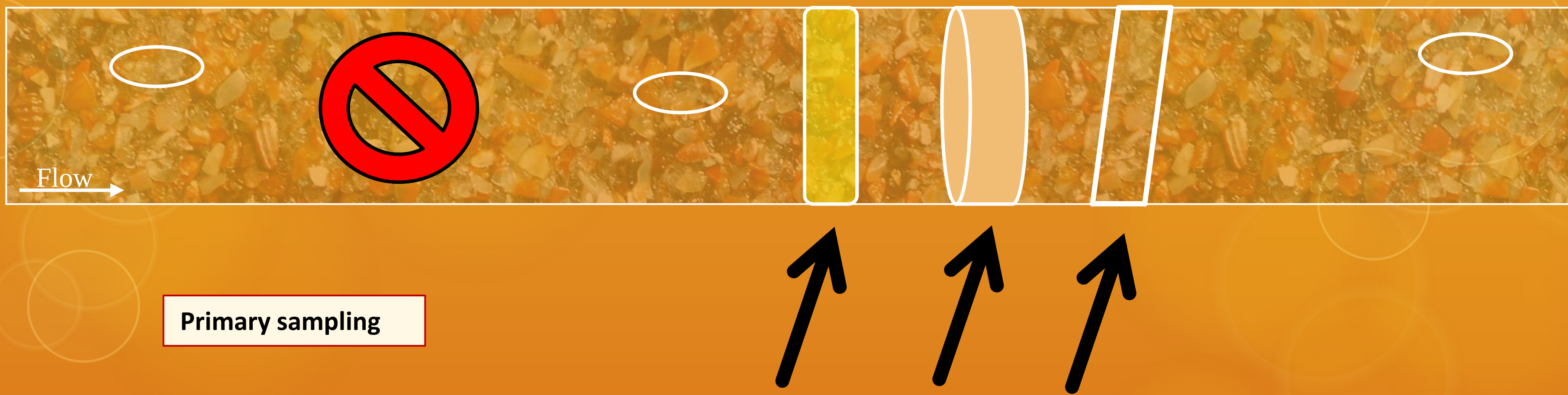


Also, introduction to *process sampling* (*dynamic* 1-D lots)

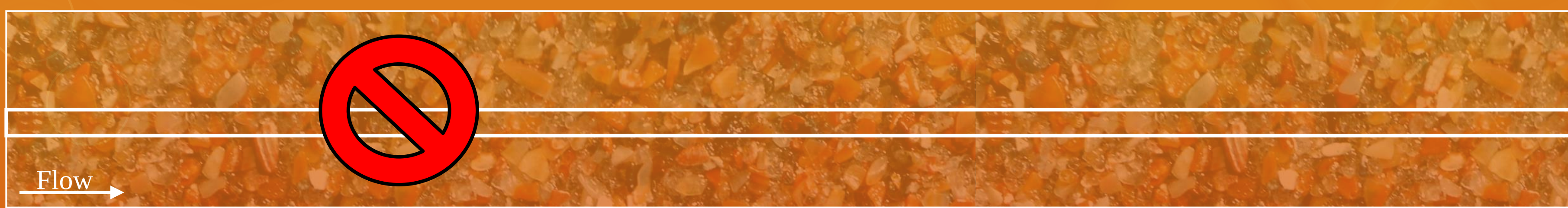

Process sampling



Sampling bias – IDE & IEE



Primary sampling

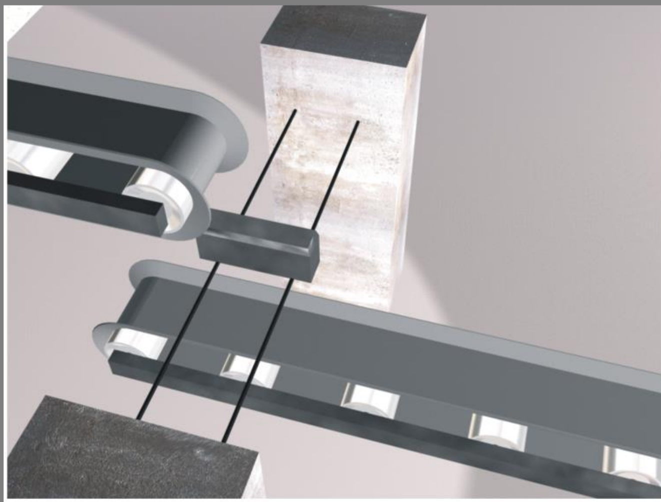


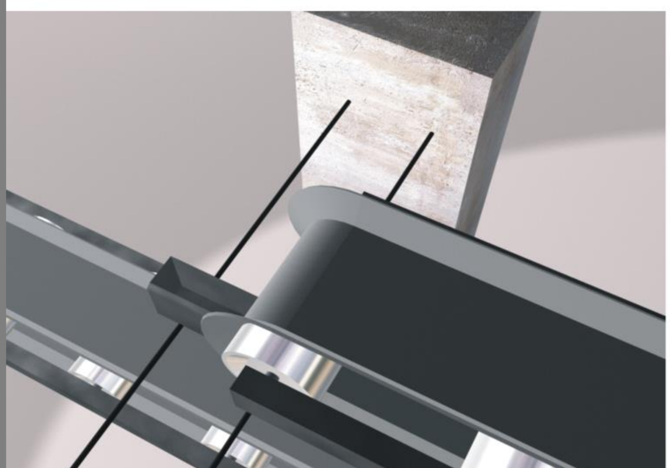
Primary sampling

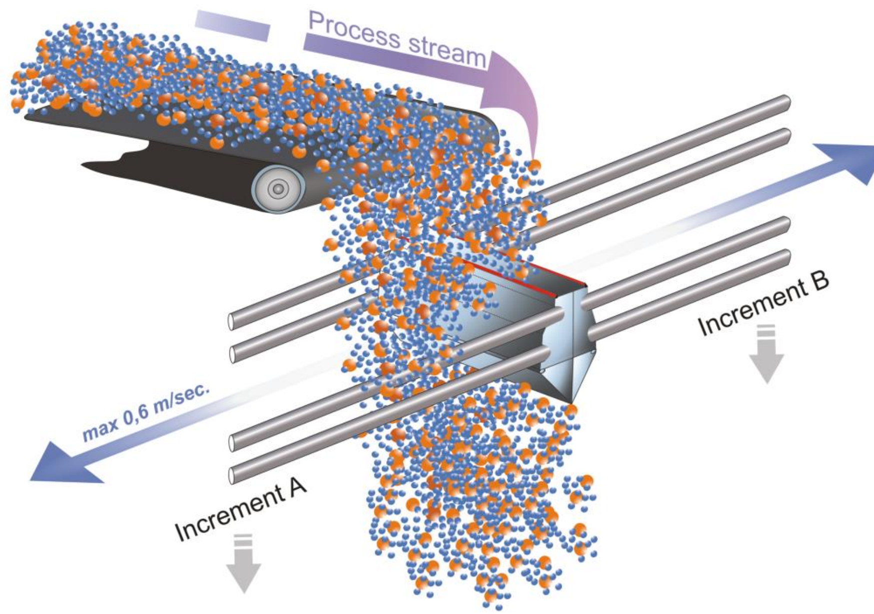
Fundamental Sampling Principle (FSP): 1-D lots

Fundamental Sampling Principle (FSP):

All increments must have the *same* (non-zero) probability of ending up in the sample






Process stream
max 0,6 m/sec.
Increment A
Increment B

Introduction to the Theory and Practice of Sampling

NEW BOOK

Kim H. Esbensen

with contributions from Claas Wagner, Pentti Minkkinen, Claudia Paoletti, Karin Engström, Martin Lischka and Jørgen Riis Pedersen

This book presents the Theory of Sampling (TOS) for all readers and audiences starting from level zero. The TOS is presented in a novel didactic framework without excessive background mathematics and statistics that often scare newcomers away. The overall objective is to present a unifying conceptual framework within which all the TOS' principles, unit operations and sampling error management rules can be understood in the easiest manner possible. This book will make the reader able to start sampling in an effective manner right away, but is also intended to inspire to further skills building and self-study. It contains a wealth of key references.

Bibliographic detail
Publication: summer 2019
ISBN: 978-1-906715-29-8
Pages: approximately 280 pp.
Publisher: IM Publications Open

Find out more and pre-order now from

https://www.impopen.com/sampling

EXAMPLE: lot dim. transformation (LDT)

or, rather: Process sampling in practice

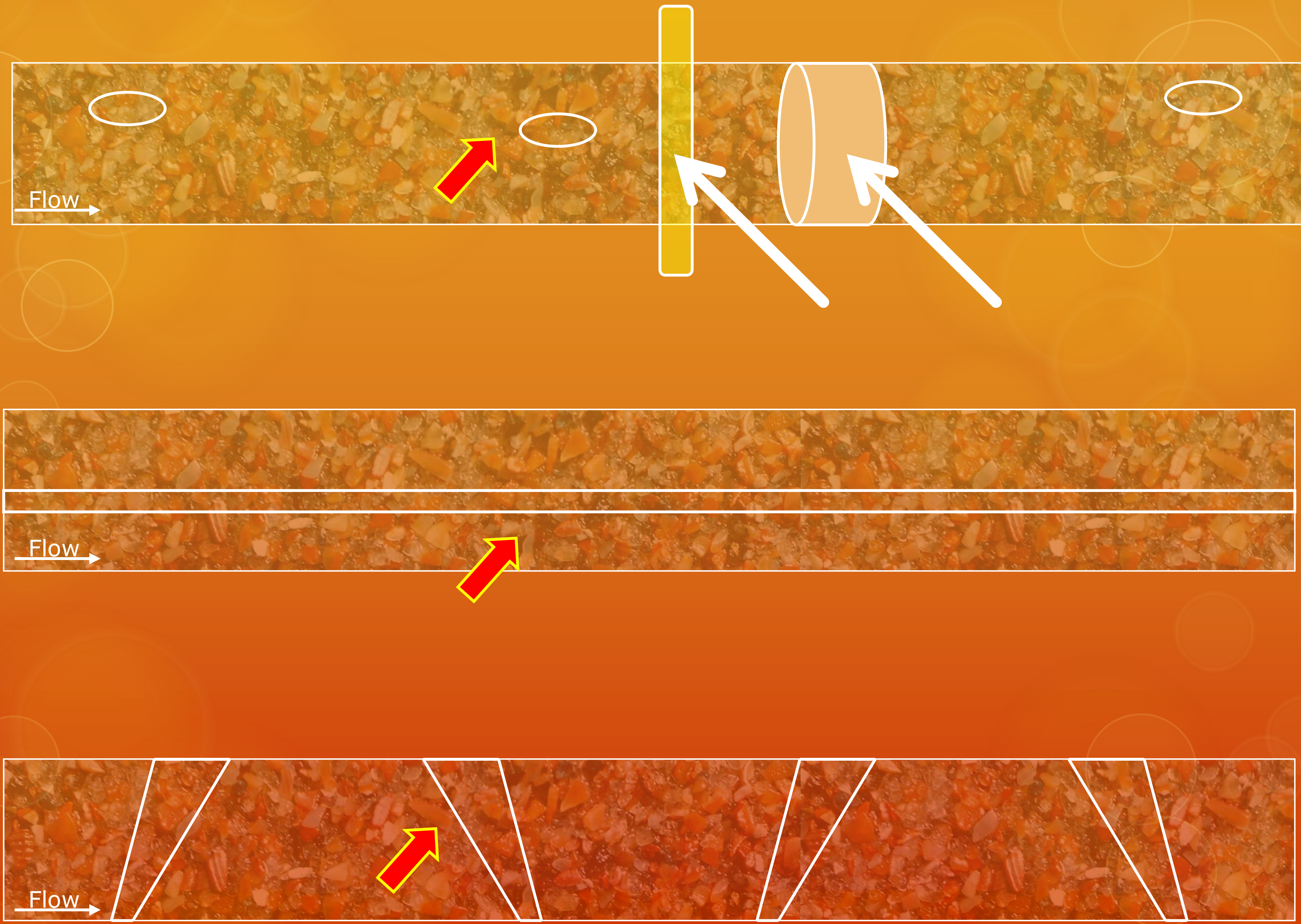
Optimal sampling localisation: 1-D transportation “bottle-necks”

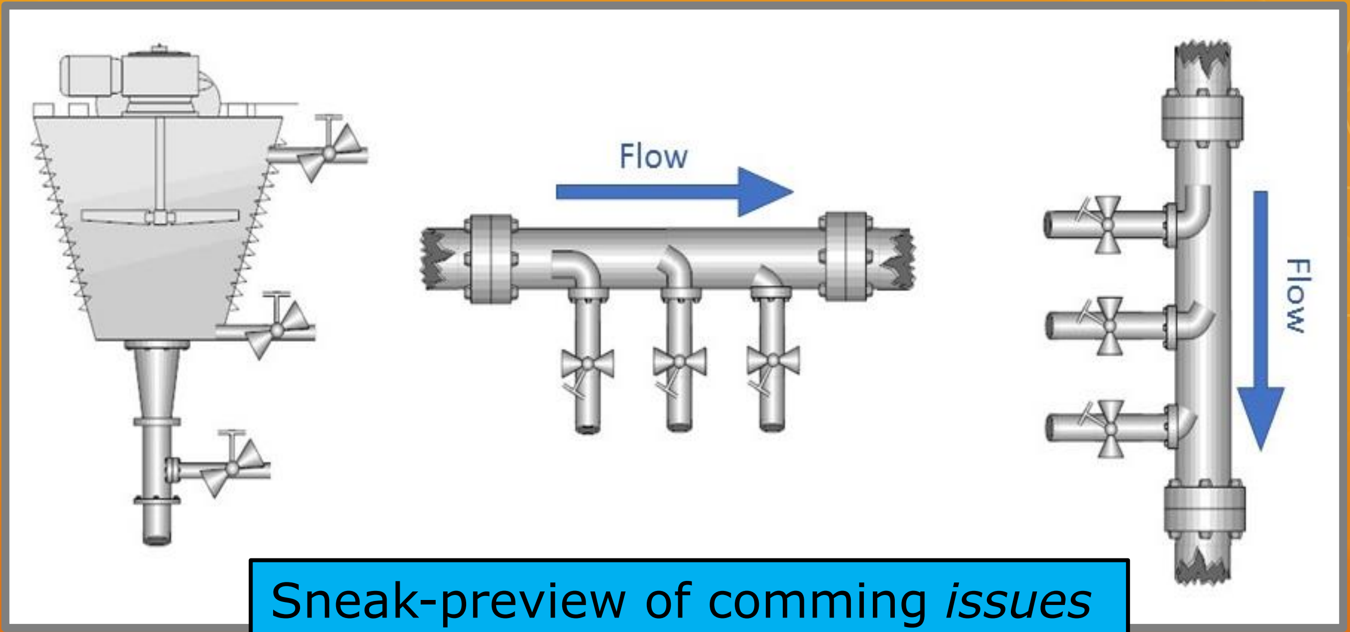
Off-loading - or

transportation …

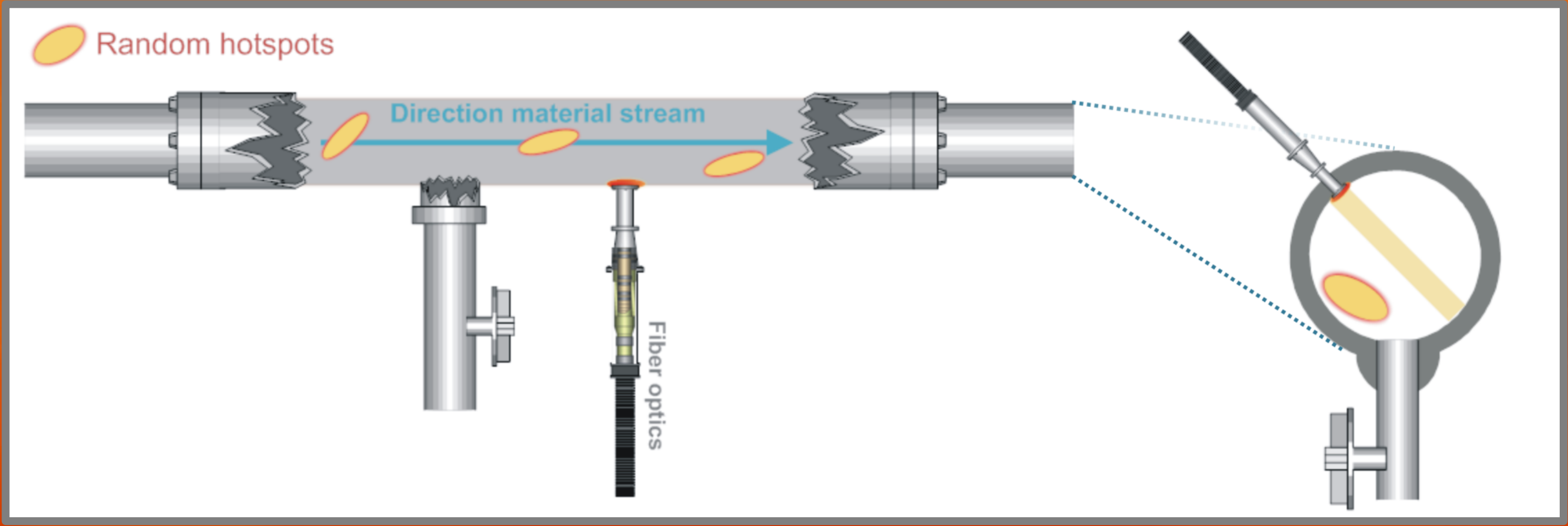
from 3-D lots

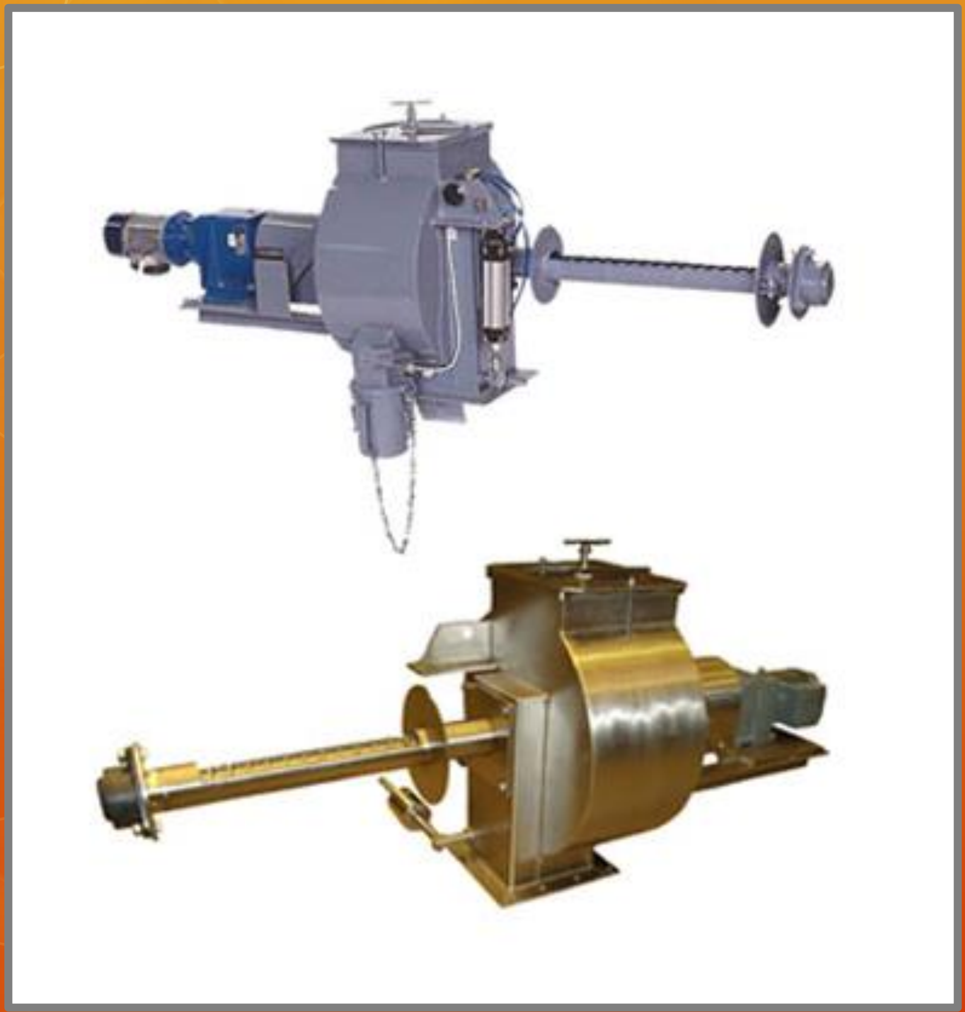
TOS-correct
sampling site: 1-D


Flow
Flow
Flow

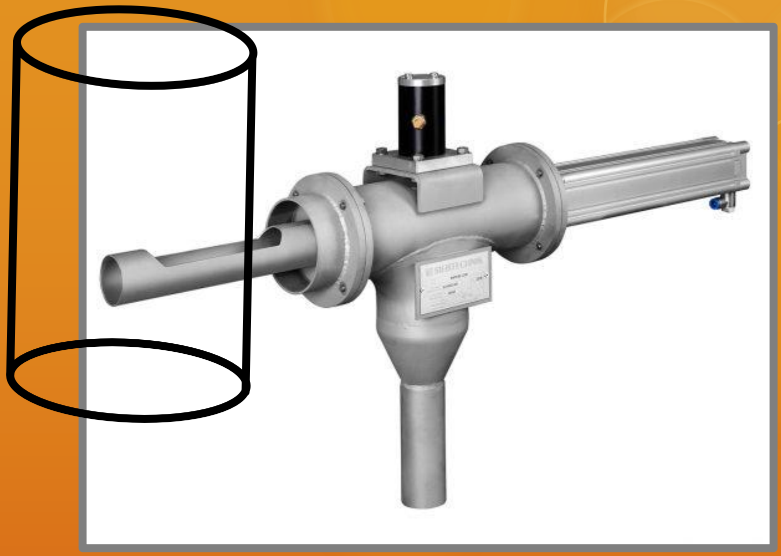
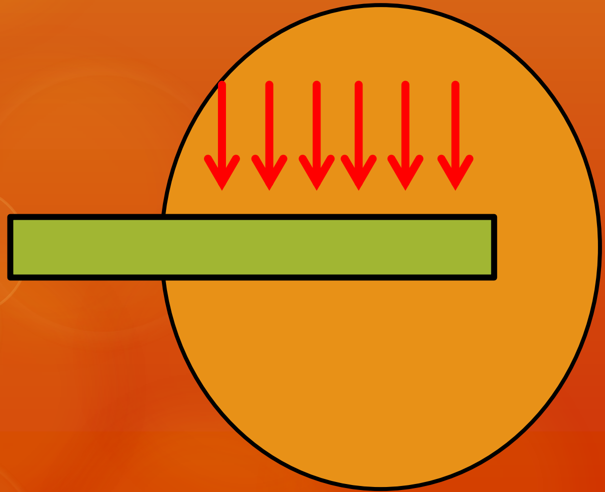
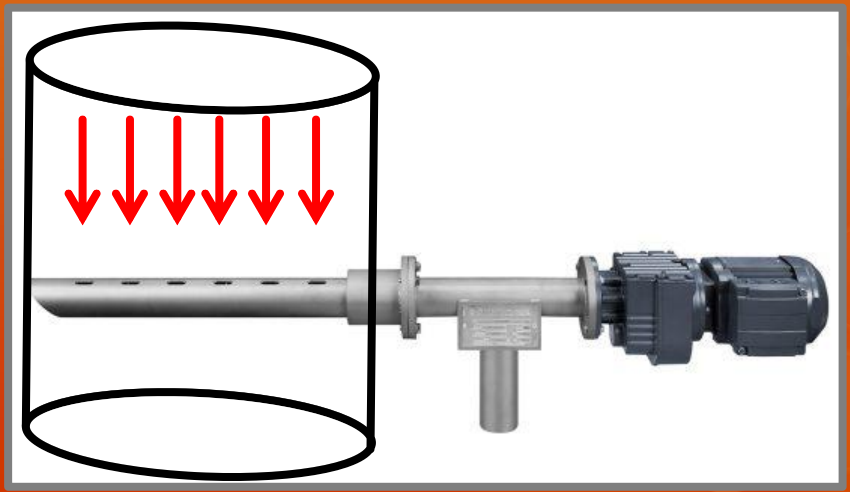


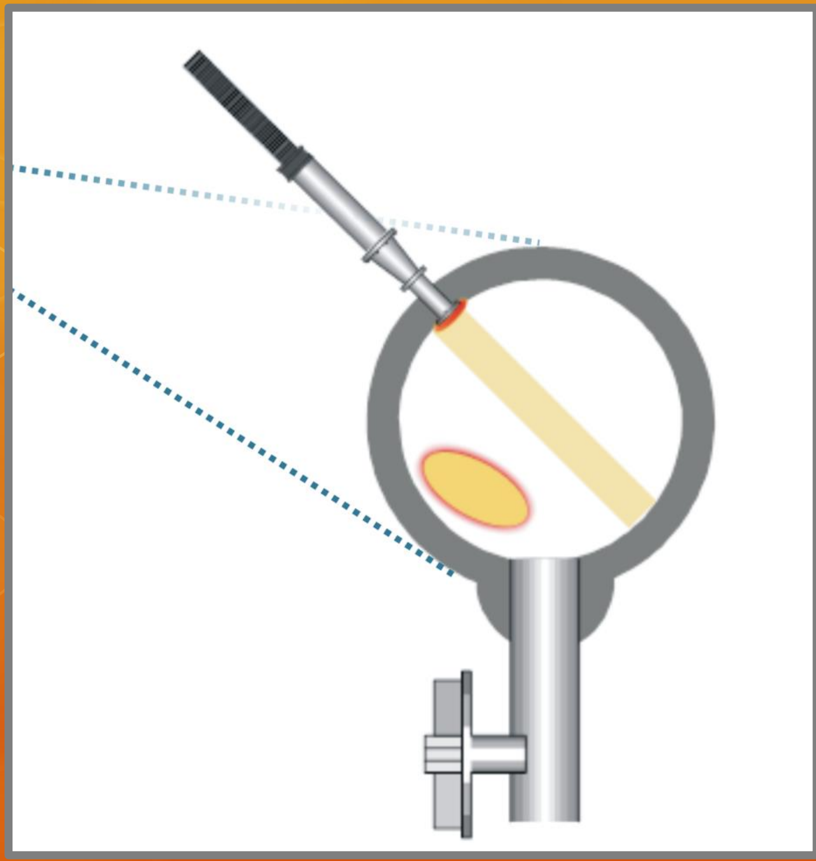
Sneak-preview of comming *issues* regarding 1-D process sampling



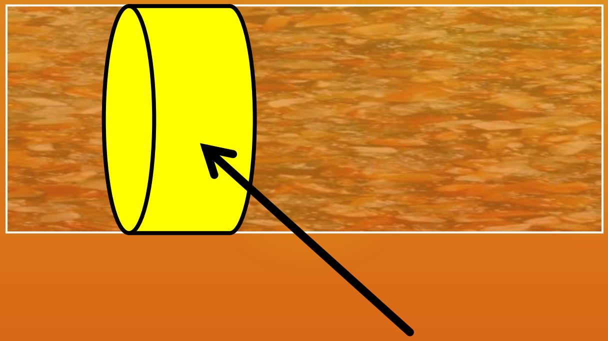




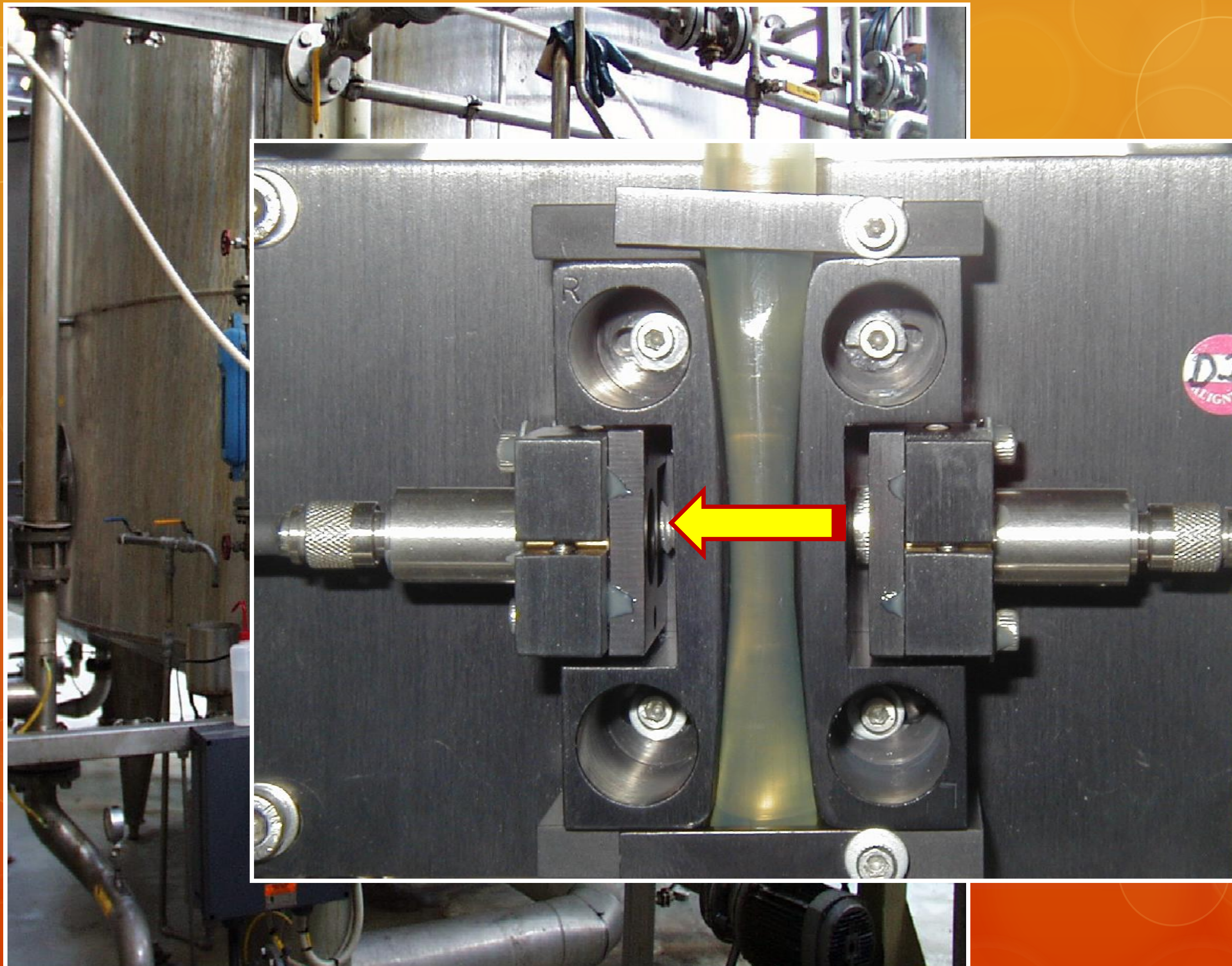


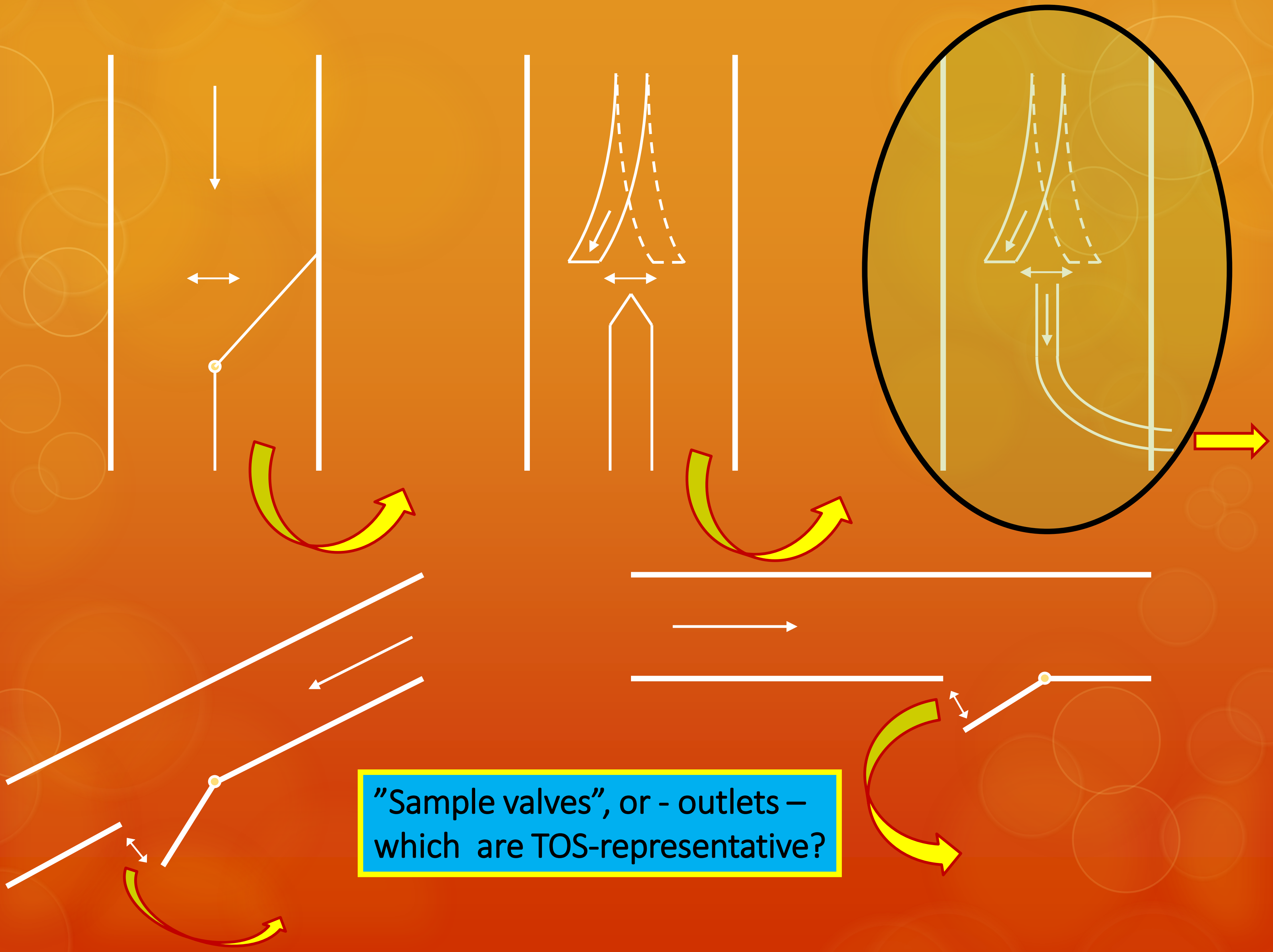
RSV



Increment = full slice!

Which demands to the ducted flow must one make in order for this kind of *sampler* to be(come) (fit-for-purpose) representative?





"Sample valves", or - outlets – which are TOS-representative?

Lot Heterogeneity Characterization (LHC)

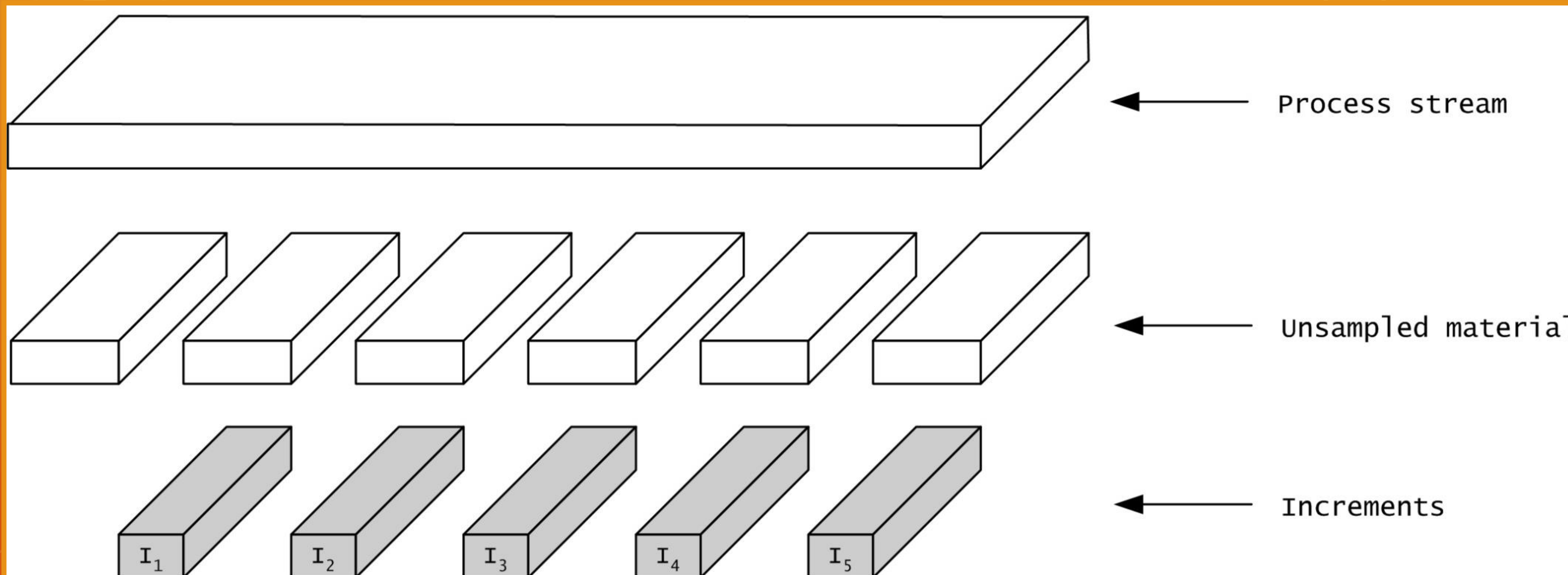
» Why? It makes *no sense* to design a sampling procedure without knowing the lot heterogeneity quantitatively

» A ***replication experiment*** will reveal TSE as well as the sampling steps generating the largest variation

» 10 (40,60) samples provides all the necessary information:

» Complete empirical sampling error estimation –

VARIOGRAPHIC ANALYSIS (1-D case)


Process stream
Unsampled material
Increments
I1
I2
I3
I4
I5

Process sampling – Variographic data analysis

SUO: Variography (variographics)

1-dimensional heterogeneity characterization

1-D lots: processes, long stationary piles, ordered series etc.

Valuable information about lot (process) *variation* (trends, upsets, periodic phenomena.

Also: variance decomposition – process “understanding”

Fo
ac

Sy
eq rting
po

St s
is
ex

Ra process

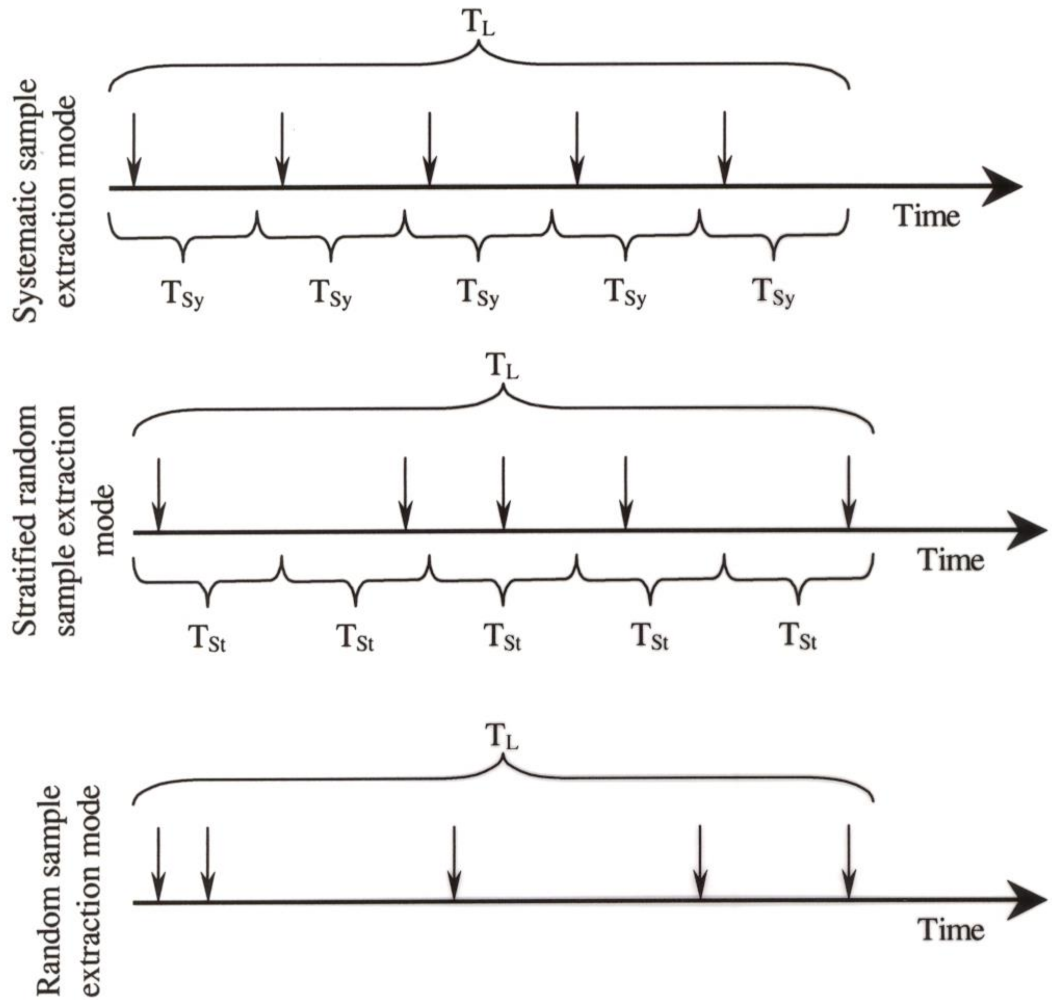
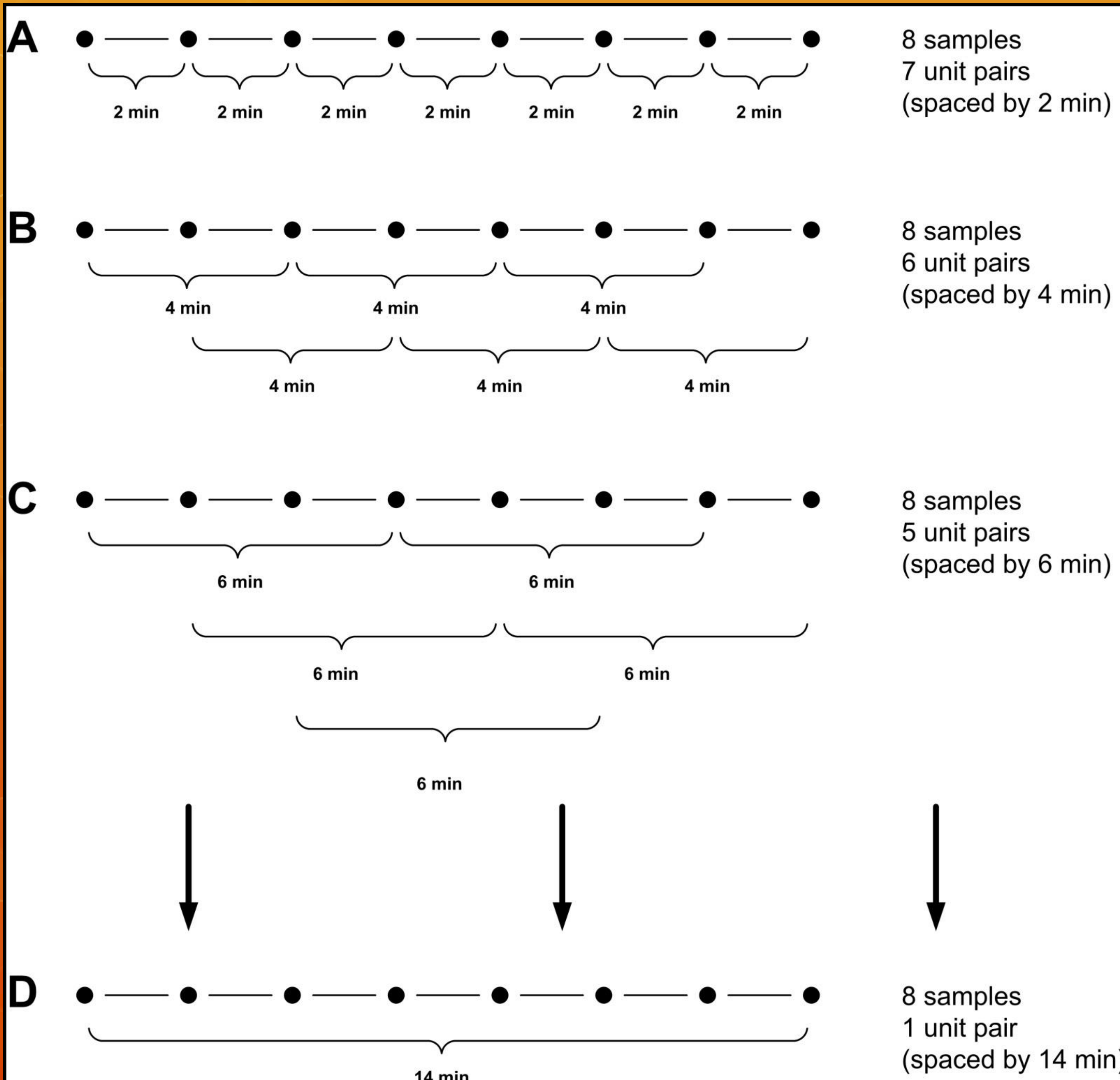


Illustration of the different sample extraction modes. The vertically arrows (↓) represent sample extractions. Notice that the number of sample extractions (Q) for systematic sample extraction mode is equal to T_L/T_{Sy}. The number of sample extractions (Q) for the stratified random sample extraction mode is equal to = T_L/T_{St}.



$$\boxed{j = \frac{\theta}{\theta_{min}}}$$

Reminder: Heterogeneity contribution: h

Heterogeneity contribution of a group to the lot (h_n) – "group" = "increment"

$$h_n = \boxed{\frac{a_n - a_L}{a_L}} \times \boxed{\frac{M_n}{\overline{M_n}}}$$

a_n: group grade
a_L : lot grade
M_n: group mass

Compositional differences group-lot (compositional heterogeneity)

Group size

Compositional difference is weighted by group size

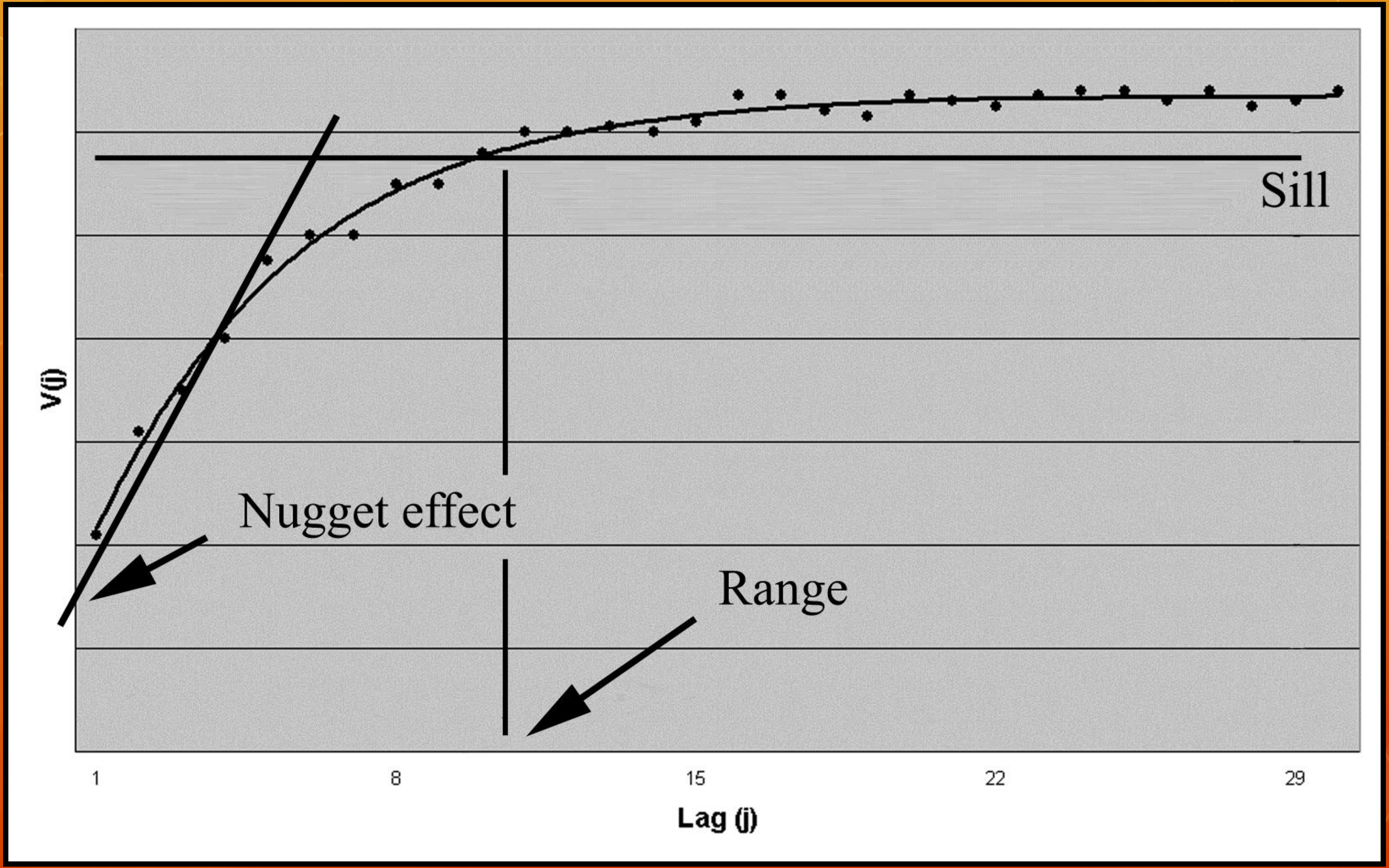
$$V(j) = \frac{1}{2(N_U - j)} \sum_m (h_{m+j} - h_m)^2$$

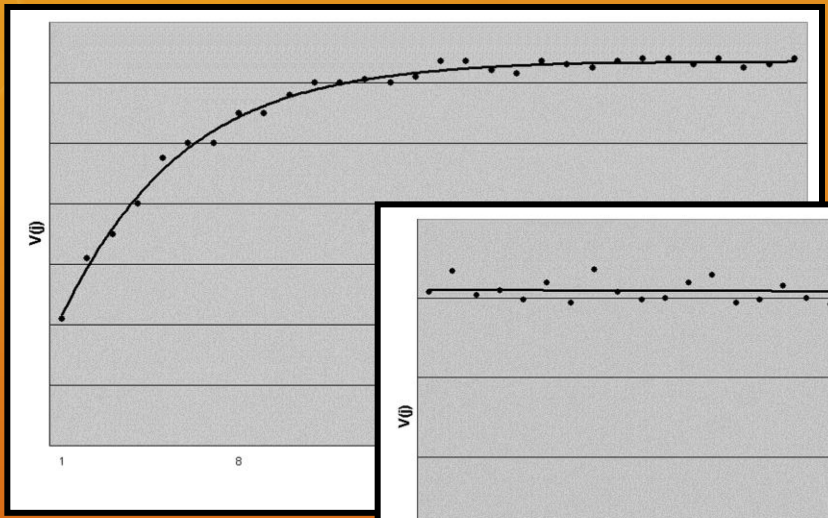
$$V(j) = \frac{1}{2(N_U - j)a_L^2} \sum_m [a_{m+j} - a_m]^2$$

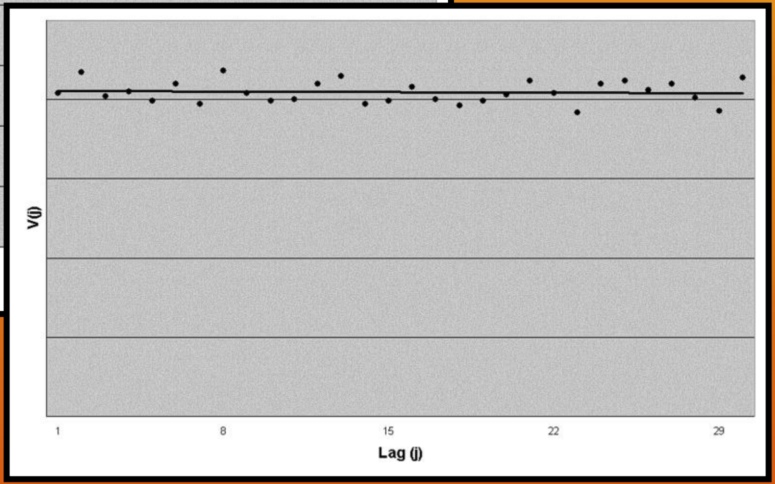
V(j) = Variogram function [relative (h_m) or absolute (a_m)

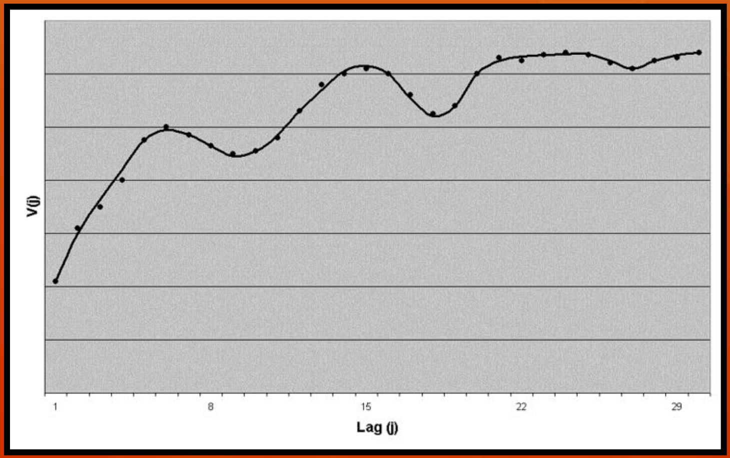
	B	C	D	E	F	G	H	I	J	K	L	M
1	Hq (Pred Values)	Lag (j)	V(j)	Q-j	1/(2(Q-j))	sum(hq+j-hq)^2	Lag1	Lag2	Lag3	Lag4	Lag5	Lag6
2												
3	15.04	1	0.245	207	0.002	102	0.00214	0.21641	0.15936	0.04268	0.64609	2.13949
4	14.99	2	0.409	206	0.002	169	0.17548	0.12454	0.06396	0.57381	2.00619	1.34351
5	14.57	3	0.455	205	0.002	186	0.00436	0.45132	0.11465	0.99501	0.5479	1.09161
6	14.64	4	0.490	204	0.002	200	0.36699	0.1637	1.13103	0.64996	0.95805	3.47114
7	15.24	5	0.573	203	0.002	233	1.02091	2.78656	1.99374	0.13913	1.5808	0.07054
8	14.23	6	0.638	202	0.002	258	0.43415	0.16128	1.9138	5.14246	1.62818	0.74909
9	13.58	7	0.652	201	0.002	262	0.0662	4.17099	8.56499	3.74384	2.3238	3.2436
10	13.83	8	0.668	200	0.003	267	3.18623	7.12516	2.81434	1.60554	2.38301	5.35876
11	15.62	9	0.699	199	0.003	278	0.78199	0.01153	0.26822	0.05823	0.28079	1.30599
12	16.50	10	0.730	198	0.003	289	0.98347	1.96616	1.26698	0.1256	4.10913	6.36351
13	15.51	11	0.699	197	0.003	275	0.16851	0.01793	0.40615	1.07205	2.34365	2.22189
14	15.10	12	0.708	196	0.003	277	0.07651	1.09788	0.3905	1.2553	1.16662	1.67314
15	15.38	13	0.745	195	0.003	291	0.59475	0.8127	1.95161	1.84063	2.46521	3.23137
16	16.15	14	0.750	194	0.003	291	2.79793	4.70109	4.52796	5.48169	6.59873	3.62027

$$V(j) = \frac{1}{2(Q_{total} - j)} \sum_{q=1}^{Q_{total}-j} \left(h_{q+j} - h_q\right)^2$$

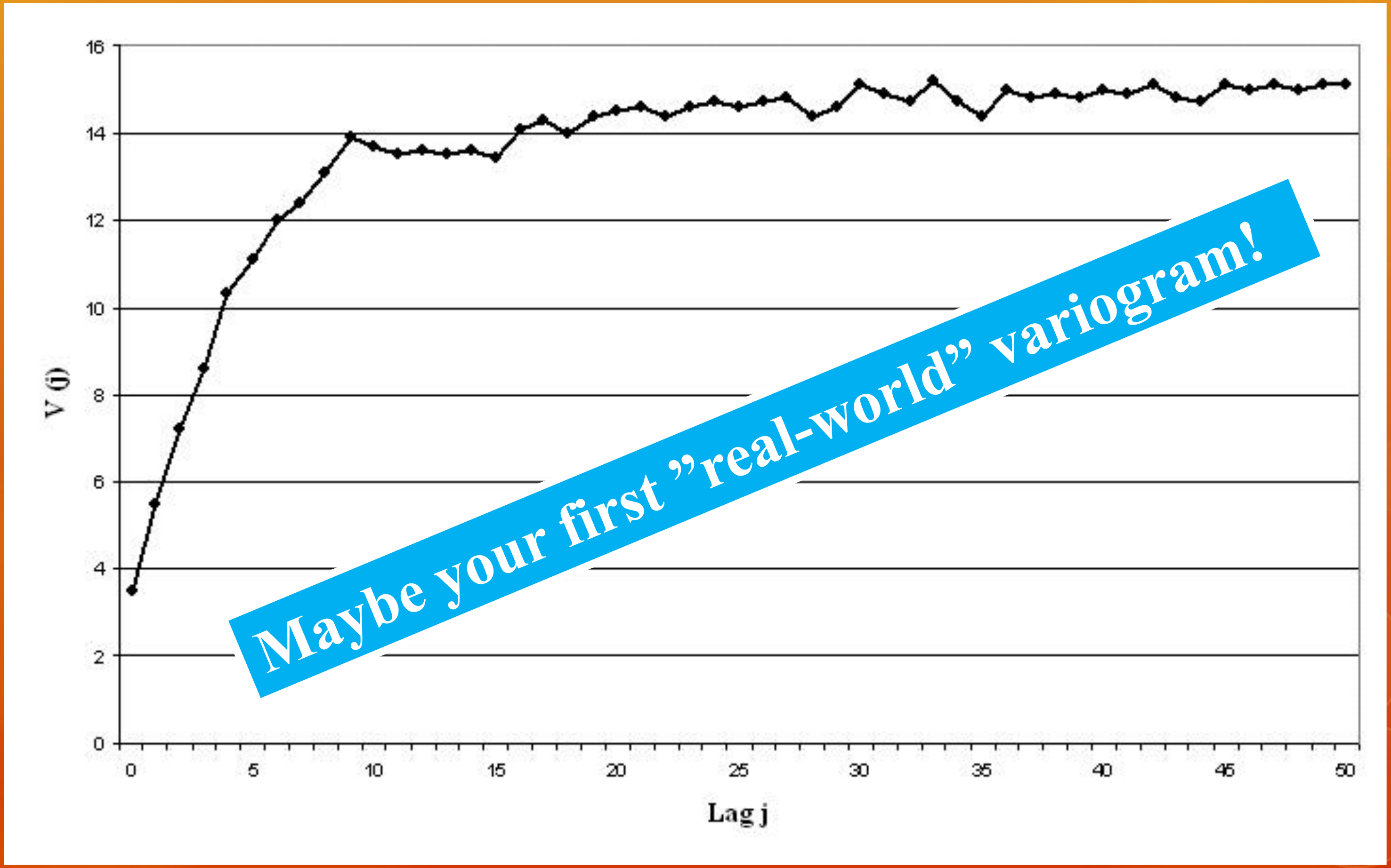

Sill
Nugget effect
Range
V(j)
1
8
15
22
29
Lag (j)


V(j)
1
8

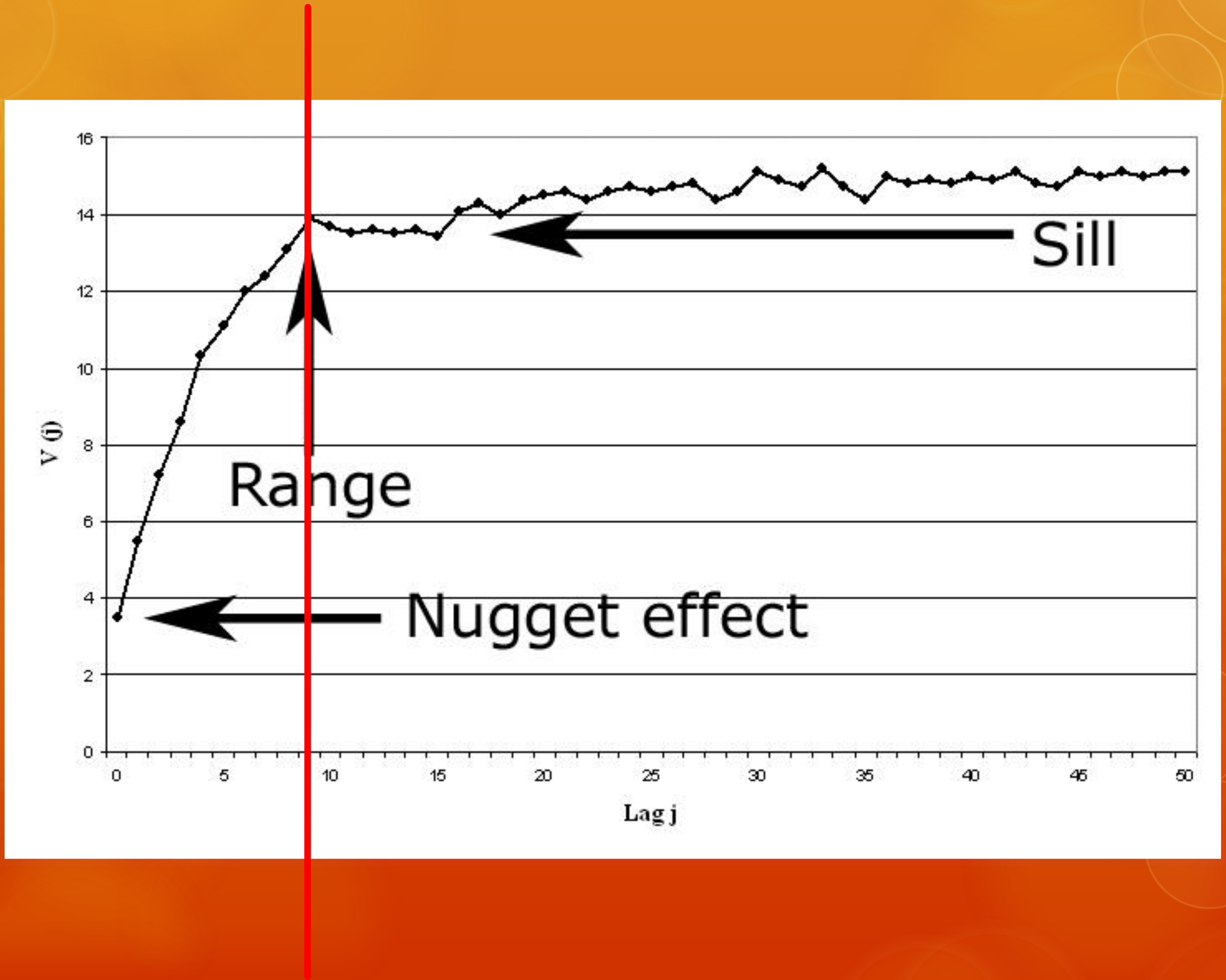

V(j)
1
8
15
22
29
Lag (j)

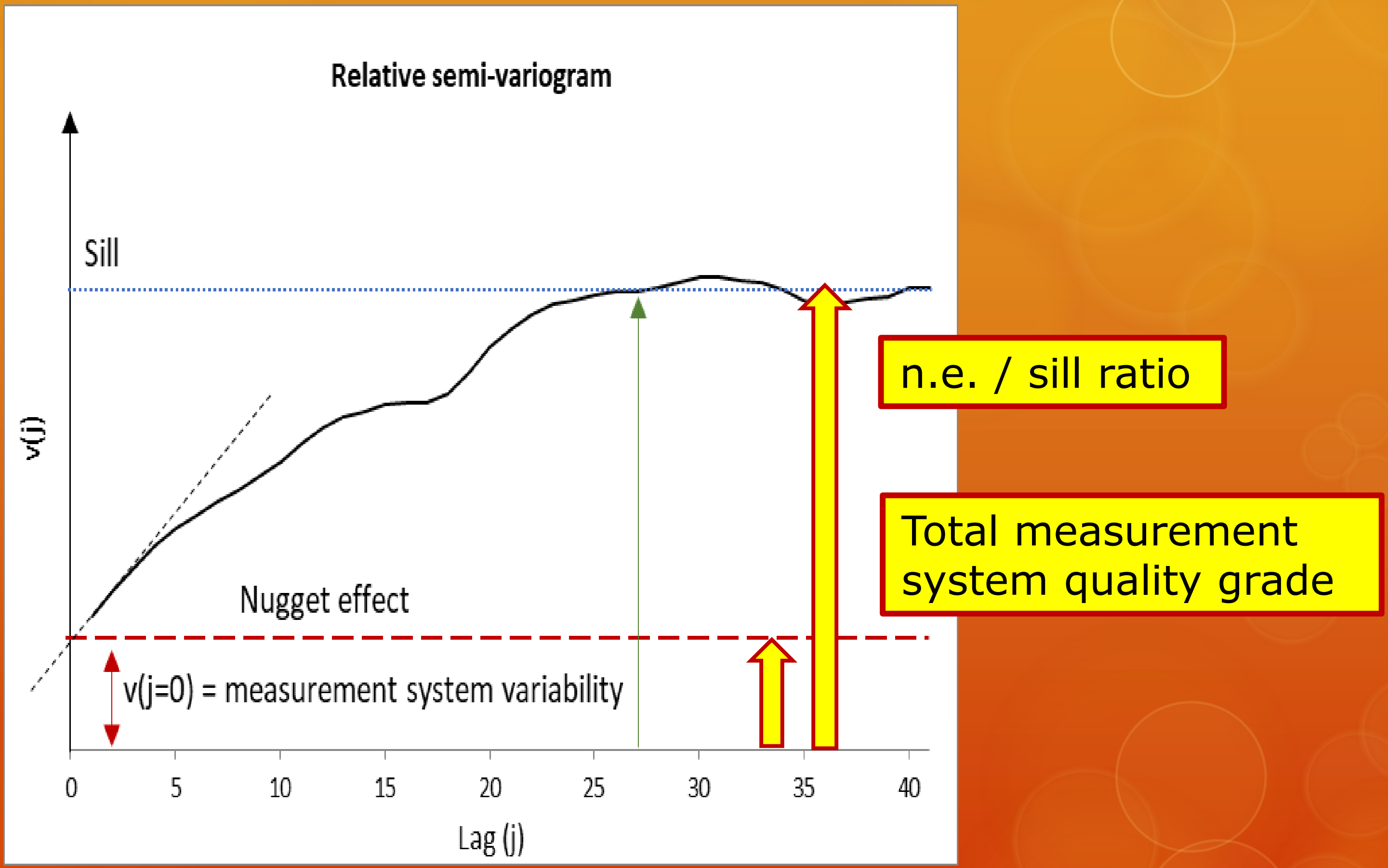

V(j)
1
8
15
22
29
Lag (j)

ACABS Research Group Aalborg University
Esbjerg, Denmark



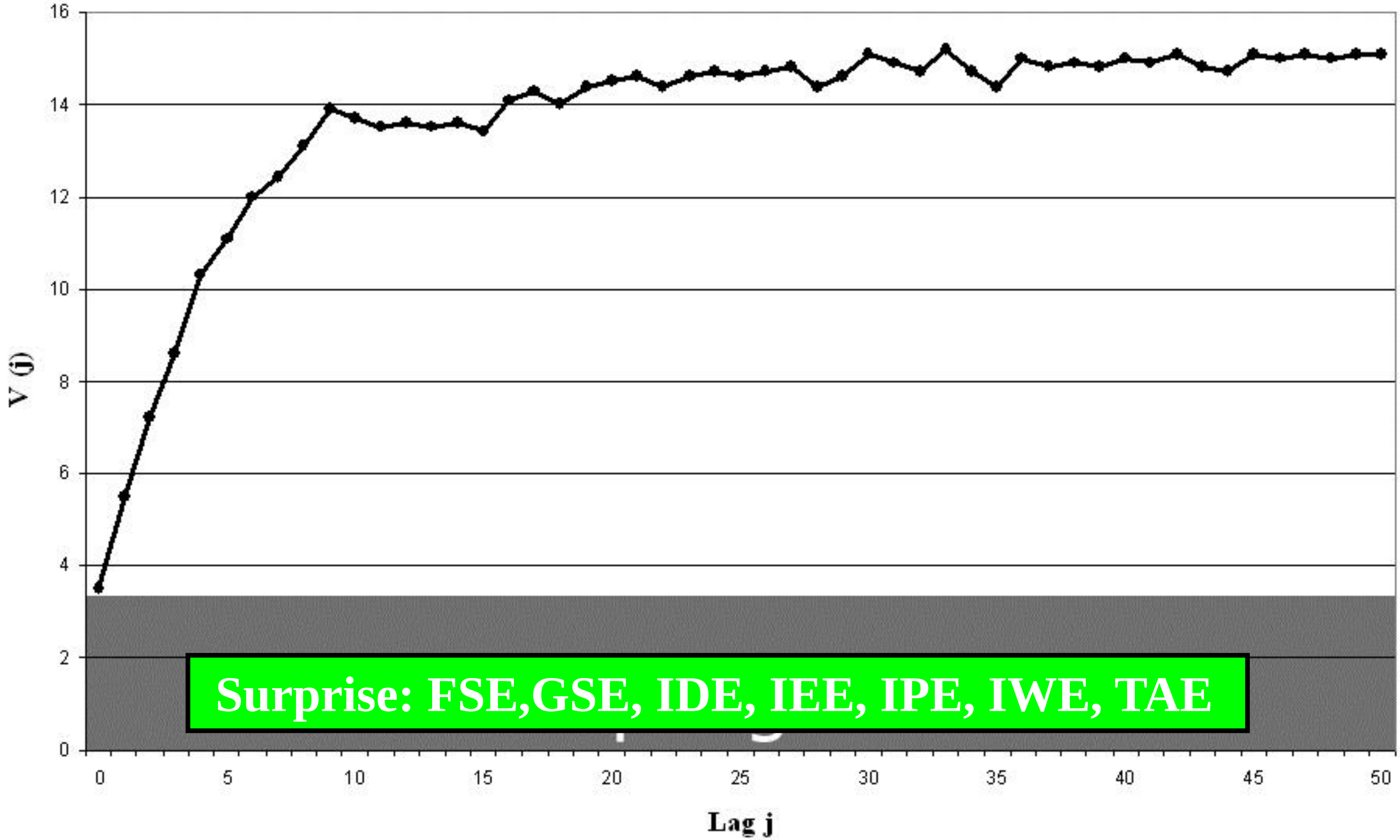
Aalborg University
Esbjerg, Denmark

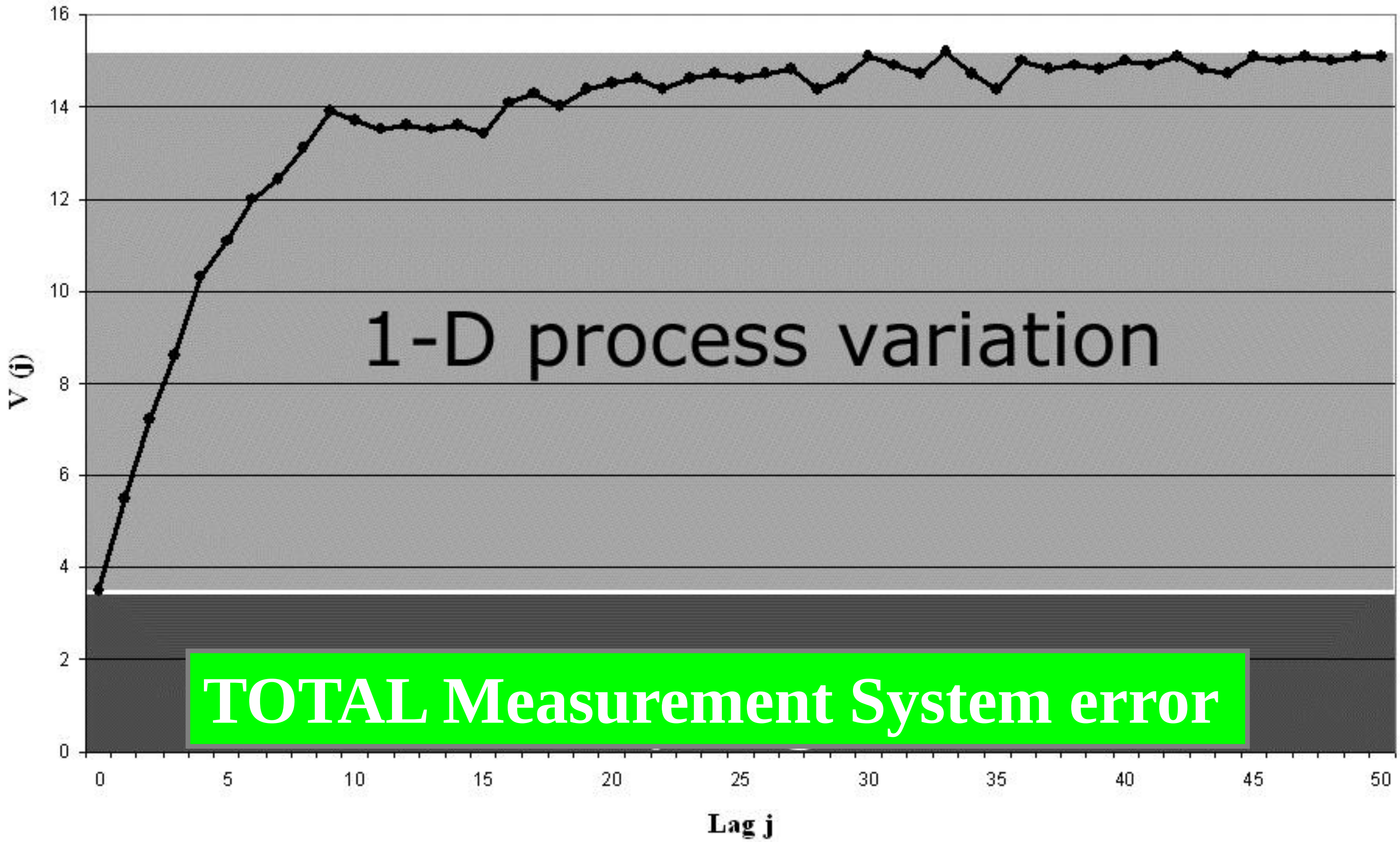



Relative semi-variogram
Sill
Nugget effect
v(j=0) = measurement system variability
v(j)
0
5
10
15
20
25
30
35
40
Lag (j)
n.e. / sill ratio
Total measurement system quality grade

b

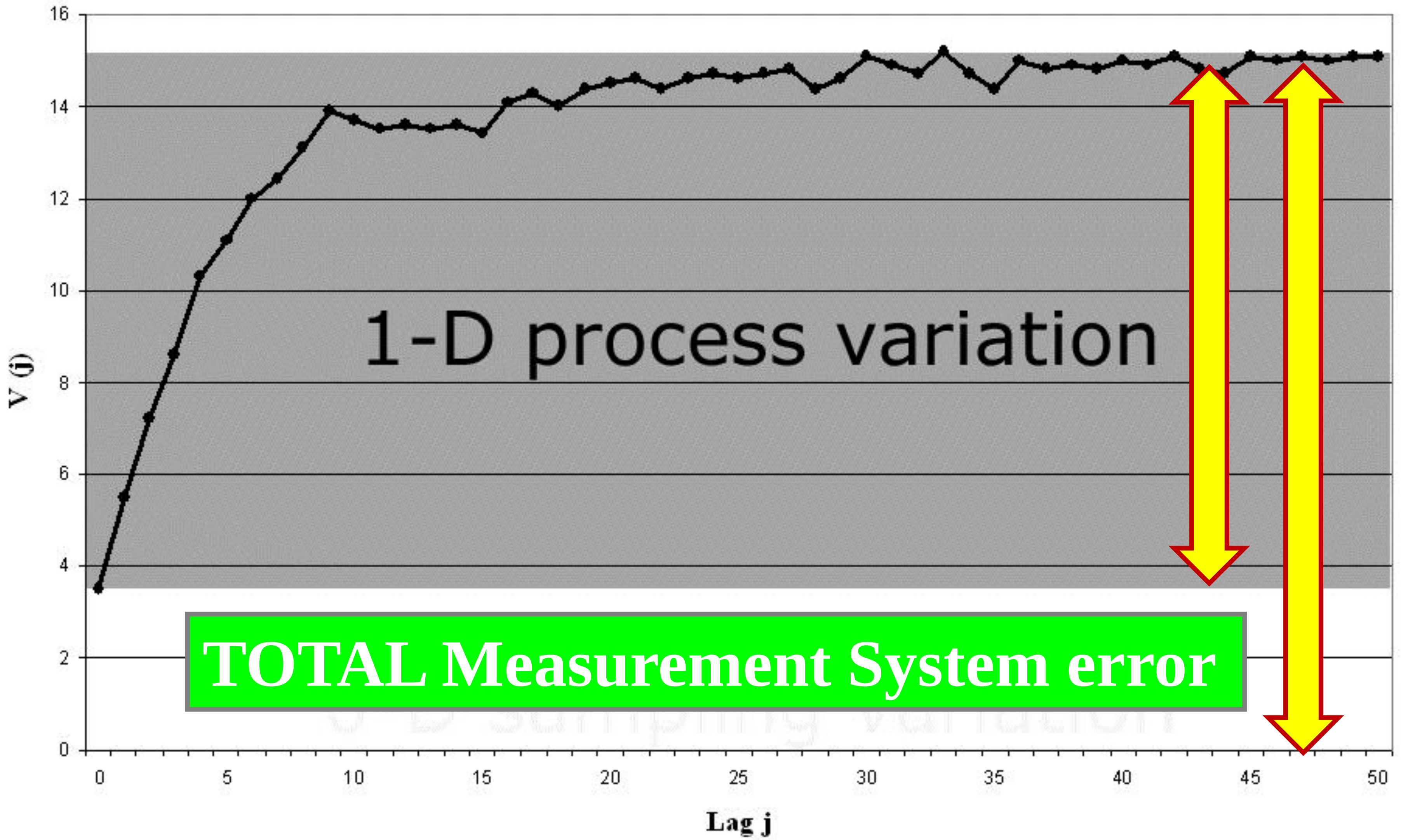
c

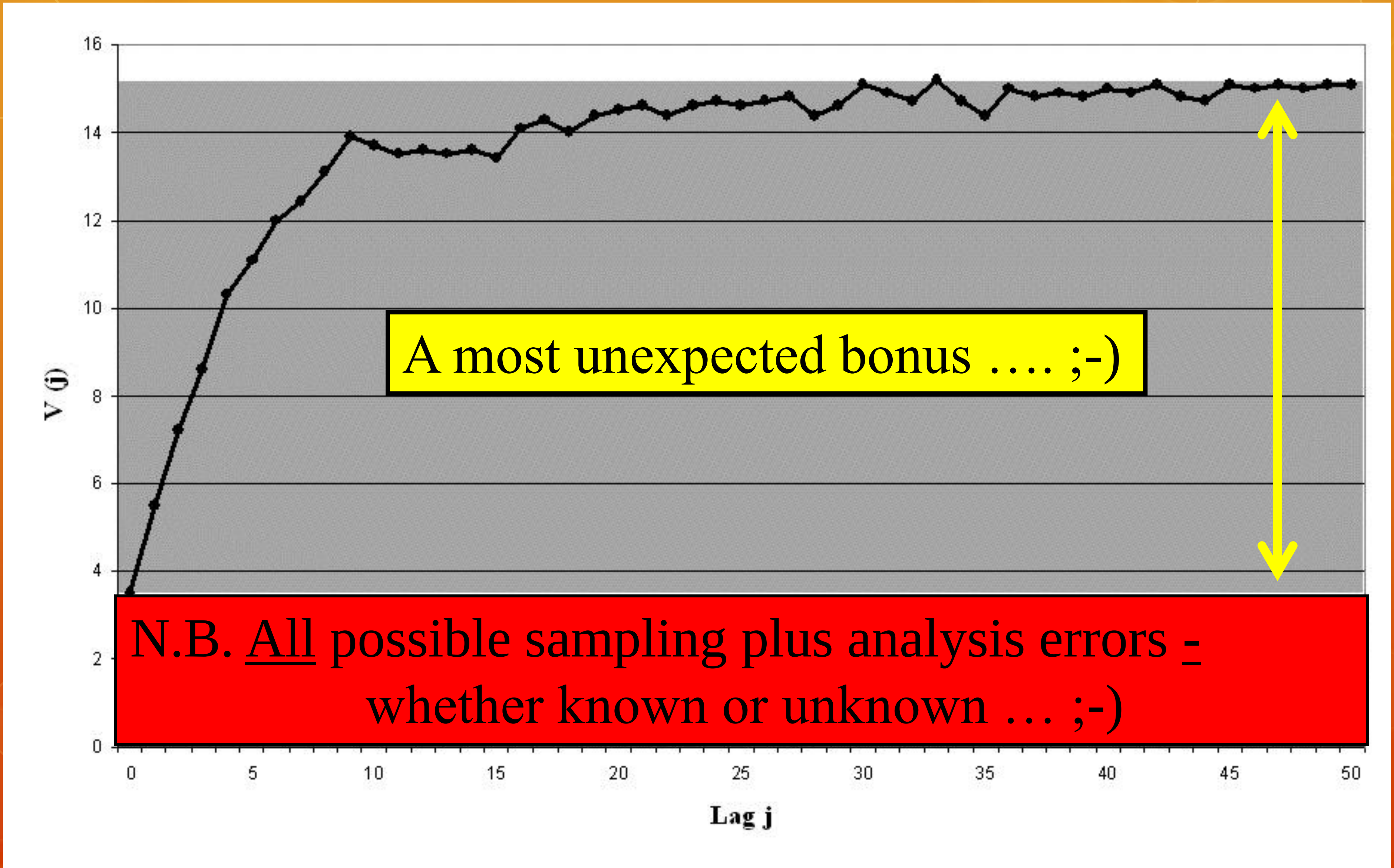

V (j)
16
14
12
10
8
6
4
2
0
0
5
10
15
20
25
30
35
40
45
50
Lag j
Surprise: FSE,GSE, IDE, IEE, IPE, IWE, TAE

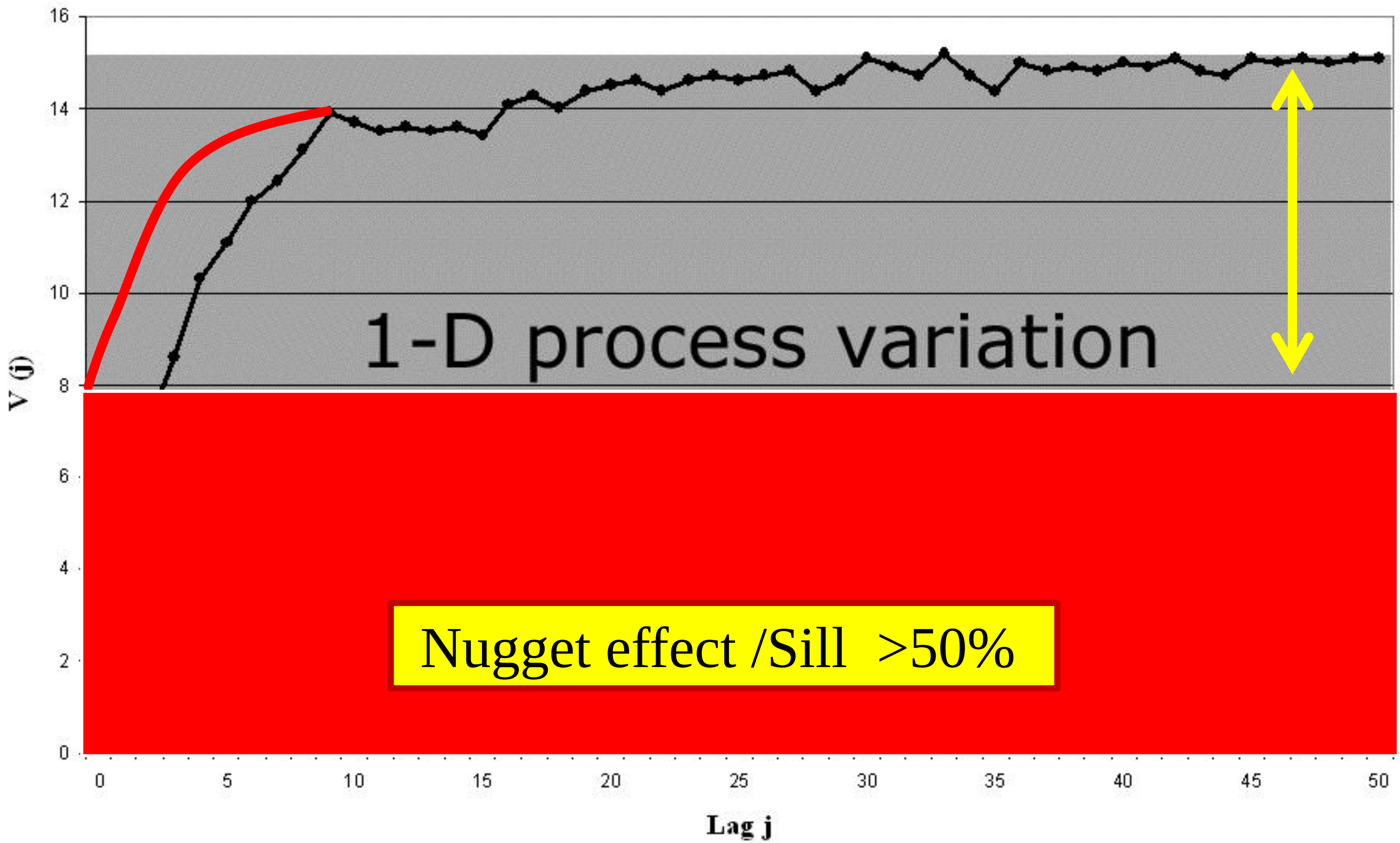

16
14
12
10
8
6
4
2
0
V (j)
1-D process variation
TOTAL Measurement System error
0
5
10
15
20
25
30
35
40
45
50
Lag j

ACABS Research Group

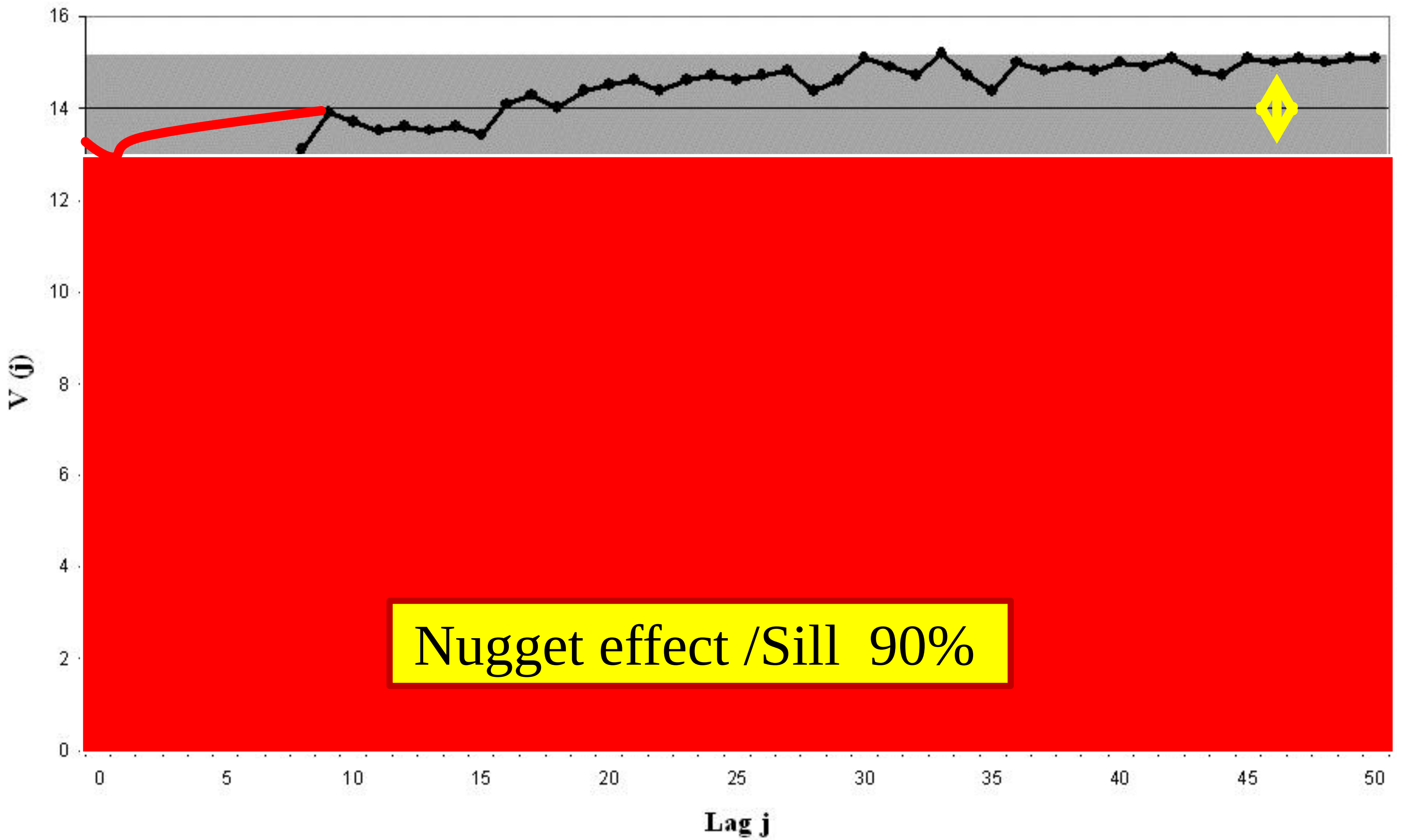
Aalborg University
Esbjerg, Denmark




16
14
12
10
8
6
4
2
0
V (j)
0
5
10
15
20
25
30
35
40
45
50
Lag j
A most unexpected bonus …. ;-)
N.B. All possible sampling plus analysis errors -
whether known or unknown … ;-)

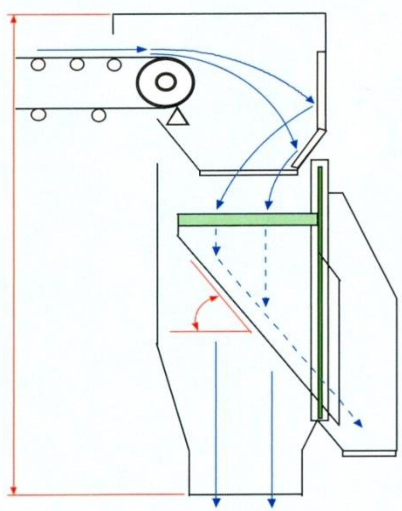


16
14
12
10
8
6
4
2
0
V (j)
0
5
10
15
20
25
30
35
40
45
50
Lag j
1-D process variation
Nugget effect /Sill >50%


16
14
12
10
8
6
4
2
0
V (j)
0
5
10
15
20
25
30
35
40
45
50
Lag j
Nugget effect /Sill 90%

PIERRE GY'S THEORY OF SAMPLING
and
C.O. INGAMELLS' POISSON PROCESS
APPROACH

PATHWAYS TO REPRESENTATIVE SAMPLING
and
APPROPRIATE INDUSTRIAL STANDARDS



Doctoral Thesis

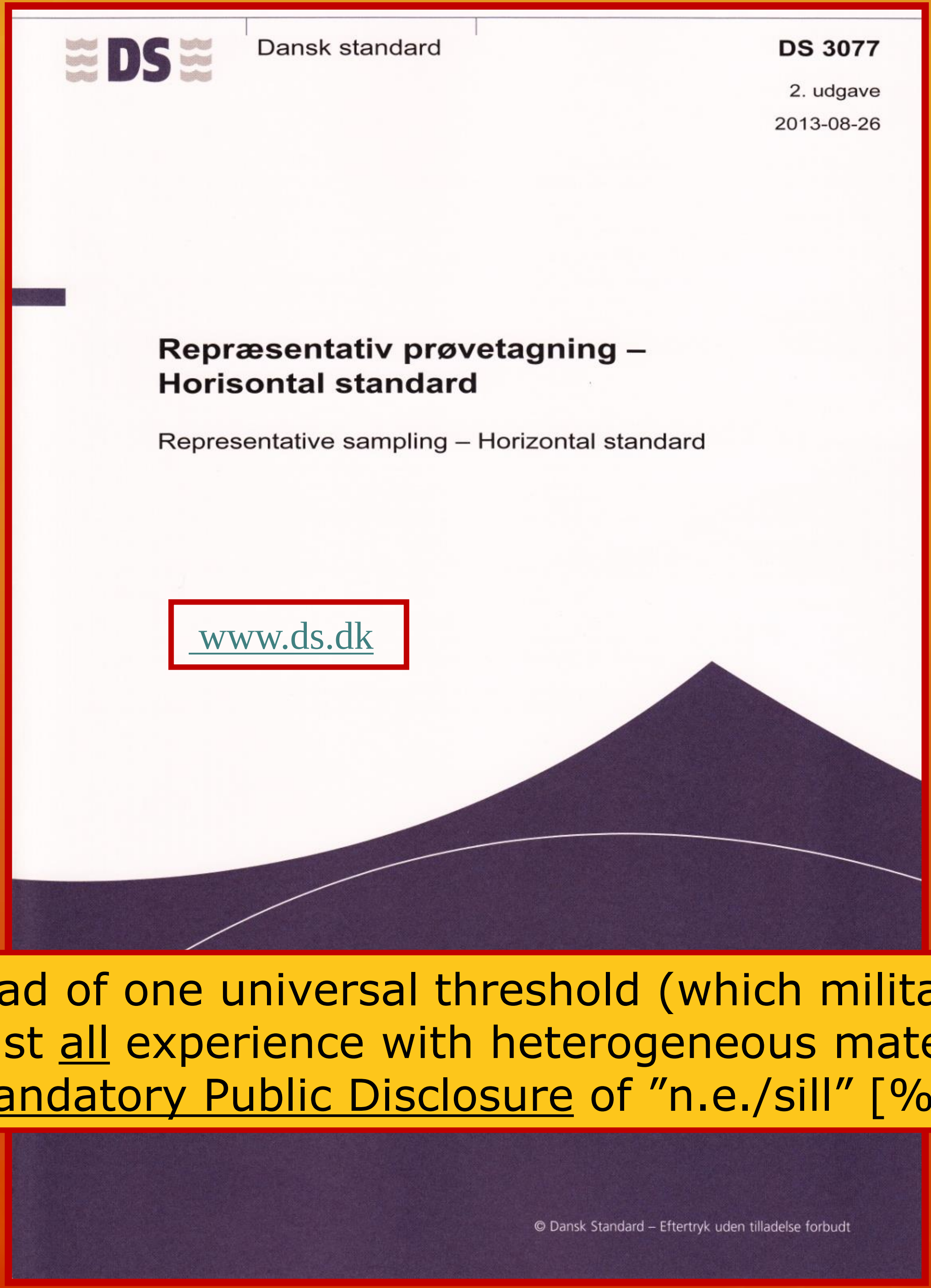
Francis F. Pitard

Aalborg University, Campus Esbjerg, Denmark
June, 2009

PIERRE GY'S THEORY OF SAMPLING
and
C.O. INGAMELLS' POISSON PROCESS APPROACH

PATHWAYS TO REPRESENTATIVE SAMPLING
and
APPROPRIATE INDUSTRIAL STANDARDS


16%
35%
WCSB4
ANGLOGOLD ASHANTI



Dansk standard

DS 3077

2. udgave

2013-08-26

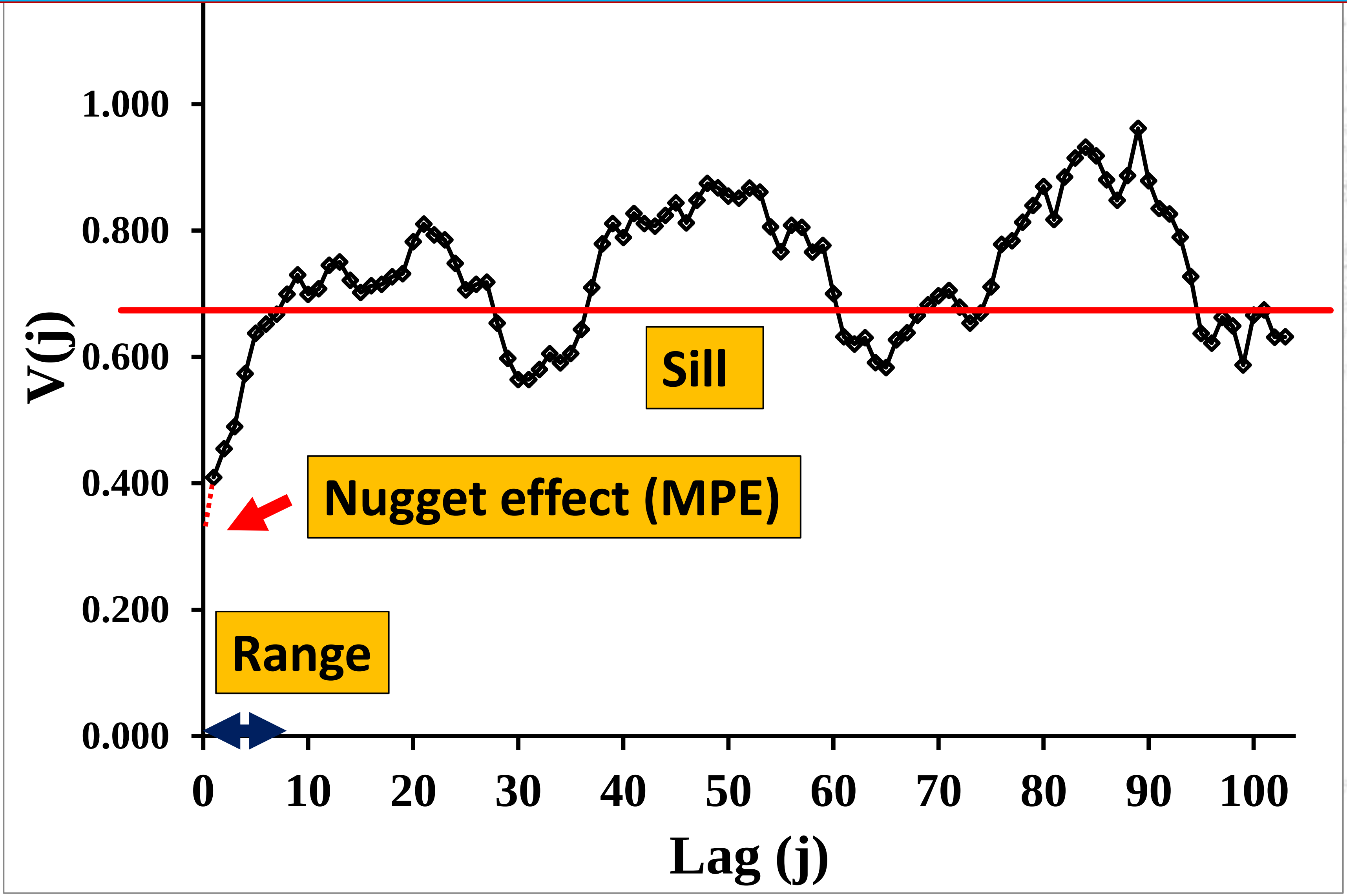
Repræsentativ prøvetagning – Horisontal standard

Representative sampling – Horizontal standard

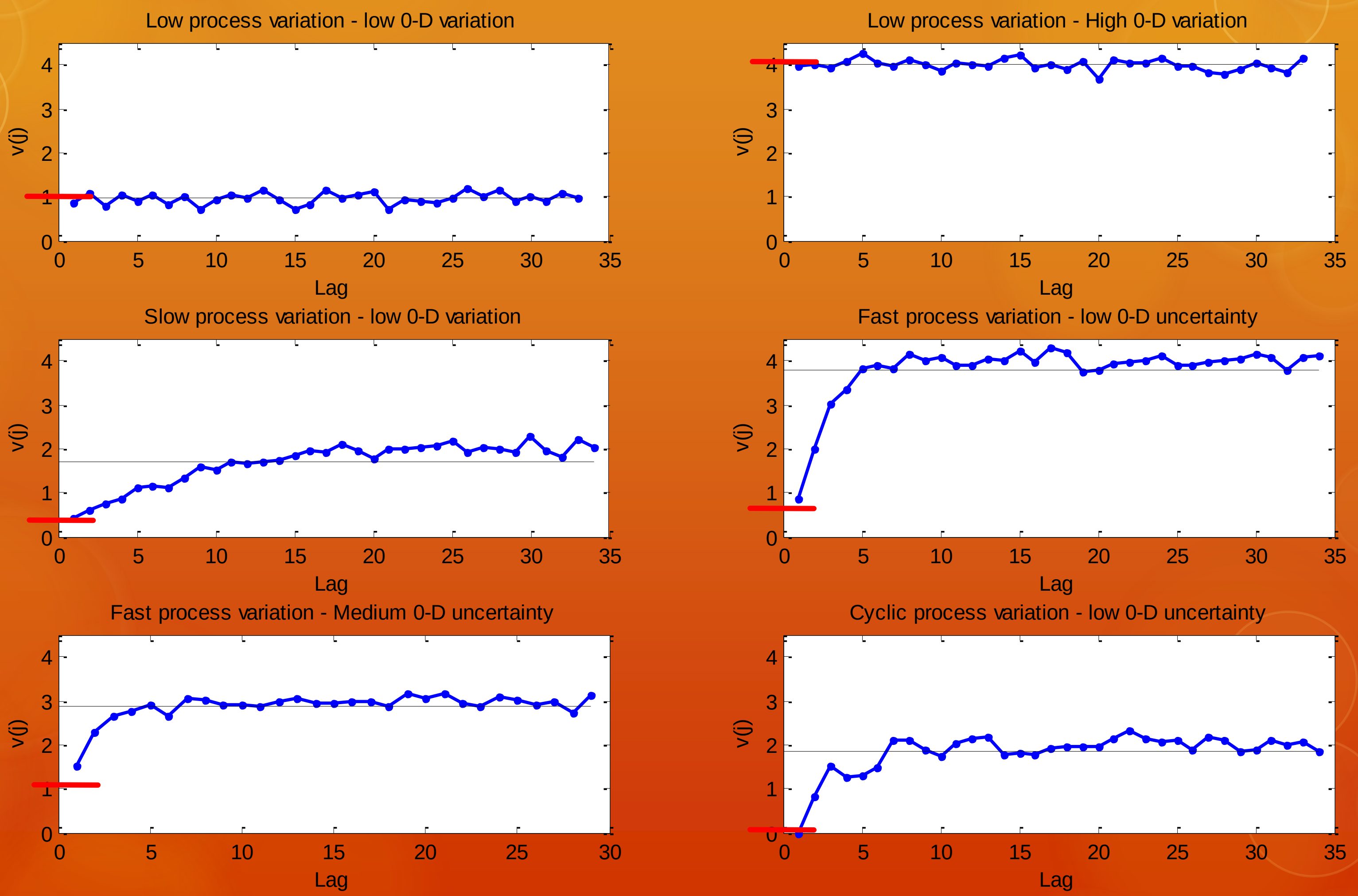
www.ds.dk

Instead of one universal threshold (which militates against all experience with heterogeneous materials - - Mandatory Public Disclosure of ”n.e./sill” [%] - -

Extracting TSE+TAE information from real time measurements through variographic analysis



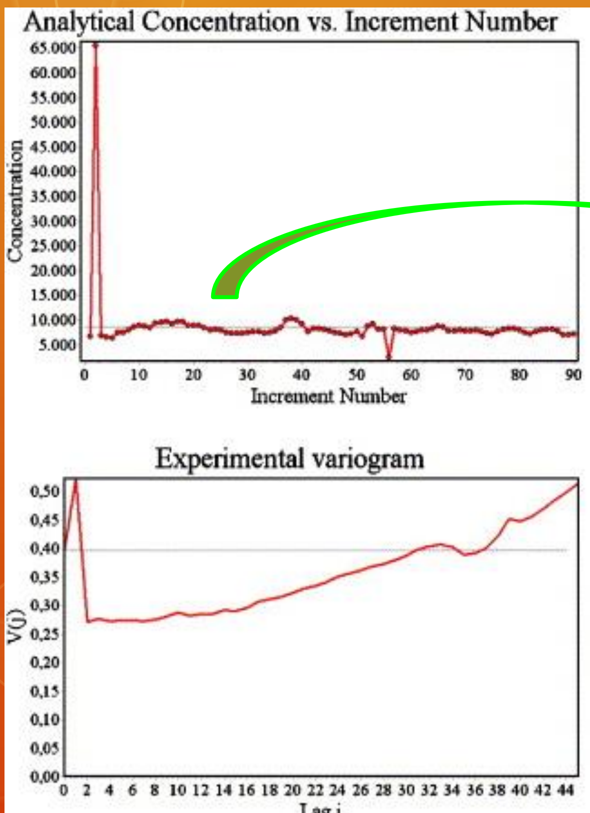
Variogram: a powerful corporate quality control tool

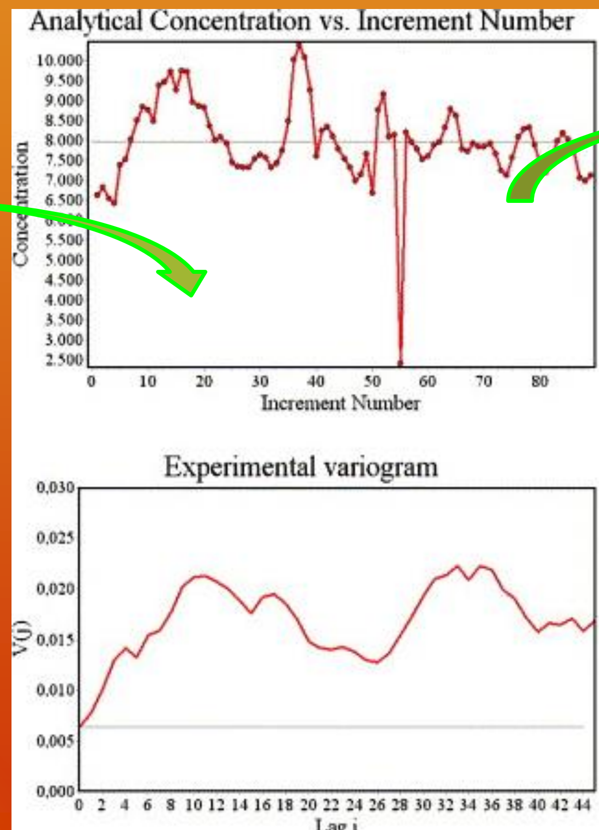


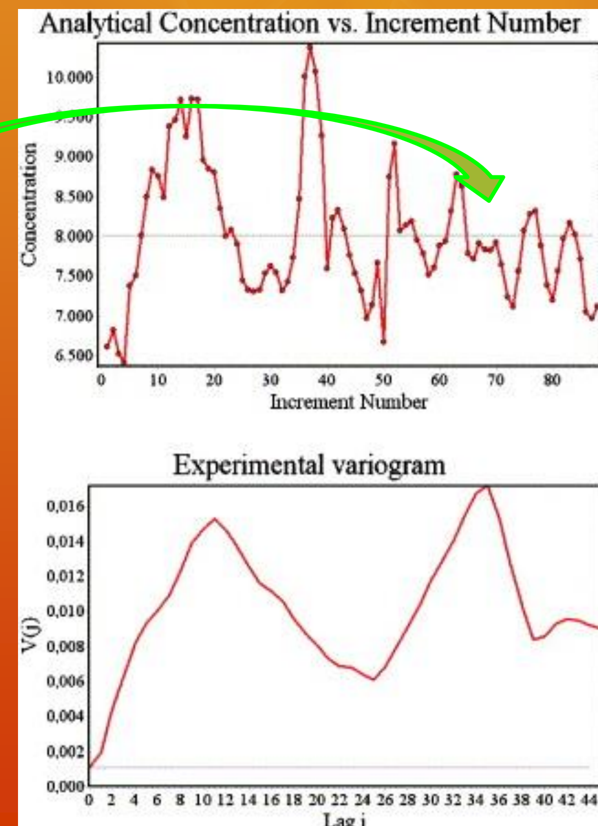
From raw data to variogram

Outliers significantly afect the variogram

ALL outliers should be removed - *sequentially*



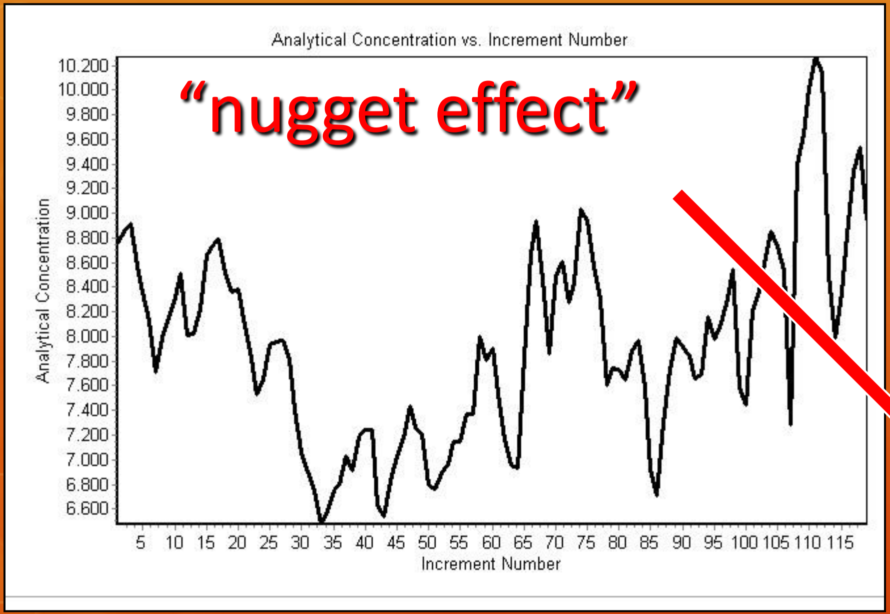




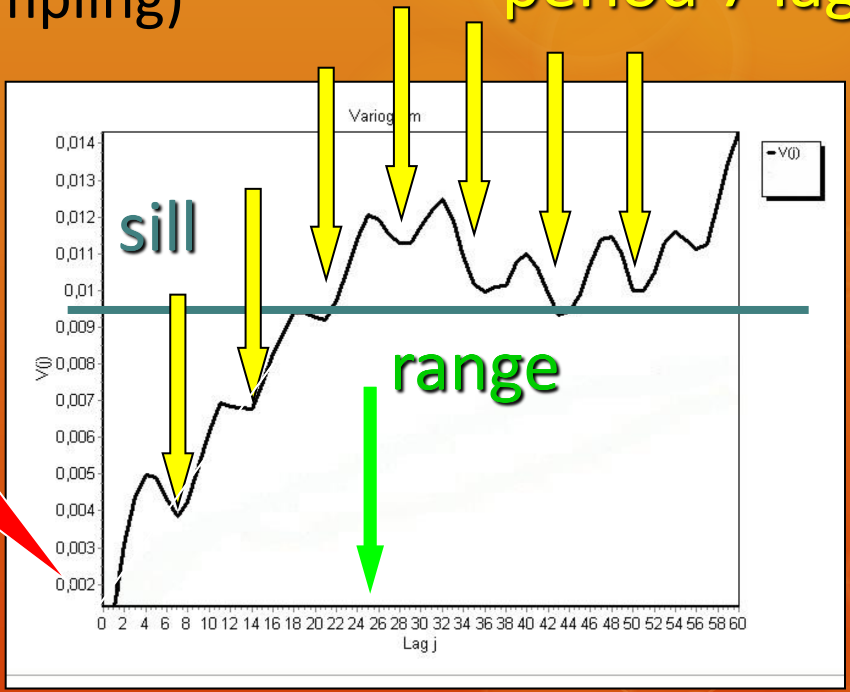
Process Sampling Variographics (1-D lot)

Ribe Biogas powerplant (daily sampling)

cycle with period 7 lags



Analytical grade (CH_4 yield m^3)

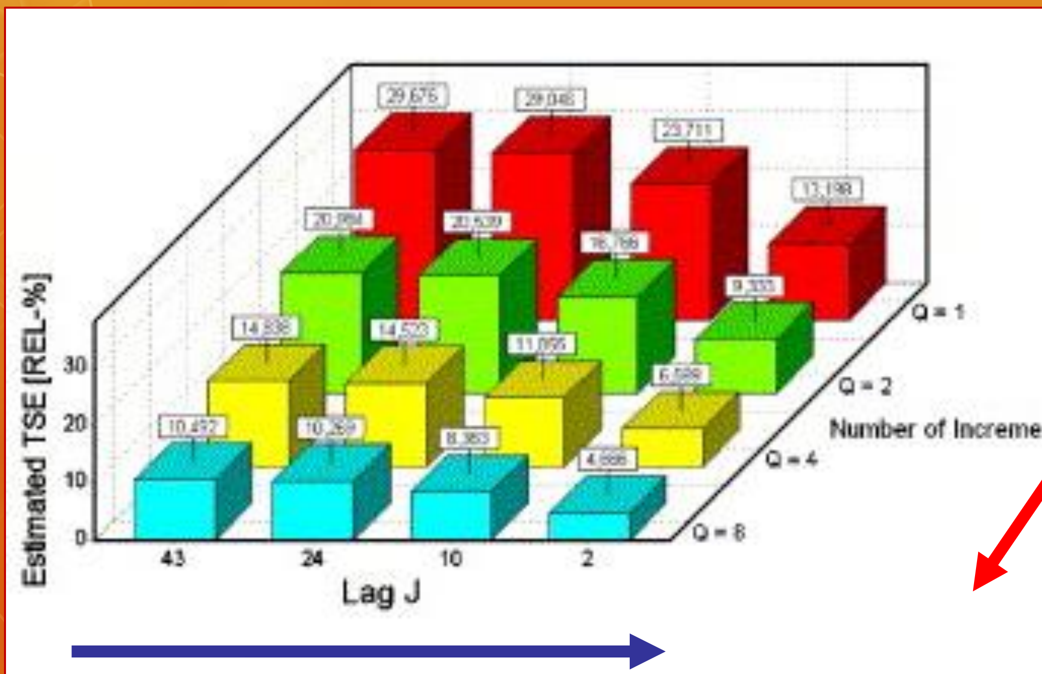


Variogram and characteristic features

Decreasing Total Sampling Errors (1-D lots)

Sampling error plot

Total Sampling Error - f(V(j), Q, j)



Q ↑
TSE error ↓

Lag ↓, sampling rate ↑
TSE ↓

Direction of steepest error descent ...
Conditioned on a preselected error level

Process sampling – applications

KeLDA (incl. intro to variographic 1-D analysis)

LKAB complete corporate variographic survey

Representative Sampling: Theory of Sampling (TOS)

TOS - Axiomatic exposé

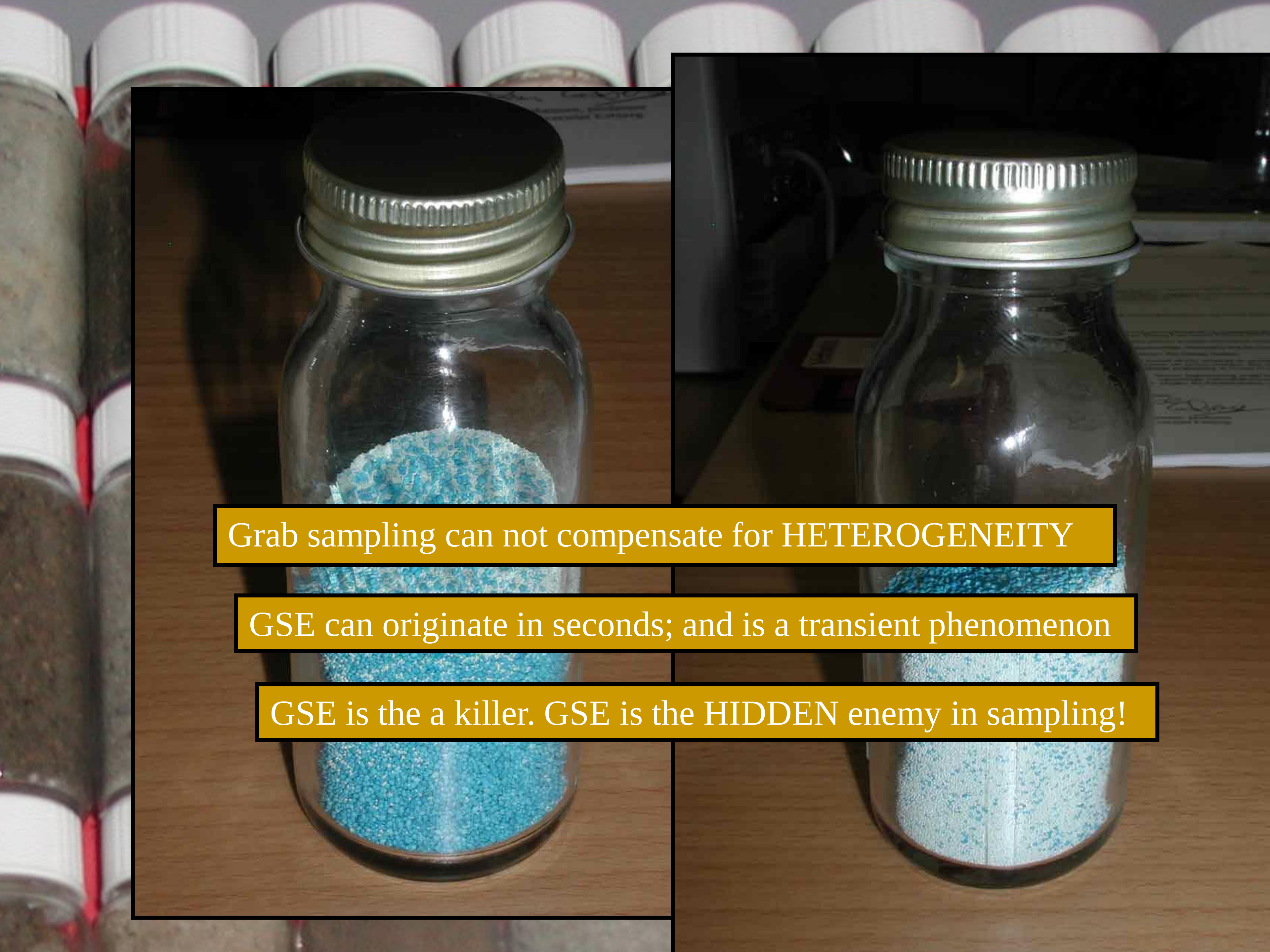
Governing principles (GP) – Sampling unit operations (SUO)

1. FSP: Fundamental Sampling Principle
2. SSI: Sampling Scale Invariance
3. PSC: Sampling Correctness (bias-free sampling)
4. PSS: Sampling Simplicity (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
7. SUO: Composite Sampling
8. SUO: Comminution
9. SUO: Mixing / Blending
10. SUO: Representative Mass Reduction (Sub-sampling)

The analytical laboratory

TOS in the laboratory – TOS in the laboratory


4405


Grab sampling can not compensate for HETEROGENEITY
GSE can originate in seconds; and is a transient phenomenon
GSE is the a killer. GSE is the HIDDEN enemy in sampling!

What you see – is <u>not</u> what you get ... ;-)

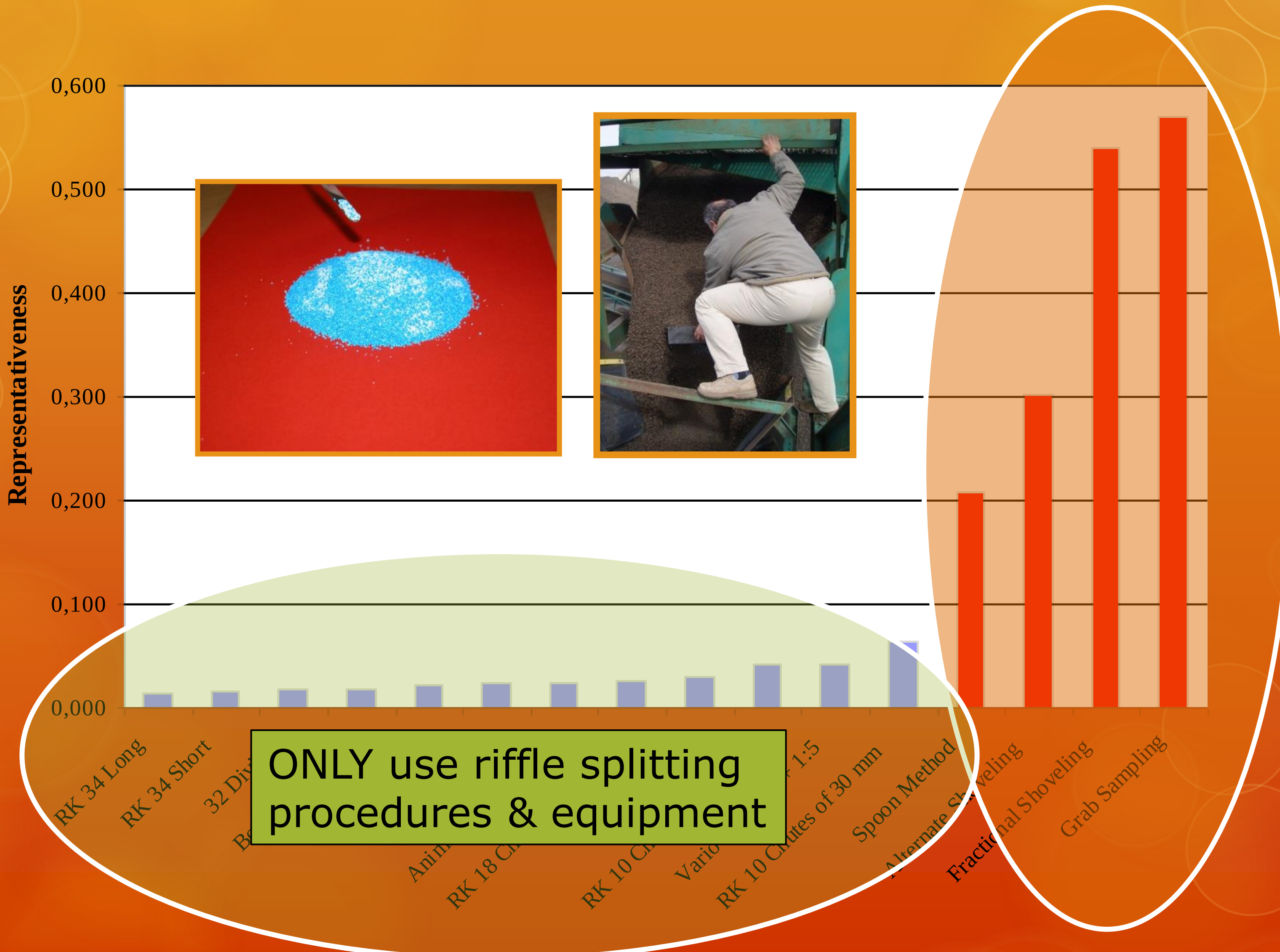
Some improvements are implemented easily

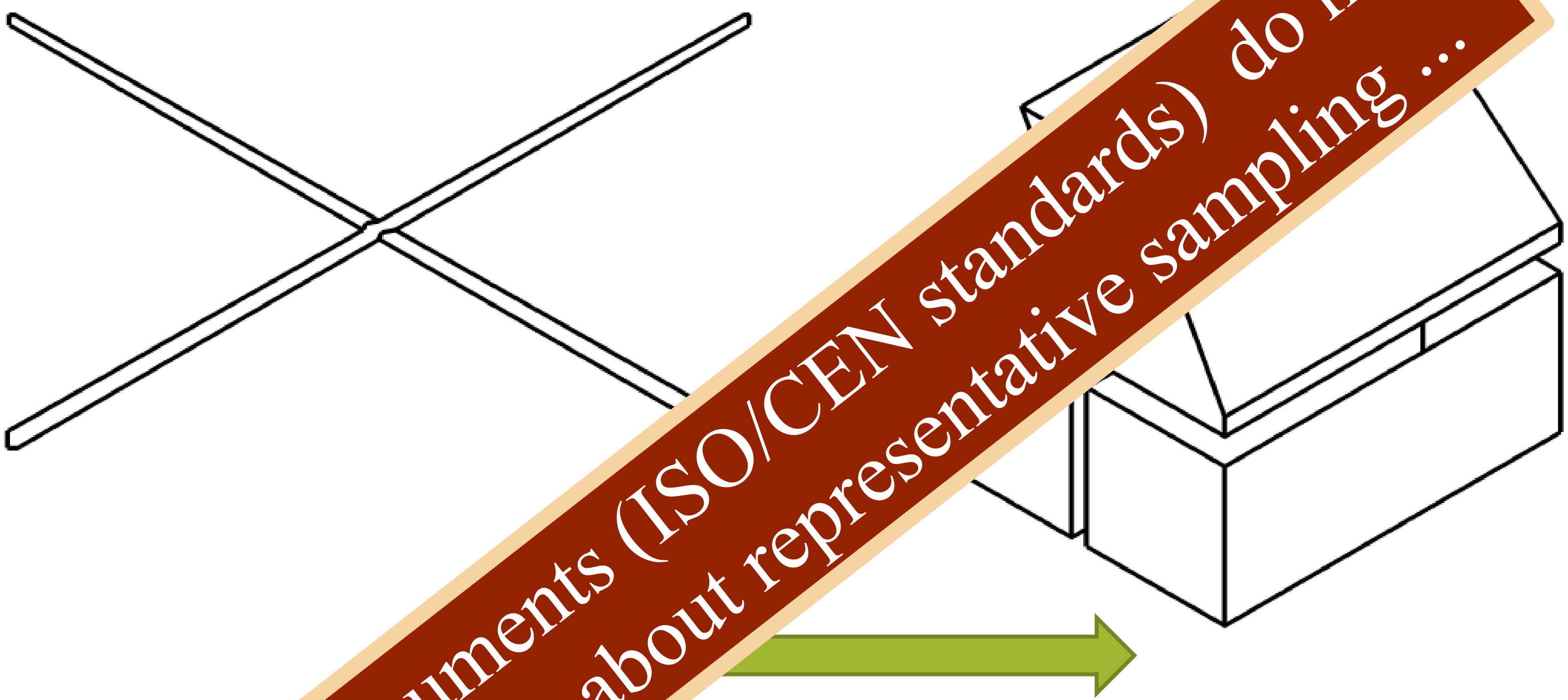
REPRESENTATIVE MASS REDUCTION IN SAMPLING

- a critical review of techniques and hardware

Lars Petersen, Casper K. Dahl & Kim H. Esbensen

Chemometrics and Intelligent Laboratory Systems, vol. 74 (2004) 95-114


0,600
0,500
0,400
0,300
0,200
0,100
0,000
Representativeness
RK 34 Long
RK 34 Short
RK 10 Chutes of 30 mm
Spoon Method
Fractional Shoveling
Grab Sampling
ONLY use riffle splitting procedures & equipment



Fig[…] […]on

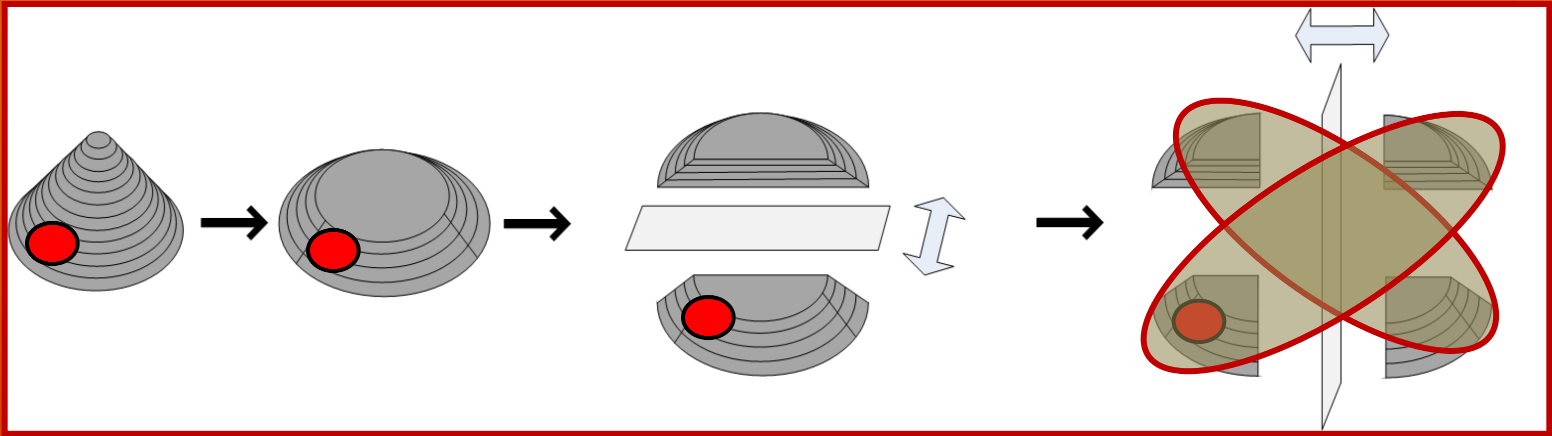
Figure B.14 – Riffle divider : multiple-slot divider (of the type with partitions and plates) with two collection boxes

Many documents (ISO/CEN standards) do not know enough about representative sampling ...

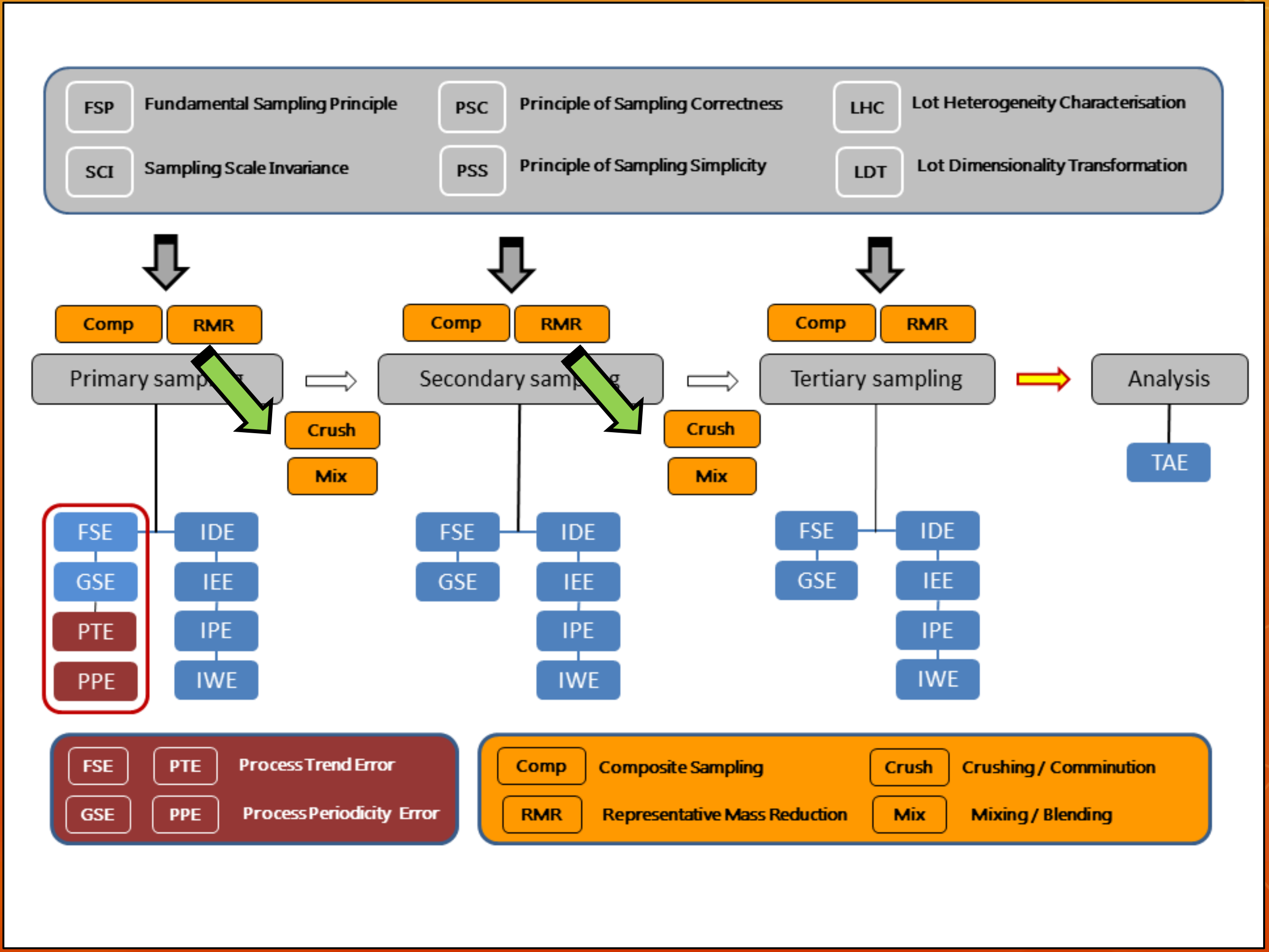

.. Just another "radial riffle splitter"

”Sampling Hall of Shame – BIG TIME
”Coning & Quartering”

An often overlooked factor: HIGHLY INSUFFICIENT lot pre-MIXING !!!

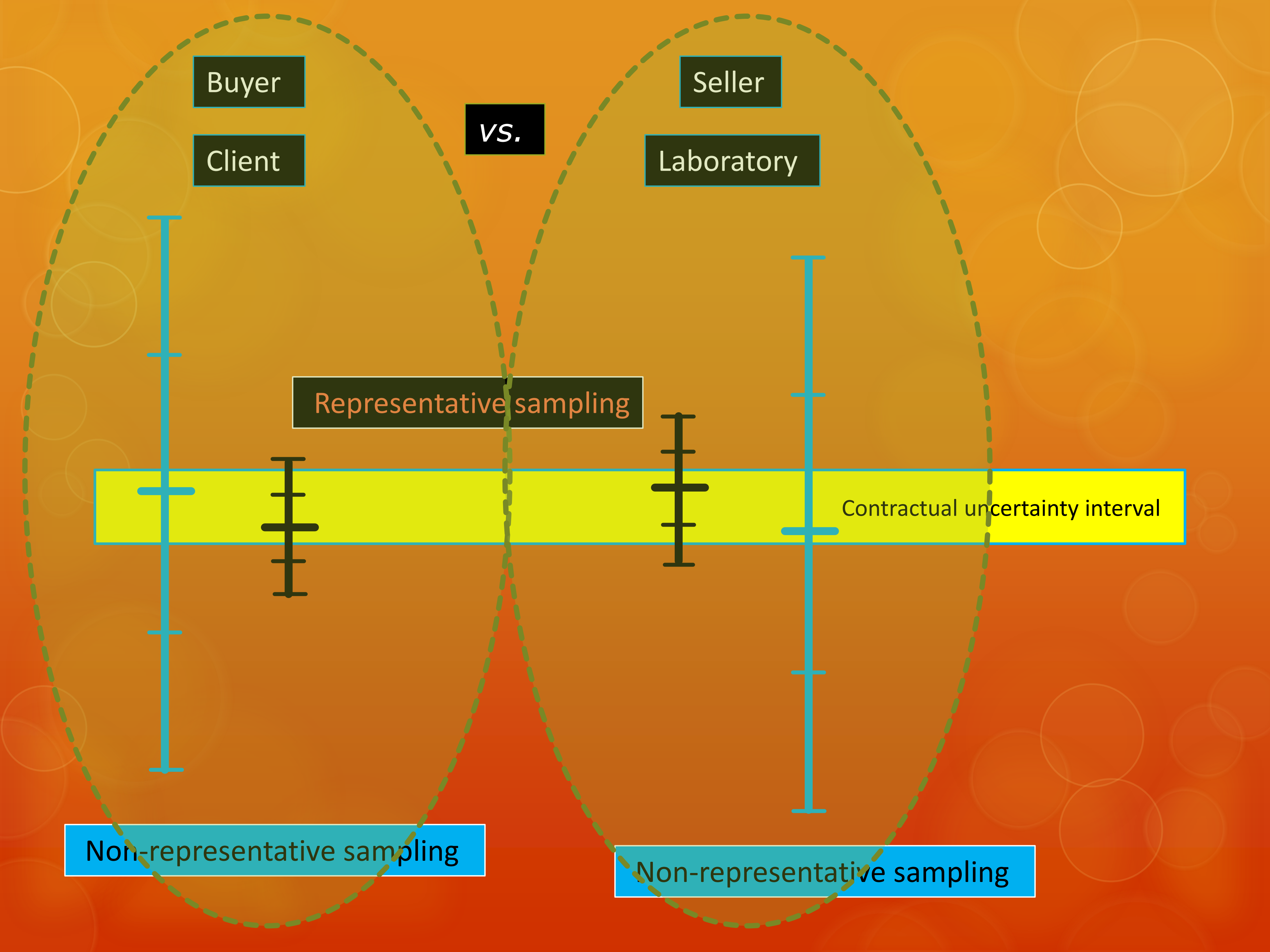


Theory of Sampling (TOS) – everything in a glance



Fundamental insights -

- ...a HUGE business opportunity ...


Buyer
Client
vs.
Seller
Laboratory
Representative sampling
Contractual uncertainty interval
Non-representative sampling
Non-representative sampling

The ultimate context & a big surprise

- Ethical and moral obligations <u>for</u> representative sampling

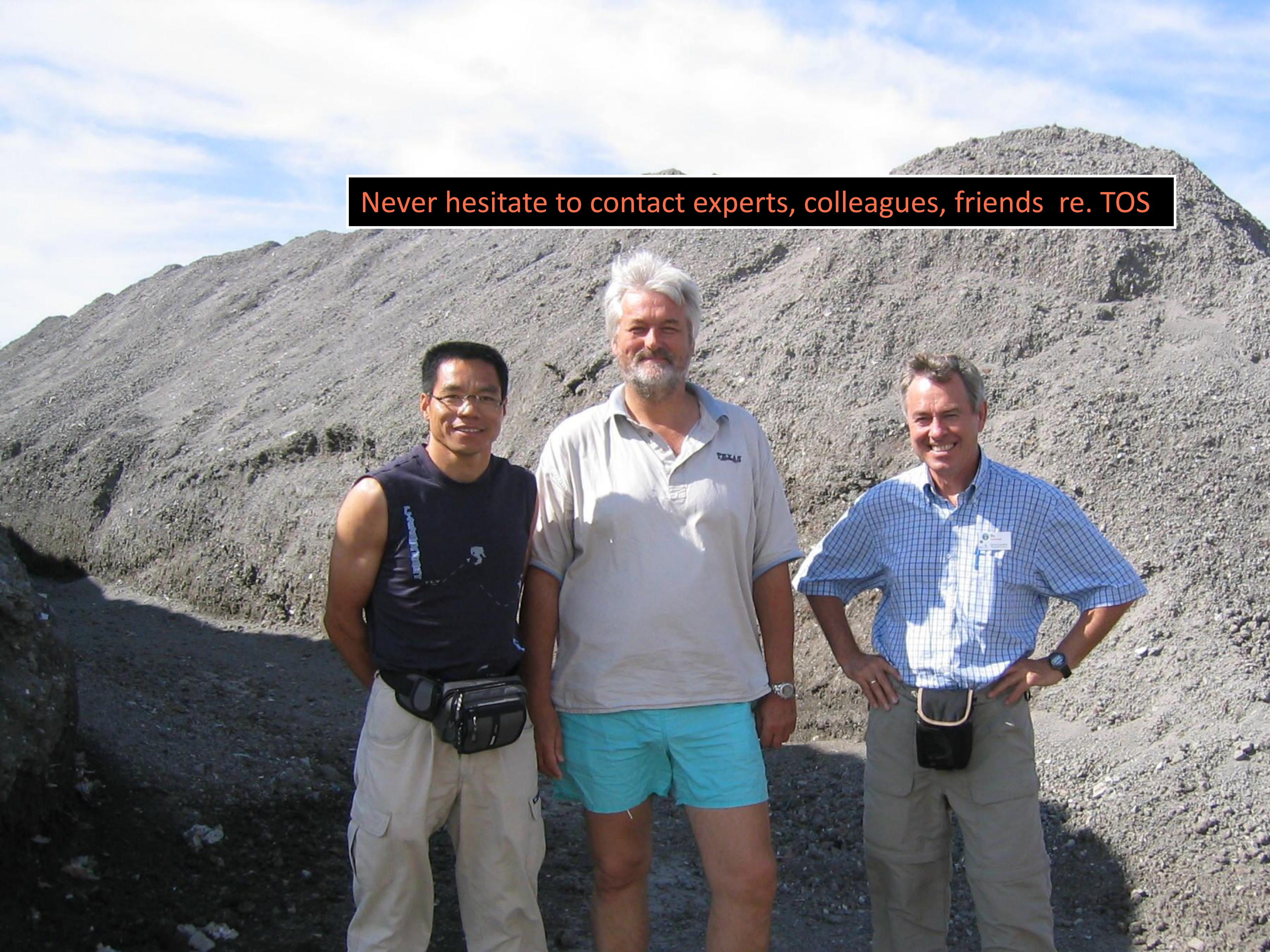
vs.

- ”Why should this company be the first / only company using more ressources and money than our competitors in order to reach optimal accuracy and precision? ? ? ?”

- ”A Tale of Two Laboratories I: The Challenge”
- ”A Tale of Two Laboratories I: The Resolution”
- ”Sampling committment – and what it takes”

- <u>This</u> is KHE Consulting’s business ethics!

Courtesy: KHE Consulting


Never hesitate to contact experts, colleagues, friends re. TOS


33

Thank you for your attention!

khe.consult@gmail.com

www.kheconsult.com

Workshop documentation and further background literature - a primer syllabus

1) **DS3077 (2013) Representative sampling – Horizontal Standard**

2) Esbensen, K.H, Wagner, C. (2014) **Why we need the Theory of Sampling**. *The Analytical Scientist*

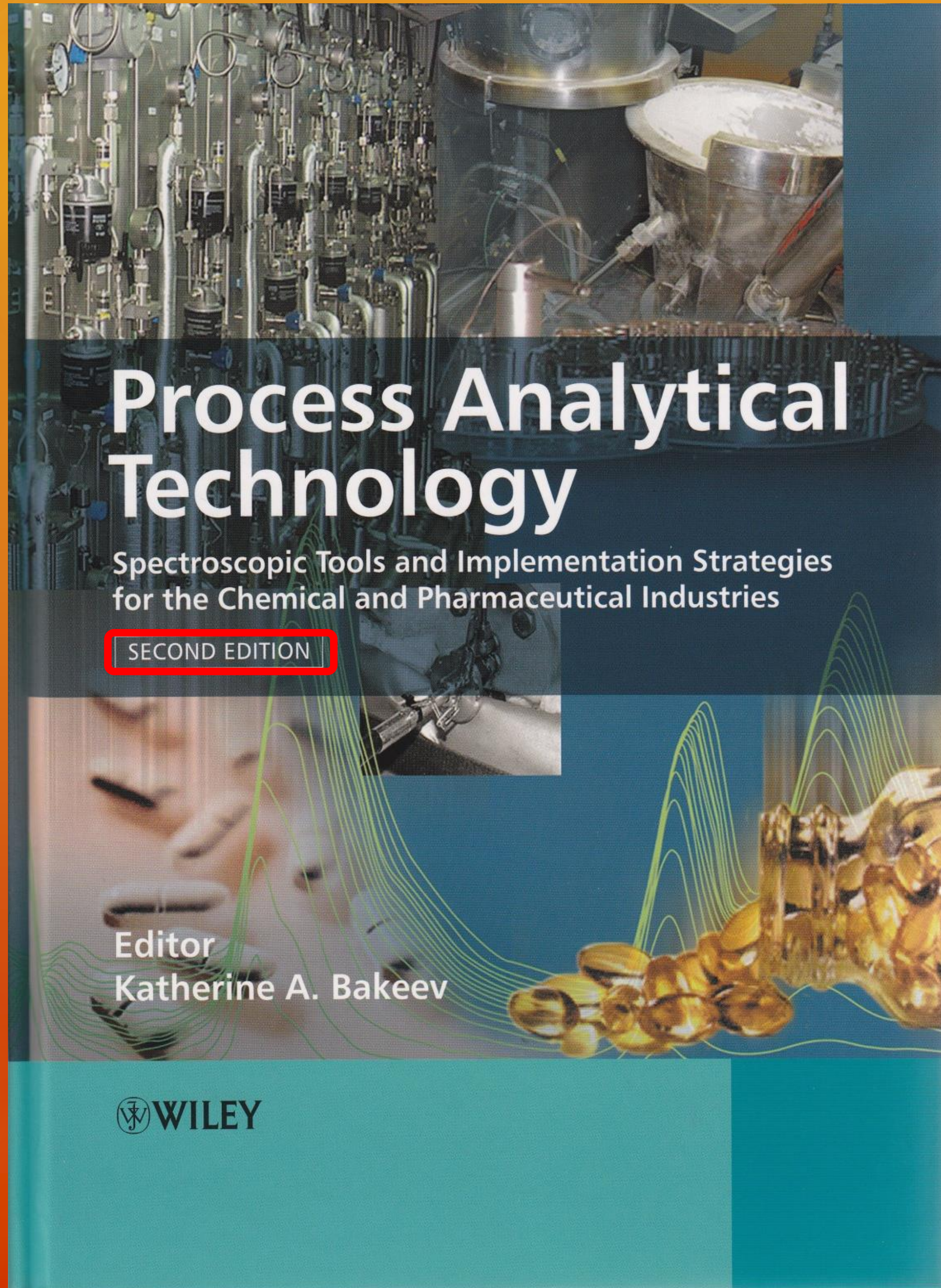
3) Esbensen, K.H, Wagner, C. (2014) **Theory of Sampling (TOS) versus Measurement Uncertainty (MU) – a call for integration**. *Trends in Analytical Chemistry (TrAC)*

4) Esbensen, K. H. Romañach, R. J. Román-Ospino, A. D.(2018) **Theory of Sampling (TOS): A Necessary and Sufficient Guarantee for Reliable Multivariate Data Analysis in Pharma ceutical Manufacturing** in *Multivariate Analysis in the Pharmaceutical Industry*, Ferreira, Menezes, Tobyn, M., (Eds.) pp 53-91. Academic Press ISBN 978-0-12-811065-2

5) Minnitt, R.C.A. & Esbensen, K.H. (2017) **Pierre Gy's development of the Theory of Sampling: a retrospective summary with a didactic tutorial on quantitative sampling of one-dimensional lots.** TOS Forum **7,** p. 7-19. doi: 10.1255/tosf.96

6) Esbensen, K.H, Román-Ospino, A,D, Sanchez, A, Romañach, R.J. (2016). **Adequacy and verifiability of pharmaceutical mixtures and dose units by variographic analysis – A call for a regulatory paradigm shift.** Intl. Jour. Pharmaceutics, vol. 499, p. 156-174.

7) Esbensen, K.H, Paoletti, C, Theix, N. (2015) (Eds) Journal AOAC International, Special Guest Editor Section (SGE): pp. 249-320 **Sampling for Food and Feed Materials (Open Access)**


Process Analytical Technology
Spectroscopic Tools and Implementation Strategies for the Chemical and Pharmaceutical Industries
SECOND EDITION
Editor
Katherine A. Bakeev
WILEY

“PROCESS SAMPLING (TOS) – the missing link in PAT”

Kim H. Esbensen & P. Paasch-Mortensen

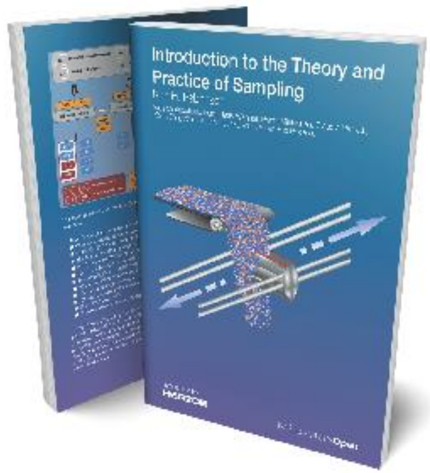
Bakeev, K. (Ed.)
PROCESS ANALYTICAL TECHNOLOGY, 2.nd Ed.(*2009*)
(chapter 3)

Introduction to the Theory and Practice of Sampling

NEW BOOK

Kim H. Esbensen

with contributions from Claas Wagner, Pentti Minkkinen, Claudia Paoletti, Karin Engström, Martin Lischka and Jørgen Riis Pedersen



This book presents the Theory of Sampling (TOS) for all readers and audiences starting from level zero. The TOS is presented in a novel didactic framework without excessive background mathematics and statistics that often scare newcomers away. The overall objective is to present a unifying conceptual framework within which all the TOS' principles, unit operations and sampling error management rules can be understood in the easiest manner possible. This book will make the reader able to start sampling in an effective manner right away, but is also intended to inspire to further skills building and self-study. It contains a wealth of key references.

Bibliographic detail
Publication: summer 2019
ISBN: 978-1-906715-29-8
Pages: approximately 280 pp.
Publisher: IM Publications Open

Workshop att.s - a signed copy ;-)

Find out more and pre-order now from

https://www.impopen.com/sampling

TOS literature portal (Open Access)

http://www.impublications.com/tos-forum

http://www.spectroscopyeurope.com/articles/sampling

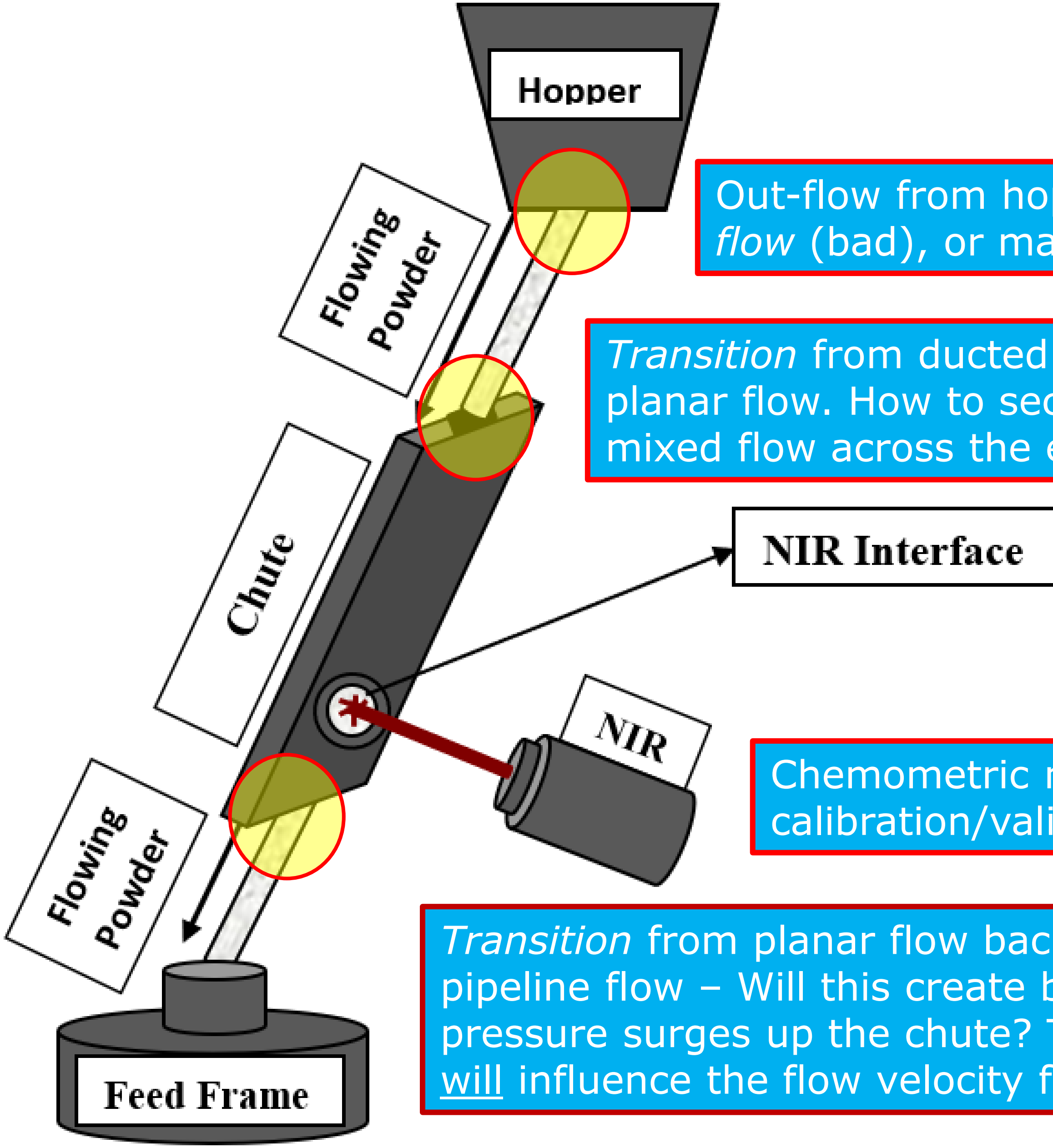
Process sampling – current issues …

The hidden elephant in the room

- - a fundamental <u>difference</u> of critical importance:
- a <u>sample cell</u> ... ... is containing the sample to do analysis


The hidden elephant in the room …

- - a fundamental <u>difference</u> of critical importance:
- a <u>sampling cell</u> … … is sampling <u>and</u> doing the analysis

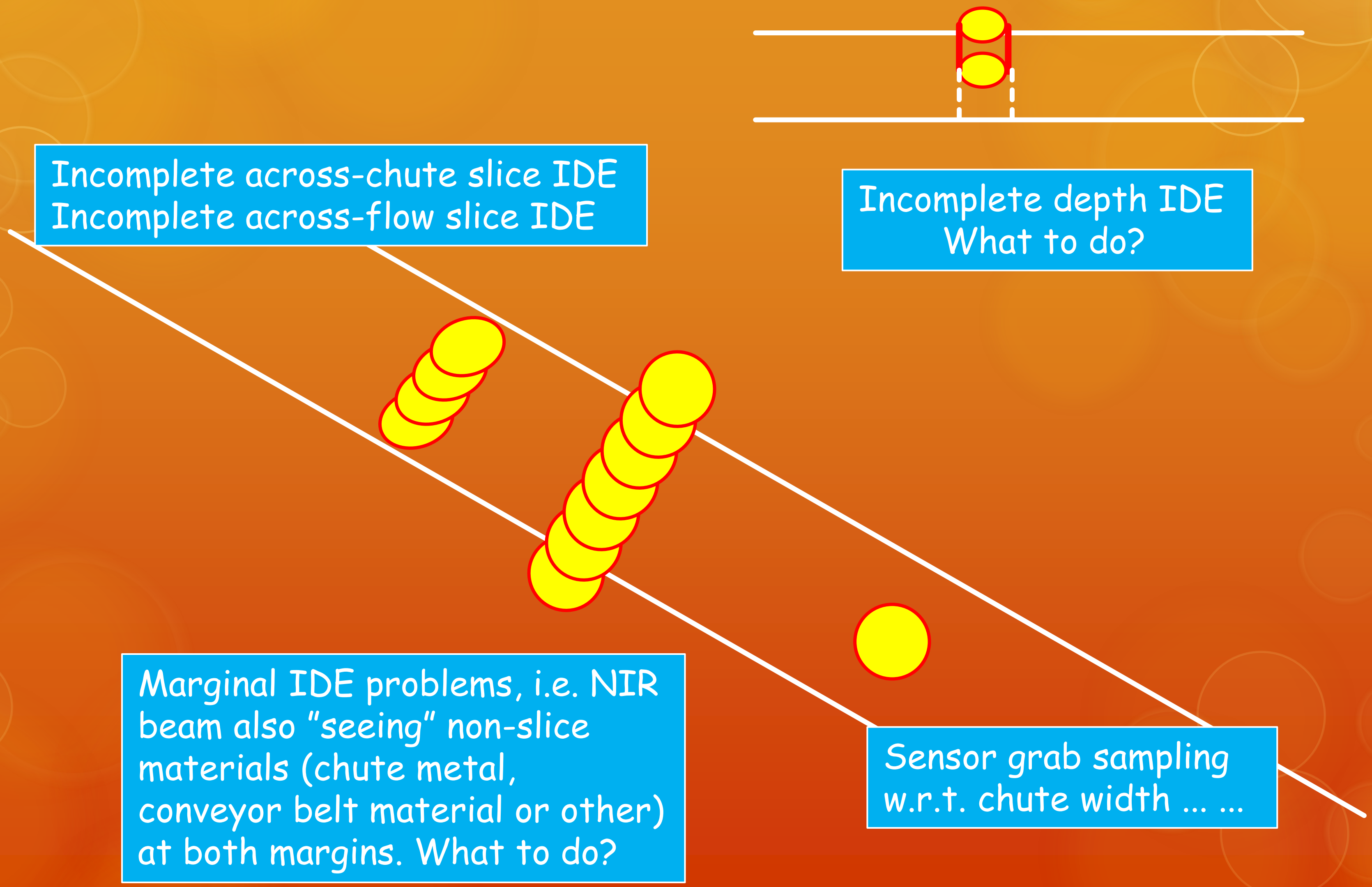


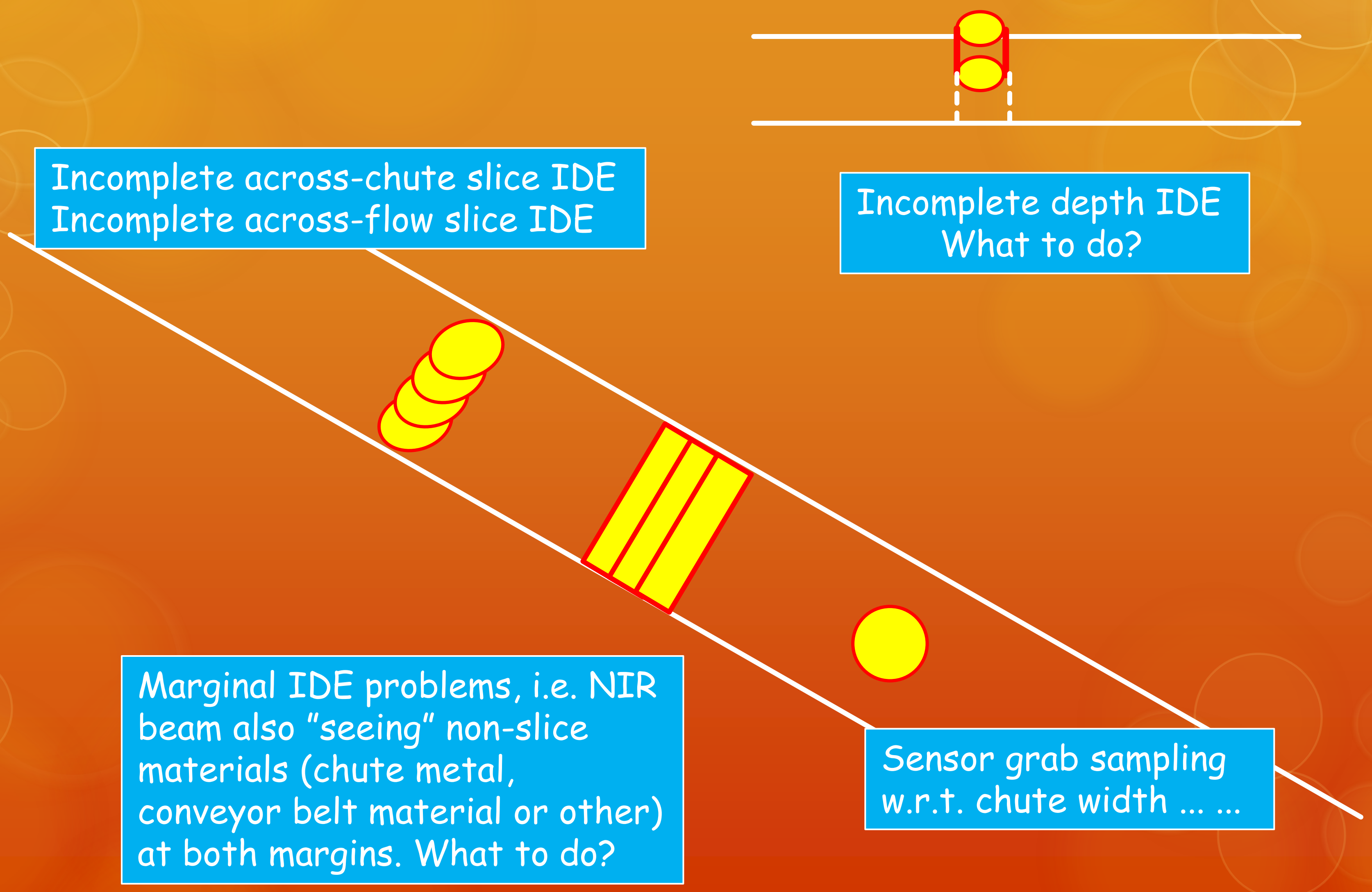
Out-flow from hopper, *funnel flow* (bad), or mass flow (good)

Transition from ducted pipeline flow to planar flow. How to secure a uniform, well-mixed flow across the entire chute width?

Chemometric multivariate calibration/validation issues

Transition from planar flow back to pipeline flow – Will this create back-pressure surges up the chute? This <u>will</u> influence the flow velocity field.


Incomplete across-chute slice IDE
Incomplete across-flow slice IDE
Incomplete depth IDE
What to do?
Marginal IDE problems, i.e. NIR beam also "seeing" non-slice materials (chute metal, conveyor belt material or other) at both margins. What to do?
Sensor grab sampling w.r.t. chute width ... ...


Incomplete across-chute slice IDE
Incomplete across-flow slice IDE
Incomplete depth IDE
What to do?
Marginal IDE problems, i.e. NIR beam also "seeing" non-slice materials (chute metal, conveyor belt material or other) at both margins. What to do?
Sensor grab sampling w.r.t. chute width ... ...