7th LBMA Assaying and Refining Conference

Keynote Speech:

Sampling: Theory and Practice

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The primary objective of the 2001 AMIRA P754 project, ‘Metal Accounting and Reconciliation’, was to improve the auditability and transparency of Metal Accounting from mine to product and thus to assist in good corporate governance.

Project areas had broad coverage from precious metals to commodities and from mine to product. One of the major deliverables was the development of a Code of Practice for Metal Accounting for the Mining and Metallurgical Industry.

The aim of the Code was to provide standard generic procedures and guidelines for obtaining credible figures of metal quantities processed and produced, and methods for obtaining a Metal Balance, and to be recognised and accepted as the Industry standard for best practice in this area.
A major point of the conclusions was:

Metal balancing and reconciliation techniques can be combined with the CI/CO approach, provided they are adapted to suit the special requirements of aligning commercial and technical estimation.

Simulation techniques are recommended for both metal balancing and reconciliation.

However …

*at least some knowledge of the errors associated with each measurement* (including sampling and assaying) *is essential.*
In this context, and with respect to subsequent implementation of results and recommendations, it was felt that the time had come to take stock over how efficient these objectives have been met ….

- and an invitation to the present lecturer resulted.

This keynote lecture deals *exclusively* with the *sampling* issues involved in this endeavor.
It is generally *assumed* that the melt is well mixed due to stirring caused by the electromagnetic fields in induction furnaces ... 

This is a crucial assumption

How well is this verified?
A quotation (from earlier LBMA conf.)

"... avoid the uncertainty related to systematic errors by proper process concept and by appropriate sampling; when inhomogeneity of the sampled material can be presumed, sample the material where its fineness can be expected to be lower" ...

1. So heterogeneity does occur ... ...
2. All the world’s precious metals do not crop out of the ground as material ‘ready-for-the-crucible’ ... ;-) 
3. Where is the authoritative manual/standard/GLP?
Manual sampling - by “professionals” …

A grab-sample, representative of 54 ton material?
Sampling is not so much material (lot) dependent --- sampling is much more up against lot *heterogeneity*
DS 3077 (2013). A minimum sampling competence encompasses FSP, TOS’ paradigm of sampling correctness, five sampling errors (CSE/ISE) and four Sampling Unit Operations (SUO)
The keynote invitation turns out to be timely - since all stakeholders, scientific and regulating agencies and authorities today actually have access precisely to the desired *standardized* procedures for sampling – but how well is this known?

2013 saw the publication of the world’s first universal standard for representative sampling, DS 3077 (2013), called a “horizontal standard” since it describes all generic principles and procedures with which to be able to guarantee representative sampling at all stages, and indeed at all scales from “mine to product” (“from lot to analysis” in the standard’s parlance). This is good stuff!
The horizontal nature of this standard also means it is designed to be *matrix-independent*, i.e. the principles can be applied to all types of commodities, materials and process irrespective of composition.

It turns out that it is highly advantageous to focus on the heterogeneity (only), which brings about a dramatic reduction of the complexities that is normally envisaged when addressing sampling. It is no longer necessary to ask: representative sampling? Well how in the view of so many different materials … … *(this must be complex!)*

The Theory of Sampling (TOS) to the fore …
Sneak preview: Theory of Sampling (TOS)

Rules for representative sampling in practise

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 fundamental insight … where all sampling starts

1. Sampling is practically never a one-shot operation

2. Sampling is always a multi-stage process:
   i) Primary sampling +
   ii) Representative Mass-reduction

Principle of Sampling Simplicity (PSI)
The analytical result – is but an *estimate* of $a_L$

**Who’s responsible …?**

Sampling errors at all stages

Primary reject

Tertiary reject

Final reject
Primary sampling representativity: - a key issue in all sampling situations

Which is always followed by: secondary sampling / mass-reduction/ handling & sample preparation(s) … Cannot be neglected either

Propagation of errors:

\[ s_x = \sqrt{\sum s_i^2} \]

Example:

\[ s_x = (55\%)^2 + (35\%)^2 + (1.5\%)^2 = (65\%)^2 \]

GOAL: \( x = m \)

“Analytical process” always contains several sampling & preparation steps – usually primary sampling dominates!
The arch-enemy: HETEROGENEITY!

Identical issue – at all scales !!!
The arch-enemy: HETEROGENEITY!

Identical issue – at all scales !!!
Analyte concentrations: 25% .... 1% .... 100 ppm

- 25%
- 10%
- 1%
- 1000 ppm
- 500 ppm
- 100 ppm
\( \text{CH}_L \) and \( \text{DH}_L \) constitutes the operative handles on heterogeneity – allowing to treat all types of lots (materials/forms/compositions in a complete unified manner. The general rules are codified in TOS.
Fundamental Sampling Principle (FSP):

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

Spear sampler core
Heterogeneity (hidden)
Sampling in the laboratory: What’s the difference w.r.t. the field/plant etc?

..... ONLY the SCALE ...... !!!

Sampling at all scales - N.B. Identical problems N.B.
Representative Sampling: Theory of Sampling (TOS)

**Governing Principles** (sampling in practise)

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)
"Correct" sampling errors

"Incorrect" sampling errors

- three sources of errors

Pierre Gy
SAMPLING FOR ANALYTICAL PURPOSES

Pierre Gy
Repræsentativ prøvetagning – Horizontal standard
Representative sampling – Horizontal standard
Representative Sampling: Theory of Sampling (TOS)

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/splitting)
Four practical Sampling Unit Operations (SUO)

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

Theory & Practise of Sampling (TOS):
- Practical procedures … …
- 4 Sampling Unit Operations (SUO):

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

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.

1. $\nabla \cdot \mathbf{D} = \rho_v$
2. $\nabla \cdot \mathbf{B} = 0$
3. $\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$
4. $\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J}$
Governing principles (GP) & Sampling Unit Operations (SUO)

1. FSP: Fundamental Se Invariance
2. PSC: Sampling Correctness (bias-free sampling)
3. PSS: Sampling Simplicity (sampling principle)
4. SSI: Sampling Scal (primary sampling + mass-reduction)
5. LDT: Lot Dimensionality Transformation
6. LHC: Lot Heterogeneity Characterization (0-D, 1-D)
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8. SUO: Comminution
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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 horizontal standard (2013).
More to the Principle of Simplicity

1. Sampling is **never** a one-shot operation

2. Sampling is **always** a multi-stage process:
   
   i)  Primary sampling  +  
   
   ii) Representative Mass-reduction

Focus on representative mass-reduction ...
Representative Mass Reduction

Representative mass reduction
Device and method examples:

- Fractional shoveling
- Grab Sampling
- Rotational dividers
- Spoon method
- Boerner divider
- Riffle splitters
REPRESENTATIVE MASS REDUCTION IN SAMPLING
- a critical review of techniques and hardware

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

Chemometrics & Intelligent Laboratory Systems, 74 (2004) 95-114
Representative Sampling: Theory of Sampling (TOS)

**Governning Principles (sampling in practise)**

1. FSP: Fundamental Sampling Principle
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Incorrect Sampling Errors (ICS)

IDE
IEE
IPE
IWE
FSE
GSE

Correct Sampling Errors (CSE)

Process Sampling Errors (PSE)

Theory of Sampling (TOS)

Measurement Uncertainty (MU)

Total Analytical Error (TAE)

Total Sampling Error (TSE)
Theory of Sampling (TOS)

Incorrect sampling errors (ICS)

Correct sampling errors (CSE)

Process sampling errors (PSE)

Measurement Uncertainty (MU)
Important terminology and understanding for analysis
- and for sampling_plus_analysis

Sampling process: BIAS + imprecision (TOS: a varying, an inconstant BIAS)!

Analytical process: BIAS + imprecision (statistical concept: a constant BIAS)
The Practical Summary:

A set of only $6 + 4$ unit operations can be used to handle \textit{(almost)} all sampling problems, always respecting TOS
Usually only a sub-set of the 10 SUO’s is necessary

It is strongly recommended to become “TOS-literate” …

\begin{itemize}
\item 10 SUO’s can be implemented for all 3-dim & 1-dim sampling – \underline{always} …
\item 10 SUO’s can \underline{usually} be implemented for 2-dim sampling (\textit{creative experience})
\item 10 SUO’s can only be implemented for 3-dim sampling \underline{with great difficulty} …
\end{itemize}
Repræsentativ prøvetagning – Horisontal standard

Representative sampling – Horizontal standard
Low priority problems

Top priority problems

Problems to be solved after performing a feasibility study

Problems that are not worth too much attention

Effect of problem

Cost of fixing problem

Courtesy: Francis Pitard Sampling Consultants
Note:
Elimination of (all) Incorrect Sampling Errors (ISE)

TOS’ Preventive Paradigm (TPP)

Principle of Sampling Correctness (PSC)

Causes: sampling variation
- FSE
- GSE
- IME
- IPE
- IWE
- TAE

IDE (cyclicity)

Bias Test(s)
- Round Robin test(s)
- “Correction factors”
- “Effects estimation”

Effect of problem

Cost of fixing problem

(trends)
References


DS 3077 (9 page free preview)*
http://webshop.ds.dk/product/M278012/standard.aspx

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

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

*) Attachments to conference handouts
Never hesitate to contact experts, colleagues, friends re. TOS
..... and here is your best friend, colleague and expert:

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TOS – the critical success factor ...

- Automatic sampling
- Sample transport to the laboratory
- Sample handling
- Laboratory control system
- Sample preparation
- Automation of analysis
Figure 2 Typical sample shapes used for metal analysis in the iron and steel industry. (Reproduced by permission of Herzog Maschinenfabrik GmbH.)
Fig. 4-21 Contours of solidified steel fraction during sampling (1: liquid 0: Solid)
Representative Sampling: Theory of Sampling (TOS)

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GP no 6: Heterogeneity characterisation

Objective: “Cover” the largest heterogeneity gradient

!! Heterogeneity characterisation essential !!
Lesson learned: There is no such thing as one approach that "fits-all-sizes" (i.e. covers all types of heterogeneity). !! Heterogeneity characterisation essential !!