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The use of Collaborative Trial in Sampling for the Validation of Measurement Procedures

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AMC The Analytical Methods Committee

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Presentation Overview

- Overview of the VaMPIS approach
- Setting a Target Uncertainty (TU or FFP-MU) for VaMPIS (OU approach)
- Using a Collaborative Trial in Sampling (CTS) to estimate Measurement Uncertainty (MU)
- Practical example based on existing data
- Conclusions

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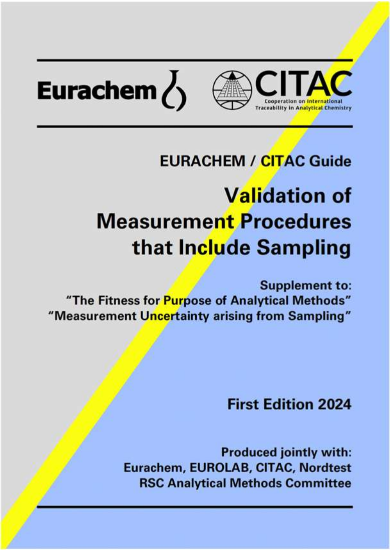
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EURACHEM / CITAC Guide

Validation of Measurement Procedures that Include Sampling

Supplement to:
"The Fitness for Purpose of Analytical Methods"
"Measurement Uncertainty arising from Sampling"

First Edition 2024

Produced jointly with:
Eurachem, EUROLAB, CITAC, Nordtest
RSC Analytical Methods Committee

Validation of Measurement Procedures that Include Sampling (VaMPIS)

Eurachem supplementary guidance to "The Fitness for Purpose of Analytical Methods" and "Measurement Uncertainty arising from Sampling– Dec 2024

"...aims to explain how to validate an overall measurement procedure from the moment that a primary sample is selected (and usually extracted) from a particular sampling target, until the reporting of a measurement result."

Rationale:
Sampling is part of the measurement process
- Includes sample storage, preparation, processing

Often an important component of Measurement Uncertainty (MU)

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The VaMPIS approach

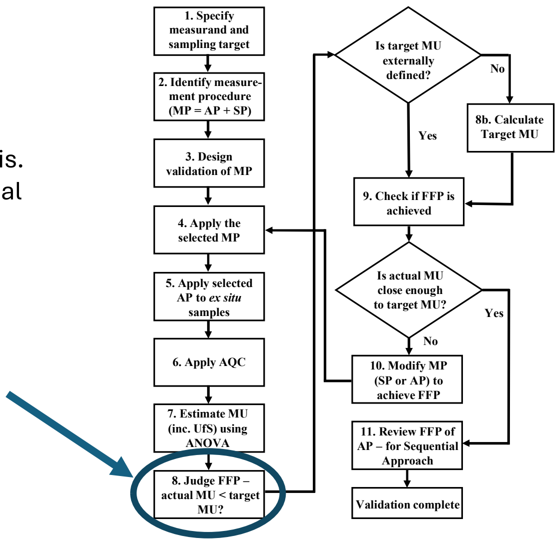
MU is considered the key metric to demonstrate
***** Fitness for Purpose (FFP) *****

MU combines uncertainty from sampling ***and*** analysis.
- Potential improvement on validation of analytical method in isolation

VaMPIS Requires a **target MU** (**TU**, or FFP-MU)
- to compare with the measured MU

TU May be set by an official body such as an industry regulator

OR – Can be set using **Optimised Uncertainty** (OU) approach



VaMPIS flowchart

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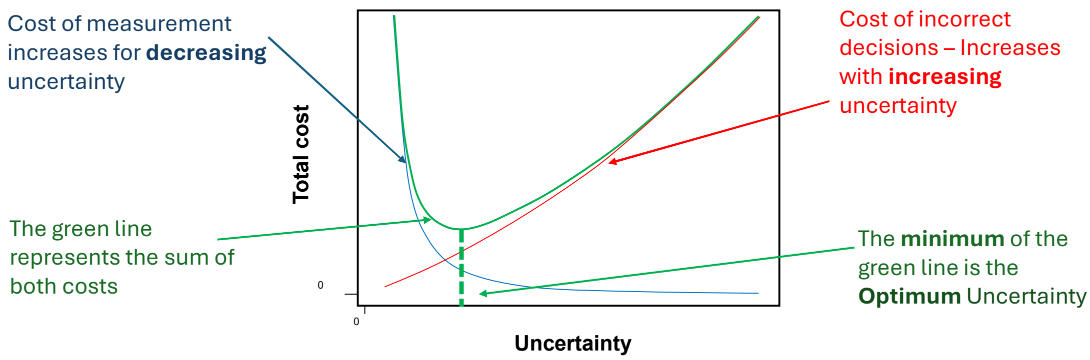
Optimised Uncertainty (OU) approach to setting TU



The OU approach calculates a TU that minimises the overall cost
- including the potential consequences of incorrect decisions

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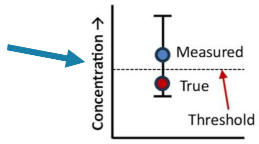
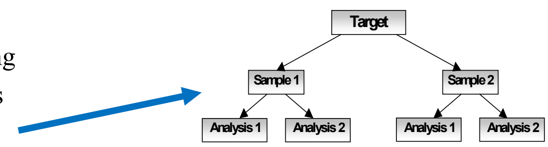
Optimised Uncertainty (OU) approach - Inputs

- A threshold value, below (or above) which a measurement value (and hence sampling target) is deemed compliant (e.g. by Regulator)



- Cost of acquiring each sample (whether primary or duplicate)
- Cost of analysing each sample (whether in lab or field)

- Component of uncertainty arising from sampling
- Component of uncertainty arising from analysis
  - e.g. using Duplicate Method / ANOVA



- Consequence cost of making an incorrect decision
- A concentration value at which to optimise (c_m)

- These two parameters will be specific to **false positive** or **false negative** scenarios

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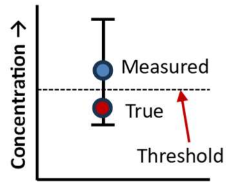
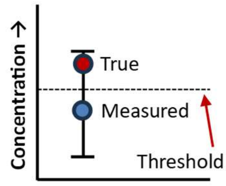
Optimised Uncertainty (OU) approach – Consequence costs

Losses that arise from rejecting a batch of material that is in fact compliant (e.g. disposal, re-assignment, remediation): **False Positive** scenario



Losses due to accepting a batch of material that is in fact non-compliant (e.g. legal costs, litigation, loss of reputation): **False Negative** scenario



Consequence costs need only to be broad estimates!

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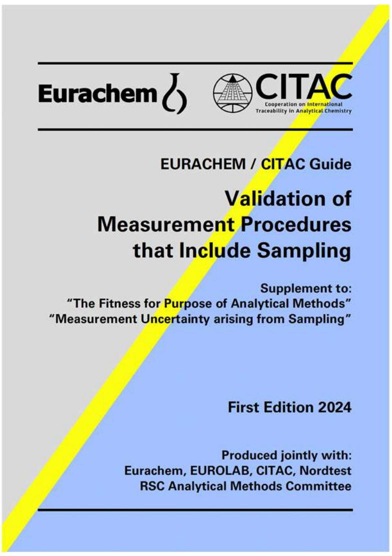

VaMPIS Guide provides two examples where MU has been estimated using the Duplicate Method

'Sequential' approach (where analytical method is already validated) on *ex situ* analysis (i.e. in-lab), and an **'integrated'** approach (where analytical method has NOT been previously validated), in this case measurements made *in situ*

An alternative approach to MU estimation is also suggested:
Using a Collaborative Trial In Sampling (CTS)
- A more realistic estimate of MU in practice?

Collaborative trial in sampling

Multiple samplers independently sample the same sampling target

This enables the inclusion of some **systematic effects** in the overall estimate of MU
- e.g. Between-Sampler Bias

So a CTS gives a more realistic estimate of MU than the duplicate method (single sampler) because it includes the effect of using **different samplers**
It could also potentially increase the scope of a validation exercise by being applied at **different sampling targets** of the same type

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CTS example – Moisture in butter

Data drawn from a Sampling Proficiency Test (SPT)
9 participants/samplers
Independent interpretation of one sampling protocol (=CTS)

In brief
Sampling target: 20 t of fresh butter – 804 blocks, 25 kg each
6 blocks selected at random
Increments (~100 g) taken using a half-round metal tube 2 cm diameter

Each 100 g increment was measured separately for this SPT
- Gravimetric determination of moisture content
- Analysed in duplicate (**analytical duplicates**)

The arithmetic mean was then calculated to estimate the result that would be obtained from a single composite measurement

Entire process was repeated with a different set of 6 blocks - **sample duplicates**

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Implementing the OU approach

MU estimated using Duplicate Method (RANOVA*), to provide input to OU software (OptiMU)*

MU estimated for:

- 6-fold measurement of each increment in composite, including between-sampler bias
- Single analysis of composite sample (by calculation of average values), including between-sampler bias
- Equivalent values for Duplicate Method with single sampler, i.e. not including between sampler effects

*AMC Software – Google Search RSC AMC SOFTWARE

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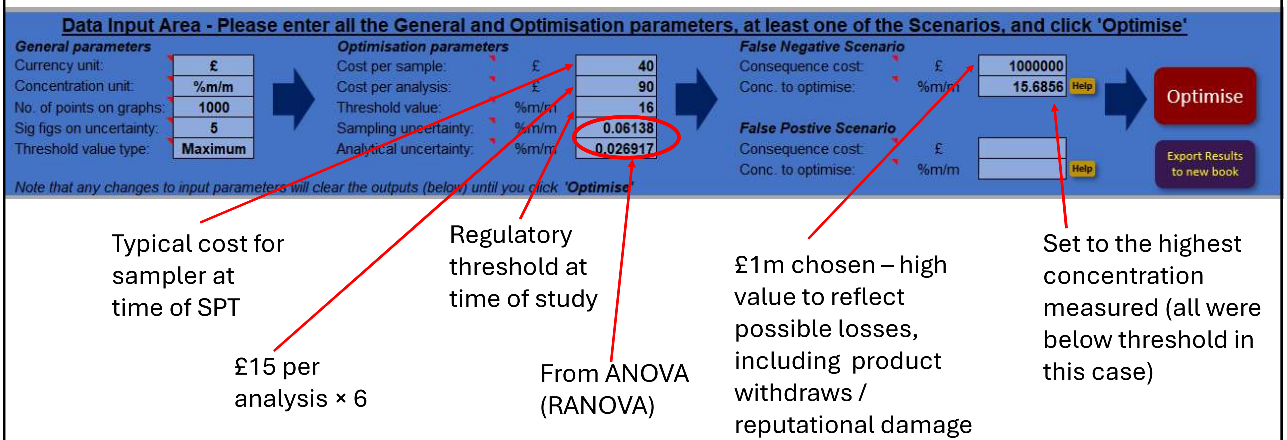
Example inputs to OU software (OptiMU)

6-fold analysis (each increment in composite sample)



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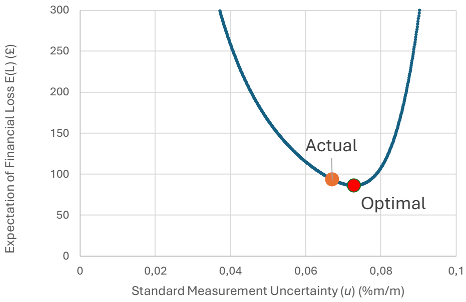
Results of applying OU approach: 6-fold

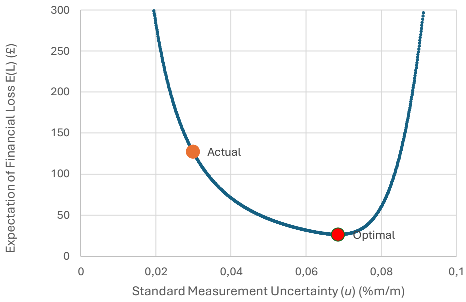
CTS – Including sampler Bias



Actual MU: 0.067 % m/m
Optimal MU: 0.073 % m/m

Close enough – consider FFP

DM – Not including between sampler



Actual MU: 0.030 % m/m
Optimal MU: 0.068 % m/m

Suggests less money could be spent on measurements to achieve FFP

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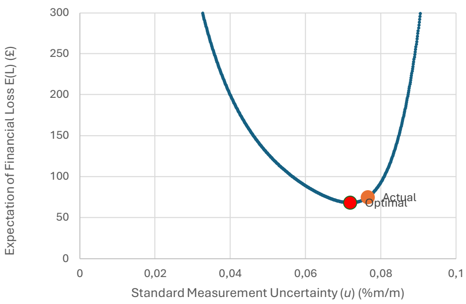
Results of applying OU approach: single fold

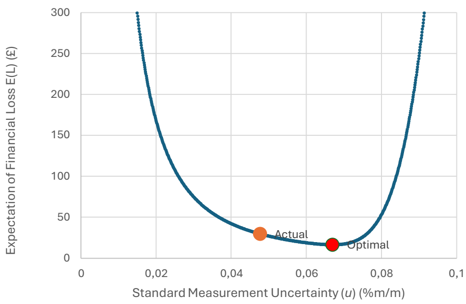
CTS – Including sampler Bias



Actual MU: 0.077 % m/m
Optimal MU: 0.072 % m/m

Again, can consider FFP

DM – Not including between sampler



Actual MU: 0.048 % m/m
Optimal MU: 0.067 % m/m

Also suggests money could be saved on measurement procedure

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Conclusions

- Applying the Optimised Uncertainty (OU approach) suggested in the VaMPIS Guide requires an estimate of overall Measurement Uncertainty (MU), including sampling
- When data from a particular Collaborative Trial in Sampling (CTS) were used to estimate MU, it was found that:
  - if between-sampler bias was included, the measurement methods **were fit-for-purpose**, for both multi-fold and single fold measurements
  - if **no between sampler effects were included** in the estimate (equivalent to a single sampler using the Duplicate Method), the OU approach suggested that costs could be cut by using a less precise measurement method
- This demonstrates that between-sampler effects can make a **large contribution** to the overall MU – especially when the sampling target is not very heterogeneous
- Further suggests there is a potential usefulness of **CTS in the validation of measurement procedures that include sampling.** Particularly if the validation is intended to be generic, e.g. applying to measurements made in different locations by different samplers

Acknowledgements

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Breakout session 7

Improving approaches to UfS* estimation & the Validation of Measurement Procedures that Include Sampling (VaMPIS)

Facilitators:

Peter Rostron: Working Group on Uncertainty from Sampling, UK Royal Society of Chemistry Analytical Methods Committee

Steve Ellison: LGC Fellow (Statistics / Analytical Science)

*Uncertainty from Sampling