Measurement Uncertainty -
An Analytical Chemistry perspective

S Ellison

LGC Limited

Introduction

- Where measurement uncertainty comes from
- How uncertainty is assessed in analytical chemistry
  - Propagation of uncertainty
  - Use of method performance data
- Special cases
  - Uncertainties near zero
  - Large uncertainty

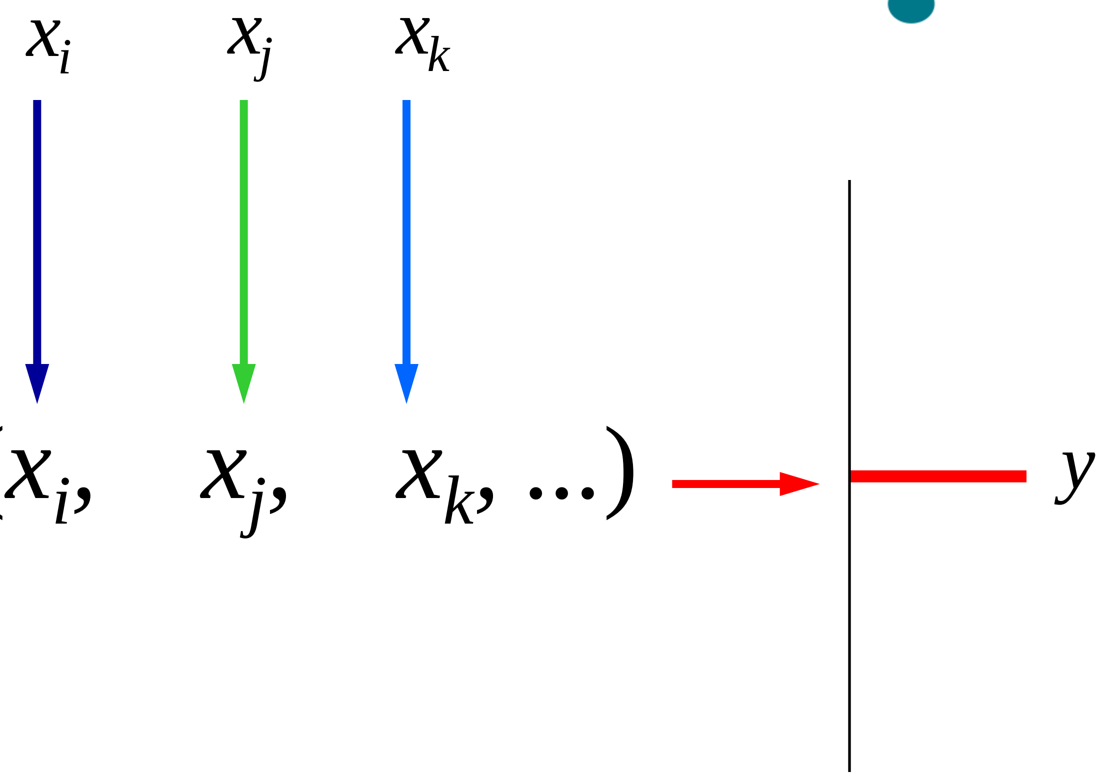
What is Measurement Uncertainty?

"A parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand"

(ISO Guide)

The number after the ±

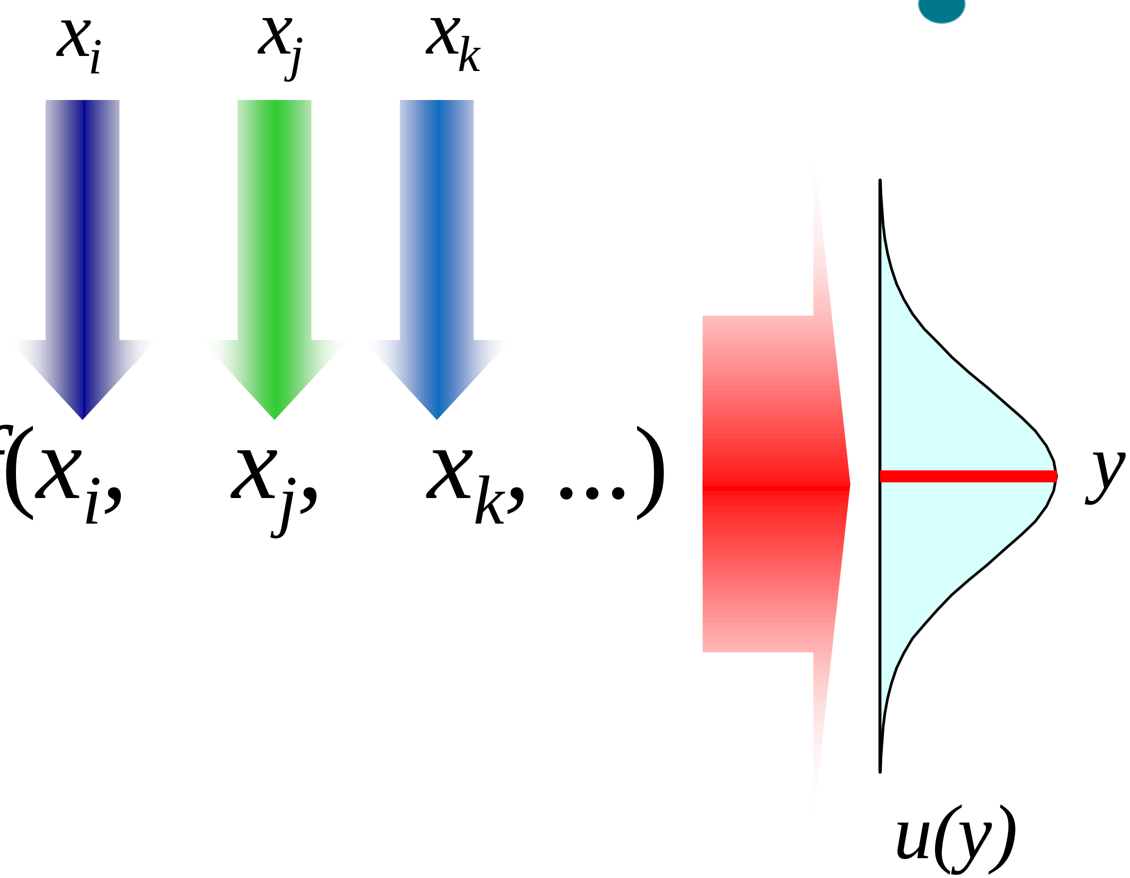
Where uncertainty comes from



$$y = f(x_i, \quad x_j, \quad x_k, \ldots)$$

Where uncertainty comes from

$$y = f(x_i, \quad x_j, \quad x_k, \ldots)$$



Assessing uncertainty: ISO Guide approach

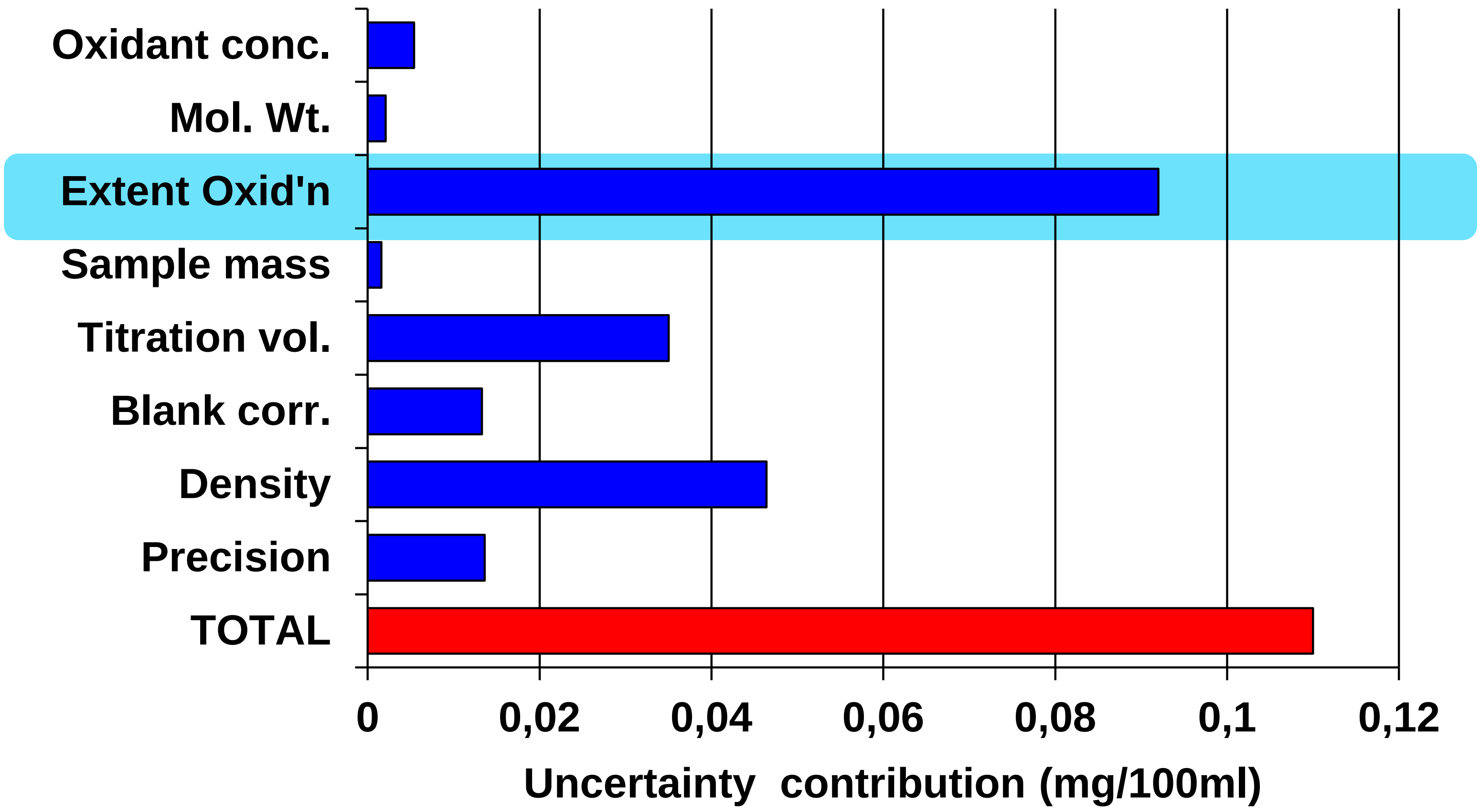
- Specify the measurand
  - including complete equation
- Quantify significant uncertainties in all parameters
  - A: from statistics of repeated experiment
  - B: by any other means (theory, certificates, judgement...)
- Express as standard deviation
- Combine according to stated principles

Sources of Uncertainty

- Sampling
- Sample/matrix effect
- Method
- Extraction/Recovery
- Analyst effects
- Laboratory effects
- Computational effects
- Random effects
- Calibration standards
- Conditions of measurement
- Corrections for known effects

- **Does not include mistakes!**

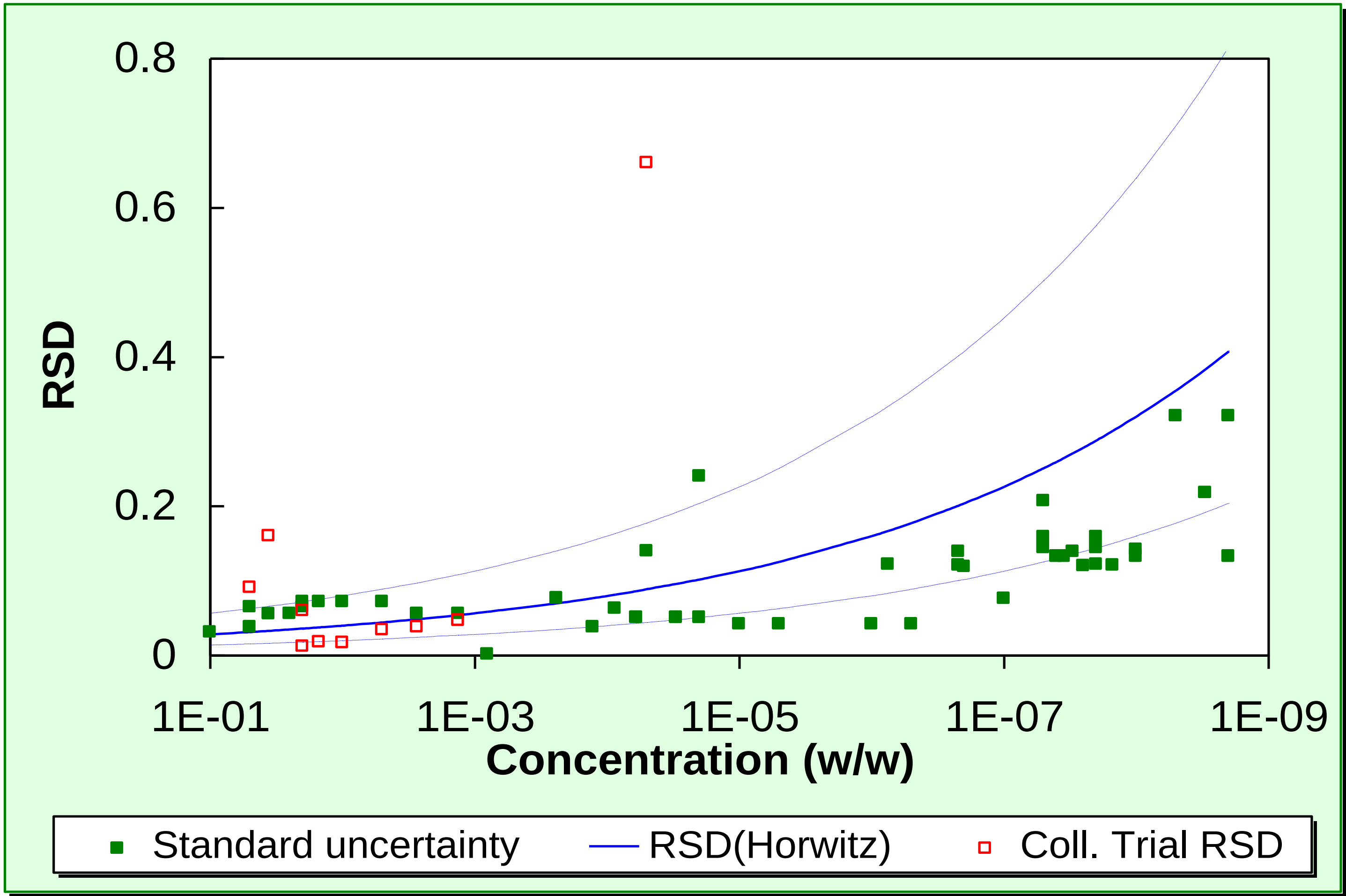
Example: Forensic alcohol standard titration



Implementing ISO in Chemistry
Building models

- Every determinand is unique
  - Every element, every molecule, every formulation
- Every 'matrix' is unique
  - Different interactions with substrate
- Interactions with environment and substrate rarely understood
- **Models are difficult to build!**

Comparing *u* with s_R



Testing labs underestimate measurement uncertainty using the GUM

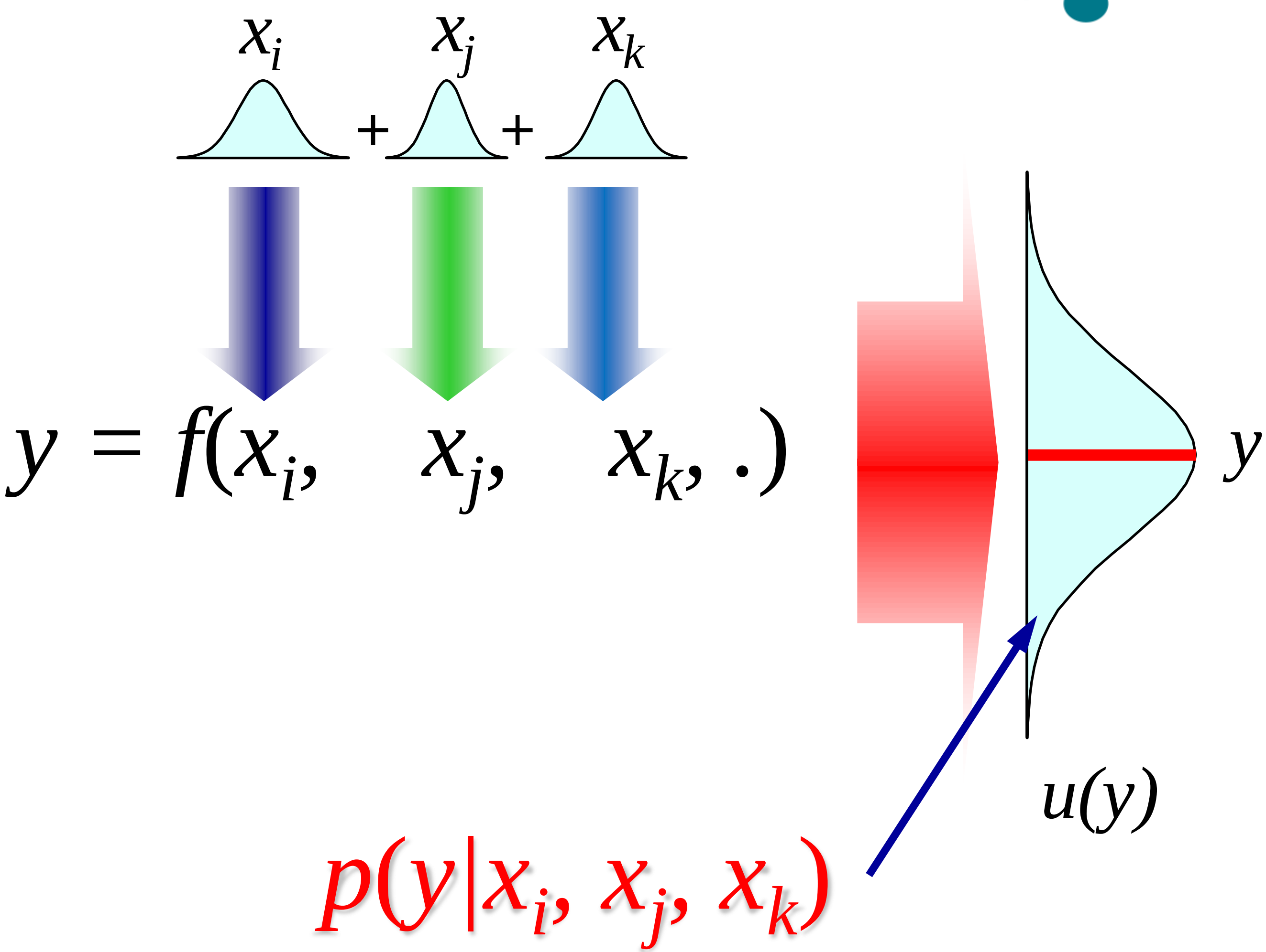
NML
UK NATIONAL MEASUREMENT LABORATORY
FOR CHEMICAL AND BIO-MEASUREMENT
HOSTED AT LGC

Validation and Interlaboratory studies

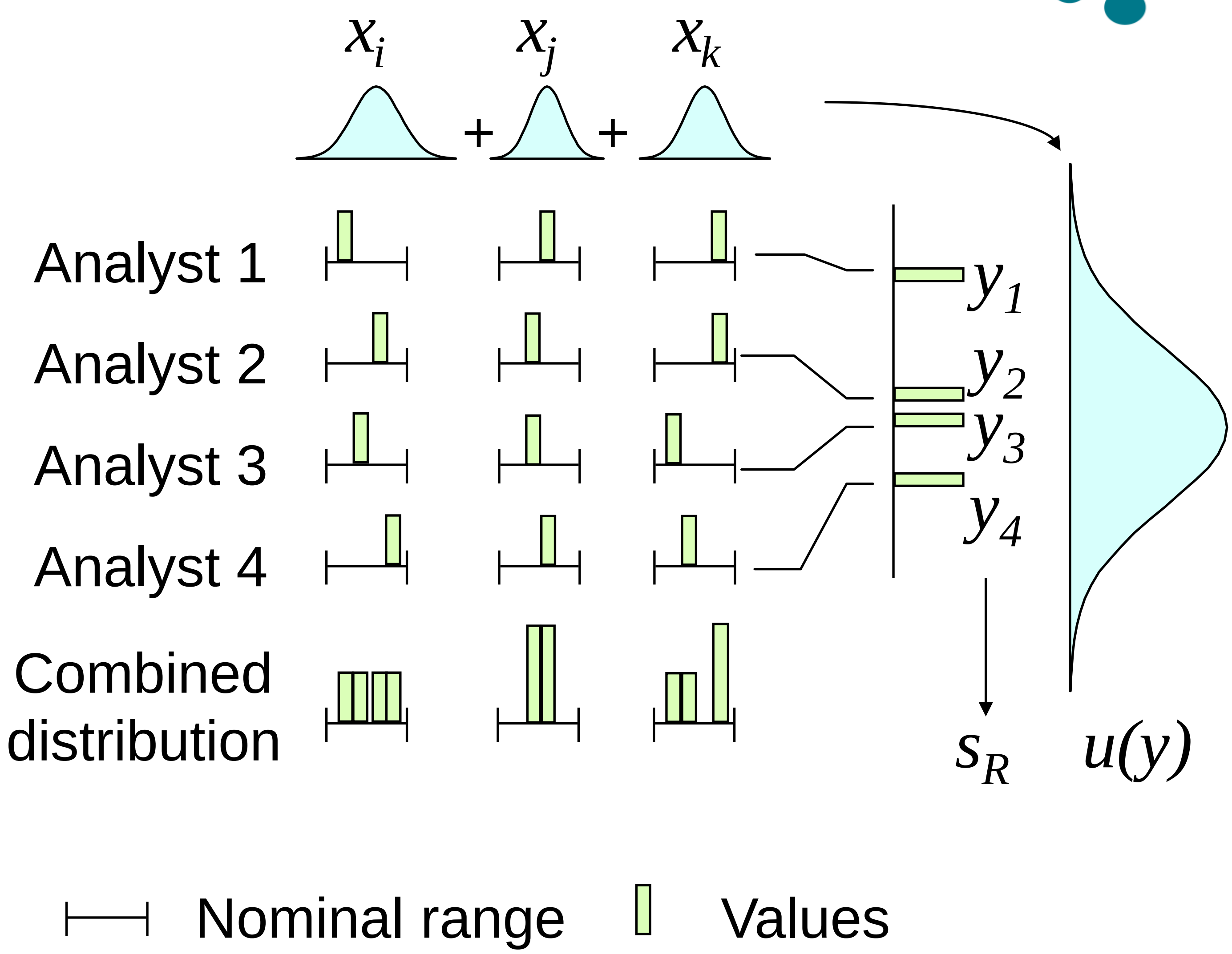
- Validation:
  - Experimental studies to establish method performance
  - Aim: Reasonable Assurance of adequacy

- Uncertainty estimation:
  - Experimental and theoretical studies of method performance
  - Aim: Quantification of accuracy

Method performance and MU



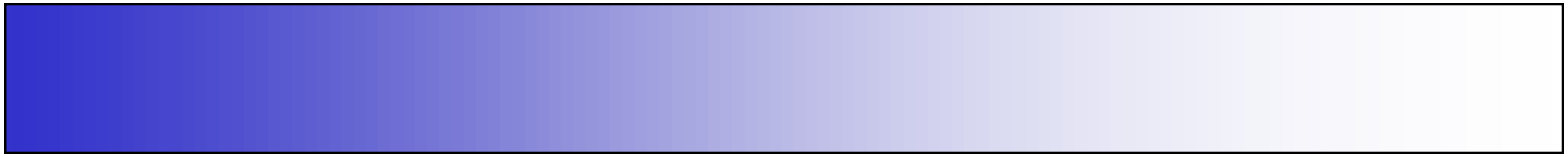
Method performance and MU



Real World problems

"Well characterised"
quantified effects,
differentiable, continuous,
traceable

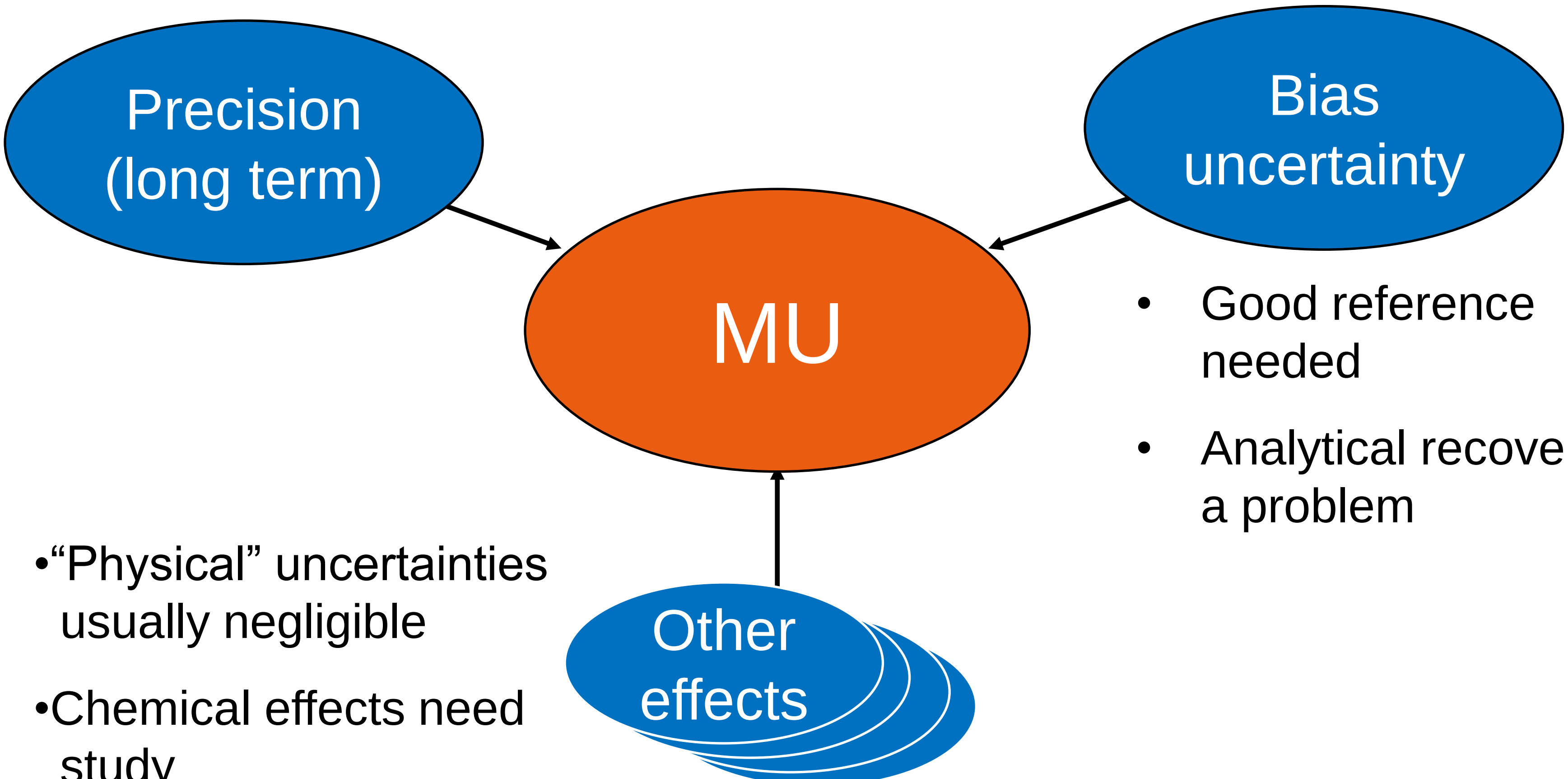
Poorly characterised;
Unpredictable effects;
Input parameters unclear



WELL ← **Measurement model applies** → **POORLY**

POORLY ← **Whole method study applies** → **WELL**

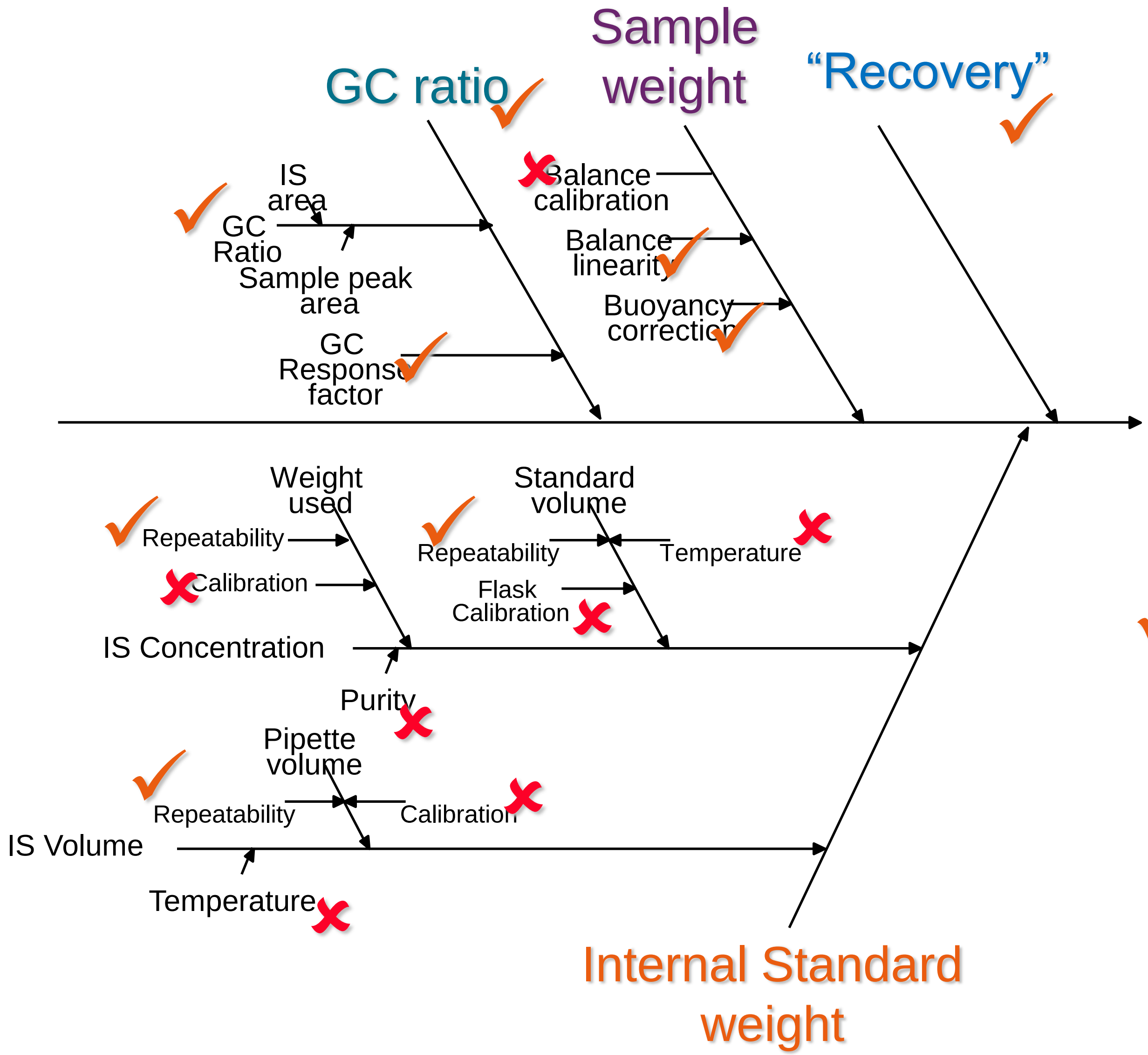
A simpler model



- Good reference needed
- Analytical recovery a problem

- “Physical” uncertainties usually negligible
- Chemical effects need study

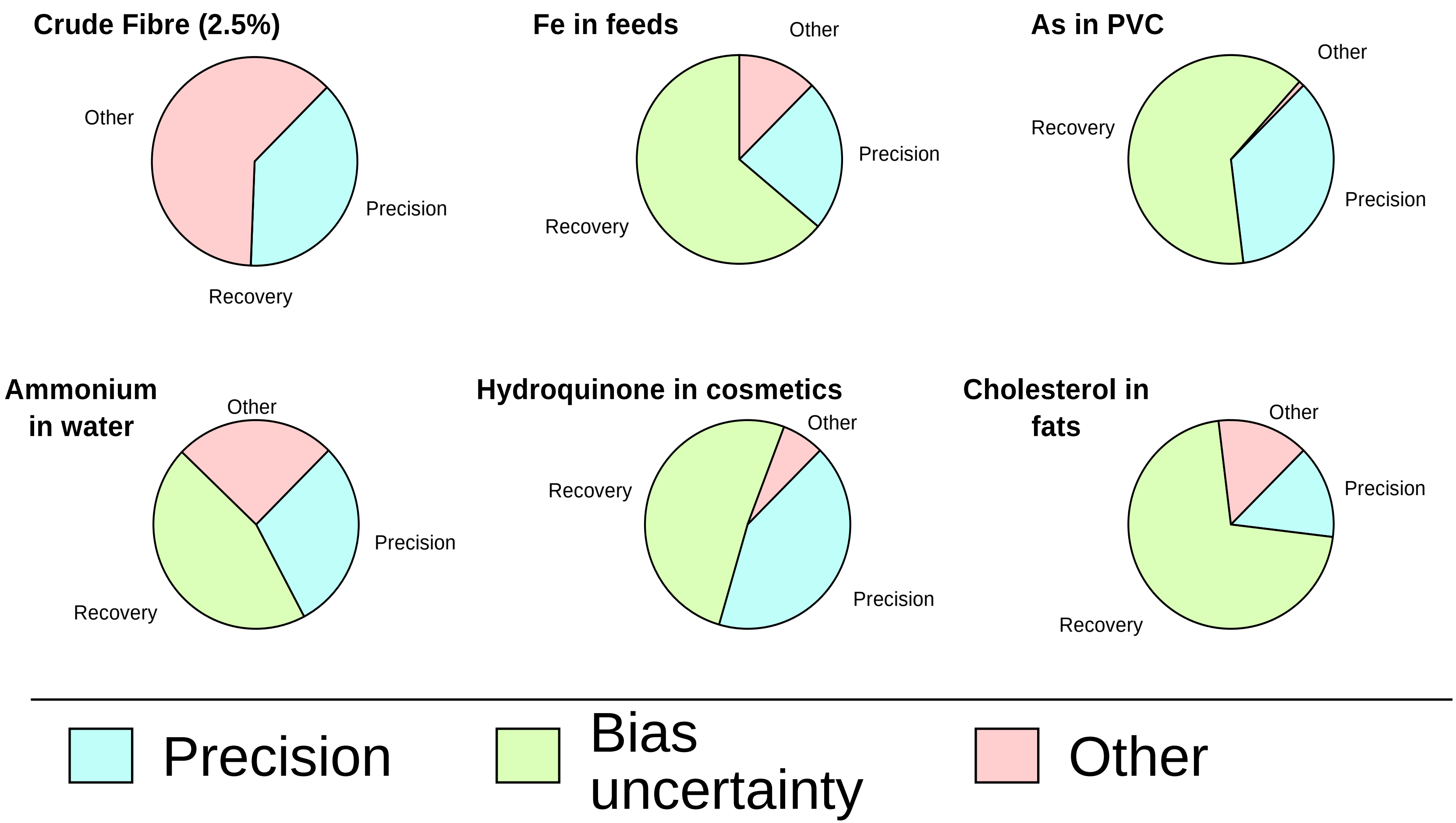
Validation experiment coverage



✓ Experiment:

Recovery for representative matrices, levels (replicated)

"Precision and Bias" Contributions to uncertainty



Most uncertainty in chemical testing relies on validation data

backed by identification of major uncertainty sources

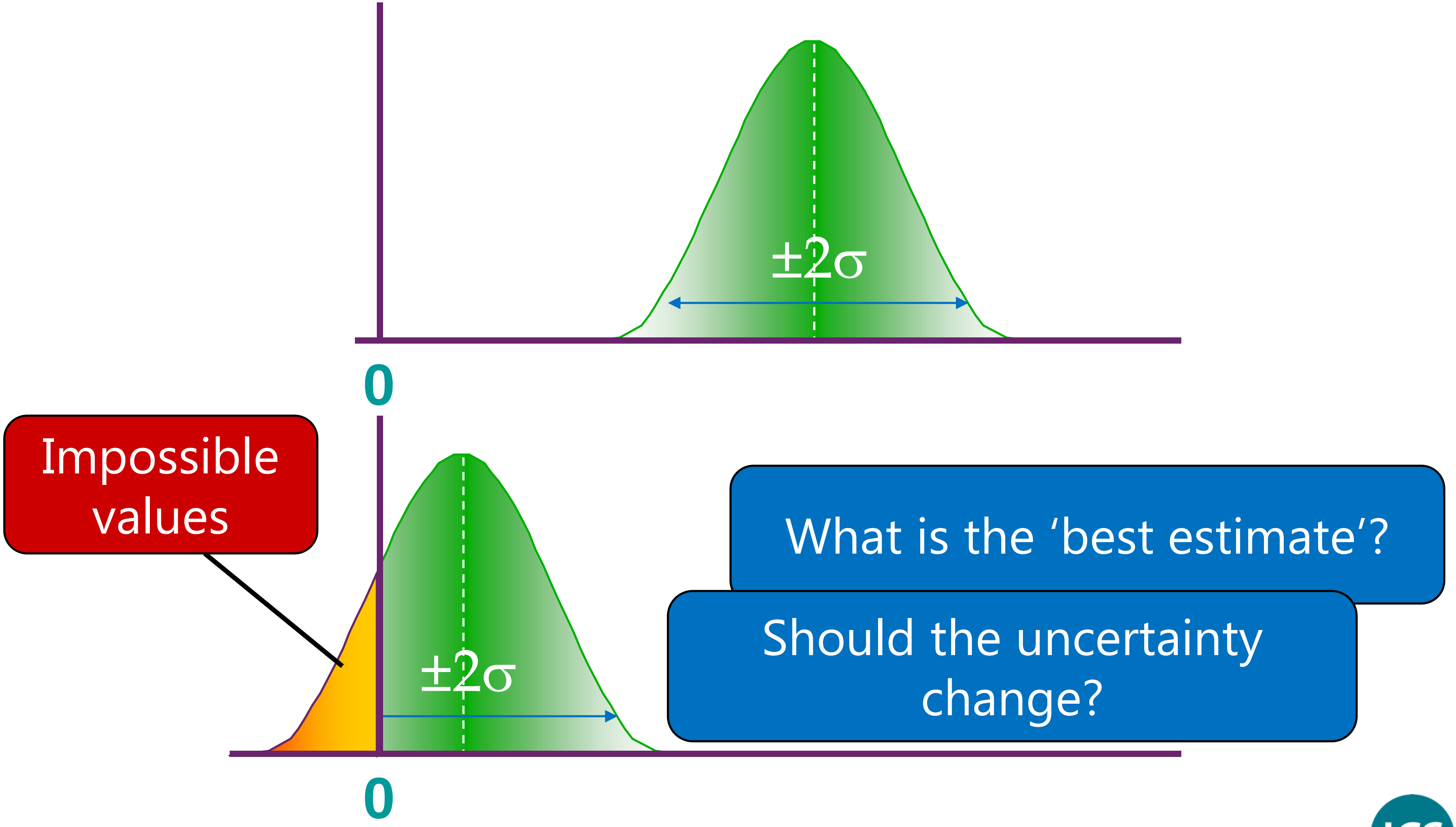
UK NATIONAL MEASUREMENT LABORATORY
FOR CHEMICAL AND BIO-MEASUREMENT
HOSTED AT LGC

Common problems

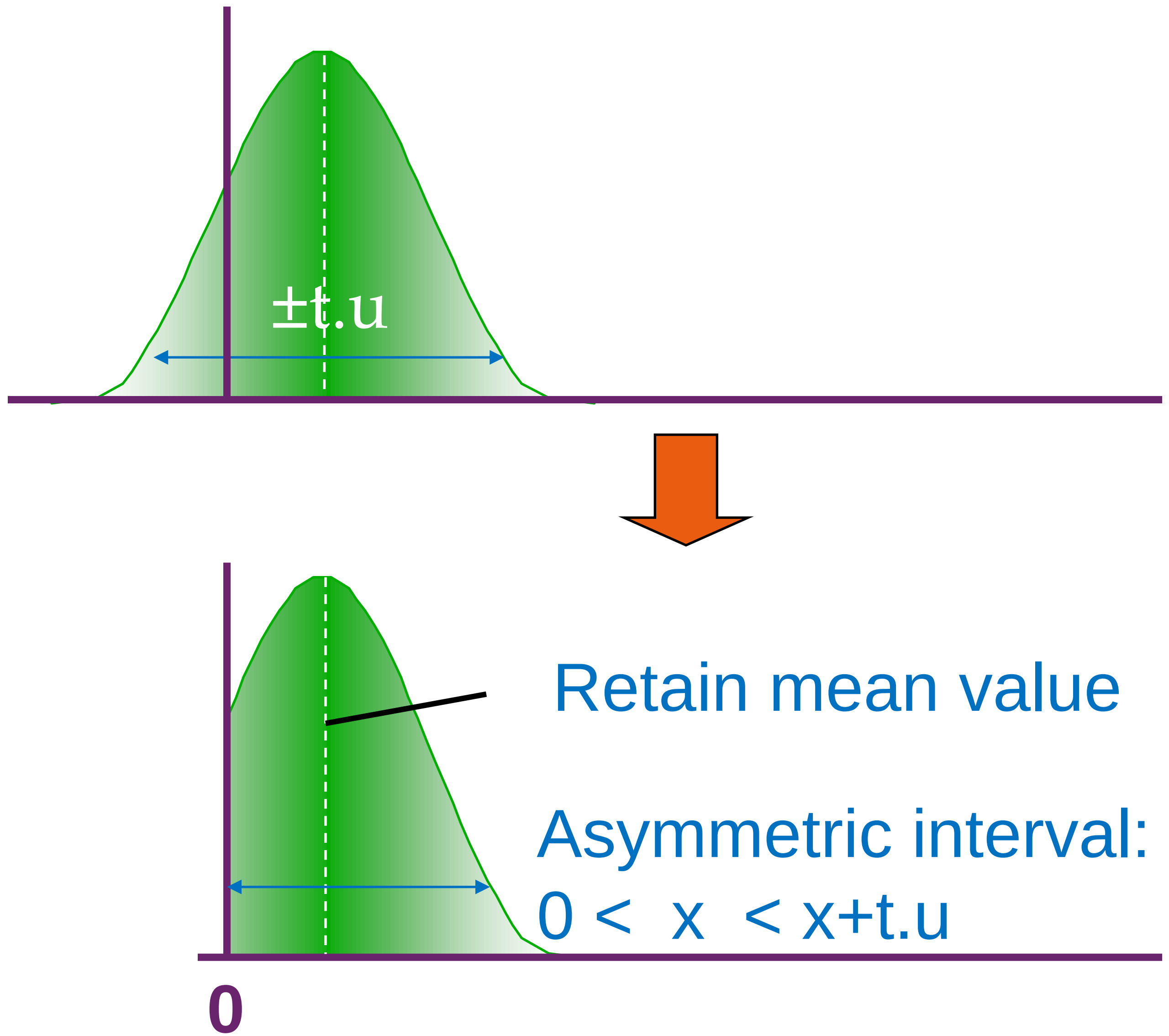
Uncertainty near zero

Uncertainties proportional to ‘true value’

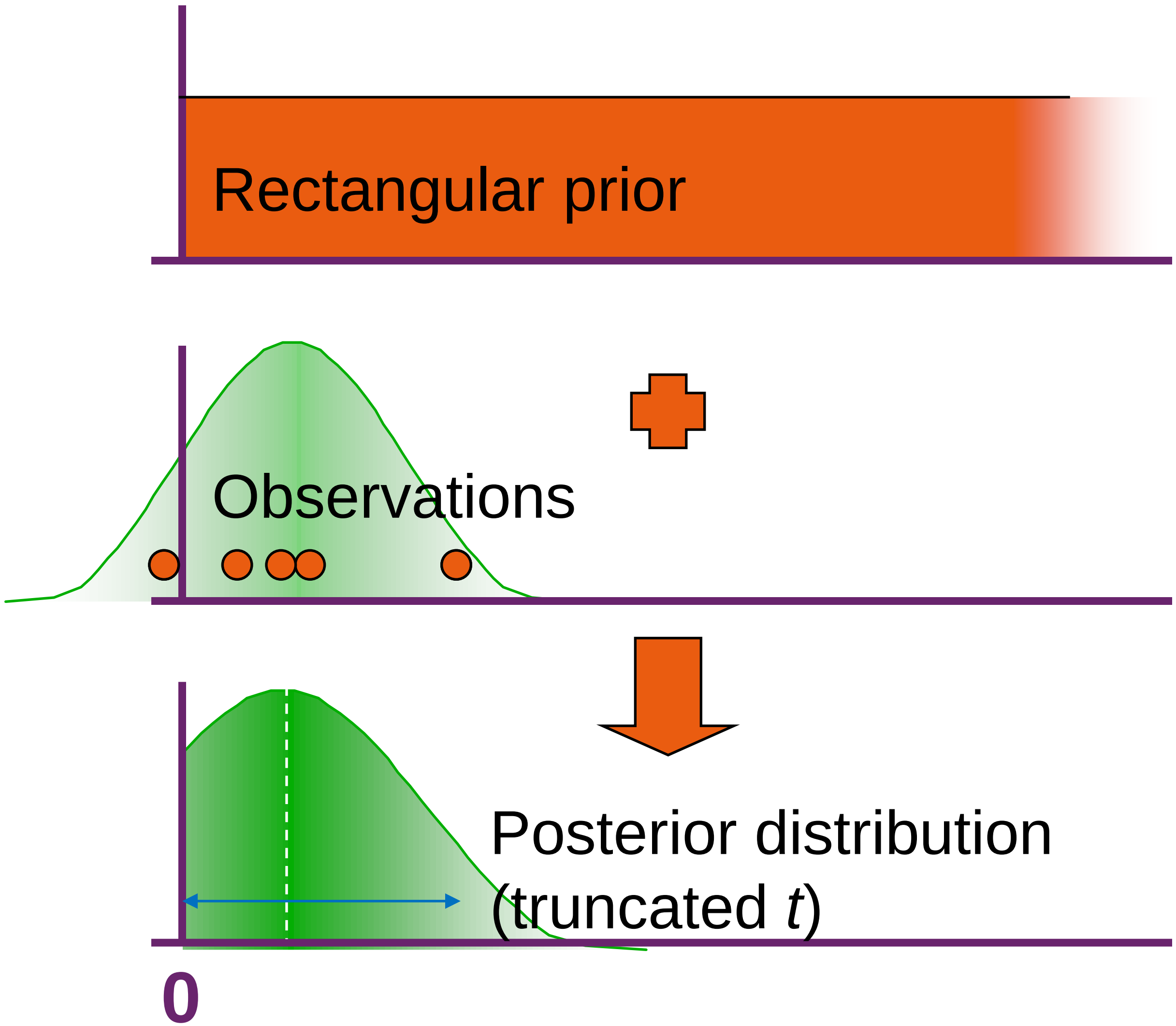
Uncertainty near zero/100%



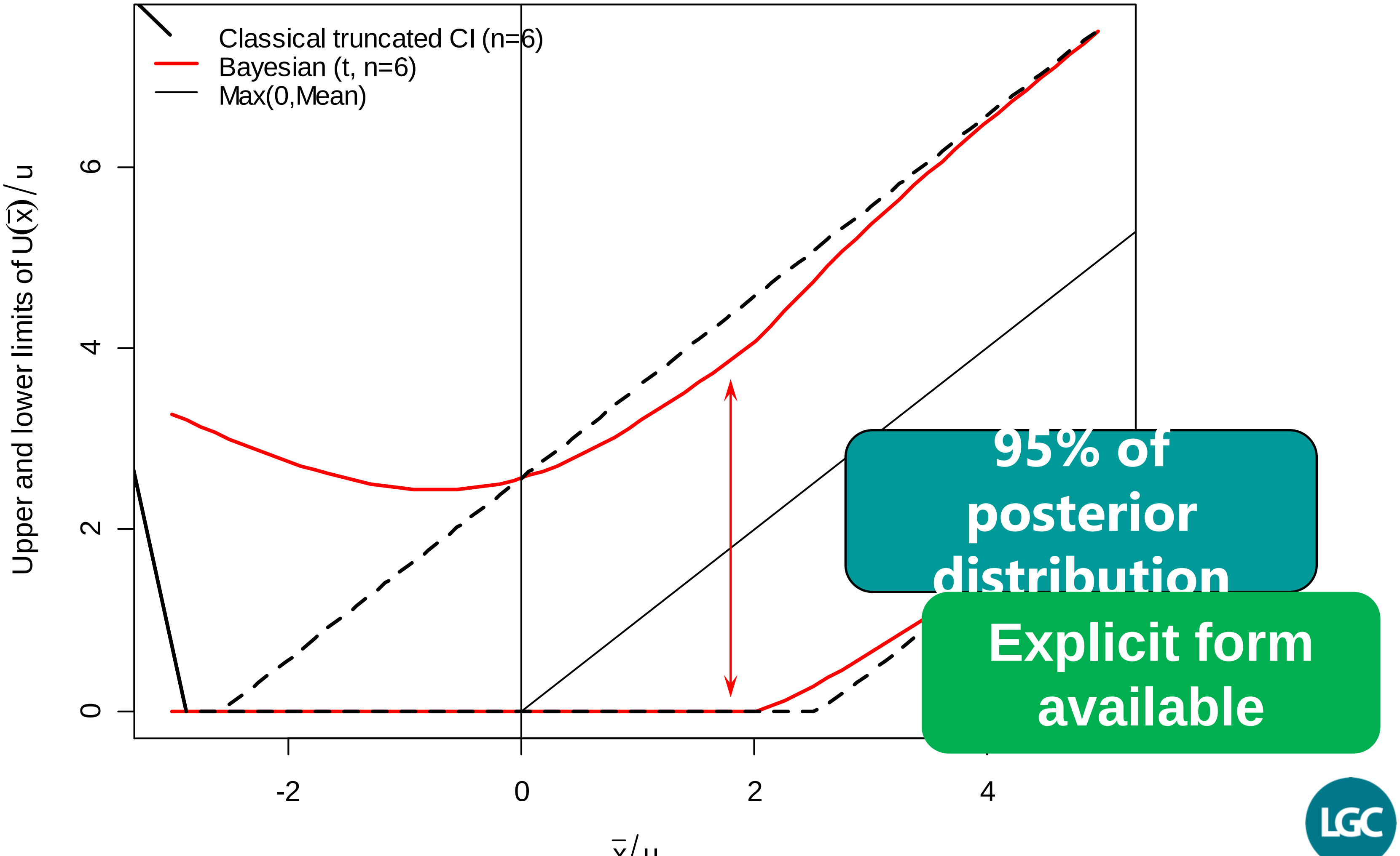
Truncation provides accurate coverage



Bayesian approach



Bayesian intervals don't disappear



Conclusions

- Measurement uncertainty in analytical chemistry can be assessed by
  - Modelling and estimation based on inputs
    Appropriate for metrology labs
  - By observing the actual dispersion in extended experiments
    Best for testing labs
- Bayesian methods can help in special cases
  - … and need not require simulation